Drop Size Distribution Analysis of Mechanically Agitated Liquid-Liquid Dispersions

A thesis submitted to The University of Manchester for the degree of Doctor of Philosophy in the Faculty of Science and Engineering

2017

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<tr>
<td>( \dot{m} )</td>
<td>mass flow rate</td>
<td>[kg s(^{-1})]</td>
</tr>
<tr>
<td>( \dot{Q} )</td>
<td>volumetric flow rate</td>
<td>[m(^3) s(^{-1})]</td>
</tr>
<tr>
<td>( \ell )</td>
<td>size of an eddy</td>
<td>[m]</td>
</tr>
<tr>
<td>( \ell_0 )</td>
<td>size of the largest eddies</td>
<td>[m]</td>
</tr>
<tr>
<td>( \ell_\eta )</td>
<td>Kolmogorov length-scale</td>
<td>[m]</td>
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<td>( \ell_{DI} )</td>
<td>eddie size limit in-between the inertia and dissipative subrange(s)</td>
<td>[m]</td>
</tr>
<tr>
<td>( \ell_{ED} )</td>
<td>eddie size limit in-between the inertia and the energy containing subrange(s)</td>
<td>[m]</td>
</tr>
<tr>
<td>( \bar{I} )</td>
<td>identity tensor</td>
<td>[-]</td>
</tr>
<tr>
<td>( \bar{d}_{32} )</td>
<td>Sauter mean diameter</td>
<td>[( \mu )m]</td>
</tr>
<tr>
<td>( \bar{d}_{a,G} )</td>
<td>geometric mean droplet size</td>
<td>[m]</td>
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<td>( \bar{d}_{ab} )</td>
<td>generic mean droplet size</td>
<td>[m]</td>
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<td>( \bar{E} )</td>
<td>mean kinetic energy per unit mass</td>
<td>[m(^2) s(^{-2})]</td>
</tr>
<tr>
<td>( \bar{P} )</td>
<td>mean pressure</td>
<td>[Pa]</td>
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<td>( \bar{t}_{res,S} )</td>
<td>mean residence time in the rotor-stator</td>
<td>[s]</td>
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<td>( \bar{t}_{res,T} )</td>
<td>mean residence time in the tank</td>
<td>[s]</td>
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<td>( \bar{t}_{res} )</td>
<td>mean residence time</td>
<td>[s]</td>
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<tr>
<td>( \bar{\pi}_i )</td>
<td>mean velocity vector in the ( i )th direction</td>
<td>[m s(^{-1})]</td>
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<td>[-]</td>
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<tr>
<td>( A )</td>
<td>area</td>
<td>[m(^2)]</td>
</tr>
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<tr>
<td>( A_i )</td>
<td>( i )th fit constant</td>
<td>[-]</td>
</tr>
<tr>
<td>( a_v )</td>
<td>Interfacial surface per unit volume</td>
<td>[m(^2) m(^{-3})]</td>
</tr>
</tbody>
</table>
Nomenclature

\( B_b \) birth-rate due to drop breakage \([s^{-1}]\)
\( B_c \) birth-rate due to drop coalescence \([s^{-1}]\)
\( B_i \) \(i\)th fit constant  
\( C \) Kolmogorov constant \( C = 1.5 \)  
\( c_n \) constant in Pope’s construction function in Eq. 2.77  
\( C_g \) glucose concentration \([\text{mol L}^{-1}]\)
\( C_i \) \(i\)th fit constant  
\( C_L \) length-scale proportionality constant (Eq. 2.95)  
\( c_L \) constant in Pope’s construction function in Eq. 2.76  
\( C_S \) clearance in-between the bottom of the tank and the stirrer \([\text{m}]\)
\( C_s \) solute concentration \([\text{mol m}^3]\)
\( C_u \) velocity proportionality constant (Eq. 2.94)  
\( C_{L,j} \) fitting constant for large daughter drop correlation for variable \(j\) (see Chapter 7)  
\( C_{s,j} \) fitting constant for small daughter drop correlation for variable \(j\) (see Chapter 7)  
\( CI \) confidence interval  
\( D \) diameter of the stirrer \([\text{m}]\)
\( d \) diameter \([\text{m}]\)
\( D_b \) death-rate due to drop breakage \([s^{-1}]\)
\( D_c \) death-rate due to drop coalescence \([s^{-1}]\)
\( d_i \) diameter of drops in class size \(i\) \([\text{m}]\)
\( D_1 \) diameter of the midsection of the filament at \(t = 0\) (see Section 4.A) \([\text{m}]\)
\( D_{50} \) median or 50\(^{\text{th}}\) percentile \([\text{m}]\)
\( D_{95} \) 95\(^{\text{th}}\) percentile \([\text{m}]\)
\( d_{\text{max}} \) maximum drop diameter \([\text{m}]\)
\( D_{\text{mid}} \) diameter of the midsection of the filament \([\text{m}]\)
\( E \) energy density \([\text{J kg}^{-1}]\)
\( E \) kinetic energy per unit mass \([\text{m}^2 \text{s}^{-2}]\)
\( E(\kappa) \) energy spectrum function as a function of the eddie wave-number [-]
\( F \) force \([\text{N}]\)
\( f(d_i) \) frequency of the droplets of diameter of class size \(i\) [-]
\( F_a(d_i) \) cumulative frequency by area of drops of class size \(i\) [-]
\( f_a(d_i) \) frequency by surface of drops of class size \(i\) [-]
\( F_k \) tensile force acting on the column’s ends \([\text{N}]\)
\( F_n(d_i) \) cumulative frequency by number of drops of class size \(i\) [-]
\( f_n(d_i) \) frequency by number of drops of class size \(i\) [-]
\( F_v(d_i) \) cumulative frequency by volume of drops of class size \(i\) [-]
Nomenclature

\( f_v(d_i) \) frequency by volume of drops of class size \( i \) [-]
\( f_v \) fitted frequency distribution by volume of the daughter drop distribution [-]
\( f_{v,n,L} \) frequency of the \( i \)th drop size after \( n \) passes through the rotor-stator for the large drops [-]
\( f_{v,n,s} \) frequency of the \( i \)th drop size after \( n \) passes through the rotor-stator for the small drops [-]
\( f_{v,n,T} \) frequency of the \( i \)th drop size after \( n \) passes through the rotor-stator for the whole distribution [-]
\( f_{v,Rec} \) frequency of the \( i \)th drop size for the recycle arrangement [-]
\( f_{v,s} \) fitted frequency distribution by volume of the satellite drop distribution [-]
\( f_{v,T} \) fitted frequency distribution by volume of the whole distribution [-]
\( G \) Gibbs free energy [J]
\( G \) shear elastic modulus [Pa]
\( g \) acceleration of gravity \( g = 9.81 \text{ m s}^{-2} \)
\( h \) parallel disk/plate gap size [m]
\( h(V' - V,V) \) coalescence efficiency [-]
\( h_i \) parallel disk \( i \)th gap size [m]
\( H_T \) height of the tank [m]
\( k \) pre-exponential factor of Generalised Newtonian Models [-]
\( k \) turbulent kinetic energy per unit mass \( \text{[m}^2\text{s}^{-2}] \)
\( k_1 \) power-inertia proportionality constants [-]
\( k_1, k_2 \) fitting constants in the Sisko model (Eq. 2.22) [-]
\( K_i \) \( i \)th fit constant [-]
\( K_P \) laminar power constant [-]
\( K_S \) Metzner-Otto mean shear constant [-]
\( K_{P,Z} \) zero-flow laminar power constant [-]
\( L \) characteristic or integral length scale [m]
\( L \) length of the inner cylinder of the concentric cylinder rheometer tool [m]
\( L(t) \) length as a function of time [m]
\( L_0 \) length at time zero [m]
\( L_b \) clearance of the concentric cylinder rheometer tool [m]
\( l_W \) length of the Wilhelmy plate [m]
\( M \) torque \( \text{[N m}^{-1}] \)
\( m(V') \) number of fragments due to drop breakage [-]
\( M_{adj} \) adjusted torque [N m]
\( M_{m,0} \) measured torque with inviscid fluid [N m]
\( M_{m,f} \) measured torque with viscous fluid [N m]
\( MAE \) mean absolute error \([-]\)
\( Mo \) mode \([m]\)
\( Mo_L \) mode of the large daughters \([m]\)
\( Mo_n \) mode of the distribution after \( n \) passes through the rotor-stator \([m]\)
\( Mo_s \) mode of the small daughter droplets \([m]\)
\( Mo_x \) Mode, \( x \) denotes if the distribution is by number, surface or volume \([m]\)
\( Mo_{n,L} \) mode of the large distribution after \( n \) passes through the rotor-stator \([m]\)
\( Mo_{n,s} \) mode of the small distribution after \( n \) passes through the rotor-stator \([m]\)
\( Mo_{Rec} \) mode of distribution using the recycle arrangement \([m]\)
\( N \) speed of the stirrer \([s^{-1}]\)
\( n \) exponential factor of Generalised Newtonian Models \([-]\)
\( n \) number density in Population Balance Equations \([-]\)
\( n \) number of passes \([-]\)
\( n_{cont} \) number of passes in the continuous arrangement \([-]\)
\( n_{ri} \) refractive index \([-]\)
\( P \) pressure \([Pa]\)
\( p \) dynamic viscosity ratio of the dispersed and continuous phases \([-]\)
\( P' \) pressure fluctuation \([Pa]\)
\( p(d_i) \) probability density of the droplets of diameter of class size \( i \) \([m^{-1}]\)
\( P_a(d_i) \) cumulative probability by surface of the droplets of class size \( i \) \([-]\)
\( p_a(d_i) \) probability density by surface of the droplets of diameter of class size \( i \) \([m^{-1}]\)
\( P_F \) power draw due to flow \([W]\)
\( P_L \) power losses \([W]\)
\( P_n(d_i) \) cumulative probability by number of the droplets of class size \( i \) \([-]\)
\( p_n(d_i) \) probability density by number of the droplets of diameter of class size \( i \) \([m^{-1}]\)
\( P_S \) power draw by the stirrer \([W]\)
\( P_T \) power draw in the absence of flow \([W]\)
\( P_v(d_i) \) cumulative probability by volume of the droplets of class size \( i \) \([-]\)
\( p_v(d_i) \) probability density by volume of the droplets of diameter of class size \( i \) \([m^{-1}]\)
\( p_{v,L}(d_i) \) probability density by volume of the large daughter droplets of diameter of class size \( i \) \([m^{-1}]\)
\( p_{v,s}(d_i) \) probability density by volume of the small daughter droplets of diameter of class size \( i \) \([m^{-1}]\)
\( p_{v,T}(d_i) \) probability density by volume of the small and large daughter droplets of diameter of class size \( i \) \([m^{-1}]\)
### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$pn$</td>
<td>pump number</td>
<td>[-]</td>
</tr>
<tr>
<td>$R$</td>
<td>radius of the rheometer’s geometry tool</td>
<td>[m]</td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant</td>
<td></td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant</td>
<td>$R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$</td>
</tr>
<tr>
<td>$r$</td>
<td>radius of the rheometer’s geometry tool</td>
<td>[m]</td>
</tr>
<tr>
<td>$R^2$</td>
<td>coefficient of determination</td>
<td>[-]</td>
</tr>
<tr>
<td>$r_1$, $r_2$</td>
<td>radius of curvature</td>
<td>[m]</td>
</tr>
<tr>
<td>$R_i$</td>
<td>radius of the inner cylinder of the concentric cylinder rheometer tool</td>
<td>[m]</td>
</tr>
<tr>
<td>$R_p$</td>
<td>radius of the outer cylinder of the concentric cylinder rheometer tool</td>
<td>[m]</td>
</tr>
<tr>
<td>$r_r$</td>
<td>radius of the du Nouy ring</td>
<td>[m]</td>
</tr>
<tr>
<td>$r_w$</td>
<td>radius of the du Nouy wire</td>
<td>[m]</td>
</tr>
<tr>
<td>$s$</td>
<td>standard deviation</td>
<td>[m]</td>
</tr>
<tr>
<td>$S_b$</td>
<td>drop breakup source term</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$S_c$</td>
<td>drop breakup coalescence source term</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$s_G$</td>
<td>geometric standard deviation</td>
<td>[m]</td>
</tr>
<tr>
<td>$s_{z,L}$</td>
<td>standard deviation of log ($d_i/M_{0L}$) of the daughter drops</td>
<td>[-]</td>
</tr>
<tr>
<td>$s_{z,s}$</td>
<td>standard deviation of log ($d_i/M_{0L}$) of the satellite drops</td>
<td>[-]</td>
</tr>
<tr>
<td>$T$</td>
<td>diameter of the tank</td>
<td>[K]</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td>[s]</td>
</tr>
<tr>
<td>$U$</td>
<td>plate velocity</td>
<td>[m s$^{-1}$]</td>
</tr>
<tr>
<td>$u$</td>
<td>velocity</td>
<td>[m s$^{-1}$]</td>
</tr>
<tr>
<td>$u'_i$</td>
<td>velocity fluctuation vector in the $i$th direction</td>
<td>[m s$^{-1}$]</td>
</tr>
<tr>
<td>$u_0$</td>
<td>characteristic velocity of the largest eddies</td>
<td>[m s$^{-1}$]</td>
</tr>
<tr>
<td>$u_i$</td>
<td>velocity vector in the $i$th direction</td>
<td>[m s$^{-1}$]</td>
</tr>
<tr>
<td>$u_\eta$</td>
<td>Kolmogorov velocity</td>
<td>[m s$^{-1}$]</td>
</tr>
<tr>
<td>$V$</td>
<td>volume of the mother drop</td>
<td>[m$^3$]</td>
</tr>
<tr>
<td>$V'$</td>
<td>volume of the daughter drop</td>
<td>[m$^3$]</td>
</tr>
<tr>
<td>$V_T$</td>
<td>volume of the tank</td>
<td>[m$^3$]</td>
</tr>
<tr>
<td>$V_{\text{swept}}$</td>
<td>swept volume</td>
<td>[m$^3$]</td>
</tr>
<tr>
<td>$W_{bf}$</td>
<td>width of the baffles</td>
<td>[m]</td>
</tr>
<tr>
<td>$X$</td>
<td>dimensionless factor (see Section 4.A)</td>
<td>[-]</td>
</tr>
<tr>
<td>$x_i$</td>
<td>$i$th direction</td>
<td>[m]</td>
</tr>
</tbody>
</table>

### Greek symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>angle of the cone and plate rheometer tool</td>
<td>[rad]</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>interphase contact angle</td>
<td>[°]</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>parameter in the Fréchet or Weibull probability density function</td>
<td>[-]</td>
</tr>
<tr>
<td>$\beta$</td>
<td>constant in Pope’s construction function Eq. 2.77</td>
<td>[m]</td>
</tr>
<tr>
<td>$\beta$</td>
<td>du Noiü ring force correction factor</td>
<td>[-]</td>
</tr>
</tbody>
</table>
\( \beta \) parameter in the Fréchet or Weibull probability density function

\( \beta(V', V) \) daughter drop size distribution

\( \dot{\gamma} \) shear strain rate

\( \dot{\gamma}_{\text{app},1}, \dot{\gamma}_{\text{app},2} \) apparent shear strain rate measured for gap sizes \( h_1 \) and \( h_2 \)

\( \dot{\gamma}_{ij} \) rate-of-strain tensor

\( \dot{\gamma}_{\text{real}} \) real shear strain rate

\( \dot{\varepsilon} \) extensional strain rate

\( \eta \) dynamic viscosity

\( \eta_0 \) zero shear dynamic viscosity

\( \eta_c \) shear dynamic viscosity of the continuous phase

\( \eta_d \) shear dynamic viscosity of the dispersed phase

\( \eta_e \) shear dynamic viscosity of the emulsion

\( \eta_s \) shear dynamic viscosity of a suspension

\( \eta_{\text{ext}} \) extensional dynamic viscosity

\( \eta_{\text{inf}} \) infinite shear dynamic viscosity

\( \eta_{\text{pl}} \) plateau dynamic viscosity of a Bingham fluid

\( \eta_r \) relative viscosity

\( \Gamma \) adsorbed solute per unit area

\( \gamma \) shear strain

\( \kappa \) dilatational viscosity

\( \kappa \) wave number of the eddies

\( \kappa' \) dimensionless wave number of eddies (\( \kappa' = \kappa L \))

\( \kappa_G \) shape factor of the Generalised Gamma distribution

\( \lambda \) Taylor microscale

\( \lambda \) relaxation time of an elastic material

\( \lambda(V' - V, V) \) coalescence frequency

\( \lambda_G \) scale factor of the Generalised Gamma distribution

\( \mu \) Newtonian dynamic viscosity

\( \mu_c \) Newtonian dynamic viscosity of the continuous phase

\( \mu_d \) Newtonian dynamic viscosity of the dispersed phase

\( \mu_{\text{ext}} \) extensional Newtonian dynamic viscosity

\( \mu_{\text{ext}} \) extensional dynamic viscosity of a Newtonian fluid

\( \nu \) kinematic viscosity

\( \Omega \) angular velocity

\( \Omega(V) \) breakup frequency

\( \varepsilon \) mean energy dissipation per unit mass

\( \phi \) volume fraction

\( \phi_0 \) volume fraction at which the emulsion starts to become elastic
Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_L$</td>
<td>Volume fraction of the large daughter drops</td>
<td>[-]</td>
</tr>
<tr>
<td>$\phi_m$</td>
<td>Maximum random packing fraction</td>
<td>[-]</td>
</tr>
<tr>
<td>$\phi_n$</td>
<td>Volume fraction of drops that have passed $n$ ($n = 0, 1, 2...$) times through the rotor-stator</td>
<td>[-]</td>
</tr>
<tr>
<td>$\phi_s$</td>
<td>Volume fraction of the small daughter drops</td>
<td>[-]</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
<td>[-]</td>
</tr>
<tr>
<td>$\rho_c$</td>
<td>Density of the continuous phase</td>
<td>[kg m$^{-3}$]</td>
</tr>
<tr>
<td>$\rho_d$</td>
<td>Density of the dispersed phase</td>
<td>[kg m$^{-3}$]</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Interfacial tension</td>
<td>[N m]</td>
</tr>
<tr>
<td>$\sigma_y$</td>
<td>Yield stress</td>
<td>[Pa]</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Stress</td>
<td>[Pa]</td>
</tr>
<tr>
<td>$\tau_c$</td>
<td>Stress experienced by a drop by the continuous phase</td>
<td>[Pa]</td>
</tr>
<tr>
<td>$\tau_d$</td>
<td>Stress inside the drop</td>
<td>[Pa]</td>
</tr>
<tr>
<td>$\tau_G$</td>
<td>Shape factor of the Generalised Gamma distribution</td>
<td>[-]</td>
</tr>
<tr>
<td>$\tau_\eta$</td>
<td>Kolmogorov time-scale</td>
<td>[s]</td>
</tr>
<tr>
<td>$\tau_{ij}$</td>
<td>Stress tensor</td>
<td>[Pa]</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Energy dissipation per unit mass</td>
<td>[m$^2$ s$^{-2}$]</td>
</tr>
<tr>
<td>$\epsilon_{max}$</td>
<td>Localized maximum energy dissipation per unit mass</td>
<td>[m$^2$ s$^{-2}$]</td>
</tr>
<tr>
<td>$\text{Ca}$</td>
<td>Capillary number</td>
<td>$\text{Ca} = \frac{\eta \dot{\gamma} d \sigma^{-1}}{}$</td>
</tr>
<tr>
<td>$\text{Ca}'$</td>
<td>Capillary number of a concentrated emulsion</td>
<td>$\text{Ca}' = \frac{\eta \dot{\gamma} d \sigma^{-1}}{}$</td>
</tr>
<tr>
<td>$\text{Ca}_\text{crit}$</td>
<td>Critical Capillary number</td>
<td>$\text{Ca}_\text{crit} = \frac{\eta \dot{\gamma} d \sigma^{-1}}{}$</td>
</tr>
<tr>
<td>$\text{Fr}$</td>
<td>Froude number</td>
<td>$\text{Fr} = \frac{N^2 D g}{U^2 m \rho}$</td>
</tr>
<tr>
<td>$N_Q$</td>
<td>Pumping number</td>
<td>$N_Q = \frac{n m \rho^{-1} N^{-1} D^3}{D^5 \rho^2}$</td>
</tr>
<tr>
<td>$P_0$</td>
<td>Power number</td>
<td>$P_0 = \frac{P_S N^{-3} D^{-5} \rho^{-1}}{}$</td>
</tr>
<tr>
<td>$P_0$</td>
<td>Reynolds number-independent Power number</td>
<td>$P_0 = \frac{P_S N^{-3} D^{-5} \rho^{-1}}{}$</td>
</tr>
<tr>
<td>$P_{0U}$</td>
<td>Free-flow Power number</td>
<td>$P_{0U} = \frac{P_S N^{-3} D^{-5} \rho^{-1}}{}$</td>
</tr>
<tr>
<td>$P_{0Z}$</td>
<td>Zero-flow Power number</td>
<td>$P_{0Z} = \frac{P_S N^{-3} D^{-5} \rho^{-1}}{}$</td>
</tr>
<tr>
<td>$Re$</td>
<td>Characteristic Reynolds number</td>
<td>$Re = \frac{N D^2 \mu}{\rho}$</td>
</tr>
<tr>
<td>$Re_\lambda$</td>
<td>Taylor-scale Reynolds number</td>
<td>$Re_\lambda = \frac{u' \lambda \nu}{\rho}$</td>
</tr>
<tr>
<td>$Re_L$</td>
<td>Turbulence Reynolds number</td>
<td>$Re_L = \frac{u_0 \delta_0 \nu^{-1}}{}$</td>
</tr>
<tr>
<td>$Vi_C$</td>
<td>Calabrese’s viscosity group</td>
<td>$Vi = \frac{\mu_d N D (\rho_c / \rho_d) \rho^{-1/2}}{}$</td>
</tr>
<tr>
<td>$Vi_H$</td>
<td>Hinze’s viscosity group</td>
<td>$Vi_H = \frac{\mu_d \rho^{-1/2} \sigma^{-1/2} \rho^{-1/2}}{}$</td>
</tr>
<tr>
<td>$We$</td>
<td>Weber number of the impeller</td>
<td>$We = \frac{\rho_c N^2 D^3 \sigma^{-1}}{}$</td>
</tr>
<tr>
<td>$We_{crit}$</td>
<td>Critical Weber number of the drops</td>
<td>$We_{crit} = \frac{\tau_c d \sigma^{-1}}{}$</td>
</tr>
</tbody>
</table>
Nomenclature

We_d  Weber number of the drop  \( We_d = \frac{\tau_c d \sigma}{1} \)

Acronyms

ANOVA  Analysis of variance
CaBER  Capillary breakup extensional rheometer
CFD  Computational Fluid Dynamics
CMC  critical micelle concentration
cmc  Carboxymethyl cellulose sodium salt
DA  Dimensional analysis
DSD  Drop Size Distribution
DVLO  Derjaguin, Landau, Verwey and Overbeek theory
FBRM  Focused beam reflectance measurement
GGf  Generalised Gamma function
GNM  Generalised Newtonian Model
HLB  hydrophile-lipophile balance
O/W  Oil-in-water emulsion
ORM  Optical reflectance measurement
PBE  Population Balance Equations
PDF  Probability density function
PIV  Particle image velocimetry
PVM  Particle video microscope
SGS  Smagorinsky sub-grid
SiOil  Silicon oil
SLES  Sodium laureth sulphate
SOP  Standard Operation Procedure
W/O  Water-in-oil emulsion
Drop Size Distribution Analysis of Mechanically Agitated Liquid-liquid Dispersions
Sergio Carrillo De Hert - Ph.D. Thesis

Abstract

Many daily life products consist of mixtures of oil and water. When an immiscible material is dispersed an interface in-between the two phases is created which gives rise to rheological phenomena which can be exploited for product formulation; this is the case in products such as hand-creams and food products. Furthermore emulsions are used to transport hydrophobic materials, for example, many pharmaceuticals are injected as emulsions into the bloodstream. The performance of such products depends on their microstructure, which is determined by its formulation and how its constituents are mixed together; therefore the microstructure depends on the properties of the dispersed phases, the emulsifier used, the equipment used and its processing conditions.

Emulsified products are seldom mono-dispersed due to the complex drop breakup mechanism in the turbulent fields inside the equipment in which the phases are forced together. The chaotic breakup mechanism of highly viscous dispersed phases yield complex and broad drop size distributions (DSD) as a result of the dominating viscous cohesive stresses inside the parent drop. Former studies have used the Sauter mean diameter and/or the size of the largest drop as the characteristic measure of central tendency of the DSD to correlate their results and to prove mechanistic or phenomenological models; however these parameters in isolation are insufficient to characterise the whole DSD of highly polydisperse emulsions.

In this dissertation a vast amount of silicon oils of different viscosity were used as dispersed phase to study the effect of various processing conditions and formulations on the resulting DSD. The effect of several formulation and processing parameters were studied for two different mixing devices: stirred vessels and in-line high-shear mixers. (1) For stirred vessels, the effect of stirring speed, continuous phase viscosity and dispersed phase volume fraction were studied in combination with the viscosity of the dispersed phase for steady-state systems. (2) For in-line high-shear mixers a model that links batch and multi-pass continuous emulsification for multimodal DSD was derived from a transient mass balance. Processing parameters such as time and volume, flow rate and number of passes through the mixer, and stirring speed were studied for a wide dispersed phase viscosity range.

The analytical methodology implemented included the use of one or more probability density functions to describe the shape of the DSD. The models proposed gave reasonable approximations of the Sauter mean diameter and allowed to study the drop size changes and the relative amount of different types of drops resulting from different breakup mechanisms.
Declaration

I declare that no portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Sergio Carrillo De Hert
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Dedication

To the memory of my beloved grandfather, Jozef De Hert, and beloved grandmother, Irene Lemeire, who always fostered my academic formation and seeded my scientific curiosity at the very early stages of my life.
Acknowledgements

I am specially thankful to Dr. Thomas L. Rodgers for his supervision and advice throughout the development of this thesis. I will always be grateful for the freedom he granted me and for his prompt feedback whenever it was needed.

I would also like to acknowledge my parents for their infinite support and encouragement throughout the different stages of my studies that led me to pursue a PhD.

I would also like to express my gratitude to the wonderful people I met in SCEAS, it was thanks to them that these last years have been enjoyable. Among these people special gratitude goes to: Mayri de Rienzo, Rafael Lopez, Pablo Lopez, Linda Trihn, Ren Zhen, Angelina Frankowski and Fernando Guzman.

Last, but not least I wish to thank the Mexican Council of Science and Technology (CONACyT) for their financial support.
The Author

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In 2012 the European Union granted him a Erasmus Mundus Scholarship to enrol in the European Masters in Engineering Rheology (EURHEO) program. Throughout his two year Masters program Sergio studied in the Katholieke University of Leuven (KU Leuven) in Belgium, the University of Minho in Portugal and the University of Ljubljana. The ante penultimate granted him the degree of MSc. in Chemical Engineering (cum laude) and the ultimate granted him the degree of MSc. in Mechanical Engineering.

In 2014, Sergio entered the Ph.D. program at The University of Manchester to research under the advisor-ship of Dr. Thomas Rodgers. This thesis is the results of his time spent at the School of Chemical Engineering and Analytical Science.
Chapter 1

Introduction

Contents

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1.1 Introduction

Emulsions are mixtures of two immiscible fluids, in which one of the liquids is suspended in the form of drops in the second liquid which constitutes the continuous phase. Many industrial products such as food (Harrison and Cunningham, 1985; Wendin et al., 1997; Depree and Savage, 2001), cosmetics, detergents, adhesives, coatings (Leal-Calderon et al., 2007), pharmaceuticals (Jansen et al., 2005; Wadhwa et al., 2012; Pacek, 2015), agrochemicals and paints are emulsions.

Some examples of their uses are,

- In the pharmaceutical industry, up to 40% of new active ingredients are insoluble in water (Wadhwa et al., 2012), many of which are dosed as emulsions. For example, water-in-oil-emulsions are the most effective mean for vaccination (Jansen et al., 2005).

- For coating because these are capable of transporting oils in an aqueous continuous phase; organic insoluble materials can be transported as drops in water instead of using organic hazardous solvents. (Leal-Calderon et al., 2007).

- Bitumen can be applied to roads by preheating it at $150^\circ C$ or it can be emulsified and applied at ambient temperature (Redelius and Walter, 2006; Leal-Calderon et al., 2007).

- As reactive medium in processes such as emulsion polymerization (Holmberg, 2006).

Properties of emulsified systems, such as stability and rheology, depend on parameters such as temperature and composition but also on their drop size and drop size distribution distribution (DSD). Figure 1.1 shows the images taken (using microscopy) of two emulsions of Silicon Oil in water. At the right their respective DSD represented as an histogram by volume is shown. This Figure shows that emulsions with the same constituents can have very different micro-structure; these two emulsions differ in concentration, mean drop size and in polydispersity.

Generally speaking, an emulsion becomes more viscous as the viscosity of both phases increase, the dispersed phase volume fraction increases and its mean drop
size and its polydispersity decrease (Otsubo and Pudhomme, 1994; Larson, 1999; Derkach, 2009).

For example, in the food industry the DSD is important for the texture of foods dispersions as it determines smoothness and creaminess (Wendin et al., 1997; Depree and Savage, 2001), stability (Harrison and Cunningham, 1985; Wendin et al., 1997; Depree and Savage, 2001) and appearance (Harrison and Cunningham, 1985).

Emulsification is the process in which one immiscible fluid is dispersed and interface in-between both liquids is created. The drop size and the DSD are affected by the type of equipment used and their processing conditions. In practice, no large-scale equipment is capable of producing drops of a single size, thereby knowledge about the whole distribution is required for a full characterisation of these systems. During emulsification, the final morphology of the emulsion is the result of two phenomena,
drop breakup and drop coalescence. Therefore it is of uttermost importance to have a clear understanding of these two phenomena to create models which can aid industry improve product quality and reduce time to market. In dilute emulsions and specially with high concentrations of surfactants, coalescence can be neglected and the final morphology is depends only on drop breakage.

Numerous attempt to have a theoretical description of drop breakup have been made since the classical study by Taylor (1932) for drop breakup in laminar flows. However if small drop sizes are desired, larger amounts of power are required which makes the flow turbulent; this is the case in many applications were industrial equipment such as stirred vessels or high-shear mixers are used. Figure 1.2 shows some of the maximum drop size $d_{\text{max}}$ that can be obtained in different emulsification equipment as a function of the localized power.

Figure 1.2: Maximum drop size attained for different devices as a function of the localized energy. Adapted from (Davies, 1985).

Turbulence is by itself a complex subject of study which has captivated many scientist for over a century. Emulsification even with hindered coalescence is complex, it is affected by a large number of variables such as turbulence intensity, geometry of the device, type of surfactant, rheology of the dispersed and continuous phases, emulsification time and dispersed phase hold-up. It is well-known that drop breakage of very viscous dispersed phases is specially complex, often leading to multiple breakup and producing complex distributions (as the one shown in Fig. 1.1b). The
increase of complexity in the breakup mechanism is depicted in Figure 1.3.

![Figure 1.3](image)

**Figure 1.3:** Breakage of liquid drops of different viscosity in a turbulent field in water for similar turbulent time scales $\tau$. (a) dodecane (viscosity 1.5 mPa.s) for $\tau = 8$ ms and (b) octanol (viscosity 6.5 mPa.s) for $\tau = 10$ ms (Taken from Andersson and Andersson (2006)).

For turbulent systems the first models for drop breakup were proposed by Hinze (1955) and (Shinnar and Church, 1960). These models, often called mechanistic models, are based on stress balances and estimate the steady-state size of the largest surviving droplet in a turbulent field. Mechanistic models have serious limitations in that these are unable to predict emulsification kinetics, the shape nor the broadness of the DSD, do not account for the viscosity of the dispersed phase or dispersed phase hold-up. These models have been extended theoretically and empirically to account for dispersed phase hold-up (Doulah, 1975) and viscosity (Davies, 1985; Calabrese et al., 1986), but no serious systematic study has been done to characterise the complete DSD. Alternatively to using $d_{\text{max}}$, these models assume that the more useful Sauter mean diameter $\bar{d}_{32}$ is proportional to $d_{\text{max}}$. The $\bar{d}_{32}$ can be obtained with the equation below

$$
\bar{d}_{32} = \frac{\sum f_n(d_i)d_i^3}{\sum f_n(d_i)d_i^2}
$$

(1.1)
where \( d_i \) is the diameter of the \( i \)th droplet class and \( f_n(d_i) \) its frequency by number.

The Sauter mean diameter is particularly useful as it allows to calculate the available interfacial area \( a_v \) with the following simple equation

\[
a_v = \frac{6\phi}{d_{32}}
\]  

(1.2)

where \( \phi \) is the volume fraction of the dispersed phase. Unsurprisingly two DSD with the same \( d_{max} \) and/or \( d_{32} \) can have very different DSD. Figure 1.4a shows two DSDs with the same \( d_{32} \) and, Figure 1.4b shows four DSDs with the same \( d_{32} \) and 95th percentile \( D_{95} \) (often considered to be equivalent to \( d_{max} \)).

\[\text{Figure 1.4: Distributions (a) with } d_{32} = 4.84\mu m \text{ and, (b) } d_{32} = 4.84\mu m \text{ and } D_{95} = 66.9\mu m.\]

Another approach, which has gained popularity in the last 40 years (since the publication by Coulaloglou and Tavlarides (1977)) has been the use of Population Balance Equations. These models intend to explain drop breakup and coalescence on a phenomenological basis and do provide information the DSD and emulsification kinetics. However single drop experiments have shown that these models are based on unrealistic (Maaß and Kraume, 2012), over-simplistic assumptions (Leng and Calabrese, 2003); solving these models is arduous (involving integrodifferential equations)(Leng and Calabrese, 2003) and are not adequate for viscous dispersed phases (Solsvik et al., 2015) nor for scale-up (Leng and Calabrese, 2003).
1.2 Objectives

The main objective of this dissertation is to create models that can predict the entire DSD. As summarized in the previous Section, the DSD become more complex as the viscosity of the dispersed phase is increased, therefore the focus in this research will be on highly viscous dispersed fluids.

The mechanically stirred devices investigated in this project were the stirred vessel and the in-line high-shear mixer. The latter are continuously fed, and are placed in the pipework. They can be operated in a continuous or recycle arrangement depending if their outflow is connected to its feeding vessel or not. There are a large amount of variables that can be investigated in mechanically stirred devices and it would result impossible to study the effect of the dispersed phase viscosity on all of them throughout a Ph.D.

This dissertation is limited to the effect of viscosity on the DSD in stirred vessels and high-shear mixers, in combination with the variables listed below for each device

1. Stirred vessel
   (a) stirring speed
   (b) continuous phase viscosity
   (c) dispersed phase volume fraction

2. In-line high-shear mixers, continuous arrangement
   (a) stirring speed
   (b) flow rate feeding the mixer
   (c) number of passes through the rotor-stator

3. In-line high-shear mixers, recycle arrangement
   (a) stirring speed
   (b) flow rate feeding the mixer
   (c) volume of the feeding vessel
(d) emulsification time

The objective of this dissertation is to study how each of these variables affect the DSD of highly viscous dispersed phases.

1.3 Outline

1.3.1 Generalities

This thesis is divided in four parts:

1. **Part I** contains two chapters. Chapter 2 provides the necessary literature review and Chapter 3 elaborates on the experimental equipment and methods used which could not be thoroughly covered in the subsequent parts.

2. **Part II** contains three chapters (Chapters 4-6) in which the objectives postulated in the previous section concerning stirred vessels are addressed.

3. **Part III** encompasses Chapters 7 to 9. These part deals with the objectives presented in the previous section for in-line high-shear mixers.

4. **Part IV** was split into two chapters. General conclusions for Part II and Part III, as well as of the whole thesis are given in Chapter 10. Chapter 11 gives recommendations for future work.

Parts II and III constitute the core of the thesis and are written in journal submission format. Therefore, each of the chapters that integrate these two parts have their own introduction, literature review, methodology, results and analysis and conclusions; and can be understood separately. However, a prelude to each of these two parts was included to ease the link in-between the chapters and provide cohesion throughout this dissertation.

Each Chapter contains its own list of references and appendices. The nomenclature was kept consistent throughout this dissertation. Note that the published or submitted papers may have a different nomenclature due to journal requirements. The counter of the fitting constants (ex. $C_i$) resets for each Chapter to avoid long subindex-values.
1.3.2 Chapter description

1.3.2.1 Part I

Chapter 2 offers the relevant literature review which was necessary for Chapter 4 to 9. To understand emulsification, knowledge of the cohesive and disruptive stresses causing drop breakage is required. The cohesive forces are interfacial and viscous forces while the disruptive stresses are unknown a priori, but are likely to be related to the kinetic energy of the turbulent fluctuations. Therefore a review of the basics of interfacial phenomena, rheology and turbulence were required.

This Chapter also includes a review of two of the main approaches used to predict drop sizes: (1) mechanistic or energy balance models and (2) population balance models. The results obtained in this dissertation were mainly compared to the mechanistic models, however the population balance models due to their phenomenological nature also provide useful insights.

Lastly, a review on DSD and on drop size statistics was included.

Chapter 3 elaborates the “Materials, Equipment and Methods” sections of Chapters 4 to 9 which could not be included in the papers.

1.3.2.2 Part II

Chapter 4 has been submitted to AIChE Journal on the 3rd of August, 2017 under the name “On the steady state drop size distribution in stirred vessels. Part I: effect of dispersed phase viscosity” by Sergio Carrillo De Hert and Thomas L. Rodgers.

For this paper we emulsified a wide range of silicon oils with viscosities ranging across 6 orders of magnitude using a stirred vessel using a 6-blade pitched impeller at 5 different speeds. The silicon oils were dispersed for 24 hours, in the presence of surfactant well-above their critical micellar concentration and the concentration of the silicon oils was 1% to discard coalescence or changes in the bulk rheology of the emulsion. Many of the obtained drop size distributions were bimodal; empirical
models were obtained to estimate their maximum drop size, their polydispersity and their drop size distribution. The results were compared with the literature.

Level of contribution to the paper: planning and execution, data acquisition\(^1\), analysis and writing the paper.

Chapter 5 has been submitted to *AIChE Journal* on the 3rd of August, 2017 under the name “On the steady state drop size distribution in stirred vessels. Part II: effect of continuous phase viscosity” by Sergio Carrillo De Hert and Thomas L. Rodgers.

In this study we used the same wide range of silicon oils as in Chapter 4 keeping most conditions constant except for the continuous phase. Three different glucose aqueous solutions were tested as continuous phases. The results were in conflict with the models reported in literature, this paper offers a possible explanation for this conflict. The empirical model obtained in Chapter 4 was extended to account for the viscosity of the continuous phase.

Level of contribution to the paper: planning and execution, data acquisition, analysis and writing the paper.

Chapter 6 is ready for submission to *AIChE Journal*. The authors of this paper have agreed to wait until Parts I and II have been accepted for publication before submitting this Chapter. It will be submitted under the name “On the steady state drop size distribution in stirred vessels. Part III: effect of the dispersed phase volume fraction” by Sergio Carrillo De Hert and Thomas L. Rodgers.

Chapters 4 and 5 were further extended to account for the dispersed phase volume fraction. For this investigation, we emulsified silicon oils with viscosities across four order of magnitude using the same surfactant concentration used in Chapter 4. The steady-state drop size distribution was studied for volume fractions in the 1.0%-80% range. A model to account to predict the maximum drop, polydispersity and drop size distribution were presented. Results were compared with published literature.

\(^1\)extensional rheometry were performed by Dr. Mihaela Turcanu at Fresenius Kabi Deutschland GmbH
Level of contribution to the paper: planning and execution, data acquisition, analysis and writing the paper.

1.3.2.3 Part III

Chapter 7 has been published, its citation is:


For this investigation silicon oils with viscosities across four orders of magnitude were emulsified using an in-line high-shear mixer in a continuous arrangement. The most viscous oils produced bimodal drop size distribution. A correlation to predict the drop sizes (both types of observed drops) and drop size distribution that accounts for dispersed phase viscosity, number of passes, flow rate and stirring speed was postulated.

Level of contribution to the paper: planning and execution, data acquisition, analysis and writing the paper.

Chapter 8 has also been published, its citation is:


This paper has been recognised as a world-leading publication by *In Abstract*, which is a journal published by The University of Manchester that selects outstanding research produced by its Faculty of Science and Engineering. This paper compares the emulsification performance for three different arrangements using the same high-shear mixer’s rotor and screen. The model is based on a transient mass balance which allows to calculate the drop sizes and depletion of an original coarse emulsion.

Level of contribution to the paper: planning and execution, data acquisition\(^2\), analysis and writing the paper.

\(^2\)power draw measurements performed by Dr. Linda Trinh at The University of Manchester.
Chapter 9 has been submitted to *Chemical Engineering Research and Design* for the special issue that will be published for the “9th International Symposium on Mixing in Industrial Processes”. The submission date was on the 4th of October, 2017 under the name “Linking continuous and recycle emulsification kinetics for in-line mixers” by Sergio Carrillo De Hert and Thomas L. Rodgers.

This investigation extends the studies done in Chapters 8 and 9. The model developed allows calculation of the drop size distribution of highly viscous oils which produce bimodal distributions using high-shear mixer in recycle configuration.

*Level of contribution to the paper:* planning and execution, data acquisition and writing. Planning and analysis split in-between the two authors.

1.3.2.4 Part IV

Chapter 10 gives overall conclusions for Parts II and III and of the whole thesis.

Chapter 11 gives recommendations for future research.

1.4 Bibliography


Part I

Literature and methods
Chapter 2

Literature review

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2.1 Emulsions: basic principles

The most common types of emulsions consist of a non-polar or oily constituent and a polar or aqueous one, nevertheless different non-polar phases can also be immiscible (i.e. polymer blends such as polyethylene and polypropylene (Gonzalez-Nunez et al., 1993)).

Emulsified systems containing emulsifiers can be divided in two types depending on their size and stability: macro and microemulsions. The focus of this dissertation is on macroemulsion.

- Macroemulsions are only kinetically stabilised and their formation is not spontaneous, therefore energy must be added to create these type of systems. The droplets dispersed in macroemulsions are typically in the 0.1\mu m to 10\mu m size range. These type of emulsions scatter light and have a “milky appearance” (Butt et al., 2006).

- Microemulsions have droplets in the 2 nm to 50 nm size range, making the size of the emulsifiers not negligible and transparent. Microemulsions have a high concentration of stabilizing agents, are thermodynamically stable and form spontaneously (Butt et al., 2006). Droplet formation in microemulsions is thermodynamically favourable due to the strong adsorption of the emulsifiers. In other words, the desorption of the emulsifiers is less favourable energetically (Butt et al., 2006; Tadros, 2009).

Emulsion can also be classified depending on which constituent is dispersed and which one is the continuous phase (see Fig. 2.1); the most common types of emulsions are the water-in-oil (W/O emulsions) and the oil-in-water emulsions (O/W emulsions); nevertheless double emulsions as the ones shown in Figures 2.1c and 2.1d may be encountered (Schramm, 2014).

The volume fraction of the dispersed phase, the type of emulsifier used (Butt et al., 2006) and the viscosity of each of the phases are important parameter that determines which is the continuous and dispersed phase (Gonzalez-Nunez et al., 1993).
Figure 2.1: Some types of emulsions. (a) Oil-in-water (b) water-in-oil (c) water-in-oil-in-water (d) oil-in-water-in-oil.

Generally speaking, the material with the largest volume fraction tends to be the continuous phase, however volume fractions of $\phi > 0.99$ have been achieved, these emulsions are called “high internal phase emulsions” (Butt et al., 2006).

The nature of the surfactant plays an important role in which of the components will be the continuous phase. Two principles to determine which component is preferred as continuous phase are (Butt et al., 2006):

- Bancroft’s rule of thumb states that the continuous phase will be the one where the surfactant is more soluble.
- The hydrophile-lipophile scale (HLB) (See Table 2.1).

The viscosity ratio of both phases also plays a role on which of the constituents will be the continuous phase. In general, the least viscous components tends to be the continuous phase (Selker and Sleicher, 1965; Gonzalez-Nunez et al., 1993; Hu et al., 2005).

For stirred vessels, Hu et al. (2005) proposed a two-region model. According to their model droplet breakup occurs in the vicinity of the impeller and coalescence away from it. Their model assumes that phase inversion occurs when the coalescence rate out-paces the breakup frequency. The dispersed volume fraction of highly viscous phases is higher than for low viscous ones because coalescence probability decreases with increasing the viscosity of the dispersed phase (Yeo et al., 2002; Hu et al., 2005).
There are several processes that destabilise macroemulsions, these mechanisms happen simultaneously and the analysis of such systems is complicated because droplet size distributions (DSD) are seldom monodisperse (Tadros, 2009). Different mechanisms are shown in Figure 2.2, while a short explanation of each mechanism is described below:

1. Creaming and Sedimentation due to gravitational or centrifugal forces. When droplets are not small enough for the Brownian motion to balance the gravitational forces (sedimentation or buoyancy depending on the densities of the phases).

2. Disproportionation or Ostwald Ripening due to a difference of the finite solubility in polydisperse systems. Molecules will diffuse from small to large droplets until the first ones disappear.

3. Aggregation processes
(a) Coalescence is the fusion of two or more droplets to form larger ones by the thinning and disruption of the liquid film between the droplets (Leal-Calderon et al., 2007; Tadros, 2009).

(b) Flocculation happens in the second minimum of the Derjaguin and Landau, Verwey and Overbeek theory (known as DLVO theory). In this mechanisms, droplets aggregate but do not change size due to the Van der Waals attraction between droplets.

4. Phase inversion is the process in which the dispersed component becomes the continuous phase and is mainly affected by the volume fraction. At volume fractions close to phase inversion, there is a microstructure called co-continuous phase, in which both of the constituents are continuous (Gonzalez-Nunez et al., 1993). As mentioned above, phase inversion does not necessarily happen at $\phi = 0.5$.

### 2.2 Interfacial phenomena and surfactants

#### 2.2.1 Interfacial phenomena

Molecules experience different interactions depending if they are in the bulk or at an interface. It is energetically unfavourable for molecules to be at the interface. The energy required to bring molecules from the bulk of a fluid to the interface is known as the surface tension $\sigma$ or interfacial tension; the term surface tension normally refers to an interface in contact with a air.

Thermodynamically, the interfacial tension can be expressed in terms of the change of the Gibbs free energy $G$ related to the change of the area $A$ of the interface for a flat interface at constant temperature $T$ and pressure $P$ as (Butt et al., 2006):

$$\sigma \equiv \left. \frac{\partial G}{\partial A} \right|_{P,T}$$

(2.1)

The dispersion of two immiscible liquids is thermodynamically unfavourable since the emulsification process increases the interfacial area. Emulsions can be kinetically
stable but the phases will tend to separate (Butt et al., 2006; Tadros, 2009).

In the absence of flow, spheres are the most stable shape for emulsified droplets (or any dispersion such as bubbles) because they have the lowest area per volume ratio. Nevertheless this curvature creates a pressure difference in-between the two phases. The pressure difference $\Delta P$ between two curved phases, known as capillary or Laplace pressure, was first derived by Young in 1805 and by Laplace in 1806 (Butt et al., 2006):

$$\Delta P = \sigma \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$$  \hspace{1cm} (2.2)

Where the term $(r_1^{-1} + r_2^{-1})$ is the mean curvature; $r_1$ and $r_2$ are two perpendicular radius of curvature and are positive if these are curved towards the liquid. For a spherical droplet or bubble (in the absence of any external force) $r_1$ and $r_2$ are equal, for a drop of diameter $d$ Equation (2.2) becomes:

$$\Delta P = \frac{4\sigma}{d}$$  \hspace{1cm} (2.3)

This equation states us that the pressure inside the dispersed fluid is higher than the pressure in the continuous one.

### 2.2.2 Surfactants

Surfactants or “surface active agents” are molecules with a hydrophilic (polar) and an hydrophobic part (non-polar) that reduce the interfacial tension when adsorbed to an interface. The molecular structure of decilsulphate and the common representation of a surfactant featuring the hydrophilic head and hydrophobic tail is shown in Figure 2.3.

Surfactants adsorb and orient at interfaces, each part of the molecule stays where it is most soluble. The adsorption is dynamic, which means that surfactant molecules leave and enter the interface (Butt et al., 2006).
2.2.2.1 Classification

The most conventional surfactants can be classified into four groups depending on their structure (Butt et al., 2006):

1. Anionic surfactants have a negative charge at the end of their molecule and releases a cation.

2. Cationic surfactants have a positive charge as hydrophilic head and release an anion.

3. Nonionic surfactants have a polar hydrophilic head but do not dissociate into ions.

4. Amphoteric surfactants contain a positive and a negative charge in their molecular structure.

Griffin (1949) suggested a scale called “hydrophile-lipophile balance” (HLB) to determine the degree of hydrophobicity of a surfactant. The scale he proposed runs between 3 and 20. Surfactants with low HLB values prefer the oily phase and thus form water-in-oil emulsions, the contrary is true for high HLB values. Table 2.1 shows the behaviour and application of surfactants according to their HLB value.

2.2.2.2 Concentration

A typical behaviour of $\sigma$ on the surfactant concentration $C_s$ is depicted in Figure 2.4. The data point were digitalised from the work of Sainath and Ghosh (2014).
Table 2.1: Behaviour in water and application of surfactants according to the HLB value (from (Adamson, 1990)).

<table>
<thead>
<tr>
<th>HLB</th>
<th>Behaviour in water</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-2</td>
<td>No dispersibility in water</td>
<td></td>
</tr>
<tr>
<td>4-6</td>
<td>Poor dispersibility</td>
<td>W/O emulsifier</td>
</tr>
<tr>
<td>8-10</td>
<td>Milky dispersion</td>
<td>Wetting agent</td>
</tr>
<tr>
<td>12-18</td>
<td>Translucent to clear solution</td>
<td>O/W emulsifier</td>
</tr>
</tbody>
</table>

who investigated the effect of the concentration of sodium dodecyl sulphate in a water-silicon oil interface.

Figure 2.4: Interfacial tension $\sigma$ of water/silicon oil interface as a function of the surfactant concentration $C_s$, the surfactant used was sodium dodecyl sulphate. Modified from (Sainath and Ghosh, 2014).

For a given solute, the Gibbs adsorption isotherm establishes the relationship between the change of $\sigma$ and the concentration of adsorbed solute per unit area (slope in Fig. 2.4), also known as the surface excess $\Gamma$. For a dilute binary solution the Gibbs adsorption isotherm is (Butt et al., 2006)

$$\Gamma = -\frac{1}{RT} \frac{\partial \sigma}{\partial \ln C_s}$$

(2.4)

where $C_s$ is the solute concentration, $T$ is the temperature and $R$ is the universal constant of gases.

This equation allows to calculate $\Gamma$ from the slope the $\sigma$ vs $\ln C_s$ curve; the slope
of the fit corresponds to $-RT\Gamma$.

If $\Gamma > 0$, the solute tends to migrate to the interface and $\sigma$ decreases with the addition of solute. This is the case for surfactants and other emulsifiers (Butt et al., 2006; Tadros, 2009). On the other hand, if $\Gamma < 0$, the concentration of the solute is lower at the interface than in the bulk of the fluid. This behavior is observed in substances that do not like adsorbing at interfaces; ions are an example. The addition of substances with negative $\Gamma$ increase the surface tension upon increasing their concentration; “hard water” is an example of ions increasing the surface tension.

As shown in Figure 2.4 if the concentration of surfactant is further increased the surface tension remains almost constant, this is known as the Critical Micelle Concentration (CMC).

For concentrations below the CMC, the surfactants migrate to the interface due to their low solubility in the bulk of the fluid; however for concentrations above the CMC, surfactants aggregate and start forming soluble structures in the bulk of the fluid. Some of these structures are represented in the schematic ternary-phase diagram (Fig. 2.5). As shown this figure, surfactants can arrange in well-defined structures such as spheres (micelles), cylinders, lamellas or hexagons (Butt et al., 2006).

### 2.2.3 Interfacial tension measurement

There are several experimental methods available to measure the surface and interfacial tension. Some of these methods are shown in Table 2.2.

The most common methods used for emulsions are the Wilhelmy plate, the du Nuoy ring and the sessile and pendant drop methods (Schramm, 2014). Static tests refer to the equilibrium $\sigma$, while dynamic refer to tests which measure the interfacial tension while this is changing; the time to reach steady state depends on the diffusion and adsorption rates. In this dissertation our focus is on static interfacial properties.

The equipment available was a tensiometer with a Wilhelmy and a du Nuoy measuring probes, reason why only the measuring principles of these two methods will be reviewed.
2.2. Interfacial phenomena and surfactants

**Figure 2.5:** Schematic representation of a surfactant ternary phase diagram. Adapted from (Liu et al., 1996; Eremin, 2011)

### 2.2.3.1 du Noüy ring

The du Noüy tensiometer (du Noüy, 1919), also known as ring tensiometer is shown in Figure 2.6. In this method the force necessary to detach or push a platinum ring from/to the interface is recorded. The force $F$ is measured using a balance or torsion wire. For a wire of radius $r_w$ (Schramm, 2014):

$$
\beta F = 4\pi r_r \sigma \cos(\alpha)
$$

Where $\beta$ is a correction factor to account for the complex shape of the interface before detachment and $\alpha$ is the contact angle between the wire and the lower phase (when the ring is pulled-up).

One of the most correction methods is the one of Harkins and Jordan (1930). In this method $\beta$ is a function of two parameters:

1. the ratio of the radius of the ring $r_r$ to the radius of the wire $r_w$

2. the cube of the radius of the ring to the volume of liquid upheld. This last one is equal to the maximum pull on the ring divided by the density difference
Table 2.2: Classification of surface and interfacial tension methods (from Schramm (2014)).

<table>
<thead>
<tr>
<th>Method</th>
<th>Static</th>
<th>Dynamic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capillary rise</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>Wilhelmy plate</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>du No&quot;uy ring</td>
<td>Good</td>
<td>N/A</td>
</tr>
<tr>
<td>Drop weight</td>
<td>Good</td>
<td>N/A</td>
</tr>
<tr>
<td>Drop volume</td>
<td>Good</td>
<td>N/A</td>
</tr>
<tr>
<td>Pendant drop</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Sessile drop</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Oscillating jet</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td>Spinning drop</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>Maximum bubble pressure</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>Maximum droplet pressure</td>
<td>Good</td>
<td>Poor</td>
</tr>
</tbody>
</table>

Figure 2.6: Schematic representation of the No"uy ring tensiometer

of the phases. Figure 2.7 shows the pull in dynes as a function of the lamella height. The maximum pull is the force at the critical point, just before the lamella breaks.

Huh and Mason (1975) tabulated the $\beta$ for a wide number of parameters.

To obtain $\sigma$ the contact angle $\alpha$ needs to be equal to zero. To achieve that, the diameter of the ring has to be considerable larger than the diameter of the wire ($r_r \gg r_w$), the ring has to be parallel to the interface, the wire has to be extremely clean and made of a material of high surface energy, such as platinum (Butt et al., 2006; Schramm, 2014). This is why normally a platinum wire is used and annealed
with direct flame. Equation 2.5 thus becomes \((\cos(0) = 1)\):

\[
\sigma = \frac{\beta F}{4\pi r_r}
\]  

(2.6)

### 2.2.3.2 Wilhelmy plate

In this method, a thin plate of a material such as platinum, glass or paper (Butt et al., 2006) is placed at the interface vertically as shown in Figure 2.8. The force \(F\) that prevents the plate from being drawn into the liquid equals:

\[
F = 2l_W \sigma \cos(\alpha)
\]  

(2.7)

Where \(l_W\) is the length of the Wilhelmy plate and \(\alpha\) is the contact angle between the plate and the liquid. This method does not need any correction factors. To have an \(\alpha \approx 0^\circ\) the measuring plates are roughened and these must be clean (Weser and Rauch, 2012). The surface tension can be determined by:

\[
\sigma = \frac{F}{2l_W}
\]  

(2.8)
2.3 Rheology

Sir Isaac Newton performed a series of experiments that consisted in putting an incompressible fluid in-between two plates and measuring the force needed to slide one of the plates at various speeds. Figure 2.9 shows a schematic representation of these type of experiments. For two plates of a given area $A$, separated by a gap distance $h$ a constant force $F$ is required to maintain motion of the upper plate at a velocity $U$, therefore

$$\frac{F}{A} \propto \frac{U}{h} \quad (2.9)$$

The proportionality constant for the former equation is called viscosity $\mu$; for the axis of reference shown in Figure 2.9, $F/A$ is the shear stress $\tau_{ij}$, and $U/h$ can be re-written as $-\partial u_i / \partial x_j$ yielding

$$\tau_{ij} = -\mu \frac{\partial u_i}{\partial x_j} \quad (2.10)$$
However deformation and flow of different materials is very diverse. In classic fluid mechanics ideal liquids also know as Newtonian fluids are considered. An ideal liquid has the following characteristics (Macosko, 1994):

- Its shear viscosity $\mu$ is constant
- It has no time effects
- No normal stresses in shear flow
- The extensional $\eta_{ext}$ and shear viscosity $\eta$ follow the so-called "Trouton ratio" ($\eta_{ext}/\eta = 3$). This will be explained later in this Section.

In rheology $\eta$ is the general term for viscosity and $\mu$ is the commonly used term for viscosity of Newtonian fluids. The complete Newtonian constitutive equation for compressible fluids is (Morrison, 2001)

$$\tau_{ij} = -\mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) + \left( \frac{2}{3} \mu - \kappa \right) \left( \frac{\partial u_i}{\partial x_i} \right) I$$  \hspace{1cm} (2.11)

Where $\tau_{ij}$ is the stress tensor, $u_i$ is the velocity vector in the $i$ direction, $\kappa$ is the dilatational viscosity and $I$ stands for the identity tensor. For an incompressible fluid the continuity equation states that $\partial u_i/\partial x_i = 0$. The former equation can be rewritten in terms of the rate-of-strain tensor $\dot{\gamma}_{ij} = (\partial u_i/\partial x_j + \partial u_j/\partial x_i)$ (Morrison, 2001)

$$\tau_{ij} = -\mu \dot{\gamma}_{ij} = -\mu \left( \frac{\partial u_1}{\partial x_1} + \frac{\partial u_2}{\partial x_2} + \frac{\partial u_3}{\partial x_3} + \frac{\partial u_4}{\partial x_4} \right)$$

$$\left( \frac{\partial u_1}{\partial x_1} \frac{\partial u_2}{\partial x_2} \frac{\partial u_3}{\partial x_3} \frac{\partial u_4}{\partial x_4} \right)$$  \hspace{1cm} (2.12)

If the stress imposed on a material imposes extensional flow instead of shear flow, a different approach is required due to the nature of the flow field. Figure 2.10 shows that for uniaxial extensions the velocity in the $x_1$ is positive and stretching and the velocity components in the $x_2$ and $x_3$ directions are negative and compressing.
Therefore, the velocity vector \( u_i \) is

\[
\mathbf{u}_i = \begin{pmatrix} u_1 \\ u_2 \\ u_3 \end{pmatrix} = \begin{pmatrix} \dot{\varepsilon} \\ -\frac{1}{2} \dot{\varepsilon} \\ -\frac{1}{2} \dot{\varepsilon} \end{pmatrix}
\]  

(2.13)

where \( \dot{\varepsilon} \) is the extensional strain rate; the extensional strain and extensional strain rate are defined as

Extensional strain
\[
\varepsilon = \frac{L(t) - L_0}{L_0}
\]  

(2.14)

Extensional strain rate
\[
\dot{\varepsilon} = \frac{\partial L(t)}{L(t) \partial t}
\]  

(2.15)

Provided that \( \dot{\gamma}_{ij} = (\partial u_i / \partial x_j + \partial u_j / \partial x_i) \), \( \dot{\gamma}_{ij} \) for uniaxial extension becomes

\[
\dot{\gamma}_{ij} = \begin{pmatrix} 2 \dot{\varepsilon} & 0 & 0 \\ 0 & -\dot{\varepsilon} & 0 \\ 0 & 0 & -\dot{\varepsilon} \end{pmatrix}
\]  

(2.16)

The extensional viscosity \( \mu_{\text{ext}} \) is defined as

\[
\tau_{11} - \tau_{22} = \mu_{\text{ext}} \dot{\varepsilon}
\]  

(2.17)

Using Equation 2.16 and the shear viscosity definition in Equation 2.12, the relationship in-between \( \mu \) and \( \mu_{\text{ext}} \) can be established. For Newtonian liquids,

\[
\tau_{11} - \tau_{22} = \mu [2 \dot{\varepsilon} - (-\dot{\varepsilon})] = 3\mu \dot{\varepsilon}
\]  

(2.18)
From the former equation and Equation 2.17 it can be concluded that

$$\mu_{\text{ext}} = 3\mu$$ \hfill (2.19)

which is known as the Trouton ratio (Morrison, 2001).

Figure 2.11 shows the shear and extensional viscosity of low density polyethylene. This figure shows that at low shear strain rates $\eta_{\text{ext}} = 3\eta$, however, at larger strain rates the extensional viscosity increases while the shear viscosity decreases; this materials are known as strain hardening (Morrison, 2001).

![Figure 2.11](image_url)

**Figure 2.11:** Shear and extensional viscosity of low density polyethylene. Adapted from (Bird et al., 1987).

Other interesting types of elastic liquids are the so-called “Boger fluids”, these materials have shear independent viscosity while being elastic; some examples are dilute polymer solutions (James, 2009).

### 2.3.1 Generalised Newtonian Model (GNM)

Even though Equation 2.12 is very useful, many materials do not exhibit a Newtonian behaviour under shear. This equation has been extended empirically by making $\mu$
stress dependent (denoted by $\eta$).

\begin{align*}
\text{Power-law} & \quad \eta = k\dot{\gamma}^{n-1} & (2.20) \\
\text{Ellis} & \quad \frac{\eta}{\eta_0} = \frac{1}{1 + k\dot{\gamma}^{1-n}} & (2.21) \\
\text{Sisko} & \quad \eta = \eta_{in} + k_1\dot{\gamma}^{n-1} & (2.22) \\
\text{Cross} & \quad \frac{\eta - \eta_{in}}{\eta_0 - \eta_{in}} = \frac{1}{1 + k\dot{\gamma}^{1-n}} & (2.23) \\
\text{Carreau-Yasuda} & \quad \frac{\eta - \eta_{in}}{\eta_0 - \eta_{in}} = \frac{1}{[1 + (k\dot{\gamma})^{1-n/a}]} & (2.24) \\
\text{Bingham} & \quad \eta = \frac{\sigma_y}{\dot{\gamma}} + \eta_p & (2.25) \\
\text{Herschell-Bulkley} & \quad \eta = \frac{\sigma_y}{\dot{\gamma}} + k\dot{\gamma}^{n-1} & (2.26)
\end{align*}

Figure 2.12 shows the behaviour described by the former equations. Equations 2.20-2.24 are commonly used to describe shear thinning or shear thickening materials; and the fitting parameters ranges from two for the Power-law model to five for the Carreau-Yasuda model. In reality many material exhibit a low shear rate Newtonian plateau $\eta_0$ and high shear rate Newtonian plateau $\eta_{in}$ (Macosko, 1994; Larson, 1999; Morrison, 2001) and as shown in Figure 2.12, Equations 2.20-2.24 describe the shear-dependent region and one or both Newtonian plateaus.

Equation 2.25 and 2.26 are typically used to describe plastic behaviour. A plastic materials show little or no deformation below a so-called “yield stress” $\sigma_y$; in other words below the $\sigma_y$ the fluid behaves as a solid. Analogously to the Newton’s law of viscosity presented in Equation 2.12 for a perfect incompressible liquid under shear, Hooke’s expression for a perfect solid under shear is

$$\tau_{12} = G\gamma_{12}$$

(2.27)

Where $G$ is the shear elastic modulus and $\gamma_{12}$ is the strain (displacement in $x_1$ over a thickness in $x_2$). Concentrated suspensions of solid particles (Macosko, 1994) and concentrated emulsion show a yields stresses (Derkach, 2009).

Some of the limitations of this models include (Morrison, 2001)
2.3. Rheology

![Figure 2.12](image)

**Figure 2.12:** Behaviour of hypothetical fluids described by GNF models by Equations 2.20-2.26.

- some models fail to predict the zero-shear region
- it is not clear if these models are useful for non-shearing flows
- these models do not predict normal stresses


- elastic effects are not properly accounted for

### 2.3.2 Rheology of emulsions

The rheological behaviour of emulsions is very complex; for example, the zero-shear viscosity of emulsions blends cannot be described by a mixing rule, shear thinning occurs at relatively low shear rates and normal stresses may be present (Tucker III and Moldenaers, 2002). In this section some of the rheological phenomena and models for steady-shear will be reviewed omitting small droplets subject to Brownian motion and normal forces and when the thickness of the layer of the surfactant is negligible compared to the size of the droplet.

In her review Derkach (2009) summarized the rheological behaviour of emulsions depending on the volume fraction of the dispersed phase $\phi$ in four regions. Figure 2.13a shows a schematic representation of her classification of emulsions depending on their zero shear mechanical behaviour. It is common practice to express results as the relative viscosity $\eta_r$ which is the ratio of the viscosity of the emulsion $\eta_e$ and the continuous phase $\eta_c$. This figure shows the exponential dependency of the relative zero-shear viscosity on the volume fraction with $\phi_m$ as asymptote; beyond $\phi_m$ the emulsion behaves as a solid (for $\dot{\gamma} = 0$) giving birth to yield stresses, the regions given by Derkach (2009) are explained below

- Region I is the domain of the dilute emulsion where the viscosity is constant
- Region II is the domain of intermediate concentrations where a weakly non-Newtonian behaviour is observed
- Region III is the domain of relative high concentrations where no-Newtonian effects are strong, viscoelastic effect, yield stress and thixiotropy are possible. Droplet size become important.
- Region IV is the domain of “compressed emulsions”. The droplet concentration exceeds the maximum packing fraction $\phi_m$ of spherical particles. In this regime emulsions are viscoplastic materials and yield stresses are important.
2.3. Rheology

2.3.2.1 Dilute emulsions

The rheological properties of emulsions are, to certain extent, similar to suspensions; suspensions can be treated as the limiting case of emulsions when the viscosity of dispersed droplets is extremely high (Derkach, 2009).
A model for very dilute non-interacting spherical spheres in a Newtonian liquid was proposed by Einstein (1906). The relative viscosity of the suspension $\eta_r$ (same nomenclature for the relative viscosity of an emulsion is used) is a function of the volume fraction of the dispersed phase $\phi$:

$$\eta_r = 1 + 2.5\phi$$

(2.28)

Taylor (1932) developed the first theory for emulsions assuming that the droplets remained spherical. Analogously to Einstein’s model for suspensions, the viscosity of an emulsion $\eta_e$ rises as the droplet fraction increases $\phi$, regardless of the viscosity of the dispersed phase $\eta_d$

$$\eta_e = 1 + \frac{1 + 2.5p}{1 + p} \phi$$

(2.29)

For very viscous materials Equation 2.29 reduces to Equation 2.28.

Choi and Schowalter (1975) came up with another model for simple shear and low volume fractions (for $\phi < 10\%$ according to Tucker III and Moldenaers (2002))

$$\eta_r = 1 + \phi \frac{5\phi + 2}{2(p + 1)} \left[ 1 + \phi \frac{5(5p + 2)}{4(p + 1)} \right]$$

(2.30)

Oldroyd (1955) developed the most rigorous model (Derkach, 2009) that accounts for the resistance of the interfacial layer, this expression include other terms such as including the 2D surface shear viscosity and the dilatational viscosity.

### 2.3.2.2 Concentrated emulsions

The complexity in analysing concentrated emulsions (or suspensions) is the inputs of mutual influence of neighbour droplets. Rigorous analysis of the equations of motions using a cell model have yielded results as the ones obtained by Yaron and Gal-Or (1972)

$$\eta_r = 1 + \frac{5.5 \left[ 4\phi^{7/3} + 1 - \frac{84}{11} \phi^{2/3} + \frac{4}{p} \left( 1 - \phi^{7/3} \right) \right]}{10 \left( 1 - \phi^{10/3} \right) - 25\phi \left( 1 - \phi^{4/3} \right) + \frac{10}{p} \left( 1 - \phi \right) \left( 1 - \phi^{7/3} \right) \phi}$$

(2.31)
Interestingly, this equation was used by Tcholakova et al. (2011) to characterize their concentrated emulsion obtained with a high-shear mixer.

Phan-Thien and Pham (1997) used a differential scheme of Taylor’s model (Eq. 2.29), their method consisted in assuming that a small volume fraction of droplets is added and that this becomes the effective medium; into this effective medium a new small amount of large sizes than the previously-added droplets is introduced. Their constructive process using Equation 2.29 yielded

\[
\left( \frac{\eta_e}{\eta_c} \right)^{2/5} \left[ \frac{2\eta_e + 5\eta_d}{2(\eta_e + \eta_d)} \right]^{3/5} = (1 - \phi)^{-1} 
\]

Pal (2001) proposed two equations with the maximum packing fraction \( \phi_m \) as fitting parameter.

\[
\eta_e \left( \frac{2\eta_e + 5p}{2 + 5p} \right)^{3/2} = \exp \left( \frac{2.5\phi}{1 - \frac{\phi}{\phi_m}} \right) 
\]

\[
\eta_e \left( \frac{2\eta_e + 5p}{2 + 5p} \right)^{3/2} = \left( 1 - \frac{\phi}{\phi_m} \right)^{-2.5\phi_m} 
\]

For high \( \eta_d \), these equations reduce to two well-known equations in suspension rheology: the Mooney and the Krieger Dougherty equations. The goodness of Equation 2.34 for a large number of experimental data collected by Pal (2001) is shown in Figure 2.14.

Pal (1992) studied the effect of \( p \) and noted that at high \( \phi \) the large differences in \( \eta_c \) arise. This was expected as for very large \( p \) the droplets are less deformable and should give \( \phi_m \) similar to the ones in suspensions (\( \phi_m \approx 0.63 \)) whereas a small \( p \) should yield larger \( \phi_m \) due to the droplet’s deformability. The data for \( \eta_0 \) was fit using \( \phi_m = 0.91 \) whereas values of \( \dot{\gamma} = 100 \text{s}^{-1} \) in the shear-thinning region yielded values above unity, he obtained \( \phi_m = 1.18 \) for \( \dot{\gamma} = 100 \text{s}^{-1} \). Meaning that the equations he proposed are methods for fitting the experimental data and lack physical meaning (Larson, 1999).
Chapter 2. Literature review

2.3.2.3 Compressed emulsions

If the surfactant is chosen adequately emulsions can reach $\phi$ beyond $\phi_m$ and remain stable without phase inversion. In this regime droplets deform and the continuous phase will be confined to thin films (Larson, 1999). The emulsions become visco-elastic. The model used to describe the rheological behaviour of compressed emulsion is the GNF Herschell-Bulkley (Eq. 2.26) (Welch et al., 2006; Tcholakova et al., 2011). The models presented in this section are some of the most notable attempts to determine how the Sauter mean drop diameter $d_{32}$, $\phi$, $\sigma$ and $\eta_c$ affect $\sigma_y$ and $k_\dot{\gamma}$ in Equation 2.26.

Princen and Kiss (1986) found that $G$ could be approximated by

$$G = 3.54 \frac{\sigma}{d_{32}^{1/3}} (\phi - \phi_0)$$  \hspace{1cm} (2.35)

Where $\phi_0$ is the $\phi$ at which $G$ is zero, which depends on the droplet size distribution. The same authors latter found expressions for the $\sigma$ and $\eta_c$ (Princen and Kiss, 1989)

$$\sigma_y = 2\frac{\sigma}{d_{32}^{1/3}} [-0.080 - 0.114 \log (1 - \phi)]$$  \hspace{1cm} (2.36)

$$k_\dot{\gamma}^n = \frac{[32 \phi - \phi_0] \eta_c \dot{\gamma}}{C a^{1/2}}$$  \hspace{1cm} (2.37)
The terms in brackets in both equations are empirical functions; \( \text{Ca} \) is the dimensionless Capillary number

\[
\text{Ca} = \frac{\eta_c d^2 \dot{\gamma}}{\sigma}
\]  

(Welch et al. (2006) dispersed 75.3-86 wt.% of silicon oils with nominal kinematic viscosities \( \nu = \frac{\eta}{\rho} \) of 100 cSt and 30 000 cSt in water and tested the models of Princen and Kiss (1989) and Otsubo and Pudhomme (1994). They were not able to characterize their systems presumably because neither of the models account for polydispersity nor for \( \eta_d \).

For high shear-rates, well above \( \sigma_y \), Tcholakova et al. (2008) developed a theoretical model which accounts for dissipative energy in films formed between colliding droplets, their final expression reads

\[
k \dot{\gamma}^n = 1.2 \dot{\gamma}^{\frac{5}{6}} \left( \phi - 0.74 \right)^{\frac{3}{2}} \left( 1 - \phi \right)^{\frac{1}{2}} \text{Ca}^{0.47}
\]  

(2.39)

They validated their results in one of their later investigations (Tcholakova et al., 2011) for oils in the 3 mPa s to 1024 mPa s viscosity range, \( \phi \) up to 0.85 and \( \dot{\gamma} \) up to 1000 s\(^{-1}\).

### 2.3.3 Rheometry

A rheometer is an instrument that measures stress and deformation history on a material for which constitutive material function is unknown. There are several ways to classify rheometers. For example, they can be divided type of stress: shear and extensional rheometers; by type of straining: small, large and steady; or by type of flow field: homogeneous or nonhomogeneous (Macosko, 1994).

In this Section the focus will be on shear rheometers, however some basics on extensional rheometry will be reviewed. Most the materials used in our investigation are Newtonian and extensional properties such as the extensional viscosity \( \mu_{\text{ext}} \) follow the Trouton ratio (Eq. 2.19). Nevertheless concentrated emulsions exhibit different extensional rheological features (Wagner and Mewis, 2011). However, we found no study on the effect of \( \mu_{\text{ext}} \) in mechanically stirred devices.
Table 2.3: Advantages and disadvantages of the most common drag-flow measuring geometries (Macosko, 1994).

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sliding plates</td>
<td>simple design, homogeneous flow, linear motion, for high viscosities</td>
<td>edge limits, gap control, difficult to load</td>
</tr>
<tr>
<td>Concentric cylinders</td>
<td>for low viscosities, high shear rates, homogeneous flow if gap is big enough, good for settling materials</td>
<td>requires end correction, difficult to clean, measurement of normal stresses is impractical</td>
</tr>
<tr>
<td>Cone and plate</td>
<td>homogeneous flow if angle gap is smaller than 0.1 rad, best for normal stresses, best for shear moduli</td>
<td>high viscosities leads to edge fracture at low shear rates, inertia effects, sample evaporation, needs good alignment</td>
</tr>
<tr>
<td>Parallel disk</td>
<td>easy to load viscous samples, Vary shear rates by changing the gap size and speed, best for oscillatory rheometry, can measure normal stress differences</td>
<td>edge fracture, non-homogeneous flow. Ok for steady state measurements, sample evaporation</td>
</tr>
</tbody>
</table>

2.3.3.1 Shear rheometers

Shear rheometers can be classified in drag flow and pressure-driven flow rheometers. Some examples of drag flow rheometers are: sliding plates, concentric cylinders, cone and plate and parallel disks. Whereas some examples of pressure-driven rheometers are capillary, slit flow and axial annulus flow (Macosko, 1994).

The rheometers used for this investigation where drag flow rheometers. The advantages and disadvantages of these are listed in Table 2.3.

The concentric cylinder, parallel disc, and cone and plate geometries are known as rotational rheometers and are extremely popular. The governing equations for these rheometers can be consulted in Table 2.4, where $M$ is the torque and $\Omega$ is
the angular velocity. In Figure 2.15 the schematic representation of the geometries and their dimension variables for the three geometries are shown. The derivation of the equations of motion and boundary conditions can be found elsewhere (Macosko, 1994; Larson, 1999; Morrison, 2001).

Table 2.4: Expressions for Steady Shear Rheological Quantities for the most common types of rotational rheometers (from (Morrison, 2001)).

<table>
<thead>
<tr>
<th>Geometry</th>
<th>$\tau_{ij}$</th>
<th>$\dot{\gamma}$</th>
<th>$\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cone and plate</td>
<td>$\frac{3M}{2\pi R^3}$</td>
<td>$\frac{\Omega}{\alpha}$</td>
<td>$\frac{3M\alpha}{2\pi R^3\Omega}$</td>
</tr>
<tr>
<td>Parallel disk</td>
<td>$\frac{M}{2\pi R^3}\left[3 + \frac{d\ln\left(\frac{M}{2\pi R^3}\right)}{d\ln(\dot{\gamma})}\right]$</td>
<td>$\frac{r\Omega}{h}$</td>
<td>$\frac{M}{2\pi R^3\dot{\gamma}_R}\left[3 + \frac{d\ln\left(\frac{M}{2\pi R^3}\right)}{d\ln(\dot{\gamma})}\right]$</td>
</tr>
<tr>
<td>Concentric cylinder</td>
<td>$\frac{M}{2\pi R^3 L \frac{R_i R_o}{R_e}}$</td>
<td>$\frac{R_i \Omega}{R_e}$</td>
<td>$\frac{M\left(1 - \frac{R_i}{R_e}\right)}{2\pi R^2 L \left(\frac{R_i}{R_e}\right)^{\frac{3}{2}} \Omega}$</td>
</tr>
</tbody>
</table>

Figure 2.15: The three most common type of rotational rheometers.

For the cone and plate geometry, the smaller the angle the higher the maximum shear rate that can be measured. The same is true for parallel plates for small gap sizes. Regarding the diameter, the smaller it is, the higher the maximum obtainable shear rate (TA Instruments, 2009).

In concentrated suspensions the flow inside a rheometer may be result of slip. Slip is an adhesive failure that depends on the material as well as of the geometry and its construction material (Wagner and Mewis, 2011). Corrections for slippage
are particularly simple for the parallel-disk geometry, the real shear rate $\dot{\gamma}_{\text{real}}$ can be obtained by measuring the apparent shear rates $\dot{\gamma}_{\text{app},1}$, $\dot{\gamma}_{\text{app},2}$ at two different gap sizes $h_1$ and $h_2$ for a given applied stress $\tau$ (Wagner and Mewis, 2011)

$$\dot{\gamma}_{\text{real}} = \frac{h_1 \dot{\gamma}_{\text{app},1} - h_2 \dot{\gamma}_{\text{app},2}}{h_1 - h_2}$$ (2.40)

There are two types of commercially available rotational rheometers; namely controlled strain and controlled stress rheometers. The stress-controlled rheometer (Fig. 2.16a) consists of a motor and position sensor supported by a frictionless bearing. When stress curves are to be obtained, this instrument applies a torque in an open loop and measures the angular position of the shaft (TA Instruments, 2005). If shear rate curves are to be obtained, the system will apply the torque in a close iterative loop. The strain-controlled rheometer (Fig. 2.16b) has two main elements, the motor providing the sample deformation and the torque transducer measuring the sample torque. The motor’s friction and inertia do not affect the measurement (TA Instruments, 2005).

![Figure 2.16: The two types of commercially available rotational rheometers (from TA Instruments (2005)).](image)

2.3.3.2 Extensional rheometers

Macosko (1994) classified the type of extensional flow geometries into: extension,
compression, sheet stretching, fiber spinning, bubble collapse, stagnation flow and entrance flows; the aforementioned geometries can be used to measure the elongational viscosity $\eta_{ext}$, however a complete review on extensional rheometry is out of the scope of this dissertation. The simplest type of extensional flow is uniaxial extension, which was previously depicted in Figure 2.10. The two most common types of rheometer with this type of flow field are the “filament stretching rheometer” and the “Capillary Breakup Extensional Rheometer” (CaBER). The former is not commercially available, therefore only the working principles of the CaBER will be reviewed.

In the CaBER rheometers a sample is placed in-between two disks, afterwards the plates separate rapidly over a short distance forming a cylindrical unstable liquid neck. The diameter of the midsection of the filament $D_{mid}$ is tracked as a function of time. An example of the evolution of the filament is shown in Figure 2.17.

![Figure 2.17](image)

**Figure 2.17:** Filament evolution for glycerol (McKinley and Tripathi, 2000).

Figure 2.18 shows some examples of the midsection evolution for three different types of materials.

The dynamics of the drainage are governed by the elastic and viscous forces opposing the Laplace or capillary pressure. Renardy (1995) showed that the force balance is

$$3\eta \left( -\frac{2}{D_{mid}} \frac{\partial D_{mid}}{\partial t} \right) = \frac{F_k}{\pi \left( \frac{D_{mid}}{2} \right)^2} - \left[ \frac{\tau_{kk}}{m} - \frac{\tau_{rr}}{m} \right] - \sigma \frac{D_{mid}}{\lambda^2} \tag{2.41}$$

Each of the terms represent

(I) Hencky strain rate $\dot{\varepsilon}$, Hencky strain is defined as $\varepsilon = 2 \ln \left( D_1/D_0 \right)$. The Hencky strain rate $\dot{\varepsilon}$ can be obtained from $\varepsilon = \int \dot{\varepsilon} dt$
tensile force acting on the column ends, these are not measured by the CaBER, therefore this instrument is considered an indexer and not a real rheometer

elastic stresses, zero for Newtonian fluids

capillary pressure

For Newtonian fluids McKinley and Tripathi (2000) showed that $D_{mid}$ evolves with time according to

$$D_{mid}(t) = D_1 - 2X - \frac{1}{3} \sigma \frac{t}{\eta}$$

(2.42)

where $D_1$ is the diameter of the midsection at $t = 0$ and $X$ is a similarity solution. Several values for $X$ have been calculated, however McKinley and Tripathi (2000) revealed that the solution given by Papageorgiou (1995) ($X = 0.7127$) is the most appropriate. For power-law fluids the expression reads

$$D_{mid}(t) = D_1 - 2^{1-n} \left( \frac{2X - 1}{3} \right) \frac{\sigma}{k} t^n$$

(2.43)

And for elastic threads (Entov and Hinch, 1997)

$$D_{mid}(t) = D_1 \left( \frac{GD_1}{\sigma} \right)^{1/3} \exp \left( -\frac{t}{3\lambda} \right)$$

(2.44)
where $G$ is the filament’s elastic modulus and $\lambda$ its relaxation time.

## 2.4 Turbulence and mechanical stirring

### 2.4.1 Turbulence

An apocryphal story says that Werner Heissenberg once said:

> When I meet God, I am going to ask him two questions: Why relativity?
> And why turbulence? I really believe he will have an answer for the first.

Turbulence has motivated the research of scientists for over a century due to the intellectual challenge and to its importance. All models are incomplete and inaccurate, nevertheless as models become more accurate or complete these become very complex and less tractable (Pope, 2011).

The aim of this section is to explain some of the basic characteristics of turbulent flow. Most of the mechanistic models for maximum droplet size or mean droplet size are based on the work of Kolmogorov (Kolmogorov, 1941b,a) who made a series of hypothesis that revolutionized the field of fluid mechanics. Nevertheless the Kolmogorov model formulations are limited to fully developed turbulent flows, which might not be the case in industrial applications where finite Reynold numbers are used. Therefore it is important to be aware of its limitations.

This section starts by presenting the classical equations of change, afterwards the Reynolds equations and the turbulent kinetic energy equation are presented and finally an explanation of Kolmogorov’s theory and its limitations.

### 2.4.1.1 Equations of change

The starting point to describe turbulent flow are the classical equations of change, namely the equation of continuity and the equation of motion which are obtained by doing a mass and momentum balance respectively (Bird et al., 2007)
Chapter 2. Literature review

Equation of continuity
\[ \frac{\partial \rho}{\partial t} = - \frac{\partial (\rho u_i)}{\partial x_i} \] (2.45)

Equation of motion
\[ \frac{\partial u_j}{\partial t} + \frac{\partial (u_i u_j)}{\partial x_i} = - \frac{\partial P}{\partial x_j} - \frac{\partial \tau_{ij}}{\partial x_i} \] (2.46)

In the equation of motion ¹, each of the terms represent

(I) rate of increase of momentum

(II) rate of momentum addition by convection

(III) addition of momentum by pressure forces

(IV) rate of momentum addition by molecular transport

For incompressible isothermal fluids the density \( \rho \) is constant and Equation 2.45 reduces to
\[ \frac{\partial u_i}{\partial x_i} = 0 \] (2.47)

Combining equations 2.46 and the viscous model for Newtonian fluids (Eq. 2.12) the Navier-Stokes equation is obtained
\[ \frac{\partial u_j}{\partial t} + \frac{\partial (u_i u_j)}{\partial x_i} = - \frac{\partial P}{\partial x_j} + \nu \frac{\partial}{\partial x_i} \left( \frac{\partial u_j}{\partial x_i} + \frac{\partial u_i}{\partial x_j} \right) \] (2.48)

where \( \nu \) is the kinematic viscosity (\( \nu = \mu/\rho \)).

2.4.1.2 The Reynolds equation

It can be observed that for large Reynolds numbers Re laminar flows become turbulent. In turbulent motion the instantaneous velocity components \( u_i \) (for \( i = 1, 2, 3 \)) are random. The Reynolds decomposition consists in decomposing \( u_i \) into the mean velocity \( \bar{u}_i \) and its fluctuation \( u'_i \), for incompressible fluids
\[ u_i = \bar{u}_i + u'_i \] (2.49)

¹Tensorial notation \( \tau_{ij}, j \) is the stress direction acting on the plane \( i \).
Similarly the pressure $P$ can be decomposed into $P = \mathcal{P} - P'$. A schematic representation of the decomposition is shown in Figure 2.19. From the equation of continuity we know that the mean of the fluctuation should be zero ($\bar{u}'_i = 0$), therefore the mean square fluctuation is used $(\bar{u}'_i^2)^{1/2}$ which differs from zero.

Rewriting the Navier-Stokes equation in terms of the average velocity $\bar{u}_i$ and pressure $\mathcal{P}$ yields the Reynolds Averaged Navier-Stokes or RANS equation (Pope, 2000)

$$
\frac{\partial \bar{u}_j}{\partial t} + \frac{\partial (\bar{u}_i \bar{u}_j)}{\partial x_i} = - \frac{\partial}{\partial x_i} \left[ \nu \left( \frac{\partial \bar{u}_j}{\partial x_i} + \frac{\partial \bar{u}_i}{\partial x_j} \right) - \frac{\mathcal{P}}{\rho} - \bar{u}_i' \bar{u}_j' \right]
$$

Equation 2.50 is almost identical to Equation 2.48 except for the right term $\bar{u}_i' \bar{u}_j'$ which is generally called Reynolds stress. For three dimensional flow, there are three of the former equations which need to be solved together with the mean continuity equation $\partial \bar{u}_i / \partial x_i = 0$. Unfortunately there are more unknown variables than equations (ie. three tangential stresses $\bar{u}_1' \bar{u}_2', \bar{u}_1' \bar{u}_3', \bar{u}_2' \bar{u}_3'$ and three normal stresses $\bar{u}_1'^2, \bar{u}_2'^2, \bar{u}_3'^2$), as a consequence the problem cannot be solved and there is a closure problem. The former equations are solved by developing new models, commonly called 2-equation models, the most famous ones are the $k - \varepsilon$ models (Pope, 2000).
2.4.1.3 Turbulent kinetic energy

Analogously to the velocity, the kinetic energy can be decomposed into the mean $\overline{E}$ and turbulent kinetic energy $k$, the decomposition yields $E = \overline{E} + k$, where $k$ is

$$k = \frac{1}{2} u'_i \cdot u'_i$$  \hspace{1cm} (2.51)

A long and complicated procedure is required to obtain the mean kinetic $E$ and turbulent energy $k$ equation. The final equations read (Pope, 2000)

$$\frac{\partial \overline{E}}{\partial t} + \overline{u}_i \frac{\partial \overline{E}}{\partial x_i} = - \frac{\partial}{\partial x_i} \left[ \frac{\overline{u}_i \rho}{\rho} + \overline{u}_j u'_j u'_i - \nu \overline{u}_j \left( \frac{\partial \overline{u}_j}{\partial x_i} + \frac{\partial \overline{u}_i}{\partial x_j} \right) \right] + \frac{\overline{u}'_i \overline{u}'_j}{\partial x_j} \frac{\partial \overline{u}_i}{\partial x_i} - \nu \frac{\partial \overline{u}'_j}{\partial x_i} \left( \frac{\partial \overline{u}'_j}{\partial x_i} + \frac{\partial \overline{u}'_i}{\partial x_j} \right)$$  \hspace{1cm} (2.52)

$$\frac{\partial k}{\partial t} + \overline{u}_i \frac{\partial k}{\partial x_i} = - \frac{\partial}{\partial x_i} \left[ \frac{u'_i p'}{\rho} \right] + \frac{1}{2} \frac{\partial \overline{u}'_i \overline{u}'_j}{\partial x_j} - \nu \overline{u}'_j \left( \frac{\partial \overline{u}'_j}{\partial x_i} + \frac{\partial \overline{u}'_i}{\partial x_j} \right) - \frac{\overline{u}'_i \overline{u}'_j}{\partial x_j} \frac{\partial \overline{u}_i}{\partial x_i} - \nu \frac{\partial \overline{u}'_j}{\partial x_i} \left( \frac{\partial \overline{u}'_j}{\partial x_i} + \frac{\partial \overline{u}'_i}{\partial x_j} \right)$$  \hspace{1cm} (2.53)

The meaning of each term is (Mathieu, 2000)

(I) rate of increase of turbulent energy

(II) convection of turbulent energy by mean flow

(III) transfer of turbulent energy by pressure effects

(IV) advective transport of turbulent energy by fluctuating motion (turbulent mixing)

(V) diffusion by molecular viscous transport

(VI) turbulence production

(VII) turbulence dissipation into heat $\varepsilon$
In Equations 2.52 and 2.53 the production terms (denoted by VI) have opposite signs meaning that the Reynolds stressed remove kinetic energy from the mean flow component and transfer it to the fluctuating one. The term denoted by VII in Equation 2.53 is the dissipation of the turbulent kinetic energy $\varepsilon$. This term transforms kinetic energy into internal energy preventing an unlimited growth of turbulence (Pope, 2000).

Term VII requires simultaneous measurements in the directions. Expansion of this term for three dimensional flows yields

$$
\varepsilon = 2\nu \left[ \left( \frac{\partial u'_1}{\partial x_1} \right)^2 + \left( \frac{\partial u'_2}{\partial x_1} \right)^2 + \left( \frac{\partial u'_3}{\partial x_1} \right)^2 \right] + 2\nu \left[ \left( \frac{\partial u'_1}{\partial x_2} \right)^2 + \left( \frac{\partial u'_2}{\partial x_2} \right)^2 + \left( \frac{\partial u'_3}{\partial x_2} \right)^2 \right] + 2\nu \left[ \left( \frac{\partial u'_1}{\partial x_3} \right)^2 + \left( \frac{\partial u'_2}{\partial x_3} \right)^2 + \left( \frac{\partial u'_3}{\partial x_3} \right)^2 \right]$$

(2.54)

### 2.4.1.4 Kolmogorov’s scales of turbulence

Turbulent flows contain a wide range of coexisting space and time scales with flux of energy from the large scales to the small ones. The kinetic energy of the large scales is commonly supplied by a large scale source which produces macroscopic velocity gradients (e.g. an impeller) and is determined by the geometry of the overall flow. The kinetic energy is transferred from unstable large eddies to smaller scales through a series of inviscid processes, this process is commonly called “energy cascade” (Pope, 2000).

The eddies of size $\ell$ have a characteristic velocity $u(\ell)$ and a time-scale $\tau(\ell) = \ell/u(\ell)$. Analogously the largest eddies have a length scale $\ell_0$ (comparable with the flow scale $L$) $^2$, called characteristic length scale (Kresta, 1998; Pope, 2000) or integral length scale (Solsvik and Jakobsen, 2016) and a characteristic velocity $u_0$ and

$^2$The length scale $\ell_0$ is the hypothetical scale of the largest eddies, while $L$ is the size of the largest isotropic eddies. Therefore under isotropic assumptions these two terms are interchangeable.
a time-scale $\tau_0$. The Reynolds number for each length scale ($\text{Re} = u\ell/\nu$) decreases with $\ell$ until the eddy motion is stable and viscous dissipation occurs converting the kinetic energy into heat Pope (2000).

Kolmogorov simplified the problem of turbulence by a series of hypothesis (Kolmogorov, 1941b,a). The first one is the “hypothesis of local isotropy” which suggests that at sufficiently high Re, the small-scale eddies are statistically isotropic. In other words all information about the geometry of the large anisotropic large eddies is lost (Pope, 2000). Isotropic flows are not to be confused with an homogeneous flows.

Homogeneous turbulence implies that the quantities are independent of spatial position meaning that all the spacial derivatives of all mean turbulent quantities are zero (terms II, III, IV and V become zero in Equation 2.52). Isotropic turbulence implies that the velocity fluctuations are independent of position and angle, the terms in Equation 2.54 that become equal are (Taylor, 1935)

\[
\begin{align*}
\left( \frac{\partial u'_1}{\partial x_2} \right)^2 &= \left( \frac{\partial u'_1}{\partial x_3} \right)^2 = \left( \frac{\partial u'_2}{\partial x_1} \right)^2 = \left( \frac{\partial u'_2}{\partial x_3} \right)^2 = \left( \frac{\partial u'_3}{\partial x_1} \right)^2 = \left( \frac{\partial u'_3}{\partial x_2} \right)^2 \\
\left( \frac{\partial u'_2}{\partial x_1} \right) \left( \frac{\partial u'_1}{\partial x_2} \right) &= \left( \frac{\partial u'_3}{\partial x_2} \right) \left( \frac{\partial u'_2}{\partial x_3} \right) = \left( \frac{\partial u'_1}{\partial x_3} \right) \left( \frac{\partial u'_3}{\partial x_1} \right)
\end{align*}
\] (2.55)

Substituting the former relations in Equation 2.54 yields

\[
\varepsilon = 6\nu \left[ \left( \frac{\partial u'_1}{\partial x_1} \right)^2 + \left( \frac{\partial u'_2}{\partial x_2} \right)^2 + \left( \frac{\partial u'_3}{\partial x_3} \right)^2 \right] \] (2.56)

The first similarity hypothesis states that in every turbulent flow at sufficiently high Re, the statistics of the small-scale motion have a universal form that is uniquely determined by $\nu$ and $\varepsilon$. Using dimensional analysis for $\text{Re} = 1$ (viscous dissipation becomes effective) the so-called “Kolmogorov scales” are obtained (Kolmogorov,
2.4. Turbulence and mechanical stirring

For this size range the energy dissipation is given by $\varepsilon = \nu/\tau_0^2$. Another implication of the Kolmogorov hypothesis is that the ratios of the Kolmogorov scales $\ell_\eta$ to the largest scales $\ell_0$ can be determined by

$$\frac{\ell_\eta}{\ell_0} \sim \text{Re}_L^{-3/4}$$ \hspace{1cm} (2.60)

$$\frac{u_\eta}{u_0} \sim \text{Re}_L^{-1/4}$$ \hspace{1cm} (2.61)

$$\frac{\tau_\eta}{\tau_0} \sim \text{Re}_L^{-1/2}$$ \hspace{1cm} (2.62)

Where Re$_L$ is the Reynolds number associated to the scale of the largest eddies, also called turbulence Reynolds number

$$\text{Re}_L = \frac{u_0 \ell_0}{\nu} = \frac{k^{1/2} \ell_0}{\nu} = \frac{k^2}{\varepsilon \nu}$$ \hspace{1cm} (2.63)

For eddies of a medium size $\ell_0 \gg \ell \gg \ell_\eta$ the dissipative eddies are not affected by viscosity. Kolmogorov’s second similarity hypothesis states that in this size-range (inertia subrange) the statistic of the motion are uniquely determined by $\varepsilon$ and independent of $\nu$. The energy dissipation is simply $\varepsilon = u^2/\tau$. The scaling equations for the inertia subrange are

$$u \sim u_0 \left( \frac{\ell}{\ell_0} \right)^{2/3}$$ \hspace{1cm} (2.64)

$$\tau \sim \tau_0 \left( \frac{\ell}{\ell_0} \right)^{2/3}$$ \hspace{1cm} (2.65)
2.4.1.5 The Taylor scale

Another length-scale commonly reported in literature is the Taylor-length scale \( \lambda \). By bookkeeping the contribution of the terms in Equation 2.54 Taylor showed that Equation 2.56 reduces to (Taylor, 1935)

\[
\varepsilon = 15\nu \left( \frac{\partial u'_1}{\partial x_1} \right)^2 \tag{2.66}
\]

The Taylor microscale \( \lambda \) is defined as

\[
\left( \frac{\partial u'_1}{\partial x_1} \right)^2 = \frac{u'^2_1}{\lambda^2} \tag{2.67}
\]

The substitution \( u'^2_1 = u'^2 \) is possible because in isotropic turbulence \( u'_1 = u'_2 = u'_3 \) and therefore \( \frac{1}{3} u'_i u'_i = u'^2_1 \). From the definition of turbulent kinetic energy \( k \) (Eq. 2.51) and the local isotropy hypothesis, it can be shown that \( k = \frac{2}{3} u'^2_1 \). Therefore

\[
\lambda = \left( \frac{10\nu k}{\varepsilon} \right)^{1/2} \tag{2.68}
\]

Analogous to Equation 2.60 the following scale equivalences can be drawn

\[
\frac{\lambda}{\ell_0} = \sqrt{10} \text{Re}_L^{-1/2} \tag{2.69}
\]

\[
\frac{\lambda}{\eta} = \text{Re}_L^{-3/4} \tag{2.70}
\]

Its associated Reynolds number is

\[
\text{Re}_\lambda = \frac{u'_1 \lambda}{\nu} = \left( \frac{20}{3} \text{Re}_L \right)^{1/2} \tag{2.71}
\]

The Taylor microscale has no clear physical interpretation (Pope, 2000) but can roughly be regarded as “the diameter of the smallest eddies which are responsible for the energy dissipation” (Taylor, 1935). It’s length-scale is intermediate to that of \( \ell_\eta \) and \( \ell_0 \) and \( \text{Re}_\lambda \) is commonly used to characterize the degree of turbulence.
2.4.1.6 Kolmogorov’s Energy spectrum

The energy spectrum function $E(\kappa)$ which is defined in terms of the wave-number of the eddies ($\kappa = 2\pi/\ell$) provides information of the kinetic energy $k$ and the dissipation rate $\varepsilon$ in the eddies of different of wave-number between $\kappa$ and $\kappa + \text{d}\kappa$ per unit mass in the $\kappa_a$ to $\kappa_b$ range.

\[
k(\kappa) = \int_{\kappa_a}^{\kappa_b} E(\kappa) \text{d}\kappa \tag{2.72}
\]

\[
\varepsilon(\kappa) = \int_{\kappa_a}^{\kappa_b} 2\nu \kappa^2 E(\kappa) \text{d}\kappa \tag{2.73}
\]

By dimensional analysis the so-called “Kolmogorov -5/3 energy spectrum for isotropic turbulence” is obtained

\[
E(\kappa) = C\varepsilon^{2/3} \kappa^{-5/3} \tag{2.74}
\]

The Kolmogorov constant is normally 1.5 (Pope, 2000).

The energy spectrum for Kolmogorov’s -5/3 spectrum is limited to the inertia subrange and does not describe the full spectrum. Figure 2.20 shows the full energy spectrum for the two subranges: the anisotropic and the universal equilibrium range. The universal equilibrium range is further divided into the inertia and dissipation subranges (Pope, 2000). The solid line represents the Kolmogorov -5/3 spectrum which only describes the inertia regime.

Pope (2000) suggest defining two extra length scales which delimit the length-scale range in which the flow can be considered isotropic. The first sets the limit in-between the inertia and dissipative subrange $\ell_{DI}$. He suggests that $\ell_{DI} = 60\ell_\eta$. The second, $\ell_{EI}$ is demarks the boundary in-between the anisotropic energy containing lengthscales and the locally isotropic inertia subrange. Pope (2000) suggests $\ell_{EI} = \ell_0/6$.

2.4.1.7 Full energy spectrum

Solsvik and Jakobsen (2016) recently published a review on isotropic turbulent models for the entire spectra. The models review and the subranges covered are shown in Table 2.5.
Chapter 2. Literature review

Figure 2.20: Schematic representation of the full energy spectrum $E(\kappa)$ as a function of the eddies wave-number $\kappa$ for isotropic turbulence. The dashed line shows the full spectrum and the solid line the Kolmogorov $-5/3$ spectrum.

Table 2.5: Energy subranges for different Model Energy Spectra (from Solsvik and Jakobsen (2016)).

<table>
<thead>
<tr>
<th>Model Energy Spectrum</th>
<th>Energy containing subrange</th>
<th>Inertia subrange</th>
<th>Dissipation subrange</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kolmogorov</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Pope</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Hinze</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Lin</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>von Karman</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Pao</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

A review of these models is out of the scope of our investigation, nevertheless the model of Pope (2000) for the full spectra can give some insights on the inertia subrange range.

$$E(\kappa) = C\varepsilon^{2/3}\kappa^{-5/3}f_L(\kappa L)f_\eta(\kappa \eta)$$

where $f_L(\kappa L)$ and $f_\eta(\kappa \eta)$ are non-dimensional functions. The first function determines the shape of the energy containing subrange and tends to unity for large $\kappa L$. The second dimensionless function determines the shape of the dissipation subrange and tends to unity for small $\kappa \eta$. Both functions tend to unity in the inertia subrange.
The equations of the functions read (Pope, 2000)

\[
f_L (\kappa L) = \left( \frac{\kappa L}{[ (\kappa L)^2 + c_L]^{1/2}} \right)^{11/3}
\]

\[
f_\eta (\kappa \ell_\eta) = \exp \{ -\beta \left[ (\kappa \ell_\eta)^4 + c_\eta^4 \right]^{1/4} - c_\eta \}
\]

Where \( c_L, c_\eta \) and \( \beta \) are positive constants. According to Pope (2000) \( \beta = 5.2 \).

The constants \( c_L \) and \( c_\eta \) determined by the requirement that \( E(\kappa) \) and \( 2\nu \kappa^2 E(\kappa) \) integrate \( k \) and \( \varepsilon \) respectively (Eq. 2.72 and Eq. 2.73).

The model can be represented in dimensionless form so that it is uniquely determined by \( Re_L \), \( Re_\eta \) or \( Re_L \) (Solsvik and Jakobsen, 2016).

The normalized version dependent on \( Re_L \) is obtained by making \( \kappa = \kappa' / L \) and diving by \( kL \), Equation 2.75 becomes (Solsvik and Jakobsen, 2016)

\[
\frac{E \left( \frac{\kappa'}{L} \right)}{kL} = C \left( \kappa' \right)^{-5/3} f_L \left( \kappa' \right) f_\eta \left( \frac{\kappa' \eta}{L} \right)
\]

With normalized dimensionless functions

\[
f_L \left( \kappa' \right) = \left\{ \frac{\kappa'}{[ (\kappa')^2 + c_L]^{1/2}} \right\}^{11/3}
\]

\[
f_\eta \left( \frac{\kappa' \eta}{L} \right) = \exp \left\{ -\beta \left[ \left( \frac{\kappa'}{Re_L} + c_\eta^4 \right]^{1/4} - c_\eta } \right\}
\]

And the constrains to determine \( c_L \) and \( c_\eta \) become (from Eq. 2.72 and Eq. 2.73)

\[
\int_0^\infty \frac{E \left( \frac{\kappa'}{L} \right)}{kL} \, d\kappa' = 1
\]

\[
\int_0^\infty 2 \left( \kappa' \right)^2 \frac{E \left( \frac{\kappa'}{L} \right)}{kL} \, d\kappa' = Re_L
\]

The values of these constants are solely a function of \( Re_L \). (Solsvik and Jakobsen, 2016) solved \( c_L \) and \( c_\eta \) for different \( Re_L \), their results are shown in Figure 2.21.

Figure 2.22 shows the full normalized spectra for different turbulence Reynolds
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Figure 2.21: Resulting $c_\eta$ and $c_L$ from Eqs. 2.81 and 2.82 as a function of $Re_L$ as calculated by Solvik and Jakobsen (2016).

numbers $Re_L$. Figure 2.22 shows that as the degree of turbulence lowers, the inertia regime vanishes and the Kolmogorov $-5/3$ spectrum is not longer valid for low Reynolds numbers.

Figure 2.22: Pope’s normalized energy spectrum for different integral scale Reynolds numbers $Re_L$. 
2.4. Turbulence and mechanical stirring

Table 2.6: Impeller classes and specific types (from Hemrajani and Tatterson (2003)).

<table>
<thead>
<tr>
<th>Class</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial flow</td>
<td>Propeller, pitched blade turbine</td>
</tr>
<tr>
<td>Radial flow</td>
<td>Flat-blade impeller, Rushton and Smith turbines</td>
</tr>
<tr>
<td>High shear</td>
<td>Cowles, disk, bar, pointed blade impeller</td>
</tr>
<tr>
<td>Specialty</td>
<td>Retreat curve impeller, sweptback impeller</td>
</tr>
<tr>
<td>Up/down</td>
<td>Disks, plate, circles</td>
</tr>
</tbody>
</table>

2.4.2 Stirred vessels

2.4.2.1 Flow Patterns and Types of Impellers

A rotating impeller imparts flow and shear to the fluids. Impellers are classified depending on the type of flow that is dominant, applications and special geometries; the type of flow limiting cases are in the axial or radial direction (see Fig. 2.23)(Harnby et al., 1992).

![Figure 2.23: Axial and radial flow pattern for propellers and disc turbines respectively (Harnby et al., 1992).](image)

Nevertheless the flow patterns in stirred vessels do not follow purely axial and radial directions and the streamlines are generally mixed due to reflection from vessel surfaces and obstruction of internal elements, such as baffles. A typical classification of the types of impellers and some examples are shown in Table 2.6.
2.4.2.2 Power consumption

The power draw is a very important variable in mixing operations. It is defined as the amount of energy necessary in a period of time to generate movement of fluid within a container (Ascanio et al., 2004). If a stirred vessel such as the one shown in Figure 2.24 with a stirrer of diameter $D$, a tank of diameter $T$, a depth of liquid in the tank $H_T$, a height of the agitator from the base of the tank $C_S$ and baffles of width $W_{bf}$ in which a Newtonian fluid with dynamic shear viscosity $\mu$ and density $\rho$ are agitated with an impeller rotational speed $N$ under the effect of the acceleration due to gravity $g$; the power requirements $P_S$ will become dependent of all the previously mentioned geometrical factors, fluid properties and processing conditions.

$$P_S = f(D, N, T, H_T, C_S, W_{bf}, \mu, \rho, g)$$  \hspace{1cm} (2.83)

![Figure 2.24: Dimensions of a stirred vessel.](image)

For geometrically similar (normally correlated to $D$) or a set of experiments are performed using the same vessel, the dimensional analysis yields three dimensional
groups

\[
\text{Reynolds number} \quad \text{Re} = \frac{ND^2\rho}{\mu} \quad (2.84)
\]

\[
\text{Froude number} \quad \text{Fr} = \frac{N^2D}{g} \quad (2.85)
\]

\[
\text{Power number} \quad P_0 = \frac{P_S}{N^3D^5\rho} \quad (2.86)
\]

The Froude number \((\text{Fr})\) is the ratio of hydrodynamic and gravitational forces and is usually important in situations where vortexing occurs, it can be neglected for Reynolds numbers \((\text{Re})\) lower than 300 and if baffles or off-center stirring are used. The Reynolds number \((\text{Re})\) is the ratio of inertial forces to viscous forces. Typically the flow will be laminar for \(\text{Re} < 10\), transitional for \(10 < \text{Re} < 10^4\) and turbulent for \(\text{Re} > 10^4\) (Hemrajani and Tatterson, 2003).

Figure 2.25 shows a typical power curve. It can be seen that at low Re \((\text{Re} < 10)\) the slope is one indicating that

\[
P_0 = \frac{K_P}{\text{Re}} \quad (2.87)
\]

\[\text{Figure 2.25: Typical power curve.}\]

Where \(K_P\) is the laminar power constant. In this regime viscous forces dominate as \(P_0 \propto \mu\). Therefore \(P_S\) can be obtained by combining Equations 2.84, 2.86 and
2.87

\[ P_S = K_P N D^2 \mu \tag{2.88} \]

In the same figure the Po becomes independent of Re for Re > 10^4, therefore Po becomes independent of \( \mu \) and inertia forces dominate, this is known as the turbulent regime. The power can therefore calculated from the Re-independent power number in the turbulent regime (labelled Po_0 in Figure 2.25)

\[ P_S = P_{00} N^3 D^5 \rho \tag{2.89} \]

In-between the laminar and turbulent region, there exists a gradual transition zone in which no mathematical relationship exists between Po and Re. Cooke et al. (2012) proved that the whole power curve can be obtained by

\[ P_o = P_{00} + \frac{K_P}{Re} \tag{2.90} \]

2.4.2.3 Energy dissipation

Stirred vessels are not truly isotropic, as true isotropy requires no directional preference in three-dimensional flow and the eddies have directional preferences. Furthermore, the degree of turbulence is not the same throughout the vessel. For example Wu and Patterson (1989) found that for Rushton turbines 60% of the energy of the impeller was dissipated in the impeller region and only 40% in the bulk. Generally speaking, there are two dissipation rates of interest, the local maximum at the vicinity of the impeller \( \epsilon_{max} \) and the mean energy dissipation rate in the whole vessel \( \bar{\epsilon} \).

Despite the flow in a stirred vessel not being truly isotropic, local isotropy is assumed. Local isotropy implies that isotropy can be applied over a limited eddy size range. There have been experiments where the local isotropy has been proven for \( 50 > Re_\lambda > 800 \) Kresta (1998). The local Re_\lambda at the impeller and bulk of the
tank can be estimated by Kresta (1998)

\[
\text{Impeller } \quad \text{Re}_\lambda = 1.22 \text{Re}^{1/2} \quad (2.91)
\]

\[
\text{Bulk } \quad \text{Re}_\lambda = 0.2 \left( \frac{\text{Re}}{\text{Po}} \right)^{1/2} \left( \frac{T}{D} \right)^{3/2} \quad (2.92)
\]

As \( \text{Re}_\lambda \) will always be larger at the vicinity of the impeller, local isotropy is more likely to happen in this region than in the bulk.

Figure 2.26 shows schematically different scales present in a stirred vessel. There are many possibilities to define the largest scale of motion (ex. \( C_S/D, T, W_S, \) etc), nevertheless the Kolmogorov scale \( \ell_\eta \) can be conveniently considered as the smallest scale of motion. Kresta (1998), among others, considered that the size of the trailing vortices (left side in Fig. 2.26) mark the limit in-between the anisotropic energy containing eddies and the inertia sub range. The trailing vortices are therefore considered the integral length scale \( L \), which have a diameter of \( W_S/2 \) or \( D/10 \) (Kresta, 1998) or \( D/12.5 \) (Wu and Patterson, 1989).

![Figure 2.26: Schematic representation of the different length-scales in a stirred vessel. Modified from (Kresta, 1998)](image)

To related the turbulence in a stirred vessel with the scales reviewed in Section 2.4.1.4 the rate of dissipation \( \varepsilon \) needs to be known. In turbulent flow viscous forces are negligible compared with inertia forces, therefore all velocities will scale with tip speed and the flow characteristics can be reduced to a set of correlations independent of \( \mu \) (Kresta and Brodkey, 2003). Authors such as Wu and Patterson (1989) and
Kresta and Brodkey (2003) have assumed unidirectional flow and used assumed that \( \varepsilon \) can be calculated from the turbulence velocity and the microscale. From dimensional analysis and the energy cascade principle

\[
\varepsilon = A \frac{u_1^3}{L}
\]  

(2.93)

Where the proportionality constant \( A \) is one for local isotropy Kresta and Brodkey (2003).

From an engineering perspective, it is desirable to have Equation 2.93 as a function of easily-measurable parameters such as \( D \) and \( N \). Therefore the characteristic turbulent velocity \( u_1^3 \) of the eddies of a characteristic size \( L \) are (Kresta and Brodkey, 2003)

\[
\overline{u_1^3} = C_u ND
\]

(2.94)

\[
L = C_L D
\]

(2.95)

Where \( C_u \) and \( C_L \) are a function of the impeller and tank geometry. Substituting the former Equations 2.94 and 2.95 in Equation 2.93 yields

\[
\varepsilon \propto \frac{C_u^3 N^3 D^2}{C_L}
\]  

(2.96)

The previous equation assumes local isotropic turbulence and a constant \( L \) in the entire vessel (Ducci and Yianneskis, 2005), which limits the former assumptions to the vicinity of the impeller (Kresta, 1998).

On the other hand, the mean energy dissipation rate \( \overline{\varepsilon} \) can be obtained by calculating the power per unit mass of fluid, for tanks with \( H_T = T \)

\[
\overline{\varepsilon} = \frac{P_g}{\rho VT}
\]

\[
= \frac{4P_o \rho N^3 D^5}{\rho \pi T^2 H_T} \propto P_o N^3 D^2 \left( \frac{D}{T} \right)^3
\]  

(2.98)

Nevertheless the Equation 2.98 would estimate the mean energy dissipation of the
whole vessel $\bar{\varepsilon}$ which may be inaccurate if the local (or maximum) energy dissipation is needed. To estimate the maximum energy dissipation $\varepsilon_{max}$ the volume of the vessel needs to be replaced by the swept volume $V_{swept}$ leading to

$$\varepsilon_{max} \propto \frac{P_s}{\rho V_{swept}} \propto \rho \omega N^3 D^2$$  \hfill (2.99)

Which is basically the same as Equation 2.96.

Zhou and Kresta (1996) studied the effect of the number of baffles, $D$ and $C_S$ on $\varepsilon_{max}$ for four impellers including Rushton turbines and the pitched blade turbine (used in our experiments). They reported that the maximum $\varepsilon_{max}$ for the pitched blade turbine was located below the impeller. Their conclusions regarding geometrical factors are listed below

1. the effect of $D$ on $\varepsilon_{max}$ is larger than the theory predicted $D^2$, this was attributed to the influence of the walls of the vessel.

2. $C_S$ is important and $\varepsilon_{max}$ should be scaled by $C_S/D$ and not $C_S/T$.

3. the number of baffles has no significant effect on $\varepsilon_{max}$

4. vessels should be scaled up by $D^2$ (see Eq. 2.99) and not $D^5$ (see Eq. 2.98).

A common way to report $\varepsilon_{max}$ values in literature is by the $\varepsilon_{max}$ to $\bar{\varepsilon}$. Gabriele et al. (2009) summarized the $\varepsilon_{max}/\bar{\varepsilon}$ for pitched blade turbines (used in our studies) and these are shown in Table 2.7. The $\varepsilon_{max}/\bar{\varepsilon}$ calculated using Equation 2.93 are the “DA” ones. The “SGS” stand for the Smagorinsky sub-grid scale, which is a “Large eddie” model which solves the anisotropic flows using the Navier-Stokes equation while the small isotropic scales are modelled; the SGS closure methods will not be reviewed as it is out of the scope of our investigation. This Table shows that there is not much agreement in literature on the value of $\varepsilon_{max}/\bar{\varepsilon}$. The $\varepsilon_{max}/\bar{\varepsilon}$ DA measurements vary from 7 to 43 and the SGS vary from 3.27 to 78.
Table 2.7: Summary of some $\varepsilon_{\text{max}}/\varepsilon$ reported in literature for pitched blade turbines (from Gabriele et al. (2009)). DA stands for dimensional analysis (Equation 2.93) and SGS for the Smagorinsky sub-grid scale (not reviewed).

<table>
<thead>
<tr>
<th>Author</th>
<th>Blades</th>
<th>$D$</th>
<th>$C_S$</th>
<th>$\varepsilon_{\text{max}}/\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kresta and Wood (1993)</td>
<td>4</td>
<td>$T/2$</td>
<td>$T/4$</td>
<td>36.5 (DA)</td>
</tr>
<tr>
<td>Zhou and Kresta (1996)</td>
<td>4</td>
<td>$T/3$</td>
<td>$T/3$</td>
<td>38.83 (DA)</td>
</tr>
<tr>
<td>Sheng et al. (2000)</td>
<td>4</td>
<td>0.35$T$</td>
<td>0.46$T$</td>
<td>7 (DA)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.5 (SGS)</td>
</tr>
<tr>
<td>Khan (2005)</td>
<td>6</td>
<td>$T/3$</td>
<td>$C_S = T/3$</td>
<td>43 (DA)</td>
</tr>
<tr>
<td>Gabriele et al. (2009)</td>
<td>6</td>
<td>0.45$T$</td>
<td>$T/4$</td>
<td>13 (DA)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.27 (SGS)</td>
</tr>
</tbody>
</table>

2.4.2.4 Shear rate

The analysis in the previous parts of this Chapter have assumed that the materials are Newtonian (Eq. 2.12), however if the materials are non-Newtonian, some other considerations have to be taken into account. As non-Newtonian fluids are shear rate $\dot{\gamma}$-dependent, an estimation of the average $\dot{\gamma}$ in the vicinity of the impeller is necessary to calculate the effective viscosity $\eta$ and its the Reynolds number $Re$.

2.4.2.4.1 Newtonian fluids  For the laminar regime, the model proposed by Metzner and Otto (1957) has been validated by many authors (Doraiswamy et al., 1994). According to Metzner and Otto (1957), the average $\dot{\gamma}$ is proportional to the agitation rate $N$

$$\dot{\gamma} = K_s N$$  \hspace{1cm} (2.100)

A different analysis to determine $\dot{\gamma}$ can be derived using the kinetic energy expression (Eq.2.53), from term VIII in this equation we obtain that

$$\varepsilon = \nu \dot{\gamma}^2$$  \hspace{1cm} (2.101)
The global $\dot{\gamma}$ can be estimated by substituting Equations 2.97 and 2.86 in Equation 2.101 (Gabelle et al., 2013)

$$\dot{\gamma} = \left( \frac{\varepsilon}{\nu} \right)^{\frac{1}{2}} = \left( \frac{P_S}{\nu \rho V_T} \right)^{\frac{1}{2}} = \left( \frac{P_o N^3 D^5}{\nu V_T} \right)^{\frac{1}{2}} \quad (2.102)$$

Using Equations 2.84 and 2.87, we obtain the expression for $\dot{\gamma}$ in the laminar regime

$$\dot{\gamma} = \left( \frac{K_P D^3}{V_T} \right)^{\frac{1}{2}} N = \left[ \frac{4 K_P}{\pi} \left( \frac{D}{T} \right)^3 \left( \frac{H_T}{T} \right)^{-1} \right]^{\frac{1}{2}} N \quad (2.103)$$

which is homologous to Equation 2.100 in that both are linearly dependent on $N$. For the turbulent regime we obtain

$$\dot{\gamma} = \left( \frac{P_o D^5}{\nu V_T} \right)^{\frac{1}{2}} N^{3/2} = \left[ \frac{4 P_o}{\pi} \operatorname{Re} \left( \frac{D}{T} \right)^3 \left( \frac{H}{T} \right)^{-1} \right]^{\frac{1}{2}} N \quad (2.104)$$

Which shows that the $\dot{\gamma}$ in the turbulent regime has a larger dependency on $N$ than the linear relationship proposed by Metzner and Otto (1957).

### 2.4.2.4.2 Power-law fluids

For power law fluids ($\eta = k \dot{\gamma}^{n-1}$), substituting Equation 2.100 (Metzner and Otto, 1957) in the Reynolds number definition for stirred vessels yields

$$\operatorname{Re} = \frac{\rho N D^2}{k \dot{\gamma}^{n-1}} = \frac{\rho N D^2}{k (K_s N^{n-1})} = \frac{\rho N^{2-n} D^2}{k K_s^{n-1}} \quad (2.105)$$

The average shear $\dot{\gamma}$ concept proposed by Metzner and Otto (1957) is only applicable in the laminar regime. Many studies have shown that $\dot{\gamma}$ in the turbulent regime would be much higher and the Metzner-Otto approach results in an over-prediction of the power consumption (Doraiswamy et al., 1994; Gabelle et al., 2013).
Using Equation 2.101, Gabelle et al. (2013) derived

\[ \dot{\gamma} = \left( \frac{\rho \varepsilon}{k \dot{\gamma}^{n-1}} \right)^{\frac{1}{2}} \]

(2.106)

\[ = \left( \frac{\rho \varepsilon}{k} \right)^{\frac{1}{n+1}} \]

(2.107)

\[ = \left( \frac{\rho P_0 D^5}{k V_T} \right)^{\frac{1}{n+1}} N^{\frac{3}{n+1}} \]

(2.108)

\[ = 4 \frac{\rho}{\pi k} P_0 \left( \frac{D}{T} \right)^2 \left( \frac{D}{H_T} \right) D^2 \left[ \frac{N^{4-2n} D^{7-3n} \rho^2 V_T^{n-1}}{k^2 P_0^{n-1}} \right]^{\frac{1}{n+1}} \]

(2.109)

Compared to Equation 2.100, the previous equation decreases the apparent viscosity and therefore increases its Reynolds number; substituting Equation 2.108 in Equation 2.20 and Equation 2.84

\[ \text{Re} = \left( \frac{N^{4-2n} D^{7-3n} \rho^2 V_T^{n-1}}{k^2 P_0^{n-1}} \right)^{\frac{1}{n+1}} \]

(2.110)

which reduces to Equation 2.84 for a Newtonian fluid \((n = 1)\). Gabelle et al. (2013) argued that this approach predicts their results (for a Rushton turbine) using particle image velocimetry (PIV) better when compared to using Equation 2.100 in the turbulent regime. Sanchez Perez et al. (2006) used this approach for bubble column reactors.

### 2.4.3 High-shear mixers

High-shear mixers or rotor-stators are devices in which the mixing element or rotor, in close proximity to a fixed element or stator. These devices rotate at very high-speeds \((10 \text{ m s}^{-1} \text{ to } 50 \text{ m s}^{-1})\) and produce very high shear rates \((2 \times 10^4 \text{ s}^{-1} \text{ to } 1 \times 10^5 \text{ s}^{-1})\) (Zhang et al., 2012). The local energy dissipation by rotor-stators may be three orders of magnitude greater than those experience in a stirred vessel (Atiemo-Obeng and Calabrese, 2003).

There are numerous geometrical variations in their design. Atiemo-Obeng and Calabrese (2003) classified them in three categories: (1) colloid mills and toothed
devices (2) axial discharge impellers and (3) radial discharge impellers. The Silverson type belong to the latter group and will be the focus of attention.

Any of the aforementioned rotor-stators can be operated in a batch or continuous arrangement (in-line) (Atiemo-Obeng and Calabrese, 2003). Figures 2.27 and 2.28 show the working principles of the Silverson-type devices in batch and in-line arrangements respectively. The main difference being that former is submerged into the vessel and the later is connected to the pipework.

![Image](a) ![Image](b) ![Image](c) ![Image](d)

**Figure 2.27:** Working principles of Silverson high-shear mixers (a) suction, (b) shear by the rotor, (c) shear through the perforations and (d) expulsion to the bulk of the vessel (from Silverson Machines (2015)).

![Image](a) ![Image](b) ![Image](c)

**Figure 2.28:** Working principle of the in-line rotor-stators (a) suction, (b) shear by rotor, (c) shear through perforation and expulsion to the pipework (from Silverson Machines (2015))

There is also a wide variety of rotors and stators or screens available. Some examples for screens for lab-scale mixers commercialized by Silverson are shown in Figure 2.29.

2.4.3.1 Flow patterns

The flow fields in Silverson-type rotor-stators are complicated and unsteady due to the blades passing.
Mortensen et al. (2011) did two dimensional particle image velocimetry images using a batch high-shear mixer with a transparent stator (plexiglass). Figure 2.30 shows some of their obtained results for three different blade positions and two different views. They noted the appearance of several transient stagnation zones (thick black line in Fig. 2.30) and that the jet stream going outwards occupies a small area of the slot. In the first row of the same Figure it can be noted that the velocity of the jet stream is higher than that of the impeller (Mortensen et al., 2011).

On the second row, when the blade blocks the opening a vortex is formed due the abrupt jet re-direction of the flows: intake at the back of the blade and discharge at the front. The place where the vortex is formed is where the turbulent energy is the highest. Mortensen et al. (2011) found that cavitation bubbles can be formed due to the strength of the vortex. They found that cavitation started for $N = 1000 \text{ min}$, but recognized that this phenomena might be geometry and size dependent (Mortensen et al., 2011).

As the blade passes the vortex migrates outwards and its strength reduces resulting in the implosion of the bubble.
Figure 2.30: Mean velocity magnitude normalized by rotor tip speed for different rotor positions (top to bottom) for two different views. (from Mortensen et al. (2011)).

2.4.3.2 Power consumption for in-line high-shear mixers

Power draw in in-line rotor-stators differs from the traditional stirred vessel in that power draw increases with flow rate. Kowalski (2009) developed a three term model

\[
P_S = P_{T1} + P_{T2} + P_{T3} \tag{2.111}
\]
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Where

(I) $P_T$ is the typical power necessary to spin the rotor in the absence of flow (see Sec: 2.4.2.2). If the flow is turbulent $P_T$ becomes independent of Re. The turbulent $P_T$ for zero flow will be renamed $P_{TZ}$ to facilitate discussion.

(II) $P_F$ is the power requirements due to the flow. Kowalski (2009) proposed that $P_F$ can be calculated by $P_F = k_1 \dot{m} N^2 D^2$. Where $k_1$ is a proportionality constant and $\dot{m}$ is the mass flow rate into the chamber.

(III) $P_L$ is the power lost (ex: vibration, noise, kinetic energy losses at the entrance, etc). These losses may be accounted for by substracting the “y-intercept” of a measured power vs $N^2$ for the turbulent regime (see Eq. 2.89) and measured power vs $N$ for the laminar regime (see Eq. 2.88).

Expanding terms I and II yield (Cooke et al., 2012)

Turbulent regime
$$P_S = P_{TZ} \rho N^3 D^5 + k_1 \dot{m} N^2 D^2 \quad (2.112)$$

Laminar regime
$$P_S = K_{PZ} N^2 D^3 \mu + k_1 \dot{m} N^2 D S^2 \quad (2.113)$$

Total
$$P_S = K_{PZ} N^2 D^3 \mu + P_{TZ} \rho N^3 D^5 + k_1 \dot{m} N^2 D^2 \quad (2.114)$$

Equation 2.114 can be rearranged by diving it by $N^3 D^5 \rho$ to obtain

$$P_{O} = \frac{K_{PZ}}{Re} + P_{TZ} + k_1 N_Q \quad (2.115)$$

where $N_Q$ is the dimensionless pumping number ($N_Q = \dot{m}/\rho N D^3$) and is obtained by determining $\dot{m}$ for different $N$ with the valves surrounding the rotor-stator fully open and with the rotor-stator acting as the only pump.

Closing valves surrounding the rotor-stator ($\dot{m} = 0$) allows to obtain $K_{PZ}$ or $P_{TZ}$ depending the regime (Cooke et al., 2012).

The power draw when the valves are fully open is maximum $P_{S, max}$ for a given $N$. The power number for these conditions can be renamed $P_{OU}$. With these
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considerations, Equation 2.112 can be rearranged (Cooke et al., 2012) to obtain

\[ P_{S,\text{max}} = P_0 U \rho N^3 D^5 = (P_0 Z + k_1 N_Q) \rho N^3 D^5 \tag{2.116} \]

\[ k_1 = \frac{P_0 U - P_0 Z}{N_Q} \tag{2.117} \]

Therefore \( k_1 \) can be estimated by carrying out experiments without flow and experiments using the rotor-stator as a pump.

2.4.4 Power draw measurement

As reviewed in Section 2.4.2.2, the power draw needs to be determined \( P_S \) experimentally. There are several way to determine \( P_S \), the advantages and disadvantages of some of these methods have been summarized by (Ascanio et al., 2004) and are shown in Table 2.8. This Section will only cover the working principles torquemeters because it was the one used in our investigations.

The working principle of the torquemeters are based on Newton’s third law. A stirrer produces a mechanical force to which the fluid presents resistance. This resistance produces a torque upon the stirrer which is transmitted to the shaft. Torquemeters have a transducer coupled to a shaft and a signal amplifier. Whenever torque is applied to the shaft, the strain generates a change in the electrical resistance of the gauges and produces an electrical signal that is directly proportional to the \( M \) applied. (Ascanio et al., 2004).

\[ P_S = M \Omega \tag{2.118} \]

Where \( M \) is the measured torque and \( \Omega \) is the angular velocity. The angular velocity is

\[ \Omega = 2\pi N \tag{2.119} \]

Substituting the equation above in Equation 2.118 yields

\[ P_S = 2\pi N M \tag{2.120} \]
Table 2.8: Advantages and disadvantages of power consumption measurement techniques (from Ascanio et al. (2004)).

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages/ Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical</td>
<td>√ simple</td>
</tr>
<tr>
<td></td>
<td>√ little instrumentation</td>
</tr>
<tr>
<td></td>
<td>√ low investment</td>
</tr>
<tr>
<td></td>
<td>× power losses must be discounted</td>
</tr>
<tr>
<td></td>
<td>× difficult to determine losses</td>
</tr>
<tr>
<td></td>
<td>× friction losses may represent 70% of total power</td>
</tr>
<tr>
<td>Calorimetric</td>
<td>√ high precision</td>
</tr>
<tr>
<td></td>
<td>√ friction losses do not need to be considered</td>
</tr>
<tr>
<td></td>
<td>× relationships are complicated</td>
</tr>
<tr>
<td></td>
<td>× requires highly sensitive instrumentation</td>
</tr>
<tr>
<td></td>
<td>× thermistors’ position is important and can alter flow pattern</td>
</tr>
<tr>
<td>Dynamometers</td>
<td>√ good option for bench and pilot scale</td>
</tr>
<tr>
<td></td>
<td>√ wide torque range</td>
</tr>
<tr>
<td></td>
<td>√ precision measurement if losses are taken into account</td>
</tr>
<tr>
<td></td>
<td>× high investment</td>
</tr>
<tr>
<td></td>
<td>× not suited for industrial level</td>
</tr>
<tr>
<td>Torquemeters</td>
<td>√ wide torque range</td>
</tr>
<tr>
<td></td>
<td>√ little instrumentation</td>
</tr>
</tbody>
</table>

Because a portion of the reaction torque is due to friction in bushing, bearings or seals, the $M$ due to these losses needs to be subtracted (Ascanio et al., 2004).

Once $M$ has been corrected for losses, $P_0$ and $\varepsilon$ can be calculated as reviewed in Section 2.4.2.2.

### 2.5 Droplet breakup in the laminar regime

There are practically no data or fundamental analysis for drop dispersion in stirred tanks under laminar conditions (Leng and Calabrese, 2003). Dispersion can occur in laminar conditions. Laminar flow fields are highly dependent on geometry and even in laminar conditions the droplet behaviour is difficult to analyse. Most fundamental studies have focused on single drops in homogeneous shear and extensional flows (Leng and Calabrese, 2003). Extensive reviews are given by Tucker III and Moldenaers (2002) and by Guido and Greco (2004).
In an idealized laminar shear flow field, with low Re and negligible inertia effects, the forces driving the deformation are shear stresses, while the resistance force is the Laplace pressure (Eq. 2.2), dimensional analysis (first derived by Taylor (1932)) reveals that drop size data can be correlated by two dimensionless numbers, namely the capillary number Ca and the viscosity ratio $p$.

$$Ca = \frac{\eta c \dot{\gamma} d}{\sigma} \quad (2.121)$$

It can be noted that if Ca is small interfacial forces dominate, the opposite is true for the disruptive shear. Taylor (1932) theorised that drop burst occurs when a critical Capillary number $Ca_{crit}$ is reached and that the $Ca_{crit}$ is $p$ dependent.

Karam and Bellinger (1968) used a concentric-cylinder geometry and a camera to study the effect of $p$ on the $Ca_{crit}$. His results are summarized in Figure 2.31. Karam and Bellinger (1968) emphasizes that the breakup of a droplet into two equally-sized drops is rare and that a wide range of sizes is obtained even under uniform shear. They found that for simple shear there is a U-shaped dependence of the $Ca_{crit}$ on $p$; there is an upper and a lower limit beyond which a droplet cannot break. Breakup can only occur for a well defined interval of $p$. For low $p$, the viscous forces cannot overcome the interfacial forces and for very high $p$, the drop becomes highly deformed but does not break. They also noticed that some drops breakup become unstable after the cessation of flow, they attributed this phenomena to internal recirculation inside the drops.

Furthermore, Taylor (1932, 1934) and Grace (1982) found that an elongation-flow field is more effective for droplet breakup; for elongational fields $Ca = \eta \dot{\varepsilon} d / \sigma$. The $Ca_{crit}$ as a function of $p$ are commonly represented in the so-called “Grace plots”. Figure 2.32 a schematic representation of the curves for shear and elongational flows. According to these type of plots, drop breakup occurs when $Ca > Ca_{crit}$ for the respective type of stress applied. Some interesting features can be noticed in Figure 2.32; for shear flow (1) there is a minimum $Ca_{crit} = 4$ when $p = 1$ and (2) drop breakup does not occurs for $p > 4$. Whereas elongational flow fields can break any type of drops regardless of $p$. 
Rumscheidt and Mason (1962) classified drop breakup depending on the viscosity ratio as follows:

- $p < 0.5$ Drop becomes S-shaped and tiny drops break from its ends (tip streaming)
- $p > 0.2$ The drop breaks through the centre with the formation of two large drops and three satellite ones
- $p < 2$ The drop extend into a cylinder and eventually breaks
- $p > 4$ The drop becomes deformed and aligns with the flow, the drops did not break in their experiments

On the other hand, Tucker III and Moldenaers (2002) gave another generalisation on the drop-burst mechanisms (see Fig. 2.33):
2.5. Droplet breakup in the laminar regime

Figure 2.32: Critical Capillary number $C_{a, \text{crit}}$ for breakup in simple shear and 2D-elongational flow as a function of the viscosity ratio $p$. Adapted from (Grace, 1982).

- $p \ll 1$ Drops assume a S-shape, and small droplets are released from the ends (tip streaming).
- $p \approx 1$ The central portion of the droplets gradually necks until the droplet breaks into two daughter droplets, with small satellite drops in-between.
- $Ca \gg C_{a, \text{crit}}$ The droplet stretches into a slender fibril, which subsequently breaks up by capillary-wave instability (also called Rayleigh instability).

Figure 2.33: Breakup mechanisms zones for simple shear flow. Adapted from (Tucker III and Moldenaers, 2002).
For concentrated emulsions, droplets breakage occurs at a lower $\text{Ca}_{\text{crit}}$. Jansen et al. (2001) proved experimentally for $0.1 < p < 22$ the so-called “mean field theory”, which considers that the forces experienced by a drop are proportional to the viscosity of the surrounding emulsion. The Ca and \( p \) for concentrated emulsion (\( \text{Ca}' \) and \( p' \) respectively) become

\[
\text{Ca}' = \frac{\eta e \gamma d}{\sigma} \\
p' = \frac{\eta d}{\eta e}
\]

which shifts the Grace curve downwards and to the right. This implies that more viscous dispersed droplets can be broken if the system if the dispersed volume fraction is high.

\section*{2.6 Droplet break-up in the turbulent regime}

\subsection*{2.6.1 Energy balance models}

The so-called “mechanistic models” are derived from energy balances in-between the cohesive and disruptive stresses. The cohesive one are considered to be the interfacial forces, although viscous stresses should also be considered for highly viscous dispersed phases. These models recognise the very complex phenomena occurring during emulsification and are limited in that these estimate the diameter of the largest surviving drop $d_{\text{max}}$.

Sprow (1967) proposed that $d_{\text{max}} \propto \bar{d}_{32}$, ever since these two term have been used interchangeably in literature. This is due to the relevance of $\bar{d}_{32}$ in many processes and because it is used as the measure of central tendency to characterise emulsions. For example, the rheological models reviewed in Section 2.3.2 use $\bar{d}_{32}$ as characteristic size of the dispersions. A more thorough review on the $\bar{d}_{32}$ to $d_{\text{max}}$ ratio (used as measure of polydispersity), along with its limitations can be found in Section 2.7.3 and in Chapter 4.

Furthermore, these models were derived considering the “local energy dissipation”
2.6. Droplet break-up in the turbulent regime

\( \varepsilon \), as turbulence in mechanically agitated vessels or in rotor-stators is not homogeneous (maximum at the vicinity of the impeller), the maximum energy dissipation \( \varepsilon_{\text{max}} \) (at the impeller’s surroundings) should be considered for systems in steady-state as recommended by Davies (1985) and by Zhou and Kresta (1998). As discussed previously in Section 2.4.2.3, estimating \( \varepsilon_{\text{max}} \) is difficult, nevertheless \( \varepsilon_{\text{max}} \propto \overline{\tau} \) is considered to apply and therefore Equation 2.99 can be used.

These models can be represented in a dimensionless form when emulsification is carried out in the turbulent regime for constant Po.

The disruptive forces are considered to be the kinetic energy of the surrounding eddies, or viscous stresses depending on the size range of the droplets. As reviewed in Section 2.4.1.4, Kolmogorov (1941a) hypothesized that for infinite Reynolds numbers, there is a scale range in which viscous forces are negligible and the flow can be considered isotropic. If drops are in this size range emulsification \((L >> d >> \ell_\eta, \ell_\eta \text{ given by Eq. } 2.57)\), emulsification is said to occur in the “turbulent inertia regime”.

On the other hand, if the drops are smaller than \( \ell_\eta \), drop breakage is said to occur in the “viscous sub-range”. The two main models proposed for this size range are the viscous-inertial and viscous-viscous depending if inertial or if viscous shear stresses are the dominant disruptive stresses.

The theories developed by Hinze (1955) and by Shinnar and Church (1960) have been the backbone of most mechanistic models. The models have been extended to account for the viscosity of the dispersed phase mainly by Calabrese et al. (1986a) and Wang and Calabrese (1986), empirically they have been extended to account for coalescence (Pacek et al., 1998), turbulence dampening (Doulah, 1975; Brown and Pitt, 1972) and for the type of impeller (McManamey, 1979). Many correlations found in literature have been summarized by Leng and Calabrese (2003) and by Singh et al. (2008).

In this Section the models of Hinze (1955), Shinnar and Church (1960) and Calabrese et al. (1986a) will be explained, while their validation and results comparison with other authors can be found in the Introduction and Literature review of the following chapters. For stirred vessels: Chapter 4 focuses on the effect of \( \mu_d \), Chapter
5 on the effect of the $\mu_c$ and Chapter 6 on the effect of the volume fraction of the dispersed phase $\phi$; and for high-shear mixers Chapter 7 focuses on the effect of $\mu_d$ and Chapter 8 on time effects.

2.6.1.1 Turbulent inertia regime

Hinze (1955) theorized that, in contrast to shear forces ($\tau = \mu_c \dot{\gamma}$) causing drop breakage in the laminar regime, dynamic pressure forces of the turbulent motions were responsible for drop breakage at high Reynolds numbers. Analogously to the theory proposed by Taylor (1932) in which drop breakup occurs at a $Ca_{\text{crit}}$ (Eq. 2.121), Hinze suggested that drop breakup occurs at a given critical Weber number $We_{\text{crit}}$. In fact, the $Ca$ and $We$ are homologous, the former being a specific type of the more general $We$. Hinze suggested that the stresses experienced by a drop in an isotropic turbulent flow field were of the order of $\tau_c = \rho_c u'^2$, yielding

$$We_{\text{crit}} = \frac{\rho_c u'^2 d_{\text{max}}}{\sigma}$$

(2.124)

Furthermore, and in analogy to Taylor’s theory, he determined that $We_{\text{crit}}$ was a function of the viscosity of the dispersed phase $\mu_d$, he formulated that the stress inside the droplet opposing deformation $\tau_d$ is given by

$$\tau_d \propto \mu_d \sqrt{\frac{\tau_c}{\rho_d}}$$

(2.125)

Through dimensionless analysis he suggested a viscous dimensionless group $Vi_H$ and the following dependency

$$Vi_H = \frac{\mu_d}{(\rho_d \sigma d)^{1/2}}$$

(2.126)

$$We_{\text{crit}} = C_1 [1 + f(Vi_H)]$$

(2.127)

If $Vi_H \to 0$, $We_{\text{crit}}$ is simply constant $C_1$. Hinze did not suggest the function $f(Vi_H)$.

As the kinetic energy of the turbulent fluctuations increase with eddie length scale
2.6. Droplet break-up in the turbulent regime

ℓ (see Section 2.4.1.6), Hinze proposed that the fluctuations of similar size to the diameter of the drop \( d_{\text{max}} \) were the ones responsible for breakup. Larger fluctuations transport the drops; while structures much smaller do not contain enough energy to cause drop burst. The square mean velocity \( \overline{u'^2} \) was estimated using Kolmogorov’s -5/3 energy spectrum (Eq. 2.74)

\[
k = \frac{1}{2} \overline{u'^2} = \int_{\kappa_1}^{\kappa_2} C \varepsilon^{2/3} \kappa^{-5/3} d\kappa = -\frac{3C}{2} \left( \frac{\varepsilon}{\kappa} \right)^{2/3} \bigg|_{\kappa_1}^{\kappa_2} \tag{2.128}
\]

As the eddies responsible for drop breakup are in the \( d \to 0 \) to \( d_{\text{max}} \) size range, the corresponding wavelengths of the eddies causing drop burst are range from \( \kappa_1 \to \infty \) to \( \kappa_2 \propto 1/d_{\text{max}} \), yielding

\[
\overline{u'^2} \propto (\varepsilon d)^{2/3} \tag{2.129}
\]

Substituting Equation 2.129 in Equation 2.124 and rearranging

\[
d_{\text{max}} \propto \left( \frac{\sigma}{\rho c} \right)^{3/5} \varepsilon^{-2/5} \tag{2.130}
\]

Shinnar and Church (1960) were the first ones to use the former equation for stirred vessels. As discussed previously, turbulence inside vessels is not homogeneously distributed (see Section 2.4.2.3), however the mean energy dissipation rate \( \varepsilon \) can be estimated by Equation 2.98 yielding

\[
d_{\text{max}} \propto \left( \frac{\sigma}{\rho c} \right)^{3/5} (N^3 D^2)^{-2/5} \tag{2.131}
\]

which can be re-arranged into

\[
\frac{d_{\text{max}}}{D} \propto \left( \frac{\rho c N^2 D^3}{\sigma} \right)^{-3/5} \tag{2.132}
\]

The right term inside the parenthesis is regarded as the Weber number of the impeller

\[
\text{We} = \frac{\rho c N^2 D^3}{\sigma} \tag{2.133}
\]
The final equation in its dimensionless form reads

\[ \frac{d_{\text{max}}}{D} = C_2 \text{We}^{-3/5} \]  

(2.134)

The former equation has been widely utilised to describe dilute systems with negligible viscous resistance inside the drops. The proportionality constant is a function of the type of the impeller and the geometrical features of the emulsification vessel.

2.6.1.1.1 Effect of the dispersed phase volume fraction Many authors have noticed an increase in drop size with \( \phi \), this has been attributed to drop coalescence (Coulaloglou and Tavlarides, 1976; Delichatsios and Probstein, 1976; Pacek et al., 1998), turbulence dampening (Brown and Pitt, 1972; Lagisetty et al., 1986; Cohen, 1991; Maaß et al., 2012) or both (Coulaloglou and Tavlarides, 1977; Desnoyer et al., 2003; Gäbler et al., 2006; Angle and Hamza, 2006). For any of the two aforementioned reasons, Equation 2.134 has been extended empirically to

\[ \frac{d_{\text{max}}}{D} = C_2 (1 + C_3 \phi) \text{We}^{-3/5} \] 

(2.135)

\[ \frac{d_{\text{max}}}{D} = d_{\text{max}}^0 (1 + C_3 \phi) \] 

(2.136)

where \( d_{\text{max}}^0 \) is the maximum drop diameter as \( \phi \to 0 \). Typically values for \( C_3 \) range in-between 2.5 and 10.

Doulah (1975) hypothesized that the increase in drop size was due to an increase of \( \mu_c \) and that this increase affected the scales of the turbulent eddies. Supposed two systems with energy dissipation \( \varepsilon_1 \) and \( \varepsilon_2 \) with their respective kinematic viscosity \( \nu_1 \) and \( \nu_2 \), but that these share the same energy spectrum and same \( \ell_\eta \) (Eq. 2.57). The following correlation can be derived

\[ \frac{\varepsilon_1}{\varepsilon_2} = \left( \frac{\nu_2}{\nu_1} \right)^3 \] 

(2.137)
Similarly the ratio of Equation 2.134 for these two hypothetical systems becomes

\[
\frac{d_{\text{max}}}{d^0_{\text{max}}} = \left( \frac{\nu_2}{\nu_1} \right)^{6/5}
\]

(2.138)

Using the equation for dilute suspensions derived by Einstein (1906) (Eq. 2.28)

\[
\frac{d_{\text{max}}}{d^0_{\text{max}}} = \left( \frac{\rho_c}{\rho_d} \right)^{6/5} \left( 1 + 2.5\phi \right)^{6/5}
\]

(2.139)

which is very similar to

\[
d_{\text{max}} = d^0_{\text{max}} (1 + 3\phi)
\]

(2.140)

Doulah (1975) argues that \( C_3 = 3 \) due to viscous effects. The limitations of these model with the background given in Section 2.3.2 where the rheological behaviour of emulsions were reviewed.

### 2.6.1.1.2 Effect of the dispersed phase viscosity

Calabrese et al. (1986a) extended the model developed by Hinze (1955) by including the resistance stresses inside the droplet. He balanced the cohesive Laplace pressure (Eq. 2.3) and the resistance stresses of the drop \( \tau_d \) (Eq. 2.125) with the disruptive turbulent energy fluctuations \( \tau_c = \rho_c u'^2 \), \( u'^2 \) given by Equation 2.129) yielding

\[
\rho_c \varepsilon^{2/3} d_{\text{max}}^{2/3} = C_4 \frac{\sigma}{d_{\text{max}}} + C_5 \frac{\mu_d}{d_{\text{max}}} \left( \frac{\rho_c \varepsilon^{2/3} d_{\text{max}}^{2/3}}{\rho_d} \right)^{1/2}
\]

(2.141)

\[
d_{\text{max}} = C_6 \left( \frac{\sigma}{\rho_c} \right)^{3/5} \varepsilon^{-2/5} \left[ 1 + C_7 \frac{\mu_d}{\sigma} \left( \frac{\rho_c}{\rho_d} \right)^{1/2} \left( \varepsilon d_{\text{max}} \right)^{1/3} \right]
\]

(2.142)

which is a transcendental equation. Equation 2.142 reduces to Equation 2.130 for \( \mu_d = 0 \); if the viscous resistance is much larger than the cohesive Laplace pressure Equation 2.142 reduces to

\[
d_{\text{max}} = C_8 \mu_d^{3/4} (\rho_c \rho_d)^{-3/8} \varepsilon^{-1/4}
\]

(2.143)
For a stirred vessel, Equation can be rearranged using the previously defined Weber number in Equation 2.133 and introducing a new definition of the the dimensionless viscosity group $V_{iC}$ (first introduced in (Wang and Calabrese, 1986))

$$
\frac{d_{max}}{D} = C_9 \text{We}^{-3/5} \left[ 1 + C_{10} V_{iC} \left( \frac{d_{max}}{D} \right)^{1/3} \right]^{3/5}
$$

(2.144)

where

$$
V_{iC} = \frac{\mu_d N L}{\sigma} \left( \frac{\mu_c}{\rho_d} \right)^{1/2}
$$

(2.145)

Equation 2.144 reduces to Equation 2.134 for $V_{iC} \to 0$ and $V_{iC} \to \infty$, the dimensionless form of Equation 2.143 is

$$
\frac{d_{max}}{D} = C_{11} \left( \frac{\mu_d}{\mu_c} \right)^{3/4} \left( \frac{\rho_c}{\rho_d} \right)^{3/8} \text{Re}^{-3/4}
$$

(2.146)

As Re is a function of $\mu_c$, the former equation does not consider any $\mu_c$-dependency. Equation 2.144 was extended by Calabrese et al. (1986b) to account for the dispersed phase volume fraction $\phi$

$$
\frac{d_{max}}{D} = C_9 \left( 1 + 3\phi \right) \text{We}^{-3/5} \left[ 1 + C_{10} (1 - 2.5\phi) V_{iC} \left( \frac{d_{max}}{D} \right)^{1/3} \right]^{3/5}
$$

(2.147)

2.6.1.2 Viscous subrange regime

These models were theoretically-derived for drops smaller than $\ell_\eta$, the inertial stress model for $d_{max} < \ell_\eta$ and the shear stress model for $d_{max} << \ell_\eta$. Due to the large amount of energy required to reach those drop sizes, there is few experimental evidence of the applicability of these models using water as continuous phase. Rueger and Calabrese (2013) could correlate their results using the viscous subrange-inertia stress model for his emulsions produced using a high shear mixer.

The mechanistic models for the inertia regime predict no effect of $\mu u_c$, however there has been experimental evidence that increasing $\mu_c$ has an effect on $d_{max}$. This has been attributed to an increase of $\ell_\eta$ (see Eq. 2.57). For stirred vessels Boxall et al. (2012) correlated their results obtained by emulsifying water in highly viscous
oils using the viscous subrange-shear stress model. However their stirred vessels were
doubtfully in the turbulent regime or carried out at a constant Po. Vankova et al.
(2007) emulsified silicon oil in various glycerol/water solutions and also found an
effect of $\mu_c$ on $d_{max}$, they correlated their results using the turbulent
inertia model for low $\mu_c$ and using the viscous subrange-shear stress model for higher
$\mu_c$.

For rotor-stators, Hall et al. (2011) also found a dependency on $\mu_c$, however it was
weaker than predicted by any of the two viscous subrange model. They concluded
that this was due to $d_{max}$ and $\ell_\eta$ being of an comparable size.

It is worth mentioning that the viscous subrange-inertia stress model has been
heavily criticised by Bourne and Baldyga (1994) among others. The reason for the
criticism is that for drops smaller than $\ell_\eta$ the disruptive stresses should be viscous
and not inertial.

The models reviewed below were developed by Shinnar and Church (1960) for
inviscid dispersed phases. Padron Aldana (2005) expanded these models for viscid
drops.

2.6.1.2.1 Inertia stresses Through dimensional analysis, Shinnar and Church
(1960) determined that the turbulent velocity fluctuations in the sub-Kolmogorov
scale are given by

$$u'^2 \propto \frac{\rho_c \varepsilon}{\mu_c} d^2$$

Substituting the former equation in Equation 2.124 lead to

$$d_{max} = C_{12} \left( \frac{\mu_c}{\rho_c^2} \right)^{1/3} \varepsilon^{-1/3}$$

$$\frac{d_{max}}{D} = C_{13} (WeRe)^{-1/3}$$

Padron Aldana (2005) extended the previous equation to account for $\mu_d$ following
the same procedure as Calabrese et al. (1986a) for the turbulent inertia regime. The
final expression in its dimensionless form is

\[
\frac{d_{\text{max}}}{D} = C_{14} (\text{WeRe})^{-1/3} \left[ 1 + C_{15} \text{ViCRe}^{1/2} \frac{d_{\text{max}}}{D} \right]^{1/3}
\] (2.151)

For the high viscosity case

\[
\frac{d_{\text{max}}}{D} = C_{16} \left( \frac{\mu_d}{\mu_c} \right)^{1/2} \left( \frac{\rho_c}{\rho_d} \right)^{1/4} \text{Re}^{-3/4}
\] (2.152)

2.6.1.2.2 Shear stresses The model developed by Shinnar and Church (1960) if the disruptive stress is shear, can be derived combining the expression for \( \text{Ca}_{\text{crit}} \) (see Eq. 2.121) and considering that the shear rate \( \dot{\gamma} \) are obtained as previously described by Equation 2.101. For a drop of diameter \( d_{\text{max}} \) and for a \( \text{Ca}_{\text{crit}} \) independent of \( \mu_d \) the following expression can be obtained

\[
d_{\text{max}} = C_{17} \sigma \left( \frac{\mu_c}{\rho_c} \right)^{-1/2}
\] (2.153)

In its dimensionless form

\[
\frac{d_{\text{max}}}{D} = C_{18} \text{We}^{-1} \text{Re}^{1/2}
\] (2.154)

As reviewed in Section 2.5, \( \text{Ca}_{\text{crit}} \) is a function of the viscosity ratio \( p \), Padron Aldana (2005) suggested the function to have the form \( 1 + \tau_d/\tau_c \), however this correlation has no been proven. The final expression in its dimensionless form reads

\[
\frac{d_{\text{max}}}{D} = C_{19} \text{We}^{-1} \text{Re}^{1/2} \left( 1 + C_{20} \text{ViCRe}^{-1/4} \right)
\] (2.155)

For \( \text{ViC} \to 0 \), it reduces to Equation 2.154 and for very viscous dispersed phases to

\[
\frac{d_{\text{max}}}{D} = C_{21} \left( \frac{\mu_d}{\mu_c} \right) \left( \frac{\rho_c}{\rho_d} \right)^{1/2} \text{Re}^{-3/4}
\] (2.156)
2.6.2 Population Balance Equations

2.6.2.1 Basics

Population Balance Equations (PBE) are a tool used for modelling systems composed of a discrete number of entities interacting with their environment (continuous phase). Therefore they have been used in multiphase systems such as suspensions, emulsion, aerosols and foams in processes such as crystallisation, milling, polymerisation, fermentation, boiling, emulsification, etc (Ramkrishna and Singh, 2014; Solsvik and Jakobsen, 2016). The dispersed phases such as bubbles, drops or solid particle have distribution properties such size and composition which are tracked by the different terms in the PBE (Solsvik and Jakobsen, 2015).

The source terms account for the birth and death of these entities; provided that the birth and death processes involve entities with different characteristic, these are integral terms; therefore PBE are integro-differential equations. In emulsification the birth and death events are called drop breakage and drop coalescence. PBE can be derived from continuum mechanic principles, statistical Boltzmann-like equations and probability principles (Solsvik and Jakobsen, 2015).

For droplets of a volume $V$ breaking into droplets of size of volume $V'$ entering and leaving at a velocity $u_i$ a control volume (with coordinates $x_i$) through different mechanisms such as convection, breakup or coalescence; the number density $n$ becomes (Liao and Lucas, 2009)

$$\frac{\partial n(V', x_i, t)}{\partial t} + \frac{\partial}{\partial x_i} [u_i(V', x, t)n(V', x, t)] = S_b + S_c$$

(2.157)

where

(I) Accumulation

(II) Droplets entering and leaving the control volume due to convection, if the flow is considered uniform this term becomes zero. This term is used when PBE are couples with computation fluid dynamics (CFD) (Liao and Lucas, 2009).

(III) Source term from drop breakup. Drop breakup results in the death of the
mother drop and in the birth of daughter drops. The breakup term can therefore be decomposed into the birth $B_b$ and death rates $D_b$: $S_b = B_b - D_b$.

(IV) Source term from drop coalescence. in the case of binary coalescence two mother drops coalesce to generate a single daughter drop. Analogously to breakup: $S_c = B_c - D_c$.

For uniform flow, Equation 2.157 becomes

$$\frac{\partial n(V', x_i, t)}{\partial t} = B_b - D_b + B_c - D_c$$

(2.158)

The model for the birth and death rates due to drop breakup are given by (Coulaloglou and Tavlarides, 1977; Liao and Lucas, 2009)

$$B_b = \int_{V'}^{\infty} m(V') \beta(V', V) \Omega(V) n(V, t) dV$$

$$D_b = \Omega(V') n(V', t)$$

where $m(V')$ is the number of drops formed from breakage of size $V'$, $\beta(V', V)$ is the distribution of daughter droplets formed from the breakup of drops of size $V$ and $\Omega(V)$ is the breakage frequency. For coalescence the birth and death rates are given by

$$B_c = \int_0^{V'} \lambda(V - V', V') h(V - V', V') n(V - V', t) n(V', t) dV'$$

(2.159)

$$D_c = n(V, t) \int_0^{\infty} \lambda(V, V') h(V, V') n(V', t) dV$$

(2.160)

where $\lambda(V' - V, V)n(V', t)n(V, t)$ is the coalescence frequency and $h(V' - V, V)$ its efficiency.

In this dissertation dilute emulsions with a high concentration of surfactant were considered, therefore coalescence was neglected and will not be reviewed.
2.6. Droplet break-up in the turbulent regime

2.6.2.2 Breakup source term

There is much disagreement on what causes drop breakage. Solsvik et al. (2015) classified the breakup criteria into six. The list below describes the criteria while the number in parenthesis the number of models, modifications and extensions of each criteria reviewed in (Solsvik et al., 2015). Each of the models suggests a different breakup frequency $\Omega(V)$.

(I) turbulent kinetic energy of the drop is larger than a critical value (10)

(II) turbulent velocity fluctuation around the surface of the drop becomes greater than a critical value (2)

(III) turbulent kinetic energy of the hitting eddies are larger than a critical value (6)

(IV) drop breaks if the turbulent inertia stress becomes greater than the Laplace pressure of the smallest daughter particle (2)

(V) combination of III and IV (4)

(VI) drop breaks if the turbulent inertia stress in the continuous phase is larger than the Laplace pressure (5)

As an example, in the classical model proposed by Coulaloglou and Tavlarides (1977)

$$\Omega(V) = K_1 \frac{\epsilon^{\frac{1}{3}}}{V^\frac{2}{3}} \exp\left(-\frac{K_2 \sigma}{\rho_d \epsilon^{\frac{2}{3}} V^\frac{5}{9}}\right)$$

The previous equation states that $\Omega(V)$ increases with $\epsilon$, $\rho_d$ and decreases with $\sigma$. Regarding the effect of $V$ on $\Omega$, some models indicate that $\Omega$ increases monotonously while other predict a maximum (as in the model of Coulaloglou and Tavlarides (1977)) (Liao and Lucas, 2009).

The distribution of daughter droplets $\beta(V', V)$ is naturally linked to the number of number of drops produced $m(V')$, the most predominant assumption found in literature is binary breakup (Sajjadi et al., 2013; Solsvik et al., 2015); this will be discussed later in this Section. Sajjadi et al. (2013) classified the different models for $\beta(V', V)$ found in literature in two: (1) statistical and (2) empirical or
phenomenological. The statistical-based models that have been used in literature are the normal, beta, uniform and random distributions (Sajjadi et al., 2013; Solsvik et al., 2015). For example, (Coulaloglou and Tavlarides, 1977) assumed a binary breakage \( m(V') = 2 \) and a normal distribution, his equation for \( \beta(V', V) \) reads

\[
\beta(V', V) = \frac{24}{V'} \exp \left[ \frac{45(2V - V')^2}{V'^2} \right]
\]  

(2.162)

The phenomenological models are the U-shaped, M-shaped and the Bell-shaped. The U-shape predicts minimum probability of producing two droplets of the same size and highest probability of producing a very large and a very small drop. The bell-shape assumes that the droplets split into two daughter droplets within a size range difference. Finally the M-shape proposes that the probability is size dependent. The function has two maximum and three minimum probabilities (Sajjadi et al., 2013). Based on their single drop experiments, Maaß et al. (2011) argues that the M-shape distribution is the most adequate.

In the last decade, single drop breakup has been studied using high speed cameras. These studies allow to observe the deformation, breakage location, breakage time, number of daughter drops and their sizes. A complete review on the single drop experiment findings is out of the scope of this dissertation, therefore only some of the main findings will be mentioned. A recent review has been published by Hasan (2017).

Regarding binary or multiple breakup, the single drop experiments performed by Maaß et al. (2011) and Maaß and Kraume (2012) support this idea. However, Solsvik et al. (2016) used two different definitions of droplet breakup: (1) Initial breakup was defined as the one which ends after initial breakup and subsequent fragmentation of the daughter drops is neglected and (2) the breakup event encompasses a sequence of breakups. The difference between these two definitions rely on whether or not it is considered that the breakup process has finish after the initial split or after the restoration of the spherical shape. The two different definitions are shown schematically in Figure 2.34.
2.6. Droplet break-up in the turbulent regime

Figure 2.34: Schematic representation of initial breakup, independent breakup and breakup cascade models. From (Solsvik et al., 2016).

Figure 2.35 shows the number of fragments as a function of the diameter of the mother drop for petroleum drops; using both drop breakup definitions. This figure shows that a droplet can breakup in more than 100 fragments before restoring its spherical shape, that the number of fragments is a function of the size of the daughter drop, that multiple breakup is more likely for large droplets and that binary breakup is a reasonable assumption (as an average) only if the initial breakup definition is used. However Solsvik et al. (2016) argues that the final breakup definition should be used, as the initial breakup definition does not consider the energy transferred in-between two breakup events in which the drop shape has not been fully restored.

2.6.2.3 Coalescence source terms

Our main concern in this dissertation is drop breakup as 5 out the 6 results chapters deal with dilute emulsions (1%). Chapter 6 deals with concentrated emulsions, it results obvious from the collision frequency term \( \lambda(V - V', V') n(V', t)n(V, t) \), that an increase in concentration or number density \( n(V', t) \) favours coalescence; a brief
Chapter 2. Literature review

Figure 2.35: Number of daughter drop fragments as a function of the diameter of the mother drop using the two different definitions used by (Solsvik et al., 2016).

summary of the variables affecting coalescence is included.

Drops in a turbulent field collide and coalesce if the liquid film in-between two drops drain. Coalescence is considered to occur in three steps: collision, liquid film drainage and rupture (Sajjadi et al., 2013). Coalescence is determined by collision frequency $\lambda(V - V', V') n(V', t) n(V, t)$ and its efficiency $h(V, V')$.

There are three typed of models for $\lambda(V - V', V')$: (1) by turbulent fluctuations, (2) by capturing a turbulent eddie and (3) by velocity gradient Sajjadi et al. (2013). As an example, Coulaloglou and Tavlarides (1977) proposed that for drops of diameter $d'$ and $d$ (model type 1)

$$\lambda(d, d') = \frac{K_2}{1 + \phi} (d + d')^2 \left( d^{2/3} + d'^{2/3} \right)^{1/2} \varepsilon^{1/3} \quad (2.163)$$

The above equation states that collision frequency increases with $\varepsilon$, and drop size.

In the film drainage models, the mean contact time $\overline{T_c}$ needs to be larger than the time required for the film in-between two drops to reach a critical thickness $\overline{T_c}$. Coulaloglou and Tavlarides (1977) determined that the coalescence efficiency could be determined by $h(V, V') = \exp(-\overline{T_c}/\overline{T_c})$. In their model, each of the terms is
estimated by

\[
\overline{T_c} = (d + d')^{2/3} \varepsilon^{-1/3}
\]  

(2.164)

\[
\overline{t_c} = K_3 \mu_c \rho_c \varepsilon^{2/3} \frac{(d + d')^{2/3}}{\sigma^2} \left( \frac{dd'}{d + d'} \right)^4
\]  

(2.165)

leading to

\[
h(V, V') = \exp \left[ -\frac{K_4 \mu_c \rho_c \varepsilon}{\sigma^2} \left( \frac{V^{1/3} V'^{1/3}}{V^{1/3} + V'^{1/3}} \right)^4 \right]
\]  

(2.166)

The above equation indicates that \( h(V, V') \) increases with lower continuous phase viscosity \( \mu_c \), and energy input \( \varepsilon \), larger drop size (\( V' \) and \( V \)) and interfacial tension \( \sigma \). The equations above do not account for the viscosity of the dispersed phase \( \mu_d \). Chesters (1991) and Tsouris and Tavlarides (1994) have proposed models which account for \( \mu_d \), in both models coalescence efficiency decreases greatly as \( \mu_d \) increases due to an increase in \( \overline{t_c} \).

### 2.6.2.4 Limitations of the PBE

As pointed out by Leng and Calabrese (2003), one of the most obvious limitations is the difficulty of solving the PBE. Other limitations is the experimental difficulty to validate the models and that the source terms are equipment-specific and should not be used for scale-up, however these might be used for optimisation.

Other limitation is that many models do not have number and volume conservation properties (Solsvik et al., 2015), they are limited by turbulence properties, there is no enough understanding of the breakup and coalescence mechanism to make phenomenological models and are not based on physical observations (Leng and Calabrese, 2003; Liao and Lucas, 2009).

For example, single drop experiments performed by (Maaß and Kraume, 2012) found that drop breakup time increases with \( V \) as predicted by the different PBE models, but that the models consider that breakup times are an order of magnitude larger than the experimental one.

As single drop experiments have shown, the effect of interfacial tension and
specially of viscosity are poorly understood and mostly neglected (Liao and Lucas, 2009; Solvik et al., 2015; Liao and Lucas, 2009; Maass and Kraume, 2012).

2.7 Droplet size distribution

2.7.1 Drop size distribution measurement

2.7.1.1 Introduction

There are several techniques to determine the DSD of emulsions produced in mechanically stirred equipment. Abidin et al. (2013) did a comprehensive review of the most used techniques and classified them as shown in Figure 2.36. In-situ (or in-line) measurements refers to those techniques in which the DSD is measured where they are produced (e.g., stirred vessel) whereas external measurements (or off-line) refer to those in which sampling is required. External measurements have the inconvenience that coalescence might occur during sampling, if a kinetic study is performed only a small sample should be withdrawn as taking large samples might change the content of the vessel significantly. Sample coalescence might be hindered by adding surfactants and by using low dispersed phase volume fractions (Abidin et al., 2013).

In-line and off-line methods can be further divided into systems which measure a physical property of the emulsion and convert the obtained parameters into a DSD and direct image analysis where the drops are captured and sizes are measured directly by analysing the obtained images (Abidin et al., 2013).

Table 2.9 shows the measurement range, accuracy and whether or not the techniques are invasive. A thorough review of each of the techniques shown in Figure 2.36 and Table 2.9 is out of the scope of our investigation, therefore only some of the main features and working principles of the most common techniques will be done while focusing on the experimental method employed for our investigation: external laser diffraction.
2.7. Droplet size distribution

Figure 2.36: Classification of measurement techniques for Drop Size Distribution (from (Abidin et al., 2013)).

Table 2.9: Characteristics of DSD measurement techniques (from Abidin et al. (2013)).

<table>
<thead>
<tr>
<th>technique</th>
<th>measurement range [µm]</th>
<th>accuracy</th>
<th>invasive/ noninvasive</th>
</tr>
</thead>
<tbody>
<tr>
<td>FBRM</td>
<td>1 to 1000</td>
<td>low</td>
<td>invasive</td>
</tr>
<tr>
<td>ORM</td>
<td>1 to 1000</td>
<td>low</td>
<td>invasive</td>
</tr>
<tr>
<td>laser diffraction</td>
<td>0.02 to 2000</td>
<td>high</td>
<td>noninvasive</td>
</tr>
<tr>
<td>endoscope</td>
<td>5 to 5000</td>
<td>high</td>
<td>invasive</td>
</tr>
<tr>
<td>PVM</td>
<td>20 to 2000</td>
<td>high</td>
<td>invasive</td>
</tr>
<tr>
<td>stereomicroscope</td>
<td>20 to 2000</td>
<td>high</td>
<td>noninvasive</td>
</tr>
<tr>
<td>external microscope</td>
<td>5 to 3000</td>
<td>high</td>
<td>noninvasive</td>
</tr>
</tbody>
</table>

2.7.1.2 Light backscattering

The Focus Beam Reflectance Measurement (FBRM) is a technique in which a probe is directly inserted into a stream. The probe consists of a focused laser beam that spins at high speeds through a sapphire window located at the tip of the probe. When the laser beam intersects the edge of a particle, some of the light is backscattered to a detector (located in the same cylindrical probe) and induces a rise in the signal until it reaches the opposite side of the particle. The time reflectance time is measured and the chord length, which is the product of the reflectance time and the tangential velocity of the spinning laser beam, is registered (Abidin et al., 2013).

The Optical Reflectance Measurements (ORM) technique also records the chord
length by rotating a laser beam. The main difference with FBRM is that particles are tracked at a shorter distance due to the short focal point, this helps reducing the distance the laser beam has to travel across the mixture (Abidin et al., 2013).

Converting the chord lengths into DSDs is complex as the shape and optical properties of the drops need to be taken into account. These techniques are sensitive to the structure of the surface (Li et al., 2005). Li et al. (2005) compared different DSD measurement techniques including FBRM, laser diffraction (Malvern Mastersizer) and microscopy. They obtained good agreement in-between the latter two techniques and that the results obtained from the FBRM measurement deviated largely.

2.7.1.3 In-situ image analysis

In-line image analysis techniques photographs of the system are taken and the drop sizes are determined by image analysis. The main components of such techniques are a camera, a microscope and illumination. For these methods to be statistically significant, at least 250-500 drops have to be analysed within some seconds; therefore the camera frame rate is important if emulsification kinetics are studied (Abidin et al., 2013). These are time-consuming techniques because they requires processing a large number of images to build-up the DSD. The quality of the images is not only influenced by the equipment used, but by the concentration (drop images overlapping) and refractive index of the phases (interfaces easier to visualize) (Abidin et al., 2013).

The endoscope probe consists of camera placed at the upper end of an endoscope which captures images in the vicinity of the glass window located at the bottom of the endoscope.

The Particle Video Microscope (PVM) probes aslo include a camera but differentiates from the endoscope probe in that it includes focused lasers as mean of illumination to enhance the gray structure in the image and facilitate image analysis (Abidin et al., 2013).

In the stereomicroscope measurement technique, a camera with a stereomicroscope is located outside the vessel. The camera is synchronized with a flashing stroboscopic light source to enhance image quality.
2.7. Droplet size distribution

2.7.1.4 External Image Analysis

External image analysis is the simplest method to determine the DSD. It is a direct method that only requires a straightforward calibration. The most common methodology is to look at samples under the microscope and take images of them. The size distribution can later be processed using image analysis software.

This technique allows to measure particles in the $17 - 1000 \mu m$. The limitation of image analysis are mainly caused by the nature of light waves. This technique is often used for calibration of other measuring techniques that deduce the size distribution out of a property such as diffusivity or diffraction angle (Abidin et al., 2013).

2.7.1.5 Laser Diffraction Particle Sizing

Laser diffraction techniques rely on the fact that particles of different sizes scatter light with different angles. Large particles scatter light at small angles and small particles scatter light at larger angles. An example of scattered laser patterns for two different particle sizes is shown in Figure 2.37. This technique allows to measure particles in the $0.01 - 3500 \mu m$. A measuring instrument based on this principle consists of a source of coherent light of known wavelength, such as laser, a series of light intensity detectors, and some means to pass the sample through the light beam (Rhodes, 2008).

![Laser scatter patterns for two different particle sizes](image)

Figure 2.37: Laser scatter patterns for two different particle sizes (images by Powers K. in (Malvern Instruments, 2011)).

The particle size distribution of a dispersed system is obtained by measuring the
angular variation of intensity of scattered light as a laser beam passes through the sample (Malvern Instruments, 2015). The intensity data obtained in the detectors is analysed using the Fraunhofer theory or the Lorentz-Mie (referred as Mie) theory.

When light interacts with a particle, some of it is absorbed, some is refracted, some diffracted and some transmitted. These interactions are shown in Figure 2.38. The amount of light that is absorbed depends on the size of the particle and the material properties of the particle and the surrounding medium (Allen, 2003).

The Fraunhofer theory does not require the refractive indices of the phases but it can yield large errors when the refractive indices of the phases are similar (Rhodes, 2008). This theory is limited to particles that are opaque or large compared to the wavelength of light and only considers diffraction.

Mie theory requires knowledge of the real and imaginary components of the refractive index of the dispersant and sample. The real part component of the refractive index describes the refracted light and the imaginary one the absorption (Allen, 2003). Taking other interactions into account, apart from diffraction, allows to determine theoretically the size of particles smaller than the wavelength of light.

2.7.2 Basics

Droplets in an emulsion are seldom monodispersed and a variety of different sizes are present. A droplet size distribution is a list of values that define the relative amount
Droplet size distribution

Distributions can be discrete or continuous. A discrete distribution (denoted here as \( f(d_i) \)) is divided in size ranges or bands of a given width. A continuous distribution (denoted by \( p(d_i) \)) can be considered as a discrete distribution with infinite number of bands of infinitesimally small width. Experimental results are given as a discrete collection of data.

Distributions can be further expressed as frequency distributions \( f(d_i) \) or cumulative distributions \( F(d_i) \). Figure 2.39 shows an example of a \( f(d_i) \) and a \( F(d_i) \). Note that the \( F(d_i) \) runs from 0% to 100%. For a discrete distribution \( \sum f(d_i) = 100\% \) therefore their magnitude will depend on the number of different classes of \( d_i \). A frequency distribution is not to be confused with a probability density function where the area under the curve equal 100%.

![Typical differential and cumulative distributions.](image)

Frequency or cumulative distribution of droplets can be by number \( (f_n(d_i) \) and \( F_n(d_i)) \), area \( (f_a(d_i) \) and \( F_a(d_i)) \) or volume \( (f_v(d_i) \) and \( F_v(d_i)) \); for a given population of particles their distribution may be very different depending on the type of distribution used. In Figure 2.40 and example of a DSD by volume was transformed into the DSD by area and by number. As will be seen the interconversion in-between distributions has been done by several authors. If the large droplets are to be neglected it is more convenient (not to say easy) to characterize a distribution by
number, the opposite is true if the small droplets want to be neglected.

The conversion in-between distribution is very simple provided that droplets should be spherical when analysed. The conversion by volume to number and vice-versa are the most commonly used, the equation are presented below

\[
f_v(d_i) = 100 \cdot \frac{f_n(d_i) d_i^3}{\sum f_n(d_i) d_i^3}
\]

\[
f_n(d_i) = 100 \cdot \frac{d_i^3}{\sum \frac{f_v(d_i) d_i^3}{d_i^3}}
\]

Figure 2.40: Frequency distribution by volume, area and number obtained for the 1000 cSt silicon oil in water/SLES for \(N = 8.33 \text{s}^{-1}\).

2.7.2.1 Expressions of central tendency

In many practical situations it is desirable to describe a collection of data with a single number. These are known as Expressions of central tendency.

2.7.2.1.1 Mean Many different means or averages can be defined for the same distribution, depending if the basis of the distribution is the number of elements, their surface or volume. The equation to obtain the different means for discrete data
is:

\[
\overline{d}_{ab} = \left[ \frac{\sum f_n(d_i)d_i^a}{\sum f_n(d_i)d_i^b} \right] \frac{1}{a - b}
\]  

(2.169)

Where \( a \) and \( b \) define the type of mean. Table 2.10 shows some of the most common means obtained by changing the values of \( a \) and \( b \) in Equation 2.169.

**Table 2.10:** Commonly used means.

<table>
<thead>
<tr>
<th>Mean</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_{10} )</td>
<td>Arithmetic or number mean</td>
</tr>
<tr>
<td>( \overline{d}_{20} )</td>
<td>Surface mean</td>
</tr>
<tr>
<td>( \overline{d}_{30} )</td>
<td>Volume mean</td>
</tr>
<tr>
<td>( \overline{d}_{32} )</td>
<td>Volume/Surface mean or Sauter mean</td>
</tr>
<tr>
<td>( \overline{d}_{43} )</td>
<td>De Broukere mean</td>
</tr>
</tbody>
</table>

The most common mean reported for emulsification technology is the Sauter mean diameter \( \overline{d}_{32} \). This is due to the relevance of the interfacial surface per unit area \( a_v \) in chemical engineering operations where the amount of interface determines the heat, mass transfer and reaction rate. The interfacial surface per unit volume \( a_v \) and the \( \overline{d}_{32} \) are related by:

\[
\overline{d}_{32} = \frac{6\phi}{a_v}
\]

(2.170)

Figure 2.41 shows the location of different means for the same DSD shown in Figure 2.40.

### 2.7.2.1.2 Percentiles and Median

Percentiles indicate the value below a given number of occurrences in a group fall. The median or 50\(^{th}\) percentile \( D_{50} \) is read from the cumulative distribution as the 50% size; half of the particles are smaller and half of the particles are bigger than the median size. Several medians can also be found depending on the basis of the distribution. Most authors use the \( D_{95} \) as the maximum droplet diameter \( d_{\text{max}} \). The percentiles are read from the \( F_x(d_i) \).

The \( F_n(d_i) \) and \( F_v(d_i) \) and their respective \( D_{x,50} \) and \( D_{x,95} \) for the DSD previously presented in Figure 2.40 is shown in Figure 2.42. From this plot we can learn that
the percentiles are also affected by the basis of the DSD. In the same plot, it can be noticed that $F_n(d_i)$ has a straight-line appearance, indicating that much of the information of the size distribution presented in Figure 2.41 was lost.

**Figure 2.41:** Comparison between different defined means.

**Figure 2.42:** Cumulative distributions by number and volume and respective 50\textsuperscript{th} and 95\textsuperscript{th} percentiles obtained for the 1000 cSt silicon oil in water/SLES for $N = 8.33\, \text{s}^{-1}$.

### 2.7.2.1.3 Mode

The mode $Mo$ is the most frequently occurring size in a sample. It/They is/are the peak(s) or critical point(s) of the frequency distribution. Different modes can also be obtained for distributions by number, surface or volume. The
mode can be helpful if there is more than one peak in the distribution.

2.7.2.2 Moments

Moments are quantitative measures of the shape of a given distribution. Certain moments \( k \)th moments are well-defined as they have a clear meaning; moments can be classified in raw \( m_k \), central \( m_{k,c} \) and normalised \( m_{k,n} \). The meaning and result of the four first moments are shown in Table 2.11.

<table>
<thead>
<tr>
<th>Number ((k))</th>
<th>Raw ((m_k))</th>
<th>Central ((m_{c,k}))</th>
<th>Normalised ((m_{c,n}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>mean</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>variance</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>-</td>
<td>skewness</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>-</td>
<td>kurtosis</td>
</tr>
</tbody>
</table>

The previously defined means \( \bar{d}_{a,0} \) (\( a = 1 \) for a DSD by number, \( a = 3 \) by volume, etc) are also the first raw central moment \( m_1 \). The variance \( m_{2,c} \), also denoted by \( s^2 \) is the expectation of the square deviation of a variable from its mean. The skewness is a measure of the asymmetry of a distribution and the kurtosis is a measure of the “tailedness” of a distribution; flat distributions have lower kurtosis. Figure 2.43 shows the graphical representation of curves with very distinct variance, skewness and kurtosis. The moments for a continuous distribution \( p(d_i) \) are given by

\[
\text{Raw moment} \quad m_k = \int_0^\infty d_i^k p(x) dd_i
\]

\[
\text{Central moment} \quad m_{k,c} = \int_0^\infty (d_i - \bar{d})^k p(d_i) dd_i
\]

\[
\text{Normalised moment} \quad m_{k,n} = \int_0^\infty \frac{(d_i - \bar{d})^k p(d_i) dd_i}{m_{2,c}^{1/2}}
\]
and for discrete distributions

\[
m_k = \frac{\sum d_i^k f(d_i)}{\sum d(d_i)} \tag{2.174}
\]

Central moment

\[
m_{k,c} = \frac{\sum (d_i - \bar{d})^k f(d_i)}{\sum d(d_i)} \tag{2.175}
\]

Normalised moment

\[
m_{k,c} = \frac{\sum (d_i - \bar{d})^k f(d_i)}{m_{2,c}^{1/2} \sum d(d_i)} \tag{2.176}
\]

**Figure 2.43:** Schematic representations of distributions with distinct (a) variance, (b) positive and negative skewness and (c) positive and negative kurtosis.

2.7.2.3 **Dispersity of a distribution**

In statistics the standard deviation \( s \) is the square root of the variance or second central moment and is normally used to indicate how close the data points tend to be from the mean. A high \( s \) indicates that the distribution is wide, the opposite is
true for low values of $s$.

Other ways to characterize the width of a distribution is by calculating the Span or the Coefficient of Variation. These two parameter cite different percentiles. The smaller their values, the narrower the size distribution. Hall (2012) used a $\sqrt{D_{90}/D_{10}}$ to characterize the broadness of his distributions.

In emulsification technology the most common way to express the polydispersity of a distribution is by the $d_{32}/d_{\text{max}}$ ratio. For example, Nishikawa et al. (1991) reported $d_{32}/d_{\text{max}} = 0.45$; Calabrese et al. (1986a) found that $d_{32}/d_{\text{max}}$ is $\mu_d$-dependent. They found $d_{32}/d_{\text{max}} \approx 0.6$ for moderate viscous oils and $d_{32}/d_{\text{max}} \approx 0.5$ for highly viscous oil. Li et al. (2014) obtained bimodal DSD using a rotor-stator mixer and found $d_{32}/d_{\text{max}} = 0.16$. Liu and Li (2013) emulsified four crude oils of different $\mu_d$ using a batch rotor-stator mixer as they took samples at different time intervals. They obtained bimodal DSD and found that $d_{32}/d_{\text{max}}$ was independent of time but decreased as $\mu_d$ increased and the distribution broadened.

### 2.7.2.4 Probability density functions

A probability density function (PDF) describes the likelihood of a variable to acquire certain value. As the total probability (100%) is contained within the function (its integral), the probability is given by the integral of the function over a certain range.

$$\int_0^{\infty} p(d_i) \, dd_i = 100\% \tag{2.177}$$

To fit the discrete volume density distributions, as the ones reported by the Mastersizer 3000, either the probability density functions or the experimental data need to be re-scaled. The PDFs can be re-scaled by

$$f(d_i) = \frac{100}{\sum p(d_i) \cdot p(d_i)} \tag{2.178}$$

Alternatively converting the experimental data into a PDF requires numerical integration (i.e. rectangle rule, trapezium rule, Simpson’s rule, etc.) to make the area
under the curve 100%. Using the trapezoidal rule

\[ p(d_i) = \frac{100}{\sum (d_i - d_{i-1}) \left( \frac{f(d_i) + f(d_{i-1})}{2} \right)} \cdot f_x(d_i) \]  

(2.179)

Most of the attempts to fit a DSD found in literature use Normal or log-normal distribution. Before reviewing the DSD fits done by several authors, these two PDF and the Generalised Gamma function (GGf) will be reviewed.

2.7.2.4.1 Normal distribution  In the normal distribution or Gaussian distribution the mode, median and arithmetic mean coincide and 68.27% of the population lies within ±\( s \) and 95.45% lies within ±2\( s \). Its probability density \( p(d_i) \) and cumulative \( P(d_i) \) functions are

\[ p(d_i) = \frac{1}{s \sqrt{2\pi}} \exp \left[ -\frac{(d_i - \overline{d})^2}{2s^2} \right] \]  

(2.180)

\[ P(d_i) = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{d_i - \overline{d}}{\sqrt{2} s} \right) \right] \]  

(2.181)

In the former equations \( \overline{d} \) (\( \overline{d}_{10} \), \( \overline{d}_{20} \) or \( \overline{d}_{30} \)) and \( s \) (in its respective basis) are the arithmetic average (Eq. 2.169) and the square root of the variance (Eq. 2.172 for \( k = 2 \)). These equations can be used to fit the distributions by number, surface or volume if their corresponding \( \overline{d} \) and \( s \) are used.

![Figure 2.44: Density and cumulative normal and log-normal distributions.](a) Linear axes  (b) Semi-logarithmic axes
2.7.2.4.2 Log-normal distribution Alternatively, if the logarithm of the data
is normally distributed, the data can be expressed with a Log-normal or Galton
distribution. In the Log-normal distribution the geometric mean, geometric mode
and the median coincide. Its functions are

\[
p(d_i) = \frac{1}{s_G \sqrt{2\pi}} \exp \left[ -\frac{[\log(d_i) - \bar{d}]^2}{2s_G^2} \right]
\]

(2.182)

\[
P(d_i) = \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{\ln d_i - \bar{d}}{\sqrt{2s_G}} \right) \right]
\]

(2.183)

Where \(\bar{d}\) is the arithmetic mean of \(\log d_i\) (also known as geometric mean) and \(s_G\) is
the standard deviation of \(\log d_i\) of the distribution. Its \(Mo\) is given by

\[
Mo = \exp(\bar{d} - s^2)
\]

(2.184)

2.7.2.4.3 Generalised Gamma distribution Unlike the two former distribu-
tions, the Generalised Gamma function (GGf) has three fitting parameters. The GGf
is flexible in that other well-known distribution can be generated depending on the
values given to its parameters \(\kappa_G\), \(\tau_G\) and \(\lambda_G\). The subfamilies that the Generalised
Gamma function can generate are listed in Table 2.12. Additionally the log-normal
distributions is obtained for \(\tau_G \rightarrow \infty\) (Morteza Khodabin, 2010). Its frequency and
cumulative distribution functions are

<table>
<thead>
<tr>
<th>Distribution</th>
<th>(\kappa_G)</th>
<th>(\tau_G)</th>
<th>(\lambda_G)</th>
</tr>
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<tr>
<td>Exponential</td>
<td>1</td>
<td>1</td>
<td>(\lambda_G)</td>
</tr>
<tr>
<td>Gamma</td>
<td>(\kappa_G)</td>
<td>1</td>
<td>(\lambda_G)</td>
</tr>
<tr>
<td>Weibull</td>
<td>1</td>
<td>(\tau_G)</td>
<td>(\lambda_G)</td>
</tr>
<tr>
<td>Generalised normal</td>
<td>(\tau_G)</td>
<td>2</td>
<td>(\lambda_G)</td>
</tr>
<tr>
<td>Half normal</td>
<td>(\frac{1}{2})</td>
<td>2</td>
<td>(\sqrt{2s})</td>
</tr>
<tr>
<td>Rayleigh</td>
<td>1</td>
<td>2</td>
<td>(\sqrt{2s})</td>
</tr>
<tr>
<td>Maxwell-Boltzmann</td>
<td>(\frac{3}{2})</td>
<td>2</td>
<td>(\lambda_G)</td>
</tr>
<tr>
<td>Log-normal</td>
<td>(\kappa_G)</td>
<td>(\infty)</td>
<td>(\lambda_G)</td>
</tr>
</tbody>
</table>
\[ p(d_i) = \frac{\kappa_G}{\lambda_G \Gamma(\tau_G)} \left( \frac{d_i}{\lambda_G} \right)^{\tau_G \kappa_G - 1} \exp \left[ - \left( \frac{d_i}{\lambda_G} \right)^{\kappa_G} \right] \] (2.185)

\[ P(d_i) = \frac{\gamma_G \left[ \tau_G \left( \frac{d_i}{\lambda_G} \right)^{\kappa_G} \right]}{\Gamma(\tau_G)} \] (2.186)

Where \( \Gamma() \) and \( \gamma() \) are the gamma function and the incomplete gamma function.

Its mean \( \overline{d} \), variance \( s^2 \) and mode \( M_o \) are

\[ \overline{d} = \frac{\lambda_G \Gamma\left( \kappa_G + \frac{1}{\tau_G} \right)}{\Gamma(\kappa_G)} \] (2.187)

\[ s^2 = \frac{\lambda_G^2 \Gamma\left( \kappa_G + \frac{2}{\tau_G} \right)}{\Gamma(\kappa_G)} \left[ \frac{\lambda_G \Gamma\left( \kappa_G + \frac{1}{\tau_G} \right)}{\Gamma(\kappa_G)} \right]^2 \] (2.188)

\[ M_o = \lambda_G \left( \tau_G - \frac{1}{\kappa_G} \right)^{\frac{1}{\gamma_G}} \] (2.189)

The effect of each of the three parameters \( \lambda_G \), \( \tau_G \) and \( \kappa_G \) is shown in Figure 2.45 in a semi-log plot. The PDS was converted into a volume density distribution using equation (Eq. 2.178). In this Figure it is shown that \( \lambda_G \) is a scale factor, \( \tau_G \) controls the skewness and \( \kappa_G \) its broadness. The GGf only allows for negatively skewed distributions.

### 2.7.3 Previous attempts to describe the DSD

There have been several attempts to describe the DSD of emulsions using PDF. Some of these works are summarized in Table 2.13. This Table shows that some authors have used normalized distributions. This is done because once \( \overline{d}_{32} \) has been calculated using the correlations in the Energy Balance Section (Section 2.6.1) the whole distribution can be fit with only one variable.

For example Chen and Middleman (1967) normalized their distribution by \( \overline{d}_{32} \),
by making

$$X_i = \frac{d_i}{d_{32}}$$

(2.190)

The $d_{32}$-normalized normal distribution becomes

$$p_v (X_i) = \frac{1}{s_v \sqrt{2\pi}} \exp \left[ \frac{-(X_i - \bar{X})^2}{2s_v^2} \right]$$

(2.191)

where the normalized mean $\bar{X}$ and standard deviation are

$$\bar{X} = \frac{\sum d_i^3 X_i}{\sum d_i^3}$$

(2.192)

$$s_v^2 = \frac{\sum d_i^3 (d_i - \bar{X})^2}{\sum d_i^3}$$

(2.193)
Similar modifications have been done for log-normal distributions and using $\bar{d}_{30}$ and $D_{v,50}$ (see Table 2.13).

Many authors have reported bimodal DSD (Brown and Pitt, 1972; Laso et al., 1987; Nishikawa et al., 1991; Chatzi et al., 1991; Pacek et al., 1998; Hall et al., 2011), however only Nishikawa et al. (1991) attempted to use multiple functions to fit the DSDs. Some authors (Calabrese et al., 1986a; Li et al., 2014; Liu et al., 2013) have converted the distribution by volume to a distribution by number to get rid of bimodality. The effect of converting a distribution by volume to a distribution by number when these are bimodal has been explained in Section 2.7.2.

Another way in which bimodality has been neglected is by fitting the DSD to its cumulative form. Pacek et al. (1998) recognised that fitting to the cumulative tends to smooth variations, Table 2.13 shows this has been a very common practice, this becomes specially obvious when the cumulative distributions by number are fit. This effect was shown previously when the $f_v(d_i)$ in Figure 2.41 was converted into $F_n(d_i)$ in Figure 2.42.

An important feature that was not mentioned by the authors reviewed in Table 2.13, is if their fits give a good estimate of the $\bar{d}_{32}$ or if their fit is merely qualitative.

### 2.8 Bibliography


<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Function(s)</th>
<th>Technique</th>
<th>Bimodality</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noro (1978)</td>
<td>$F_n(d_i)$</td>
<td>Photography</td>
<td>No</td>
<td>For stirred vessel. For colloid mill</td>
</tr>
<tr>
<td>Nishikawa et al. (1991)</td>
<td>Normal</td>
<td>Microscopy</td>
<td>Yes</td>
<td>DSD by number and volume fit with a combination of two and three normal distributions respectively. $F_n(d_i/D_{n,50})$</td>
</tr>
<tr>
<td>Vankova et al. (2007)</td>
<td>Log-normal</td>
<td>PVM</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Boxall et al. (2010)</td>
<td>Log-normal</td>
<td>PVM</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Singh et al. (2008)</td>
<td>$f_n(d_i)$</td>
<td>Microscopy</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Liu et al. (2013)*</td>
<td>Log-normal</td>
<td>Fréchet</td>
<td>LD</td>
<td>DSD by volume converted to a DSD by number to fit with a single PDF. Same as above</td>
</tr>
<tr>
<td>Li et al. (2014)*</td>
<td>Fréchet</td>
<td>LD</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Qi et al. (2015)</td>
<td>Log-normal</td>
<td>PVM</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Sprow (1967)</td>
<td>$F_v(d_i)$</td>
<td>Schwarz and Coulter counter</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Calabrese et al. (1986a); Wang and Calabrese (1986) ⊥</td>
<td>Normal and Log-normal</td>
<td>Photography</td>
<td>No</td>
<td>$F_v(d_i/\overline{d}_{32})$ Low and intermediate viscosity by normal distribution by volume or number, high viscosities by log-normal distribution by number</td>
</tr>
<tr>
<td>Nishikawa et al. (1991)</td>
<td>Normal</td>
<td>Microscopy</td>
<td>Yes</td>
<td>See above $F_v(d_i/\overline{d}_{32})$. Notes that bimodal DSD could be fit by a single cumulative function.</td>
</tr>
<tr>
<td>Pacek et al. (1998) †</td>
<td>Log-normal</td>
<td>PVM</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Kraume et al. (2004)</td>
<td>Normal</td>
<td>Endoscope</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Vankova et al. (2007)</td>
<td>Normal</td>
<td>PVM</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Chen and Middleman (1967)</td>
<td>Normal</td>
<td>Photography</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>Brown and Pitt (1972)</td>
<td>Normal</td>
<td>Photography</td>
<td>Yes</td>
<td>$f_v(d_i/\overline{d}_{32})$, reported bimodality, got rid of large mode</td>
</tr>
<tr>
<td>Hall et al. (2011)*</td>
<td>Log-normal</td>
<td>LD</td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</table>

* Rotor-stator; ⊥ depending on $\mu_d$; † best fit; ◊ multiple fit


Weser, C. and Rauch, T. (2012). Tensiometer k11 mk4 with display panel kb0803 [user manual].


Chapter 3

Materials, equipment and methods

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3.1 Introduction

This chapter covers in more details the materials, equipment and methodology used for the subsequent chapters, which are presented in journal format. To avoid excessive repetition, figures that were reported in Chapters 4-9 are only referenced in this chapter.

Chapter 3 was possible as many chapters share the materials used and/or the equipment and/or the methodology. For example:

- In all studies Silicon Oil was used as dispersed phase.
- In all studies sodium laureth sulfate (SLES) was used as surfactant, and the same mass per volume of SLES was dissolved.
- Chapters 4,6-9 used water as continuous phase and Chapter 5 used glucose solutions.
- The concentration of the dispersed phase was kept at 1v.% in Chapters 4,5,7-9 but varied in Chapter 6.
- The same stirred vessel was used for Chapters 4-6.
- The same rotor-stator was used for Chapters 7-9.
- Power measurements for both devices were obtained using a torque meter
- All emulsions were analysed using the Mastersizer 3000 (Malvern Instruments, Malvern, UK).

3.2 Materials

3.2.1 Dispersed phases

Silicon Oils (SiOil) or poly-dimethyl siloxanes, are clear Newtonian fluids which are available in a wide range of viscosities. These are inert and safe to use in the laboratory. The SiOils were acquired were from 200 Fluid series (Dow Corning, Michigan, USA), which are commercialized by their kinematic viscosity in centistokes
3.2. Materials

To expand our SiOil inventory, we mixed some of the acquired SiOils. The full list of SiOils used throughout our investigations is shown in Table 3.1.

Table 3.1: Density $\rho_d$, viscosity $\mu_d$ and refractive index $n_{ri}$ for the different SiOils used at 25°C.

<table>
<thead>
<tr>
<th>SiOil [cSt]</th>
<th>$\rho_d$ [kg m$^{-3}$]</th>
<th>$\mu_d$ [Pa s]</th>
<th>$n_{ri}$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>750</td>
<td>$4.88 \times 10^{-4}$</td>
<td>1.375</td>
</tr>
<tr>
<td>10</td>
<td>934</td>
<td>$9.58 \times 10^{-3}$</td>
<td>1.399</td>
</tr>
<tr>
<td>50</td>
<td>960</td>
<td>$4.91 \times 10^{-2}$</td>
<td>1.402</td>
</tr>
<tr>
<td>350</td>
<td>970</td>
<td>$3.28 \times 10^{-1}$</td>
<td>1.403</td>
</tr>
<tr>
<td>1000</td>
<td>970</td>
<td>$9.47 \times 10^{-1}$</td>
<td>1.404</td>
</tr>
<tr>
<td>*2760</td>
<td>970</td>
<td>$2.75 \times 10^{0}$</td>
<td>1.404</td>
</tr>
<tr>
<td>*4500</td>
<td>970</td>
<td>$4.34 \times 10^{0}$</td>
<td>1.404</td>
</tr>
<tr>
<td>*7600</td>
<td>970</td>
<td>$7.36 \times 10^{0}$</td>
<td>1.404</td>
</tr>
<tr>
<td>10000</td>
<td>970</td>
<td>$1.05 \times 10^{1}$</td>
<td>1.404</td>
</tr>
<tr>
<td>12500</td>
<td>970</td>
<td>$1.34 \times 10^{1}$</td>
<td>1.404</td>
</tr>
<tr>
<td>30000</td>
<td>970</td>
<td>$2.95 \times 10^{1}$</td>
<td>1.404</td>
</tr>
<tr>
<td>(50000)</td>
<td>970</td>
<td>$4.92 \times 10^{1}$</td>
<td>1.404</td>
</tr>
<tr>
<td>100 000</td>
<td>970</td>
<td>$1.07 \times 10^{2}$</td>
<td>1.404</td>
</tr>
</tbody>
</table>

*Obtained by mixing 1000 and 10 000 cSt SiOil, \(\uparrow\) obtained by mixing 30 000 and 100 000 cSt SiOil.

Their density $\rho_d$ was taken from the Safety Data Sheet provided by Dow Corning.

Their shear viscosity $\mu_d$ was determined experimentally using a DV2T Viscometer (Brookfield Viscometers, Essex, UK) using different spindles depending on the viscosity of the materials. These experiments were done using a water bath to control the temperature to 25°C.

The elastic properties of the 1000, 10 000, 30 000 and 100 000 cSt SiOils were assessed with a HAAKE CaBER (Thermo Fischer Scientific, Massachusetts, USA). The experiments were performed at 25°C. The starting height in-between the plates was 3 mm, the final height was adjusted to 3 mm. The extensional viscosity $\mu_{ext}$ as a function of extensional-strain-rate $\dot{\varepsilon}$ can be consulted in the Appendix of Chapter 4. As shown in the Appendix, the Silicon Oils did not exhibit non-Newtonian properties and their Trouton ratio was 3, as for any Newtonian material.

Finally the refractive index $n_{ri}$ was obtained using a RFM390 Refractometer (Belling-ham & Standley, Kent, UK) controlling the temperature at 25°C.

It is worth noticing that $\rho_d$ of the 0.65 cSt SiOil is quite different from the rest
Chapter 3. Materials, equipment and methods

of the SiOils, and as will be seen in Sections 3.2.3 their interfacial tension is also different.

### 3.2.2 Continuous phases

With exception of the investigation performed for Chapter 5, the continuous phase for all our systems contained a fixed amount of surfactant which was diluted in water.

The surfactant used was Texapon N701 (Cognis, Hertfordshire, UK). Texapon N701 contains approximately 70 wt.% of sodium laureth sulfate (SLES), which is an anionic surfactant of yellowish appearance consisting of a mixture of alkyl ether sulphates \( (\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_n\text{OSO}_3\text{Na}) \) and water and other impurities. According to the manufacturer, Texapon N701 has a density in-between 900 kg m\(^{-3}\) and 1100 kg m\(^{-3}\).

The SLES contained in Texapon N701 has an average molecular weight of 420 g mol\(^{-1}\) (El-Hamouz, 2007). Figure 3.1 shows the surface tension as a function of SLES concentration as obtained by El-Hamouz (2007). He determined that its CMC was in-between 0.1 mmol L\(^{-1}\) and 0.2 mmol L\(^{-1}\), but as shown in Figure 3.1, \( \sigma \) remains practically constant at values as small as 0.04 mmol L\(^{-1}\) or 0.0128 g L\(^{-1}\). The reason for not having a sharper transition at the CMC (as in Fig. 2.4) is unknown (El-Hamouz, 2007).

For the experiments performed in Chapter 4 the continuous phase consisted of 27.85 g of Texapon N701 dissolved in 1880 ml of water. Therefore

\[
C_s = \frac{100 \times (27.85 \text{ g Texapon}) \left(\frac{0.7 \text{ g SLES}}{\text{g Texapon}}\right)}{(27.85 \text{ g Texapon}) + 1880 \text{ g water}} = 1.02 \text{ wt.}%
\]

This concentration is equivalent to 10.23 g L\(^{-1}\), which is 800 times larger than the CMC (SLES aqueous solution-air interface). The same amount of surfactant was used for the emulsions produced in Chapter 4 and Chapter 5. The continuous phases used for Chapter 4 included glucose solutions. As glucose has a higher density than water, the concentration by weight percentage is lower but the molar concentration is constant. In Chapter 5 we studied the effect of dispersed phase volume fraction
3.2. Materials

Figure 3.1: Surface tension as a function of SLES concentration (from El-Hamouz (2007)).

φd. For most of these experiments the amount of surfactant (in grams) was kept constant. As a results the surfactant concentration in water increases as solutions as φd increases, this is shown in Table 3.2.

Table 3.2: Amount of materials used for emulsion prepared with different φd in Chapter 5.

<table>
<thead>
<tr>
<th>φ</th>
<th>Water [L]</th>
<th>SiOil [L]</th>
<th>Texapon [g]</th>
<th>C_s [% wt.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.030</td>
<td>1.880</td>
<td>0.060</td>
<td>27.85</td>
<td>1.02</td>
</tr>
<tr>
<td>0.100</td>
<td>1.743</td>
<td>0.197</td>
<td>27.85</td>
<td>1.10</td>
</tr>
<tr>
<td>0.250</td>
<td>1.453</td>
<td>0.487</td>
<td>27.85</td>
<td>1.32</td>
</tr>
<tr>
<td>0.375</td>
<td>1.209</td>
<td>0.731</td>
<td>27.85</td>
<td>1.58</td>
</tr>
<tr>
<td>0.500</td>
<td>0.966</td>
<td>0.974</td>
<td>27.85</td>
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<tr>
<td>0.600</td>
<td>0.770</td>
<td>1.169</td>
<td>27.85</td>
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<tr>
<td>0.700</td>
<td>0.576</td>
<td>1.364</td>
<td>27.85</td>
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<tr>
<td>0.800</td>
<td>0.366</td>
<td>1.574</td>
<td>27.85</td>
<td>4.95</td>
</tr>
</tbody>
</table>

For the high-shear mixer experiments (Chapters 7-9), 9.9 L of continuous phase were prepare, all containing 1.04 wt.% of SLES. The continuous phases were prepared by mixing $142.94 \text{ g of Texapon in } 9.77 \text{ L of water.}$

$$C_s = 100 \frac{(142.94 \text{ gTexapon}) \left(\frac{0.7 \text{gSLES}}{\text{gTexapon}}\right)}{(142.94 \text{gTexapon}) + 9770 \text{gwater}} = 1.04\text{ wt.%} \quad (3.2)$$

The study for Chapter 5 involved using glucose aqueous solutions to increase the
viscosity of the continuous phase. The glucose acquired was Sweet M01632 (Cargill, Minnesota, USA), which contain 82.7 wt.% and water. Aqueous glucose solutions have a Newtonian behaviour. The molar mass of pure glucose is 180.16 g mol\(^{-1}\).

Sweet M01632 was never used directly, it was always used as the continuous phase containing SLES. The solutions were prepared by mixing 660.0 g, 1094.0 g and 1282.2 g for the 1.50 mol L\(^{-1}\), 2.50 mol L\(^{-1}\) and 2.93 mol L\(^{-1}\) respectively. The solutions were prepared using a 2 L volume flask, an example of the concentration calculation is given below

\[
\frac{1282.2 \text{ g Sweet M0162}}{1 \text{ g Sweet M0162}} \cdot \frac{0.827 \text{ g Glucose}}{180.16 \text{ g mol}} = 2.94 \text{ mol L}^{-1}
\]

(3.3)

A volume of 1.88 L of the glucose solutions were poured into the vessel and mixed with 27.85 g of Texapon N701 before adding the dispersed phase. The properties of the prepared aqueous Glucose/SLES solutions are shown in Table 3.3.

**Table 3.3:** Density \(\rho_d\), viscosity \(\mu_d\) and refractive index \(n_{ri}\) for the different SiOils used at 25°C.

<table>
<thead>
<tr>
<th>(C_g) [mole/L]</th>
<th>(\rho_c) [g m(^{-3})]</th>
<th>(\mu_c) [Pa s]</th>
<th>(n_{ri}) [-]</th>
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</thead>
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<tr>
<td>0</td>
<td>997</td>
<td>(1.04 \times 10^{-3})</td>
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</tr>
<tr>
<td>1.5</td>
<td>1098</td>
<td>(2.65 \times 10^{-3})</td>
<td>1.372</td>
</tr>
<tr>
<td>2.5</td>
<td>1166</td>
<td>(5.73 \times 10^{-3})</td>
<td>1.398</td>
</tr>
<tr>
<td>2.93</td>
<td>1194</td>
<td>(9.79 \times 10^{-3})</td>
<td>1.409</td>
</tr>
</tbody>
</table>

The \(\mu_d\) and \(n_{ri}\) in Table 3.3 were obtained in the same way as the properties of the SiOils in Table 3.1. The density was obtained using a pycnometer and a scale.

Another additional material was used to measure the Metzner-Otto shear constant \(K_s\). A 30 g carboxymethyl cellulose (cmc, Glentham Life Sciences, Corsham, UK) in 2 liter of water solution was prepared. The cmc solutions are shear-thinning Non-Newtonian solutions. The rheogram of this solution was obtained by a step-stress sweep in the 1.0 Pa to 100 Pa stress range using a AR-2000 stress-controlled rheometer (TA Instruments, Delaware, USA) and a 40 mm, 2° cone and plate tool. The rheogram obtained can be consulted in Figure 6.B.1 in Appendix 6.B.
Interfacial tension

The interfacial tension $\sigma$ for the SiOils and the continuous phases listed in Table 3.3 were obtained using a Tensiometer MK4 (KRUSS, Hamburg, Germany) and a platinum-iridium KRUSS Standard Ring with $r_r = 9.545\, \text{mm}$ and $r_w = 0.185\, \text{mm}$. The correction method by Harkins and Jordan (1930) was used and the equipment performed measurements until the standard deviation of five continuous measurements was smaller than $0.1\, \text{mN m}^{-1}$. The experiments were repeated thrice. The results were plotted in Figure 3.2 with $C_g$ and $\mu_d$ as parameters respectively. It is evident that the 0.65 cSt SiOil has different $\sigma$ than the rest of the SiOils of higher $\mu_d$; furthermore, the interfacial tension decreases as $C_g$ increases.

![Figure 3.2](image_url)

**Figure 3.2:** Interfacial tension in-between Silicon Oils and the continuous phases (a) as a function of $\mu_d$ and (b) as a function of $C_g$. The error bars represent one standard deviation.

It was not possible to measure $\sigma$ for the SiOils thicker than the 350 cSt SiOil using the du Nüoy ring method (also attempted with a Wilhelmy plate). The limitation of both techniques is due to the fact that highly viscous fluids take more time to flow from the lamella into the bulk and the tensiometer tends to overestimate the maximum lamella height (see Fig. 2.7) resulting in lamella rupture. The limitations of these techniques have also been reported by Lee et al. (2012). More adequate techniques for highly viscous systems are the pendant drop and the sessile drop methods; unfortunately these were unavailable. Calabrese et al. (1986) and Hall et al. (2011) also emulsified SiOil and reported that $\sigma$ was independent of the viscosity of
the SiOil, therefore we assumed that $\sigma$ for the SiOil thicker than the 350 cSt have the same $\sigma$.

### 3.3 Equipment and Methods

#### 3.3.1 Stirred Vessel

##### 3.3.1.1 Geometry

All the emulsions in Chapters 4-6 were prepared using the same Vessel and the same Pitched Blade Turbine. Their geometrical features are listed in Table 3.4.

**Table 3.4:** Geometrical characteristics of the vessel and impeller used in Chapters 4-6.

<table>
<thead>
<tr>
<th>Vessel</th>
<th>Impeller</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimension</td>
<td>Dimension</td>
</tr>
<tr>
<td>Internal Diameter</td>
<td>13.70 cm</td>
</tr>
<tr>
<td>Height vessel</td>
<td>25.40 cm</td>
</tr>
<tr>
<td>Height liquid</td>
<td>13.70 cm</td>
</tr>
<tr>
<td>Number of baffles</td>
<td>4</td>
</tr>
<tr>
<td>Width of baffles</td>
<td>1.41 cm</td>
</tr>
<tr>
<td>Thickness of baffles</td>
<td>0.59 cm</td>
</tr>
<tr>
<td>Liquid volume</td>
<td>1.97 L</td>
</tr>
<tr>
<td>Position</td>
<td>Center</td>
</tr>
</tbody>
</table>

The shaft of the impeller was coupled to a IKA RW 20 Digital Overhead Stirrer (IKA-WERKE, Staufen, Germany). The stirring speeds $N$ were determined using a CT6 Hand-Held Tachometer (Compact Instruments, Lancashire, UK).

##### 3.3.1.2 Power-draw and rheometry of emulsions

The power draw $P_S$ was obtained using torque $M$ measurements. The torque was measured using a TorqSense RWT321 1 N m torque sensor (Sensor Technology, Oxfordshire, UK) fitted to the shaft of the impeller. The working principle of torque-meters has been reviewed in Section 2.4.4. The procedure to measure $P_S$ out of $M$ measurements has been thoroughly explain by James et al. (2017).
Before starting any measurements for a given material, $M$ for $N = 0 \text{s}^{-1}$ was set to zero. Afterwards the impeller was fixed to the $N$ under study and the torque was recorded for a duration of 15 s, the impeller was accelerated to the next $N$ and the torque was measured again, this process was repeated without fixing the zero. The data exported by the sensor’s software is $N$, $M$ and time. However the measured $M$ is not only due to the forces exerted by the fluid being stirred, but include mechanical losses due to bending moments of the shaft, noise, and other losses. Equation 2.120 allows to calculate power out of $M$ measurements, substituting this equation into the $P_S$ expressions for the laminar (Eq. 2.88), transitional (Eq. 2.90) and turbulent (Eq. 2.89) regimes the following expression can be obtained (James et al., 2017)

Laminar

$$M = \frac{K_P D^3}{2\pi} N + M_{\text{losses}}$$

(3.4)

Transitional

$$M = \frac{P_{o0} \rho D^5}{2\pi} N^2 + \frac{K_P D^3}{2\pi} N + M_{\text{losses}}$$

(3.5)

Turbulent

$$M = \frac{P_{o0} \rho D^5}{2\pi} N^2 + M_{\text{losses}}$$

(3.6)

where torque losses $M_{\text{losses}}$ in the equations above are the $y$-intercept. The equations above were used to produce the power curve in Figure 5.1 in Chapter 5 by doing $M$ measurements using water, 2.90 mol L$^{-1}$ glucose solution, and five silicon oils in the 50-10 000 cSt nominal dynamic viscosity range.

In Chapter 6, we studied concentrated emulsions which are non-Newtonian fluids. Equations 3.4-3.6 are only valid for Newtonian fluids. For power-law fluids in the laminar regime, the Metzner-Otto constant $K_S$ needs to be determined to determine the average shear rate around the impeller. The procedure described below was performed for the cmc solution (rheogram shown in Fig. 6.B.1).

Combining Equation 2.87 ($K_P = PoRe$) and the previously derived Re for a power-law fluid in the laminar regime given by Equation 2.105,

$$K_P = \frac{2\pi M}{K_S^{n-1} k N^n D^3}$$

(3.7)
which can be re-arrange into the equation below to account for losses

\[
M = \frac{kKPK_S^{n-1}D^3}{2\pi}N^n + M_{\text{losses}}
\]  

(3.8)

from the previous equation \(K_S\) can be obtained from the slope of a \(M\) vs \(N^n\) plot.

The concentrated emulsions (\(\phi > 0.25\)) in Chapter 5 were shear thinning and many of these were in the turbulent regime. For the turbulent regime Po is viscosity-independent and therefore it should not be affected by the shear-thinning behaviour of the materials and Equation 3.6 should be applicable. However, as seen previously, their Re should be estimated using Equation 2.110 as recommended by Gabelle et al. (2013). Therefore their rheological characterisation is also necessary.

The rheological properties of these emulsion were also analysed using the AR-2000 rheometer but using a 50 mm parallel-plate geometry which allows to correct for slippage using Equation 2.40 by running the step-stress sweeps at different gap sizes \(h_1 = 300 \mu\text{m}\) and \(h_2 = 500 \mu\text{m}\). The experiments for each gap size were repeated at least twice. The rheograms after correcting for slippage (see Eq. 2.40) can be consulted in Appendix 6.C.

3.3.2 High-shear mixer

3.3.2.1 Arrangements and Geometry

For the studies in Chapters 7-9 the high-shear mixer used was a L5M-A Laboratory Mixer (Silverson Machines, Chesham, UK) with integrated tachometer. The lab-scale rotor-stator workheads are versatile in that these are interchangeable and some can be used as batch or in-line rotor-stators. The studies performed in this dissertation were focused on in-line rotor-stators, however Chapters 8 includes a study using the batch workhead. For all the experiments, in-line and batch, we used the same rotor and screen. The characteristics of the rotor and screen are listed in Table 3.5, while images of these are shown in Chapter 8 in Figure 8.3.

The in-line rotor-stator was operated in two different arrangements: continuous and recycle arrangement.
Table 3.5: Geometrical characteristics of the rotor-stator.

<table>
<thead>
<tr>
<th>Rotor</th>
<th>Screen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>3.0 cm</td>
</tr>
<tr>
<td>Number of blades</td>
<td>4</td>
</tr>
<tr>
<td>Height</td>
<td>1.0 cm</td>
</tr>
<tr>
<td>Blade thickness</td>
<td>0.5 cm</td>
</tr>
<tr>
<td>Maximum speed (nominal)</td>
<td>133 s⁻¹</td>
</tr>
<tr>
<td>Inner diameter</td>
<td>3.2 cm</td>
</tr>
<tr>
<td>Outer diameter</td>
<td>3.4 cm</td>
</tr>
<tr>
<td>Stator height</td>
<td>2.0 cm</td>
</tr>
<tr>
<td>Hole arrangement</td>
<td>6x40, pitched</td>
</tr>
<tr>
<td>Number of holes</td>
<td>240</td>
</tr>
</tbody>
</table>

- In the continuous arrangement the outlet of the rotor-stator is directed to a secondary tank (or process). Multi-pass processing implies that the material passes \( n \) number of times through the rotor-stator causing further drop fragmentation.

- In the recycle arrangement an in-line high-shear mixer is used to produce batches. The outlet of the high-shear mixer is directed to the feeding vessel, creating a recycle loop. It is expected that for a time \( t > 0 \) there is a mixture of drops that have passes \( n \) number of times.

Schematic representations of both arrangements are shown in Figure 8.2.

To control and assist the flow rate through the rotor-stator a peristaltic pump was used. The peristaltic pump used was a 501- single channel pumphead (Watson Marlow, Cornwall, UK). The flow rate of the pump is controlled by adjusting a knob in the 000-999 range, the knob setting was named “pump number” \( pn \) for convenience. The outflow of the pump was calibrated using a 1 L measuring cylinder, it was found that the response of the pump is non-linear. The outflow corresponding to five different \( pn \) are listed in Chapter 8 in 8.1.

For all the emulsification studied done in Chapters 7-9, coarse emulsions were prepared as starting point. All the coarse emulsions had the same SiOil concentration and surfactant concentration. The most common volume prepared was 10 L, for this volume 142.94 g of Texapon N701 were pre-dissolved in 9.77 L of tap water before pouring 100 mL of SiOil. The surfactant concentration was 1.04 wt.% (Eq. 3.2 and the SiOil concentration was 1 v.%. The dimensions of the vessel and Rushton impellers used to make the coarse emulsions are listed in Table 3.6.

Even though, Hall et al. (2011) found that the coarse drop size does not influence
the DSD at the outlet of the rotor-stator, special care to reproduce all conditions were taken, for example the mixtures were stirred for 24 h at different $N$ (see specific procedure in Chapters 7-9) to ensure that drop breakage did not occur in the vessels, the $N$ of the Rushton turbines was decreased when the peristaltic pump was turned on and the effect of the peristaltic on the DSD was studied (see Fig. 8.4).

**Table 3.6:** Geometrical characteristics of the vessel and impeller used for Chapter 7-9.

<table>
<thead>
<tr>
<th>Vessel</th>
<th>Impeller</th>
<th>Chapters 7 &amp; 8</th>
<th>Chapter 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal Diameter</td>
<td>25 cm</td>
<td>Diameter</td>
<td>7.55 cm</td>
</tr>
<tr>
<td>Height vessel</td>
<td>33 cm</td>
<td>Height</td>
<td>1.57 cm</td>
</tr>
<tr>
<td>Height liquid</td>
<td>variable</td>
<td>Disc diameter</td>
<td>7.55 cm</td>
</tr>
<tr>
<td>Number of baffles</td>
<td>0</td>
<td>Number of blades</td>
<td>6</td>
</tr>
<tr>
<td>Liquid volume</td>
<td>variable</td>
<td>Blade thickness</td>
<td>0.16 cm</td>
</tr>
<tr>
<td>Position</td>
<td>Center</td>
<td>Clearance</td>
<td>8 cm</td>
</tr>
</tbody>
</table>

### 3.3.2.2 Power-draw

As reviewed in Section 2.4.3.2, measurements with zero flow through the rotor stator and measurements allowing the rotor-stator to pump the material freely are required. Torque measurements were used to obtain the power curve of the high-shear mixer used. The working principle of the torque meters have been reviewed in Section 2.4.4 and most of the equations and methodology described in Section 3.3.1.2 was used.

The power measurements in the turbulent regime were performed by filling the rotor-stator by locating a water reservoir above the rotor-stator. Valves at the outlet and inlet of the high-shear mixer were installed.

With the valves closed, using Equation 3.6 lead to the estimation of $P_{OZ}$, whereas fully open valves (free $\dot{m}$) lead to the estimation of $P_{OU}$. To determine $N_Q$, $\dot{m}$ was measured for different $N$ with the valves fully open using a measuring cylinder. The equations to estimate $N_Q$, $k_1$, $P_{OZ}$ and $P_{OU}$ have been reviewed in Section 2.4.3.2.

For the laminar regime, a mixture of the 1000 cSt and 10 000 cSt Silicon Oil was prepared. As important temperature $T$ changes occurred due to the high viscosity of the material and high shear rates which lead to viscous heating, the $\mu$ dependency on $T$ was determined. The $\mu$ of the blend was measured at different temperatures.
using a water bath and the DV2T Viscometer. The $\mu$ dependence on temperature could be well-described by the fit

$$\mu = \frac{2398 \text{ Pa s K}}{T} - 6.32 \text{ Pa s} \quad 298 \text{ K} < T < 353 \text{ K} \quad (3.9)$$

The temperature was measured at the inlet and outlet of the rotor-stator, the arithmetic average for each measured $N$ was used for the calculations. First $K_P$, was measured using Equation 3.4 and $P_o$ using Equation 2.87 ($P_o = K_P/Re$), where the $Re$ was calculated using the $\mu$ at the average $T$.

The complete power curve (see Eq. 2.115) is presented in Figure 8.5.

### 3.4 Droplet size distribution analysis

The DSD were for all our studies were determined using a laser diffraction particle size analyser: the Mastersizer 3000. The physical principles under which this instrument works have been reviewed in Section 2.7.1.5. Images of the external components and of the flow cell of the system are shown in Figure 3.3.

![Figure 3.3: External components and flow cell of the DSD measuring system](image)

The (II) Hydro EV dispersion unit and a 500 mL (for the 0.65 cSt-4400 cSt SiOil) or 1000 mL (4400 cSt-100 000 cSt SiOil) beaker full of water are used. The dispersion unit has a stirrer which velocity can be set in the Standard Operation Procedure.
A sufficient amount of sample is then poured or gently injected into the beakers to lower its concentration. The meaningful concentration inside the Mastersizer is the so-called “obscuration rate” which depends on the amount of dispersed sample, droplet size, DSD of the sample. For wet samples, such as the ones used in our research, the target obscuration rate recommended by Malvern lies is in-between 5% and 20%. The smaller the droplets the lower the recommended obscuration rate (to avoid multiple scattering), while coarse droplets and/or very polydisperse require a 10% to 20% for the sample to be representative (Longworth-Cook, 2016).

The Hydro-EV pumps the sample through the (V) inlet of the (I) Mastersizer and through the (IV) flow cell. While the sample crosses the flow-cell, a set of red and blue lasers (sequentially) passes through the flow cell and the sample. The laser scattering is recorded by a series of detectors around the flow cell. The information recorded by the detectors is further transformed into the DSD by the software of the Mastersizer installed in the (III) computer.

The SOP Editor of the software requires information of the particle type (spherical, non-spherical or opaque), refractive and absorption indexes of the dispersed phase and refractive index of the dispersant. The option for non-spherical particles was chosen in case that the drops acquired an ellipsodial shape while passing through the flow cell, however the Mastersizer’s software allows to re-adjust the settings during data export. No difference was noticed in between the spherical and non-spherical analysis options. The measurement procedure allows to set up the background and sample measurement duration, number of consecutive measurements per sample and stirring speed of the dispersion unit. The result analysis models that can be chosen from are the “general purpose” and the “narrow modes”. The SOP for our investigations were not very different from each other (see Tab. 3.4), apart from the $n_{rr}$ which is SiOil specific, only the measurement times were tuned depending on the sample and repeatability.

Differentiation in the volume of the beaker (500 mL and 1000 mL) and sample measurement duration was necessary for the highly polydispersed DSD. We found that increasing the sampling volume made our measurements in-between samples
Table 3.7: SOP for the Mastersizer 3000.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>set-up value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of particles</td>
<td>non-spherical</td>
</tr>
<tr>
<td>Background measurement duration</td>
<td>15 s</td>
</tr>
<tr>
<td>Sample measurement duration</td>
<td>10 s (low ( \mu_d )); 200 s (high ( \mu_d ))</td>
</tr>
<tr>
<td>Number of measurements</td>
<td>5</td>
</tr>
<tr>
<td>Stirrer speed</td>
<td>1500 rpm</td>
</tr>
<tr>
<td>Analysis model</td>
<td>general purpose</td>
</tr>
</tbody>
</table>

more repeatable while increasing the sampling time did our measurement for each sample repeatable. The 1000 mL beaker was also used for the highly concentrated emulsions.

For each emulsified system, at least three samples were measured yielding a total of 15 DSD which were arithmetically averaged.

The Mastersizer’s software allows to export a large variety of statistics of the DSD, nevertheless the statistics by volume are recommended given the physics of the instrument. Typically the data exported was: the 10th, 50th, 90th percentiles, the \( \bar{d}_{32}, Mo \) and the result in sizes.

3.5 Bibliography


James, J., Cooke, M., Trinh, L., Hou, R., Martin, P., Kowalski, A., and Rodgers,


Part II

Stirred vessels
Preface

This part aims to study the effects of dispersed phase viscosity on the DSD in stirred vessel. A large number of experiments were performed using a wide variety of silicon oils of different viscosity using the same impeller and vessel, as well as the same mass of surfactant for each experiment.

The results obtained yielded a three-part peer-reviewed journal paper, each of the parts aims to tackle the effect of a variable or a combination of variables related to the effect of the dispersed phase viscosity:

1. Chapter 6 or first part of the paper studies the effect of dispersed phase viscosity across 6 orders of magnitude in combination with the effect of stirring speed for very dilute emulsions.

2. Chapter 7 or Part II studies the combined effect of the dispersed and continuous phase viscosity, also for dilute emulsions. In the experiments of this study, silicon oils with viscosities across five orders of magnitude were dispersed in glucose solutions with viscosities in the 1.0-9.8 mPa viscosity range. The power number of the systems was kept constant. Furthermore, experiments were carried at two different stirring speeds to prove that the two aforementioned variables do not affect the stirring speed dependency found in the first part of this study.

3. The third part of this study can be found in Chapter 8 and it explores the effect of dispersed phase hold-up (1.0v.%-80v.%) on the DSD for dispersed phases with viscosities across five orders of magnitude.
To my knowledge, there is not such an integral study in literature which explores the effect of these variables and their combination across such wide viscosity spectrum. Keeping the geometrical features, interfacial tension and densities constant throughout this studies allows for a more critical comparison and consistency.
Chapter 4

On the steady-state drop size distribution in stirred vessels. Part I: effect of dispersed phase viscosity


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Abstract

Previous studies on emulsification have used the maximum drop size ($d_{max}$) or Sauter mean diameter ($d_{32}$) to investigate the effect of viscosity on the drop size distribution (DSD), however these parameters fall short for highly polydispersed emulsions. In this investigation (Part I) we studied the steady-state DSD of dilute emulsions using of silicon oils with viscosities varying across 6 orders of magnitude at different stirring speeds. Different emulsification regimes were identified; our modelling and analysis is centred on the intermediate viscosity range where interfacial cohesive stresses can be considered negligible and drop size increases with viscosity. The bimodal frequency distributions by volume were well described using two log-normal density functions. In Part II (Carrillo De Hert and Rodgers, 2017b) we expanded this study by using other continuous phases of different viscosity while keeping the Power number constant, thus examining the effects of viscosity ratio.

4.1 Introduction

The properties of emulsions are linked to their microstructure. One of the most important characteristics of its microstructure is their droplet size distribution (DSD) which has a direct impact on its rheological behaviour, stability, and interfacial area. The DSD of emulsified products through mechanical mixing results from the breakup and coalescence of droplets. The latter becomes negligible for dilute emulsions and allows isolation of the break-up mechanism for its study.

Due to the complexity of turbulent fields a full theoretical description of the drop breakup process has not been possible. The breakup forces encountered in a turbulent chaotic flow pattern will be different for all the drops; nevertheless it has been possible to determine the average size of the largest drops (of diameter $d_{max}$) that can withstand these disruptive forces. Hinze (1955) determined through dimensional analysis that two dimensionless groups, the Weber number of the droplet ($We_d$) and the viscosity group ($Vi_H$), could describe the breakup process.
Chapter 4. Effect of dispersed phase viscosity in stirred vessels

\[ \text{We}_d = \frac{\tau d_{\text{max}}}{\sigma} \]  \hspace{1cm} (4.1)

\[ \text{Vi}_H = \frac{\mu_d}{\sqrt{\rho_d \sigma}} \]  \hspace{1cm} (4.2)

Where \( \tau \) is the stress experienced by the drop of diameter \( d_{\text{max}} \); \( \sigma \) is the interfacial tension in-between the dispersed and continuous phase, and \( \mu_d \) and \( \rho_d \) are the viscosity and density of the dispersed phase respectively. The breakup would occur when the \( \text{We}_d \) reached a critical value or critical Weber number (\( \text{We}_{\text{crit}} \)) number which is a function of \( \text{Vi}_H \).

\[ \text{We}_{\text{crit}} = C_1 [1 - \psi(\text{Vi}_H)] \]  \hspace{1cm} (4.3)

It has been theorized that for droplets larger than the Kolmogorov length scale \( \ell_\eta \) (for isotropic homogeneous turbulence) the stress \( \tau \) experienced by a drop is due to the kinetic energy fluctuations, this is known as the turbulent inertia regime. Kolmogorov’s length scale and the stress due to the kinetic energy fluctuations are given by (Kolmogorov, 1941; Hinze, 1955)

\[ \ell_\eta = (\frac{\mu_c}{\rho_c})^{3/4} \varepsilon^{-1/4} \]  \hspace{1cm} (4.4)

\[ \tau = C_2 \rho_c (\varepsilon d_{\text{max}})^{2/3} \]  \hspace{1cm} (4.5)

Where \( \mu_c \) and \( \rho_c \) are the viscosity and density of the continuous phase. For inviscid dispersed phases (\( \text{Vi}_H \to 0 \)) Equations 4.1, 4.3 and 4.5 yield \( d_{\text{max}} = C_3 (\rho_c/\sigma)^{-3/5} \varepsilon^{-2/5} \).

Where \( \varepsilon \) is the energy dissipation rate per unit mass, which value depends on the location in the vessel. Authors like Zhou and Kresta (1998a) have suggested that the the equilibrium drop size is determined by the maximum energy dissipation rate \( \varepsilon_{\text{max}} \) which is located in the impeller vicinity. There is much discrepancy on how to estimate \( \varepsilon_{\text{max}} \) as it depends on the method and assumptions used for its estimation (Gabriele et al., 2009). One of the scaling parameters used in literature is the \( \varepsilon_{\text{max}}/\varepsilon \)
ratio, where \( \varepsilon \) is the mean dissipation rate and can be obtained from power draw \( P_S \) measurements

\[
\varepsilon = \frac{P_S}{\rho_c V_T} \tag{4.6}
\]

Where \( V_T \) is the volume of the vessel. For fully developed turbulence in a stirred vessel with a stirrer diameter \( D \) rotating at a speed \( N \) the dimensionless Power number (\( \text{Po} = \frac{P_S \rho_c^{-1} N^{-3} D^{-5}}{} \)) becomes constant. Rushton et al. (1950) determined that \( \varepsilon = C_4 N^3 D^2 \). Combining equations 4.1, 4.3 and 4.5 Shinnar and Church (1960) concluded that for inviscid, diluted droplets larger than \( \ell_\eta \)

\[
\frac{d_{\text{max}}}{D} = C_5 \left( \frac{\rho_c N^2 D^3}{\sigma} \right)^{-3/5} = C_5 \text{We}^{-3/5} \tag{4.7}
\]

Note that the Weber number defined above is based on the stirrer and not on the stress experienced by the droplet (\( \text{We} = \frac{\rho_c N^2 D^3 \sigma}{\mu} \)).

Sprow (1967) proposed that the average drop sizes \( \overline{d}_{ab} \) are proportional to the maximum diameter.

\[
\overline{d}_{ab} = C_6 d_{\text{max}} \tag{4.8}
\]

Where \( \overline{d}_{ab} \) is

\[
\overline{d}_{ab} = \left[ \int_0^\infty f_n(d_i) d_i^a d_i^b \right]^{1/a - b} \tag{4.9}
\]

For \( a = 3 \) and \( b = 2 \) the Sauter mean diameter \( \overline{d}_{32} \) can be obtained. The \( \overline{d}_{32} \) is specially useful as it links the interfacial area to its volume through \( a_v = 6 \phi / \overline{d}_{32} \). Where \( a_v \) is the interfacial area and \( \phi \) the emulsion’s volume fraction.

Equation 4.8 made \( d_{\text{max}} \) and \( \overline{d}_{32} \) interchangable and has been widely used but several values for \( C_6 \) have been reported in literature. Nishikawa et al. (1991) found \( C_6 = 0.45 \) and Calabrese et al. (1986a) found \( C_6 \approx 0.6 \) for moderate viscous oils and \( C_6 \approx 0.5 \) for highly viscous due to the broadening of the DSD as \( \mu_d \) increases. Li et al. (2014) obtained bimodal DSD using a rotor-stator mixer and found \( C_6 = 0.16 \). Liu
and Li (2013) emulsified 4 crude oils with different viscosity using a batch rotor-stator mixer as they took samples at different time intervals. They obtained bimodal DSD and found that $C_6$ was independent of time but that $C_6$ decreased as $\mu_d$ increased and the distribution broadened. The aforementioned studies suggest that Equation 4.8 should be used with caution if a mechanistic model based on $d_{max}$ is applied to viscid materials.

Other mechanistic and empirical models apart from Equation 4.7 have been suggested and many have been summarized by Singh et al. (2008).

The three paper study by Calabrese et. al. (Calabrese et al., 1986a; Wang and Calabrese, 1986; Calabrese et al., 1986b) has been the most important to describe the effect of $\mu_d$ and $\sigma$ for viscid dispersed phases. For their mechanistic model Calabrese et al. (1986a) and Wang and Calabrese (1986) balanced the disrupting and the surface and viscous cohesive energies

$$\frac{\bar{d}_{32}}{D} = C_7 \text{We}^{-3/5} \left[ 1 + C_8 \text{Vi}_C \left( \frac{\bar{d}_{32}}{D} \right)^{\frac{7}{5}} \right]^{3/5}$$

(4.10)

Where their dimensionless viscosity group $\text{Vi}_C$ is the ratio of the viscous energy of the dispersed phase to the surface energy ($\text{Vi}_C = \mu_d ND (\rho_c/\rho_d)^{1/2} \sigma^{-1}$). If $\text{Vi}_C \to 0$ Equation 4.10 reduces to Equation 4.7; on the other hand if $\text{Vi}_C$ is very large, the interfacial forces become negligible and Equation 4.10 reduces to

$$\frac{\bar{d}_{32}}{D} = C_9 \left( \frac{\rho_c}{\rho_d} \right)^{3/8} \left( \frac{\mu_d}{\mu_c} \right)^{3/4} \text{Re}^{-3/4}$$

(4.11)

Where $\text{Re}$ is the Reynolds number $\text{Re} = \rho_c N D^2 \mu_c^{-1}$. As noted by the authors as $\mu_c$ is contained within $\text{Re}$ thus Equation 4.11 has no dependency on $\mu_c$. Calabrese et al. (1986a) performed a long series of experiments using five silicon oils as dispersed phase within the $9.60 \times 10^{-2}$ Pa s to $1.05 \times 10^1$ Pa s viscosity range in distilled water in the absence of surfactant; $\sigma$ was constant for all the SiOils and water $\sigma = 3.78 \times 10^{-2}$ N m$^{-1}$. Equation 4.10 was able to describe the results obtained by Arai et al. (1977) and most of their own results, except the ones obtained with two most
viscous SiOils (4.43 Pa s and 10.5 Pa s). For these two silicon oils, their results were well-correlated by (Calabrese et al., 1986a)

$$\frac{d_{32}}{D} = 2.1 \left( \frac{\mu_d}{\mu_c} \right)^{3/8} \text{Re}^{-3/4}$$

(4.12)

The droplet size dependency on $\mu_d$ for these SiOils was approximately half of the one in Equation 4.11 despite the large $V_{IC}$. This equations suggests that there is a $\mu_c$ dependency, but the authors did not perform any experiments to prove such dependency.

In the second part of these studies, Wang and Calabrese (1986) changed $\sigma$ systematically by using different methanol in water solutions for SiOils in the $1.0 \times 10^{-3}$ Pa s to $1.0$ Pa s $\mu_d$ range and $1.0 \times 10^{-3}$ N m$^{-1}$ to $4.5 \times 10^{-2}$ N m$^{-1}$ for the $\sigma$ range. They found that as $\mu_d$ increases the influence of $\sigma$ decreases.

The DSD may be represented by frequency or density distribution curves $f(d_i)$ or by their cumulative curves $F(d_i)$. For emulsions these are commonly by number ($f_n(d_i)$ and $F_n(d_i)$) or by volume ($f_v(d_i)$ and $F_v(d_i)$). Two emulsions may have different DSDs despite having the same mean droplet size. There have been numerous attempts to describe the droplet size distributions obtained in stirred vessels and in rotor-stators; some of the distribution functions used are summarized in Table 4.1.

Multimodality has been explicitly mentioned by several of authors listed in Table 4.1 (Brown and Pitt, 1972; Laso et al., 1987; Nishikawa et al., 1991; Chatzi et al., 1991; Pacek et al., 1998; Hall et al., 2011) while others (Calabrese et al., 1986a; Wang and Calabrese, 1986) found that the DSD broadens as $\mu_d$ increases. The broadening has been attributed to a change in the droplet breakup mechanism from bursting towards stretching by several of the aforementioned authors.

Figure 4.1 shows the viscosity ratio of the dispersed and continuous phase used in some of the most relevant studies in the field in chronological order. Despite the numerous studies on emulsification using stirred vessels and rotor-stators, it becomes evident that the effect of viscosity on polydispersity has not been addressed.

When bimodality is present, regularly one or several of the four approaches listed
Table 4.1: Types of Distributions used by Several Authors to fit the DSD.

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Function(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noro (1978)</td>
<td>Normal</td>
</tr>
<tr>
<td>Calabrese et al. (1986a)</td>
<td>Normal and Log-normal</td>
</tr>
<tr>
<td>Nishikawa et al. (1991)</td>
<td>Normal</td>
</tr>
<tr>
<td>Vankova et al. (2007)</td>
<td>Log-normal</td>
</tr>
<tr>
<td>Boxall et al. (2012)</td>
<td>Log-normal</td>
</tr>
<tr>
<td>Singh et al. (2008)</td>
<td>Log-normal</td>
</tr>
<tr>
<td>Liu et al. (2013)*</td>
<td>Fréchet</td>
</tr>
<tr>
<td>Li et al. (2014)*</td>
<td>Fréchet</td>
</tr>
<tr>
<td>Qi et al. (2015)</td>
<td>Log-normal</td>
</tr>
<tr>
<td>Sprow (1967)</td>
<td>Schwarz and Bezemer</td>
</tr>
<tr>
<td>Calabrese et al. (1986a)</td>
<td>Normal and Log-Normal</td>
</tr>
<tr>
<td>Wang and Calabrese (1986)</td>
<td>Normal</td>
</tr>
<tr>
<td>Nishikawa et al. (1991)</td>
<td>Multiple Normal</td>
</tr>
<tr>
<td>Pacek et al. (1998)</td>
<td>Log-normal</td>
</tr>
<tr>
<td>Kraume et al. (2004)</td>
<td>Normal</td>
</tr>
<tr>
<td>Vankova et al. (2007)</td>
<td>Normal</td>
</tr>
<tr>
<td>Chen and Middleman (1967)</td>
<td>Normal</td>
</tr>
<tr>
<td>Brown and Pitt (1972)</td>
<td>Normal</td>
</tr>
<tr>
<td>Hall et al. (2011)*</td>
<td>Log-normal</td>
</tr>
<tr>
<td>Carrillo De Hert and Rodgers (2017a)*</td>
<td>Generalized Gamma</td>
</tr>
</tbody>
</table>

* Rotor-stator; △ narrow gap homogenizer; ⊥ depending on \( \mu_d \); ⊤ best fit

below is used

- Fit to the cumulative distribution. As noted by Pacek et al. (1998), cumulative distributions tend to smooth out detailed variations.

- Truncate the distribution that does not follow the trend (Brown and Pitt, 1972; Groeneweg et al., 1994)

- Nishikawa et al. (1991) used two normal density functions to fit the distribution by number and three to describe the one by volume.

- Convert the distribution by volume to a distribution by number (Calabrese et al., 1986a; Li et al., 2014; Liu et al., 2013) which diminishes the contribution of the large drops.

Calabrese et al. (1986a) found that a linear-normal distribution by number or volume could describe their DSD for low to moderate \( 1.0 \times 10^{-3} \text{ Pa s} \) to \( 5.0 \times 10^{-1} \text{ Pa s} \)
4.1. Introduction

Figure 4.1: Viscosity ratio $\mu_d/\mu_c$ in relevant experimental studies on emulsification (Chen and Middleman, 1967; Sprow, 1967; Brown and Pitt, 1972; Arai et al., 1977; Noro, 1978; Calabrese et al., 1986a; Wang and Calabrese, 1986; Nishikawa et al., 1991; Laso et al., 1987; Chatzi et al., 1991; Kraume et al., 2004; Vankova et al., 2007; Singh et al., 2008; Hall et al., 2011; Boxall et al., 2012; Liu et al., 2013; Li et al., 2014; Qi et al., 2015; Carrillo De Hert and Rodgers, 2017a,b). The extended line for the study of Calabrese et al. (1986a) implies that different equations were used to fit each viscosity ratio range (see Eqs. 4.11 and 4.12).

dispersed phases. But for their high-viscosity oils (5.0 Pa s to 10 Pa s) the largest 1% of the drops contained 70% of the emulsions volume, therefore their data could only be represented using a log-normal distribution by number.

Zhou and Kresta (1998b) used four different types of impeller at different impeller speeds and off-bottom clearances and measured to study the DSD of very dilute emulsions. They classified their DSD into four categories and suggested different distribution functions for each case: (1) Long tail distribution represented by a normal distribution; (2) double peak distribution by superimposing two normal distributions; (3) skew distribution which could be represented by a Poisson distribution, an exponential distribution, a Gamma distribution or two superimposed normal distributions; and (4) skew-normal distribution which can be approximated by a normal distribution.
Chatzi et al. (1991) attributed the scarce amount of literature reporting bimodality on the inaccuracy of the photographic methods while Laso et al. (1987) noted that in photographic methods the observers tend to neglect small droplets and focus on the larger ones. The DSD analysis before 1990 included techniques such as Coulter counter (Sprow, 1967), photograph image analysis (Chen and Middleman, 1967; Brown and Pitt, 1972; Arai et al., 1977; Noro, 1978; Calabrese et al., 1986a; Wang and Calabrese, 1986; Laso et al., 1987) and microscopy (Nishikawa et al., 1991).

In our previous study (Carrillo De Hert and Rodgers, 2017a) we studied the effect of $\mu_d$ on the $f_v(d_i)$ for rotor-stator mixers using a multiple fit Generalized Gamma function. The DSD obtained in the aforementioned study showed two distinctive peaks which could be fit as the mode of the daughter drops $Mo_L$ and the mode of the satellite drops $Mo_s$ of each distribution was easily obtainable. The present study resulted more challenging as the $f_v(d_i)$ of the two types of daughter droplets were merged together in most of the DSD and the trends are more difficult to quantify.

In Part I of this study, the combined effects of $\mu_d$ and $N$ of dilute emulsions (1 v.%) with an excess of surfactant—to hinder cohesive interfacial forces—on the droplets size and DSD are studied. Throughout this investigation we intend to broaden the understanding of the droplet breakup process by providing a characterization of the $f_v(d_i)$ as bimodality arises for viscid dispersed phases.

In Part II (Carrillo De Hert and Rodgers, 2017b), we investigated the effect of $\mu_c$ on the DSD for experiments at constant $Po$; according to the theory reviewed in this section, the drop size and DSD should be independent of $\mu_c$ if $Po$ is constant, and if emulsification occurs in the turbulent inertia regime; however this is was not the case. Part II (Carrillo De Hert and Rodgers, 2017b) offers an explanation by discussing the limitations of the Kolmogorov -5/3 energy spectrum.

The narrow bars in Figure 4.1 (for the current studies: Parts I and II (Carrillo De Hert and Rodgers, 2017b)) represent the experimental range while the thick bars represent the range on which modelling was undertaken.
4.2 Materials and equipment and methods

4.2.1 Materials

Nine 200 Fluid XX Silicone Oil (dimethyl siloxane, Dow Corning, Michigan, U.S.A.) where “XX” stands for their nominal dynamic viscosity in centistokes [cSt], which will be used to facilitate discussion. Silicon Oils (SiOil) are available over a wide range of viscosity, their shear viscosity is independent of shear rate and their densities and interfacial tension are similar for most of them. Four additional SiOils with intermediate viscosities labelled as 2800 cSt, 4500 cSt, 7600 cSt and 50 000 cSt were obtained by mixing. The list of the SiOils and relevant properties are listed in Table 4.2.

Table 4.2: Density $\rho_d$, viscosity $\mu_d$ and refractive index $n_{ri}$ for the SiOils used at 25$^{\circ}$C.

<table>
<thead>
<tr>
<th>SiOil</th>
<th>$\rho_d$ [kg m$^{-3}$]</th>
<th>$\mu_d$ [Pa s]</th>
<th>$n_{ri}$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>750</td>
<td>$4.88 \times 10^{-4}$</td>
<td>1.375</td>
</tr>
<tr>
<td>10</td>
<td>934</td>
<td>$9.58 \times 10^{-3}$</td>
<td>1.399</td>
</tr>
<tr>
<td>50</td>
<td>960</td>
<td>$4.91 \times 10^{-2}$</td>
<td>1.402</td>
</tr>
<tr>
<td>350</td>
<td>970</td>
<td>$3.28 \times 10^{-1}$</td>
<td>1.403</td>
</tr>
<tr>
<td>1000</td>
<td>970</td>
<td>$9.47 \times 10^{-1}$</td>
<td>1.404</td>
</tr>
<tr>
<td>*2800</td>
<td>970</td>
<td>$2.75 \times 10^{0}$</td>
<td>1.404</td>
</tr>
<tr>
<td>*4500</td>
<td>970</td>
<td>$4.34 \times 10^{0}$</td>
<td>1.404</td>
</tr>
<tr>
<td>*7600</td>
<td>970</td>
<td>$7.36 \times 10^{0}$</td>
<td>1.404</td>
</tr>
<tr>
<td>10 000</td>
<td>970</td>
<td>$1.05 \times 10^{1}$</td>
<td>1.404</td>
</tr>
<tr>
<td>12 500</td>
<td>970</td>
<td>$1.33 \times 10^{1}$</td>
<td>1.404</td>
</tr>
<tr>
<td>30 000</td>
<td>970</td>
<td>$2.93 \times 10^{1}$</td>
<td>1.404</td>
</tr>
<tr>
<td>$^\dagger$50 000</td>
<td>970</td>
<td>$4.88 \times 10^{1}$</td>
<td>1.404</td>
</tr>
<tr>
<td>100 000</td>
<td>970</td>
<td>$1.06 \times 10^{2}$</td>
<td>1.404</td>
</tr>
</tbody>
</table>

*Obtained by mixing the 1000 and 10 000 cSt SiOils.

$^\dagger$ Obtained by mixing the 30 000 and 100 000 cSt SiOils.

The densities $\rho_d$ were taken as given by the provider. The viscosities $\mu_d$ were measured using a DV2T Viscometer (Brookfield Vicometers, Essex, UK). The refractive index $n_{ri}$ of SiOils were determined using a RFM390 Refractometer (Bellingham and Stanley Ltd, Kent, UK).

Calabrese et al. (1986a) raised some concerns about some high viscosity SiOils behaving as Boger fluids: shear viscosity independent of shear rate but with a
Chapter 4. Effect of dispersed phase viscosity in stirred vessels

extensional viscosity dependent on extensional strain rate. The extensional properties of the 1000, 10000, 30000 and 100000 cSt SiOils were investigated using a HAAKE CaBer (Thermo Fischer Scientific, Massachusetts, USA). All the SiOils behaved as Newtonian fluids under the experimental strain rates. This study can be consulted in Appendix 4.A.

As continuous phase we used a 1.0 wt.% sodium laureth sulfate (SLES) aqueous solution. The surfactant used was Texapon N701 (Cognis, Hertfordshire, UK) which contains approximately 70% concentration by weight of SLES and approximately 30% water and impurities. SLES is an anionic surfactant with molar mass and density equal to $420 \text{ g mol}^{-1}$ and $1030 \text{ kg m}^{-3}$ respectively. El-Hamouz (2007) determined that its critical micelle concentration is $8.4 \times 10^{-2} \text{ g L}^{-1}$, the concentration used in this investigation is approximately 120 times higher.

The interfacial tension were measured using a K11 Mk4 Tensiometer (KRUSS, Hamburg, Germany) with a 9.545 mm platinum-iridium ring. Measuring the interfacial tension for SiOils above a 1000 cSt was not possible with this method because the tensiometer overestimates the maximum lamella height and breaks it. The $\sigma$ between the 0.65 cSt, 10 cSt and 350 cSt SiOils and the continuous phases are shown in Table 4.3. The interfacial tension increases for the two most viscous SiOils is very similar, therefore the interfacial tension for the SiOils with viscosities greater than 350 cSt was assumed constant, as done by Calabrese et al. (1986a) and Hall et al. (2011).

Table 4.3: Interfacial tension of the SiOils and the continuous phases. The percentages represent one standard deviation.

<table>
<thead>
<tr>
<th>SiOil [cSt]</th>
<th>$\sigma$ [mN m$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>6.08 ±1.2%</td>
</tr>
<tr>
<td>10</td>
<td>9.25 ±3.0%</td>
</tr>
<tr>
<td>350</td>
<td>9.43 ±3.9%</td>
</tr>
</tbody>
</table>

4.2.2 Equipment

A 6-bladed pitched turbine inclined 45° with $D = 4.83 \times 10^{-2}$ m was used as impeller. The turbine was coupled with a RW20 (IKA-WERKE, Staufen, Germany). The
tank had a diameter $T$ of $1.37 \times 10^{-1}$ m ($D/T \approx 0.35$) and four baffles. The size of the baffles, clearance and the height of the liquid were $T/10$, $T/3$ and $T$ respectively. The volume of the vessel $V_T$ was 1.97 L.

The DSD was obtained using an off-line laser diffraction particle size analyser, the Mastersizer 3000 (Malvern Instruments, Malvern, UK), which allows to measure drops in the $10^{-3}$ µm to $3 \times 10^3$ µm range.

### 4.2.3 Method

#### 4.2.3.1 Emulsification

Once the continuous phase was poured into the vessel, the desired rotational speed of the impeller was fixed using a CT6 Hand-Held Tachometer (Compact Instruments, Lancashire, UK) and 20 mL of SiOil were injected in the impeller vicinity using a syringe. The concentration of the SiOil was 1.0% by volume.

The emulsification time for all experiments was 24 h and steady-state was verified by comparing the DSDs obtained after 24 h and 72 h for the 10 and 10 000 cSt SiOils for $N = 8.33 \text{ s}^{-1}$.

As seen in Table 4.2, $\mu_d$ was varied across several orders of magnitude. The effect of $\mu_d$ and $N$ was assessed by emulsifying the SiOils listed in Table 4.2 in the Water/SLES solution at five different $N$: 8.33 s$^{-1}$, 10.0 s$^{-1}$, 11.7 s$^{-1}$, 13.3 s$^{-1}$ and 15 s$^{-1}$.

The total number of emulsions prepared was 65, nevertheless the emulsions prepared with 7600 cSt and 10 000 cSt SiOil for the lowest stirring speeds (8.33 s$^{-1}$ and 10.0 s$^{-1}$) could not be analysed because the largest droplets were beyond the measuring limit of the instrument and due to the large diameter span of the DSD spreading across three orders of magnitude.

#### 4.2.3.2 Droplet Size Analysis

Samples were taken at the impeller vicinity using a syringe with a modified larger hub not to cause further droplet break up. Samples were analysed right after sampling to
ensure that no changes in the DSD would occur, despite that emulsion stability was verified for a period of 72 h after emulsification. At least three samples were analysed for each emulsion. Drops of the sample were added to the Hydro EV dispersion units until reaching an obscuration rate of about 5-11%.

The analysis model chosen in the instrument’s software was “General purpose” to ensure that bimodal effects were not suppressed. Three measurement cycles of 30 s were performed for the emulsions containing the 0.65 cSt -2760 cSt SiOils whereas measurement cycles of 300 s were needed for the most viscous SiOil. This was necessary due to the polydispersity of the droplets, increasing the analysis time allowed consistency in the measurements for the same sample. The $n_{ri}$ for the dispersed phases are the ones listed in Table 4.2 and the absorption index used was $1 \times 10^{-3}$ as recommended by Malvern for transparent droplets under the microscope.

### 4.3 Results and discussion

#### 4.3.1 Phenomenology

In this section some of the results will be presented to show the effect of $\mu_d$ and $N$ on the shape of the DSD. Two different behaviours were found for the 0.65 -10 000 cSt SiOils and the 12 500-100 000 cSt SiOils. In the former $\mu_d$ range, droplet size increased with $\mu_d$ and decreased with $N$; for the latter viscosity range, the maximum droplet size was independent of $\mu_d$ and $N$.

The effect of $\mu_d$ for the SiOils in the 0.65 cSt -10 000 cSt viscosity range for $N = 11.7 \text{s}^{-1}$ is shown in Figure 4.2a in a semi-log plot. As expected, the droplet size increases with $\mu_d$ and the DSD broadens. The 0.65 cSt, 10 cSt and 50 cSt SiOils yielded monomodal distributions while the rest were bimodal, presumably due to a change in the drop breakup mechanism that produces satellite droplets. Figure 4.2b shows the effect of $N$ on the DSD for the 1000 cSt SiOil. As expected the droplet size decreases with $N$. This is true for the daughter and satellite droplets.

Figure 4.3 shows the DSD for the second type of behaviour encountered where the maximum drop size is independent of $\mu_d$ (see Fig. 4.3a) and $N$ (see Fig. 4.3b).
4.3. Results and discussion

**Figure 4.2:** Examples of the resulting DSD of systems emulsified. (a) DSD for SiOils for in the 0.65 cSt - 10000 cSt viscosity range for $N = 11.7 \text{s}^{-1}$. (b) DSD for the 1000 cSt SiOil for different $N$. The shadowed areas represent one standard deviation from the mean.

**Figure 4.3:** Examples of the resulting DSD of systems emulsified. (a) DSD for SiOils for in the 10 000 - 100 000 cSt viscosity range for $N = 11.7 \text{s}^{-1}$. (b) DSD for the 100 000 cSt SiOil for different $N$. The shadowed areas represent one standard deviation from the mean.

Figure 4.4 shows the $d_{32}$ as a function of $\mu_d$ with $N$ as parameter. The vertical dashed delimits the two types of behaviours mentioned above. For the first type of behaviour (left of the dashed line), where $d_{\text{max}}$ is $\mu_d$ and $N$ dependent, $d_{32}$ increases with viscosity and levels off before decreasing sharply despite $d_{\text{max}}$ increasing. This behaviour is due to the appearance of satellite drops, which amount increase with $\mu_d$ as was previously shown in Figure 4.2a. Furthermore the curves for different $N$ are parallel.
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Figure 4.4: Effect of $\mu_d$ on the $\bar{d}_{32}$ with $N$ as parameters.

The $\bar{d}_{32}$ for the SiOils with viscosity equal and above 12 500 cSt were plotted at the right side of the dashed line in Figure 4.4; this zone is characterized by $d_{\text{max}}$ being independent of $\mu_d$ and by a decrease in $N$ dependency; all the curves seem to converge at the maximum $\mu_d$.

Equation 4.8 was tested for our emulsions using the 95th percentile as an approximation of $d_{\text{max}}$. Figure 4.5 shows the evolution of the $\bar{d}_{32}$ to $d_{\text{max}}$ ratio. It can be seen this ratio was constant for our monomodal emulsion while decreasing with $\mu_d$ for our bimodal distribution. No clear trend was found for the most viscous SiOils; as explained above, these had a different behaviour. However, this plot reveals that assuming a constant $\bar{d}_{32}/d_{\text{max}}$ result in a tenfold-miscalculation in this region.

Even though the experimental viscosity range used by Calabrese et al. (1986a) is included in our study, we did not observe a low viscosity $d_{32}$-plateau for the viscosity range where, according to their mechanistic model, interfacial forces are the primarily force resisting drop breakup. As explained by Wang and Calabrese (1986), this is attributed to the lower interfacial tensions in our systems as the systems emulsified by Calabrese et al. (1986a) were surfactant-free.
4.3. Results and discussion

4.3.2 Drop size

The drop size analysis was performed using the mode of the daughter drops $Mo_L$, alternatively $d_{max}$ could be used; but we considerer the former statistically more significant and is consistent with our previous work (Carrillo De Hert and Rodgers, 2017a). In Section 4.3.3 the DSD will be standardized by $Mo_L (f_v(d_i/Mo_L))$ and it will become evident that $Mo_L \propto d_{max}$ and why this was used. The analysis in this Section was only performed for the SiOils thinner than the 12 500 cSt SiOils.

Figure 4.6 shows the mode of the daughter droplets $Mo_L$ as a function of $\mu_d$. This curve shows a steady increase of $Mo_L$ with $\mu_d$ for each $N$ compared to the $\overline{d}_{32}$ shown previously where a plateau and decrease were observed. The comparison in-between Figures 4.4 and 4.6 show that $\overline{d}_{32}$ is not the best measure of central tendency to elucidate the drop break-up mechanism when the DSD are multimodal.

However, it can be noticed that the data obtained by the thinnest SiOil (0.65 cSt) does not follow the same trend as the thicker SiOils. This is attributed to its different properties (see Table 4.2) and $\sigma$ (see Table 4.3; furthermore Figure 4.2a shows that this oil produced a broader DSD than the other subsequent oils which also yielded monomodal distributions. Following Equation 4.7, the $Mo_L D^{-1} We^{3/5}$ against $\mu_d$ should collapse the data-points creating a master-curve. As shown in

![Figure 4.5: $\overline{d}_{32}$ to $D_{95}$ ratio as a function of $\mu_d$. The error bars represent one standard deviation from the mean.](image)
Chapter 4. Effect of dispersed phase viscosity in stirred vessels

Figure 4.6: Effect of $\mu_d$ on the $Mo_L$ with $N$ as parameters.

Figure 4.7, this standardization successfully collapses the data points for different $N$, furthermore the curve resembles the ones presented by Calabrese et al. (1986a) and Wang and Calabrese (1986) where a drop size-plateau (interfacial forces dominate) is followed by a drop size increase (as viscous forces become important). This Figure aids in delimiting the boundary of our study to the 10 cSt - 10 000 cSt SiOils where viscous cohesive forces dominate.

Figure 4.7: Dimensionless standardized $Mo_L$ as a function of $\mu_d$.

A fit was performed for the emulsions with SiOils in the 10 cSt - 10 000 cSt
viscosity range with a fixed $Mo_L \propto N^{-1.2}$ dependency.

\[
\frac{Mo_L}{N^{-6/5}} = A_1 \mu_d^{A_2}
\]  

(4.13)

The values of the fitting constants, their 95% Confidence Interval and $p$-value are listed in Table 4.4.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Coefficient</th>
<th>$p$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$4.64 \times 10^3 \pm 2.94%$</td>
<td>$5.1 \times 10^{-59}$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$0.365 \pm 3.29%$</td>
<td>$1.4 \times 10^{-31}$</td>
</tr>
</tbody>
</table>

The coefficient of determination $R^2$ and the mean absolute error $MAE$ of the fit were 0.986 and 5.39% respectively. Our dependency on $\mu_d$ disagrees with most mechanistic models found in literature; the models proposed by Arai et al. (1977) and Calabrese et al. (1986a) state that $A_2 = 0.75$ and the model proposed by Davies (1985), $A_2 = 0.6$. For their most viscous oils, Calabrese et al. (1986a) could not fit their results using their mechanistic model and proposed an empirical correlation with $A_2 = 3/8$ (Eq. 4.12), which is very similar to the value found throughout our investigation. In our previous study on the effect of dispersed phase viscosity in rotor-stators (Carrillo De Hert and Rodgers, 2017a) we found $A_2 = 0.375$, suggesting that $A_2$ is independent of the mechanical stirred apparatus used.

### 4.3.3 Droplet size distribution modelling

The DSD were normalized by $Mo_L$ to show the changes in the shape of the DSD. Figure 4.8a shows the effects of $\mu_d$ for constant $N$ and Figure 4.8b shows the effect of $N$ on the DSD for the 1000 cSt Silicon Oil. The former Figure shows that the DSDs become broader and that the amount of satellite drops increase with $\mu_d$. The latter Figure shows that for our experimental range, there is no important DSD-shape dependency on $N$. Therefore Equation 4.8 holds for different $N$ but not for $\mu_c$ for a given SiOil. Both Figures show that $Mo_L \propto d_{\text{max}}$, the 95th percentile $D_{95}$ of all the DSD was $D_{95} = 1.54 Mo_L$ with a standard deviation of 6.54%.
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Figure 4.8: Normalized DSD $f_v(d_i/Mo_L)$ (a) for different SiOils for $N = 13.3 \text{s}^{-1}$ and (b) for the 1000 cSt SiOil for different $N$.

The DSDs were modelled by fitting two log-normal distributions functions $(p(d_i/Mo_L))$ to the $Mo_L$-standardized DSD by volume. The $p(d_i/Mo_L)$ were normalized so that the sum of the frequencies equals 100%. The equations of the log-normal distribution, its normalization and the mixing rule of the two distributions are given by

\[
p \left( \frac{d_i}{Mo_L} \right) = \frac{1}{s_z \sqrt{2\pi}} \left( \frac{d_i}{Mo_L} \right) \exp \left\{ -\frac{\left[ \ln \left( \frac{d_i}{Mo_L} \right) - \bar{z} \right]^2}{2s_z^2} \right\} \tag{4.14}
\]

\[
f_v \left( \frac{d_i}{Mo_L} \right) = 100 \times \frac{p \left( \frac{d_i}{Mo_L} \right)}{\sum p \left( \frac{d_i}{Mo_L} \right)} \tag{4.15}
\]

\[
f_{v,T} \left( \frac{d_i}{Mo_L} \right) = (1 - \phi_s) f_{v,L} \left( \frac{d_i}{Mo_L} \right) + \phi_s f_{v,s} \left( \frac{d_i}{Mo_L} \right) \tag{4.16}
\]

Where $s_z$ is the standard deviation of $\ln(d_i/Mo_L)$, $\bar{z}$ is the arithmetic mean of $\ln(d_i/Mo_L)$, $\phi_s$ is the volume fraction of the satellite drops; and $f_{v,T}(di/Mo_L)$, $f_{v,L}(di/Mo_L)$ and $f_{v,s}(di/Mo_L)$ are the standardized frequency distribution by volume for the whole DSD, the daughter drops and the satellite drops respectively.

The expression for the mode $Mo$ of a log-normal distribution function is $Mo = \exp(\bar{z} - s_z^2/2)$, therefore in the case of the $Mo_L$-standardized DSD we obtain $\bar{z} = s_z^2/2$ reducing the number of fitting parameters for $f_{v,L}(d_i/Mo_L)$. 
To fit the \( M_{OL} \)-standardized DSDs the following assumptions were made:

- The standard deviation of the daughter droplets \( s_{z,L} \) is independent of \( \mu_d \) and \( N \) as \( M_{OL}/d_{max} \) is constant (see Fig. 4.8).

- The modes of both types of droplets are equidistant

\[
\bar{z}_s = \ln M_{Os} + \frac{s_{z,s}^2}{2} = A_4 + \frac{s_{z,s}^2}{2} \tag{4.17}
\]

- The standard deviation of the satellite droplets is \( N \)-independent (see Fig. 4.8b), but has a power-law dependency on \( \mu_d \):

\[
s_{z,s} = A_5 \mu_d^{A_6} \tag{4.18}
\]

- As \( \phi_s \) for the monomodal distributions is zero, increases with \( \mu_d \), the daughter droplets disappeared in short \( \mu_d \)-interval and is \( N \)-independent; we used a cumulative Weibull distribution to describe the effect of \( \mu_d \) on \( \phi_s \)

\[
\phi_s = 1 - \exp \left[ - \left( \frac{\mu_d}{\beta} \right)^{\alpha} \right] \tag{4.19}
\]

Where \( \alpha \) and \( \beta \) are fitting parameters.

Under these considerations listed above, the DSD were fitted for \( s_{z,L}, A_4, A_5, A_6, \alpha \) and \( \beta \) using the least absolute error in-between the experimental and modelled DSDs. The values obtained for the fit are shown in Table 4.5. Some examples of the fits are shown in Figure 4.10.

The value we obtained for \( s_{z,L} \) is considerably larger than the ones of Chen and Middleman (1967) and Wang and Calabrese (1986) who reported values of 0.23 and 0.24 respectively, however these are not comparable as the aforementioned authors used normal distribution functions rather than the log-normal used in our investigation.
Chapter 4. Effect of dispersed phase viscosity in stirred vessels

Table 4.5: DSD fit parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s_{z,L}$</td>
<td>0.40</td>
</tr>
<tr>
<td>$A_4$</td>
<td>-0.87</td>
</tr>
<tr>
<td>$A_5$</td>
<td>0.80</td>
</tr>
<tr>
<td>$A_6$</td>
<td>0.15</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>1.4</td>
</tr>
<tr>
<td>$\beta$</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Figure 4.9 shows the values of $\phi_s$ if it is allowed to fit “freely”, while the line represents equation 4.19 with its corresponding fit parameters found in Table 4.5. This Figure shows that a cumulative Weibull distribution is adequate for describing the $\phi_s$ dependency on $\mu_d$. The disappearance of the large daughter droplets when the thickest Silicon Oils were used explains why Equation 4.13 was unable to predict the modes of the DSD for $\mu_d > 30$ Pa s.

![Graph showing volume fraction of satellite drops $\phi_s$ as a function of dispersed phase viscosity $\mu_d$ for five different stirring speeds.](image)

**Figure 4.9:** Volume fraction of satellite drops $\phi_s$ as a function of dispersed phase viscosity $\mu_d$ for five different stirring speeds.

It is interesting noticing that the two DSD are equidistant, in our previous study on the effect of viscosity in rotor-stators (Carrillo De Hert and Rodgers, 2017a) we found the same $Mo_L$ dependency on $\mu_d$, but we found that the small droplets decreased with $\mu_d$ which was not the case for stirred vessels. The reason, a priori, is unknown.

The goodness of the fit can be assessed by comparing the $d_{32}$ obtained with the fit
with the experimental one. In the first subfigure a $N$-standardized $d_{32}$ as a function of $\mu_d$ is shown; provided that Equation 4.8 is applicable for different $N$ and that $d_{max} \propto N^{-6/5}$. It can be observed that our fit follows the trend of the experimental data. The second figure uses direct comparison. The $R^2$ and $MAE$ are 0.82 and 12.2% respectively.

### 4.4 Conclusions

A wide number of SiOils with $\mu_d$ ranging across 6-orders of magnitude were emulsified to study the changes in the steady-state drop break-up mechanism. Three different regimes were observed, namely (1) the one where interfacial forces dominate and
which has been described by Hinze (1955), Chen and Middleman (1967), Calabrese et al. (1986a) and Calabrese et al. (1986b) and many others. (2) The regime where the drops’ viscous resistance dominates which has been mainly described by Davies (1985), Calabrese et al. (1986a) and Wang and Calabrese (1986). In this regime bimodal drop size distributions were observed for the SiOils in the 50-350 cSt range. Bimodality was also observed in the same \( \mu_d \) range in our study on the effect of viscosity in rotor-stators (Carrillo De Hert and Rodgers, 2017a). (3) For very high \( \mu_d \) we observed that the maximum drop sizes decrease and become independent of \( N \); furthermore the steady-state \( \bar{d}_{32} \) of these emulsion were smaller than the ones obtained for the 10 cSt SiOils.

To describe the effect of \( \mu_d \) on the drop sizes we used the \( M_{OL} \), which was shown to be a better parameter than \( \bar{d}_{32} \) while being proportional to \( d_{max} \) for all the experimental \( \mu_d \) and \( N \). The drop size correlated well with \( \mu_d^{0.365} \), which is in agreement with our previous work (Carrillo De Hert and Rodgers, 2017a), while being in disagreement with the work of Davies (1985), Calabrese et al. (1986a), Wang and Calabrese (1986) and Vankova et al. (2007); the first three of these studies were done in the absence of surfactant, while the latter was performed did use surfactants. The sutler dependency of the DSD on \( \mu_d \) could not been explained by any mechanistic model.
Finally a methodology to fit the bimodal DSD by volume using two log-normal distributions was proposed. The fit proposed could predict the $d_{32}$ reasonably-well.

4.5 Bibliography


**Appendix**

**Appendix 4.A  Extensional rheometry**

The Newtonian behaviour of our SiOils were verified using a Capillary Breakup Extensional Rheometer, the HAAKE CaBER (Thermo Fisher Scientific, Massachusetts, USA). The measurements were obtained at 25 °C. The samples’ starting height and diameter were 3 mm and 6 mm respectively, whereas the samples’ final height were 11 mm. The surface tension used was $\sigma_s = 20.9 \text{ mN m}^{-1}$ for all the SiOils.
Chapter 4. Effect of dispersed phase viscosity in stirred vessels

The data in Figure 4.A.1 showed a linear dependency of the normalized diameter of the midsection $D_{\text{mid}}$ of the filament with time $t$ (when plotted in a linear scale) and therefore was treated a Newtonian fluid. According to McKinley and Tripathi (2000), the shear viscosity of a Newtonian fluid $\mu$ can be obtained from extensional experiments using

$$\mu = \frac{\left(\frac{2X-1}{3}\right) \sigma_s t}{D_{\text{mid}}(t) - D_1}$$  \hspace{1cm} (4.20)

Where $X$ is a dimensionless factor and $D_1$ is the diameter of the filament at $t = 0$. Several values of $X$ have been proposed, McKinley and Tripathi (2000) argues that the best value is $X = 0.7127$.

The extensional strain rate $\dot{\varepsilon}$ is given by

$$\dot{\varepsilon}(t) = -\frac{2}{D_{\text{mid}}(t)} \frac{dD_{\text{mid}}(t)}{dt}$$  \hspace{1cm} (4.21)

Figure 4.A.2 shows the shear viscosity obtained using the extensional data and Equation 4.20. The dashed lines show the viscosity obtained using a rotational rheometer. As it can be observed, the four SiOils have a Newtonian behaviour in the experimental $\dot{\varepsilon}$ rate, as these do not exhibit a dependency on $\dot{\varepsilon}$. Furthermore, the viscosity obtained from shear and extensional tests are reasonably close. The extensional viscosity $\mu_{\text{ext}}$ therefore can be obtained using the Trouton rule $\mu_{\text{ext}} = 3\mu$. 
Figure 4.A.2: Shear viscosity obtained using Equation 4.20. The dashed lines show the viscosity obtained using a rotational rheometer.
Chapter 5

On the steady-state drop size distribution in stirred vessels. Part II: effect of continuous phase viscosity


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Chapter 5. Effect of continuous phase viscosity in stirred vessels

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Abstract

In Part I (Carrillo De Hert and Rodgers, 2017c) we used silicon oils with viscosities across six orders of magnitude to investigated the effect of the dispersed phase viscosity on the DSD of dilute emulsions. In this study we expanded Part I by using three glucose aqueous solutions to thicken the continuous phases approximately an order of magnitude while keeping the Power number constant. It was found that increasing the continuous phase viscosity decreases the maximum drop size despite having drops well above the Kolmogorov length-scale. Our results are in disagreement with the mechanistic models for the turbulent inertia regime. The contradictory results were explained using the full turbulent energy spectrum proposed by Pope (2000) instead of the Kolmogorov -5/3 spectrum (for infinite Reynolds numbers). Our analysis revealed that two systems with same energy spectrum may produce different DSD, indicating that the turbulent kinetic energy was unlikely to be responsible for drop breakup in our systems.

5.1 Introduction

In this study we varied the viscosity of the continuous phase systematically in a turbulent stirred vessel. As further explained below, mechanistic models consider that the continuous phase should not influence the drop size or drop size distribution provided that the drops are larger than the Kolmogorov length-scale \( \ell_\eta \) and that the vessel is in the turbulent regime. However the mechanistic models consider that the viscosity of the continuous phase \( \mu_c \) becomes relevant if the drops are smaller than \( \ell_\eta \) or if the flow is laminar.

Due to the predictions of the models, the effect of \( \mu_c \) in turbulent vessels has not been thoroughly investigated. Most of the experimental studies shown in Figure 1 in Part I (Carrillo De Hert and Rodgers, 2017c) did not vary \( \mu_c \) systematically, and we found no studies where \( \mu_d \) and \( \mu_c \) are varied systematically to study their combined effect.

Two of the studies where \( \mu_c \) are varied systematically are the ones of Vankova
et al. (2007) and Boxall et al. (2012). Vankova et al. (2007) used a narrow-gap homogenizer to emulsify a $9.5 \times 10^{-2}$ Pas SiOil in different glycerol aqueous solutions varying $\mu_c$ from $1 \times 10^{-3}$ Pas to $1.8 \times 10^{-2}$ Pas. They found that even the drops emulsified in $3 \times 10^{-3}$ Pas glycerol solution produced smaller drops than when the $1 \times 10^{-3}$ Pas one was used. They attributed the decrease in droplet size to a change in the emulsification regime from turbulent inertia to viscous inertia as $\mu_c$ increased.

Boxall et al. (2012) emulsified deionized water in oils with viscosities in the $3.1 \times 10^{-3}$ Pas to $10^{-1}$ Pas using a stirred vessel with a 6-blade Rushton turbine with a diameter $D$ of 0.051 m at different stirring speeds. They used the mean energy dissipation rate per unit mass $\overline{\varepsilon}$ to calculate $\ell_\eta$ and were able to observe a transition from turbulent inertia to sub-Kolmogorov shear stress regimes. Their results were well correlated by the models of Hinze (1955) and Shinnar and Church (1960). Nevertheless Boxall et al. (2012) worked with very high $\mu_c$ and their experiments were not carried out at a constant Power number $P_o$, i.e. the Reynolds number ($Re$) of their systems ranged from 27 to $3.4 \times 10^3$, therefore some of their systems were mainly in the laminar and transition regimes.

5.2 Theory

As reviewed in Part I (Carrillo De Hert and Rodgers, 2017c), Hinze (1955) theorized that drops larger than $\ell_\eta$ are broken up by the kinetic energy of the turbulent fluctuations $k$. Under the assumption of isotropic turbulence, he used the Kolmogorov $-5/3$ energy spectrum and determined that the stresses experienced by the largest droplet of diameter $d_{max}$ are

$$\rho_c \overline{u'^2} = C \rho_c \left(\varepsilon d_{max}\right)^{\frac{2}{3}}$$

(5.1)

Where $\rho_c$ is the density of the continuous phase, $\overline{u'^2}$ is the average of the square of velocity differences ($k = \overline{u'^2}/2$), $\varepsilon$ is the energy dissipation rate per unit mass and $C$ is the Kolmogorov constant ($C = 1.5$)(Pope, 2000). The Kolmogorov length-scale $\ell_\eta$
is given by
\[ \ell_\eta = \left( \frac{\nu_c^3}{\varepsilon} \right)^{1/4} \]  
\[ (5.2) \]
Where \( \nu_c \) is the kinematic viscosity of the continuous phase. Turbulence in stirred vessels is not homogeneous across the whole vessel. According to Davies (1985) the steady-state DSD will be determined by the maximum energy dissipation rate \( \varepsilon_{\text{max}} \) which is located in the vicinity of the impeller (Kresta, 1998; Gabriele et al., 2009). Determining \( \varepsilon_{\text{max}} \) is difficult, however it is proportional to the mean energy dissipation rate per unit mass \( \varepsilon \). Several \( \varepsilon_{\text{max}}/\varepsilon \) have been reported in literature for different impeller geometries and have been proven to be independent of \( N \) using particle image velocimetry (Gabriele et al., 2009).

The \( \varepsilon \) can be obtained through power draw \( P_S \) measurements
\[ \varepsilon = \frac{P_S}{\rho_c V} = \frac{P_0 N^3 D^5}{V_T} \]  
\[ (5.3) \]
Where \( V_T \) is the volume of the vessel, \( P_0 \) is the dimensionless Power number \( (P_0 = P_S \rho_c^{-1} N^{-2} D^{-5}) \), \( N \) is the impeller speed and \( D \) is the diameter of the impeller. Therefore two geometrically identical systems with the same \( P_0 \), operated at the same \( N \) have the same \( \varepsilon \) and \( \varepsilon_{\text{max}} \); furthermore, if these two systems have the same \( \rho_c \), they should have the same disruptive forces (Eq. 5.1); note that for a constant \( P_0 \) all these terms are independent of \( \nu_c \).

For \( d_{\text{max}} < \ell_\eta \), Shinnar and Church (1960) determined through dimensional analysis that the stresses due to \( k \) are given by
\[ \rho_c u'^2 \propto \frac{\varepsilon d_{\text{max}}^2}{\nu_c} \]  
\[ (5.4) \]
This model, includes an effect of \( \nu_c \) on the disruptive forces, however it has been criticized arguing that the disruptive forces for \( d_{\text{max}} < \ell_\eta \) should be mainly viscous (Bourne and Baldyga, 1994). Shinnar and Church (1960) proposed another model viscous stresses being the disruptive force for \( d_{\text{max}} << \ell_\eta \); for isotropic turbulence Taylor (1935) showed that \( \varepsilon = (15/2)\nu_c (\partial u' / \partial d)^2 \), therefore the viscous shear stresses
over a distance $d$ are

$$
\mu_c \left[ \left( \frac{\partial u'}{\partial d} \right)^2 \right]^{1/2} \propto \mu_c \left( \frac{\varepsilon}{\nu_c} \right)^{3/2} = \rho_c (\nu_c \varepsilon)^{3/2}
$$

(5.5)

Where $\mu_c$ is the dynamic viscosity of the continuous phase.

Equations 5.1, 5.4 and 5.5 are the stresses of the commonly known inertia subrange ($d_{\text{max}} \gg \ell_\eta$), sub-Kolmogorov inertia stress ($d_{\text{max}} < \ell_\eta$) and sub-Kolmogorov-viscous stress models ($d_{\text{max}} \ll \ell_\eta$). As reviewed in Part I, the disruptive forces are balanced with the cohesive ones; the cohesive forces involved depend on the viscosity of the dispersed phase $\mu_d$ (Hinze, 1955; Arai et al., 1977; Calabrese et al., 1986). Hence these may be viscous ($\mu_d \to \infty$), interfacial ($\mu_d \to 0$) or both. Padron (2005) made a comprehensive review on the mechanistic models and their derivation. Table 5.1 shows the models for constant Po for the two limiting cases $\mu_d \to 0$ and $\mu_d \to \infty$.

The dimensionless numbers in this Table for a stirred vessel are

$$
\text{We}_S = \frac{\rho_c N^2 D^3}{\sigma}
$$

(5.6)

$$
\text{Re} = \frac{ND^2}{\nu_c}
$$

(5.7)

Where $D$ is the diameter of the impeller, $N$ its stirring speed and $\sigma$ the interfacial tension.

**Table 5.1:** Summary of mechanistic models for constant Po in its dimensionless form. The four columns at the right are the exponential dependencies for each parameter. From Padron (2005).

<table>
<thead>
<tr>
<th>Range</th>
<th>Model</th>
<th>$\frac{d_{\text{max}}}{D} \propto$</th>
<th>Dependency</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{\text{max}} &gt; \ell_\eta$</td>
<td>$\mu_d \to 0$</td>
<td>$\text{We}_S^{-3/5}$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$\mu_d \to \infty$</td>
<td>$\left( \frac{\mu_d}{\mu_c} \right)^{3/4}$ $\left( \frac{\rho_c}{\rho_d} \right)^{3/4} \text{Re}^{-3/4}$</td>
<td>3/4 0 -3/5 -6/5</td>
</tr>
<tr>
<td>$d_{\text{max}} &lt; \ell_\eta$</td>
<td>$\mu_d \to 0$</td>
<td>$\left( \text{We}_S \text{Re} \right)^{-1/3}$</td>
<td>0 1/3 -2/3 -1</td>
</tr>
<tr>
<td></td>
<td>$\mu_d \to \infty$</td>
<td>$\left( \frac{\mu_d}{\mu_c} \right)^{1/2}$ $\left( \frac{\rho_c}{\rho_d} \right)^{1/4} \text{Re}^{-3/4}$</td>
<td>1/2 1/4 -1/2 -3/4</td>
</tr>
<tr>
<td>$d_{\text{max}} \ll \ell_\eta$</td>
<td>$\mu_d \to 0$</td>
<td>$\left( \text{We}_S \text{Re} \right)^{1/2}$</td>
<td>0 -1/2 -1/2 -3/2</td>
</tr>
<tr>
<td></td>
<td>$\mu_d \to \infty$</td>
<td>$\left( \frac{\mu_d}{\mu_c} \right)^{1/2}$ $\left( \frac{\rho_c}{\rho_d} \right)^{1/2} \text{Re}^{-3/4}$</td>
<td>1 -1/4 -1/4 -3/4</td>
</tr>
</tbody>
</table>
5.3 Materials and equipment and methods

5.3.1 Materials

Eight of the Fluid XX Silicon Oils (SiOil, dimethyl siloxane, Dow Corning, Michigan, U.S.A.) used in Part I (Carrillo De Hert and Rodgers, 2017c) with nominal dynamic viscosity in the 10 to 100,000 cSt range and blends were emulsified for this investigation. Their \( \rho_d \) and \( \mu_d \) can be consulted in Table 5.1.

<table>
<thead>
<tr>
<th>SiOil [cSt]</th>
<th>( \rho_d ) [kg m(^{-3})]</th>
<th>( \mu_d ) [Pa s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>934</td>
<td>( 9.58 \times 10^{-3} )</td>
</tr>
<tr>
<td>50</td>
<td>960</td>
<td>( 4.91 \times 10^{-2} )</td>
</tr>
<tr>
<td>350</td>
<td>970</td>
<td>( 3.28 \times 10^{-1} )</td>
</tr>
<tr>
<td>1000</td>
<td>970</td>
<td>( 9.47 \times 10^{-1} )</td>
</tr>
<tr>
<td>*2800</td>
<td>970</td>
<td>( 2.75 \times 10^{0} )</td>
</tr>
<tr>
<td>*4500</td>
<td>970</td>
<td>( 4.34 \times 10^{0} )</td>
</tr>
<tr>
<td>*7600</td>
<td>970</td>
<td>( 7.36 \times 10^{0} )</td>
</tr>
<tr>
<td>10000</td>
<td>970</td>
<td>( 1.05 \times 10^{1} )</td>
</tr>
<tr>
<td>12500</td>
<td>970</td>
<td>( 1.33 \times 10^{1} )</td>
</tr>
<tr>
<td>30000</td>
<td>970</td>
<td>( 2.93 \times 10^{1} )</td>
</tr>
<tr>
<td>( ^\dagger )50000</td>
<td>970</td>
<td>( 4.88 \times 10^{1} )</td>
</tr>
<tr>
<td>100000</td>
<td>970</td>
<td>( 1.06 \times 10^{2} )</td>
</tr>
</tbody>
</table>

*1000 and 10 000 cSt SiOil blend.

\( ^\dagger \) 30 000 and 100 000 cSt SiOil blend.

We expanded the results obtained in Part I (Carrillo De Hert and Rodgers, 2017c) by modifying the continuous phase. The continuous phases studied were three Sweet Glucose Syrup M01632 (Brenntag, Mülheim, Germany) aqueous solutions of concentration \( C_g \) 1.50 mol L\(^{-1}\), 2.50 mol L\(^{-1}\) and 2.90 mol L\(^{-1}\). All the continuous phases contained 27.85 g of Texapon N701 (Cognis, Hertfordshire, UK), which yields 1 wt.% of Sodium Laureth Sulphate (SLES) for the systems emulsified in water (\( C_g = 0 \)). Naturally the wt.% was different depending of the continuous phase used as their \( \rho_c \) are different; the SLES concentrations ranged from 0.86% for \( C_g = 2.90 \) mol L\(^{-1}\) to 1.0% for \( C_g = 0 \) mol L\(^{-1}\).

The relevant properties of the continuous phases are shown in Table 5.2. The \( \rho_c \)
were obtained using a pycnometer and the $\mu_c$ was obtained using the same methods used to determine the properties of the SiOils in Part I (Carrillo De Hert and Rodgers, 2017c).

**Table 5.2:** Density $\rho_c$ and viscosity $\mu_c$ for the continuous phases used at 25°C.

<table>
<thead>
<tr>
<th>$C_g$ [mol L$^{-1}$]</th>
<th>$\rho_c$ [kg m$^{-3}$]</th>
<th>$\mu_c$ [Pa s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>997</td>
<td>$1.04 \times 10^{-3}$</td>
</tr>
<tr>
<td>1.50</td>
<td>1098</td>
<td>$2.65 \times 10^{-3}$</td>
</tr>
<tr>
<td>2.50</td>
<td>1166</td>
<td>$5.73 \times 10^{-3}$</td>
</tr>
<tr>
<td>2.90</td>
<td>1194</td>
<td>$9.79 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

The measured $\sigma$ for the 10 and 350 cSt SiOils and the continuous phases are shown in Table 5.3. These were obtained by the methodology described in Part I (Carrillo De Hert and Rodgers, 2017c). For a given $C_g$ the interfacial tension for the 10 and 350 cSt SiOils is very similar, therefore $\sigma$ for the SiOils with $\mu_d$ greater than 350 cSt was assumed constant as done in Part I (Carrillo De Hert and Rodgers, 2017c) and by other authors (Calabrese et al., 1986; Hall et al., 2011). The results show that $\sigma$ decreases with $C_g$.

**Table 5.3:** Interfacial tensions $\sigma$ of the SiOils and the continuous phases. The percentages represent one standard deviation.

<table>
<thead>
<tr>
<th>SiOil [cSt]</th>
<th>$\sigma$ [mN m$^{-1}$] 0 mol L$^{-1}$</th>
<th>$\sigma$ [mN m$^{-1}$] 1.50 mol L$^{-1}$</th>
<th>$\sigma$ [mN m$^{-1}$] 2.50 mol L$^{-1}$</th>
<th>$\sigma$ [mN m$^{-1}$] 2.93 mol L$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>9.25 ±3.0%</td>
<td>7.56 ±1.5%</td>
<td>6.52 ±0.8%</td>
<td>5.57 ±1.2%</td>
</tr>
<tr>
<td>350</td>
<td>9.43 ±3.9%</td>
<td>7.57 ±2.2%</td>
<td>6.46 ±1.3%</td>
<td>5.54 ±2.2%</td>
</tr>
</tbody>
</table>

### 5.3.2 Equipment and methods

The geometric features of the vessel and impeller used have been previously described in Part I (Carrillo De Hert and Rodgers, 2017c).

#### 5.3.2.1 Emulsification

The emulsions were prepared by pouring the continuous phases into the vessel, $N$ was fixed using a CT6 Hand-Held Tachometer (Compact Instruments, Lancashire,
5.4. Results and discussion

UK) and injecting 20 mL of SiOil in the impeller vicinity using a syringe. The concentration of the SiOil was 1% by volume for all systems.

Analogously to the experiments we ran in Part I (Carrillo De Hert and Rodgers, 2017c), the systems were stirred for 24 h and steady-state was verified by analysing the DSD at different times.

The drop size analysis was also carried out using the Mastersizer 3000 (Malvern Instruments, Malvern, UK) using the same operation procedure as in Part I (Carrillo De Hert and Rodgers, 2017c).

All the SiOils in the 10 to 30 000 cSt viscosity range were emulsified in the three different glucose solutions. Additionally, the 50 000 and 100 000 cSt SiOils were emulsified in the 2.90 mol L\(^{-1}\) solution. All combinations were studied for two \(N\): 10.0 s\(^{-1}\) and 13.3 s\(^{-1}\).

The total number of emulsions prepared for Part II of our investigation was 62, however the data obtained in Part I (Carrillo De Hert and Rodgers, 2017c) was also incorporated for the analysis.

5.3.2.2 Power draw and rate of energy dissipation

The \(P_o\) was estimated following the procedure described in James et al. (2017), the torque \(M\) was measured using a TorqSense RWT321 1 N m torque sensor (Sensor Technology, Oxfordshire, UK). The power draw \(P_s\) can be estimated using \(P_s = 2\pi NM\). Seven materials were used: (1) water, (2) a 2.9 mol L\(^{-1}\) glucose in water solution, (3-7) five different SiOils. The torque was measured for different \(N\) and the real torque \(M\) was obtained by subtracting the mechanical losses estimated by calculating the \(y\)-intercept through regression of measured \(M\) vs. \(N\) and measured \(M\) vs. \(N^2\) for the laminar and turbulent regimes respectively.

5.4 Results and discussion

This section is divided in three. (1) Section 5.4.1 presents the power curve obtained for the impeller used. This Section shows that all our experiments were carried out
Chapter 5. Effect of continuous phase viscosity in stirred vessels

at a constant Po. (2) Section 5.4.2 shows the combined effect of $\mu_d$ and $\mu_c$ on the droplet size and on the DSD. Analogously to the phenomenological Section in Part I (Carrillo De Hert and Rodgers, 2017c), the mode of the daughter drops $M_{oL}$ was used as fitting parameter. $M_{oL}$-normalized DSD are also presented for the different $C_g$ to ease the comparison in-between DSDs with the same dispersed phase. (3) Finally, Section 5.4.3 offers an explanation for the unexpected effect of $\mu_c$ on the drop sizes despite all experiments being carried out at constant Po and most of our emulsions yielding $d_{max}$ larger than $\ell_\eta$ which is commonly used as boundary in-between the inertia and viscous sub-ranges.

5.4.1 Power draw

Before proceeding to the main topic of our investigation, the power draw results are presented as these will become an important topic of discussion further on when our results are compared with the models based on the Kolmogorov-Hinze theory (Hinze, 1955) reviewed in Part I (Carrillo De Hert and Rodgers, 2017c).

The “power curve” is shown in Figure 5.1. The laminar power constant $K_P$ ($K_P = RePo$) and the Po plateau in the turbulent regime were 64.1 and 1.33 respectively. This curve shows that all our experiments were carried out in the turbulent regime at a constant Po.

![Power curve](image-url)
5.4. Results and discussion

5.4.2 Phenomenology, drop size and drop size distribution

In this section some of the results will be presented to show the effect of $\mu_c$, $\mu_d$ and $N$ on the shape of the DSD. In Section 5.4.3 an analysis on turbulence for our systems is presented; the analysis was necessary to explain why $\mu_c$ had an effect on the DSD despite it not being considered by any mechanistic model.

The effect of $\mu_d$ for the systems emulsified in water/SLES ($C_g = 0$) for the five different $N$ investigated were presented in Part I (Carrillo De Hert and Rodgers, 2017c). The systems with $C_g > 0$ showed a similar trend: the maximum drop size increases with $\mu_d$, the 10 and 50 cSt SiOils yielded monomodal DSD, whereas thicker oils yielded bimodal distributions, the maximum drop size reached a maximum for the 10 000 cSt SiOil before plummeting.

Figure 5.2 shows the DSD we obtained for the 50 cSt, 1000 cSt, 10 000 cSt and 100 000 cSt SiOil for $N = 13.3 \text{s}^{-1}$ for the continuous phases used. It is evident that the droplet size decreases with $\mu_c$ (or $C_g$). It can further be noticed in Figures 5.2b and 5.2c that increasing $C_g$ reduces the size of the satellite droplets and increases their amount. Interestingly 5.2c suggests that increasing $C_g$ gives birth to a third merged distributions, which droplet size is smaller than the ones obtained with low $\mu_c$. This is reasserted by Figure 5.2d where two distinct peaks with a third distribution in their valley was obtained; as demonstrated in our previous work using rotor-stators (Carrillo De Hert and Rodgers, 2017b,a), the Mastersizer 3000 is capable of separating two DSDs sharply.

According to the mechanistic model reviewed in Part I (Calabrese et al., 1986; Wang and Calabrese, 1986), interfacial cohesive forces become negligible as $\mu_d$ increases. It is worth mentioning that according to the mechanistic models presented in Table 5.1 for $\mu_d \to \infty$ a decrease in drop size is expected as incrementing $C_g$ leads to an increase in $\rho_c$. The smaller drop sizes obtained as $C_g$ increases could not be justified only by the change in $\rho_c$ ($\approx 20\%$ variation, see Tab. 5.2). This will be discussed thoroughly in Section 5.4.3, after the drop size and DSDs have been characterized.

Figure 5.3 shows the $\bar{d}_{32}$ obtained as a function of $\mu_d$ for $N = 13.3 \text{s}^{-1}$ for the
four continuous phases used in a log-log scale. It is evident that $\bar{d}_{32}$ decreases with $C_g$. The dotted line represents the limit in-between the zones where $d_{max}$ increases with $\mu_d$ (left) and where $d_{max}$ is independent of $\mu_d$ (right). This behaviour has been previously discussed in Part I (Carrillo De Hert and Rodgers, 2017c); the decrease in $\bar{d}_{32}$ can be noticed for $\mu_d < 10 \text{ Pa s}$ and is due to the increase in amount of satellite drops. It is interesting to notice that this behaviour is observed for all the continuous phases at the same $\mu_d$ despite the DSDs having a different shape. As done in Part I (Carrillo De Hert and Rodgers, 2017c) we will restrict our analysis to the emulsions to the left of the dashed line.

Figure 5.4 shows the evolution of the $\bar{d}_{32}$ to $d_{max}$ ratio as a function of $\mu_d$ for different $C_g$. The plot shows that for the 50 cSt Silicon Oil, which yielded a
monomodal distribution, $\overline{d}_{32}/d_{\text{max}}$ is independent of $\mu_c$. In Part I (Carrillo De Hert and Rodgers, 2017c), the monomodal distributions (0.65, 10 and 50 cSt SiOils) yielded the same $\overline{d}_{32}/d_{\text{max}}$ and the ratio would decrease as the amount of satellite drops increased. An increase in $\mu_c$ favoured the appearance of satellite drops, therefore the $\overline{d}_{32}/d_{\text{max}}$ is expected to be lower as $\mu_c$ increases. The indexes in Figure 5.4 and $R^2$ were obtained for the $3.28 \times 10^{-1} \text{ v to 7.36 viscosity range}$; thicker oils displayed a chaotic trend and were not fitted.

Analogously to the drop size analysis performed in Part I (Carrillo De Hert and Rodgers, 2017c), the mode of the daughter droplets $M_{OL}$ was used. Figure 5.5 shows the mode of the daughter droplets $M_{OL}$ as a function of $\mu_d$ for $N = 13.3 \text{ s}^{-1}$. Most of the results obtained for the 10 000 cSt SiOil are not shown in this plot as the daughter droplets do not exhibit a clear $M_{OL}$ (see Fig. 5.2c). The comparison in-between these plots show that $\overline{d}_{32}$ is not the best measure of central tendency to elucidate the drop break-up mechanism when the DSD are multimodal.

The first part of our analysis of variance contemplated $\mu_d$, $\rho_d$, $\mu_c$, $\rho_c$, $\sigma$ and $N$ as variables. The results of the analysis of variance with all the aforementioned variable
Chapter 5. Effect of continuous phase viscosity in stirred vessels

Figure 5.4: \( \bar{d}_{32} \) to \( d_{\text{max}} \) ratio as a function of viscosity for the different continuous phases used.

is shown in Appendix 5.A

\[
M_{OL} = A_1 \mu_d^{A_2} \mu_c^{A_3} \rho_d^{A_4} \rho_c^{A_5} \sigma^{A_6} N^{A_7}
\]  

(5.8)

The mean and 95% confidence interval (\( %CI \)) obtained for \( A_7 \) was \(-1.21 \pm 16.4\%\), which is in agreement with the Kolmogorov-Hinze (Hinze, 1955) theory for the turbulent inertia regime. An analysis on the effects of \( \mu_c, \rho_c \) and \( \sigma \) is difficult because the variables are linked (see Tab. 5.2). Provided that \( N \) is in agreement with the mechanistic models and that according to Wang and Calabrese (1986) interfacial cohesive forces are negligible for high \( \mu_c \), different models were proposed by fixing \( M_{OL} \propto N^{-6/5} \) and \( M_{OL} \propto (\text{We} D^{-3})^{-3/5} \). The mean of the fitting coefficients, \( p \)-value and 95\%\( CI \), as well as the coefficient of determination \( R^2 \) and mean absolute error \( MAE \) of the fit can be consulted in Appendix 5.A. The models using \( M_{OL} \propto N^{-6/5} \) instead of \( M_{OL} \propto (\text{We} D^{-3})^{-3/5} \) provided better fits. In the same Table it can be seen that if the kinematic viscosity \( (\nu = \mu/\rho) \) is used, the power dependency on \( \nu_d \) and \( \nu_c \) is statistically similar (based on the 95\%\( CI \)). Therefore the model
which yielded the smallest $MAE$ and has the least fitting parameters was

$$MoL = A_1 \left( \frac{\nu_d}{\nu_c} \right)^{A_2} N^{-6/5}$$

(5.9)

Where the coefficients and their 95%CI are $A_1 = 3.15 \times 10^2 \pm 8.05\%$ and $A_2 = 0.403 \pm 3.98\%$. The coefficient of determination $R^2$ and the $MAE$ of the fit were 0.954 and 12.4% respectively. The goodness of the fit using the mean coefficient value can be assessed in Figure 5.6.
If the results presented in Figure 5.7 are standardized by $\nu_c F^{-2/5} N^{-6/5}$ the $\overline{d}_{32}$ collapses into a Master curve relatively well in the $9.58 \times 10^{-3}$ Pa$s > \mu_d > 4.34$ Pa$s$ interval. The scattered results for the 10 cSt are due to the presence of a small tail in the distribution for the emulsion using the two most viscous continuous phases, presumably due to the tip-steaming mechanism which has been reported for small $\mu_c$ to $\mu_d$ ratios (Bruijn, 1993). It is unclear if the scattered results for the high-viscosity end is due to a different $\overline{d}_{32}$ dependency on $\nu_d/\nu_c$ or to experimental error. The DSD analysis of these emulsions is difficult due to sampling: a single large drop can alter the shape of the whole distribution.

![Figure 5.7:](image) Collapsed $\overline{d}_{32}\nu_c^{2/5} N^{-6/5}$ as a function of $\mu_d$. The shadowed area and the percentages represent one standard deviation from the mean.

The DSD were normalized by $Mo_L$ to show the changes in the shape of the DSD. Figure 5.8 shows the effects of $\mu_c$ on the shape of the DSD for the 1000 cSt and the 4500 cSt SiOils. The proportionality $Mo_L = 1.54 D_{95}$ found in Part I (Carrillo De Hert and Rodgers, 2017c) was also obtained; from these Figures, and the results obtained in Part I (Carrillo De Hert and Rodgers, 2017c) we concluded that the size of the large daughter drops is independent of $\mu_c$, $\mu_d$, $\sigma$ and $N$.

The effect of $\mu_d$ for the four continuous phases used is shown in Figure 5.9. For the distribution where the amount of daughter drops were not enough to obtain the $Mo_L$ directly, these were obtained by extrapolating Equation 5.9. These curves...
5.4. Results and discussion

Figure 5.8: $M_o L$-standardised DSD $f(v(d_i/M_o L))$ with $C_g$ as parameter for (a) 1000 cSt SiOil for $N = 13.3 \, \text{s}^{-1}$ and (b) 4500 cSt SiOil for $N = 10.0 \, \text{s}^{-1}$.

show that all DSD for the 10 cSt and 50 cSt Silicon Oils are monomodal and that bimodality arises somewhere in-between the 50 and 350 cSt SiOil despite $\mu_c$ changing an order of magnitude. In our previous work on the effect of $\mu_d$ on the DSD in rotor-stators (Carrillo De Hert and Rodgers, 2017b), we also found that bimodality occurred in the same $\mu_d$ range.

The degree of polydispersity increases as the normalized minimum droplet diameter also decreases with $\mu_d$. The shape of the DSD for the 7600 cSt and 10 000 cSt Silicon Oils in Figures 5.9b-5.9d suggest that at least three distribution are merged together. To our knowledge, the only study reporting trimodal DSDs has been the one of Nishikawa et al. (1991). A possible explanation is that some of the daughter drops produced from the stretching breakup mechanism suffer further breakup in the viscous turbulent regime.

Figure 5.10 shows an estimate of the volume fraction of the daughter droplets $\phi_L$, the points were obtained by fitting a log-normal distribution to the right end of the DSDs in Figure 5.9. Fitting of the whole DSDs was impractical due to the appearance of a third merged distribution. Nevertheless a clear trend can be observed in Figure 5.10, which is in agreement with the DSDs presented in Figure 5.8a: increasing $\mu_c$ favours the stretching breakup mechanism resulting in DSDs with a larger amount of satellite drops. The dashed lines in this Figure were obtained by $\phi_m = \exp \left[ - \left( \mu_d/\beta \right)^\alpha \right]$ which corresponds to subtracting a Weibull distribution to
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Figure 5.9: $M_{OL}$-standardized DSDs obtained for $N = 10 \text{s}^{-1}$ for all dispersed SiOils in (a) Water/SLES and in (b) $1.5 \text{ mol L}^{-1}$ (c) $2.5 \text{ mol L}^{-1}$ and (d) $2.9 \text{ mol L}^{-1}$ glucose aqueous solutions.

100%. A parametrization of $\alpha$ and $\beta$ was not possible.

5.4.3 Turbulence and emulsification sub-regime

The mechanistic models presented in Table 5.1 predict different dependencies on the variables depending on the size-scale of $d_{\text{max}}$ in relation with $D$ and $\ell_{\eta}$. Surprisingly we found that $\mu_c$ had a large effect on the drop size and on the DSD, despite all our experiments being at constant $Po$; furthermore, the $d_{\text{max}}$ obtained varied across two orders of magnitude (see Fig. 5.5 and $d_{\text{max}} = 1.54M_{OL}$) making it unlikely that emulsification occurs in the same emulsification regime in all our systems studied. In this section a theoretical analysis on the relevant scales under the assumption of
isotropic turbulence was performed to offer an explanation on the effect of $\mu_c$ despite $d_{\text{max}}$ being larger than $\ell_\eta$.

The theory postulated by Hinze (1955), and which was used as the starting point of the mechanistic models presented in Table 5.1 is based on the assumption that the turbulent kinetic energy $k$ is the disrupting force causing drop breakup; furthermore he assumed isotropic turbulence and that Kolmogorov -5/3 energy Kolmogorov (1941) spectrum for drops larger than the Kolmogorov scale $\ell_\eta$. The Kolmogorov -5/3 spectrum is given by

$$E(\kappa) = C_\varepsilon \kappa^{-5/3}$$

(5.10)

Where $E(\kappa)$ is the energy spectrum function and $\kappa$ is the eddy wavenumber $\kappa = 2\pi/\ell$, where $\ell$ is the size of the eddie. The turbulent kinetic energy $k$ in a given range $\kappa_1$ to $\kappa_2$ can be obtained by

$$k = \int_{\kappa_1}^{\kappa_2} E(\kappa) d\kappa$$

(5.11)

Kolmogorov’s model suggests that in the turbulent inertia regime large eddies transfer their energy to smaller eddies (kinetic energy cascade) until the Kolmogorov length-scale $\ell_\eta$ is reached and viscous dissipation takes over. However, Kolmogorov’s hypothesis is only valid for infinite $\text{Re}$ and industrial processes occur at finite $\text{Re}$. The
turbulent inertia sub-range for finite $Re$ is narrower and in some cases non-existent (Solsvik and Jakobsen, 2016). Solsvik and Jakobsen (2016) recently reviewed other models of energy spectra for isotropic turbulence, using the one proposed by Pope (2000) as benchmark. Pope’s energy spectrum describes the energy-containing range, the inertial sub-range and the dissipation range. The spectrum is given by

$$E(k) = C \varepsilon^{2/3} k^{-5/3} f_L(kL) f_\eta (\ell_\eta k)$$

(5.12)

Where $f_L(kL)$ and $f_\eta (\ell_\eta k)$ are specified dimensionless functions, which can be consulted in the original text (Pope, 2000). The term $L$ refers to the integral length scale, which is a measure of length-scale characterising the largest isotropic eddies. The Reynolds number linked to this scale of turbulence is the integral Reynolds number or the turbulence Reynolds number, $Re_L$.

$$Re_L = \frac{u'L}{\nu_c}$$

(5.13)

Where $u'$ is the fluctuating velocity centred around the stationary mean. The relationship in-between $L$ and $\ell_\eta$ is given by (Pope, 2000)

$$\frac{\ell_\eta}{L} = Re_L^{-3/4}$$

(5.14)

The energy spectrum model can normalized so that it is uniquely a function of $Re_L$ (Solsvik and Jakobsen, 2016). This normalization uses the dimensionless wave-number $\kappa' = \kappa L$.

To obtain the normalized model energy spectrum $L$ and $\ell_\eta$ need to be determined. For a pitched-blade turbine, $L$ is considered to be the size of the trailing vortices (Kresta, 1998) $L = D/10$, however values ranging from $D/12.5$ to $D/6$ have been adopted (Gabriele et al., 2009).

The determine $\ell_\eta$, $\varepsilon_{max}$ needs to be known. Gabriele et al. (2009) summarized some of the $\varepsilon_{max}/\overline{\varepsilon}$ obtained for pitched-blade turbines by several authors (Table 1 and Table 3 in Ref. Gabriele et al. (2009)). The values ranged from 3.27 to 78 for
downward pumping 45°-pitched blade turbines depending on the number of blades, the geometrical ratios of the vessel and the methodology used to determine $\varepsilon_{\text{max}}$. The authors suggest that the Smagorinsky closure method provides more realistic results than the direct and dimensional analysis methods (see discussion in Ref. Gabriele et al. (2009)). Using this method Khan (2005) determined that $\varepsilon_{\text{max}}/\bar{\varepsilon} = 78$ for a 6-PBT-D with geometric ratios $C = T/3$ and $D = T/3$; which are very similar to the ones in this study.

Despite the discrepancy on the reported $\varepsilon_{\text{max}}/\bar{\varepsilon}$, using the value reported by Khan (2005) will provide the most “optimistic” scenario (widest turbulent inertia regime). Table 5.1 shows the calculated $\bar{\varepsilon}$ and $\varepsilon_{\text{max}}$, the former was obtained from our $P_S$ measurements

$$\bar{\varepsilon} = \frac{P_S}{\rho_c V_T}$$

and the latter using the $\varepsilon_{\text{max}}/\bar{\varepsilon}$ reported by Khan (2005).

**Table 5.1:** Mean energy dissipation rate $\bar{\varepsilon}$ and maximum local energy dissipation rate $\varepsilon_{\text{max}}$ for different $N$.

<table>
<thead>
<tr>
<th>$N$ [s$^{-1}$]</th>
<th>$\bar{\varepsilon}$ [m$^2$ s$^{-3}$]</th>
<th>$\varepsilon_{\text{max}}$ [m$^2$ s$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.33</td>
<td>0.100</td>
<td>7.82</td>
</tr>
<tr>
<td>10.0</td>
<td>0.173</td>
<td>13.5</td>
</tr>
<tr>
<td>11.7</td>
<td>0.278</td>
<td>21.7</td>
</tr>
<tr>
<td>13.3</td>
<td>0.408</td>
<td>31.8</td>
</tr>
<tr>
<td>15.0</td>
<td>0.585</td>
<td>45.7</td>
</tr>
</tbody>
</table>

The localized Kolmogorov-scale in the area of $\varepsilon_{\text{max}}$ is obtained using (Kolmogorov, 1941)

$$\ell_\eta = \left(\frac{\mu_c}{\rho_c}\right)^{3/4} \varepsilon_{\text{max}}^{-1/4}$$

and $\text{Re}_L$ using Equation 5.14 and $L = D/10$.

Figure 5.11 shows the resulting Pope’s normalized energy spectra for the four studied $C_g$ for $N = 13.3$ s$^{-1}$. The dashed vertical line at $2\pi$ (left) shows the location of $L$. The solid-decaying straight line shows the Kolmogorov -5/3 spectrum (Eq. 5.10). In Figure 5.11a the dashed vertical lines indicate the location of estimated $\ell_\eta$ for the studied continuous phases and dotted lines represent the spectrum proposed by Shinnar and Church (1960) for $\kappa > \ell_\eta$ (from Eq. 5.4). The dashed lines in Figure
5.11b show the \( \kappa L \) at which a 20% (to represent a good approximation) deviation from the Kolmogorov \(-5/3\) spectra was found. It can be noted that the width of turbulent inertia sub-range shortens with \( \mu_c \). The list of calculated \( \ell_\eta \), \( \text{Re}_L \) and turbulent inertia sub-range size-range is shown in Table 5.1 for all different \( N \) and \( C_g \) studied.

![Figure 5.11: Pope's normalized Energy Spectrum for the systems studied for \( N = 13.3 \text{s}^{-1} \).](image)

(a) the vertical dashed line at the right show \( L \) (at \( 2\pi \)), the ones at the right demarcate \( \ell_\eta(\mu_c) \) and the dotted lines shows the sub-Kolmogorov spectrum theorized by Shinnar and Church (1960). (b) show the turbulent inertia range if a 20% tolerance in-between the energy spectra of Kolmogorov (1941) and Pope (2000) is considered.

**Table 5.2:** Kolmogorov scale \( \ell_\eta \) and integral turbulent Reynolds number \( \text{Re}_L \), and turbulent inertia (TI) range for the experimental \( C_g \) and \( N \).

<table>
<thead>
<tr>
<th>( C_g ) [mol L(^{-1})]</th>
<th>( N ) [s(^{-1})]</th>
<th>( \ell_\eta ) [( \mu \text{m} )]</th>
<th>( \text{Re}_L/10^2 ) [-]</th>
<th>TI range [( \mu \text{m} )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.33</td>
<td>20.0</td>
<td>15.1</td>
<td>361-4830</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>17.4</td>
<td>18.1</td>
<td>321-4830</td>
</tr>
<tr>
<td></td>
<td>11.7</td>
<td>15.5</td>
<td>21.1</td>
<td>287-4830</td>
</tr>
<tr>
<td></td>
<td>13.3</td>
<td>14.0</td>
<td>24.1</td>
<td>255-4830</td>
</tr>
<tr>
<td></td>
<td>15.0</td>
<td>12.9</td>
<td>27.1</td>
<td>241-4830</td>
</tr>
<tr>
<td>1.50</td>
<td>10.0</td>
<td>32.8</td>
<td>7.76</td>
<td>509-4830</td>
</tr>
<tr>
<td></td>
<td>13.3</td>
<td>26.5</td>
<td>10.3</td>
<td>454-4830</td>
</tr>
<tr>
<td>2.50</td>
<td>10.0</td>
<td>55.9</td>
<td>3.82</td>
<td>906-4830</td>
</tr>
<tr>
<td></td>
<td>13.3</td>
<td>45.1</td>
<td>5.09</td>
<td>762-4830</td>
</tr>
<tr>
<td>2.90</td>
<td>10.0</td>
<td>82.0</td>
<td>2.29</td>
<td>1436-4830</td>
</tr>
<tr>
<td></td>
<td>13.3</td>
<td>66.1</td>
<td>3.05</td>
<td>1208-4830</td>
</tr>
</tbody>
</table>

In Figure 5.12, the experimental \( D_{95} \) (\( D_{95} = 1.54 Mo_L \)) for \( N = 13.3 \text{s}^{-1} \) was plotted as a function of \( \mu_d \). The limits of the turbulent sub-regimes shown in Figure
5.11 are shown as dashed lines for the TI regime and $\ell_\eta$ is denoted with dotted lines. This Figure shows that most of our resulting $D_{95}$ are not in the turbulent inertia regime; as a reminder the $\varepsilon_{max}/\overline{\varepsilon}$ used was the largest reported and lower dissipation ratios would reduce the width of the TI regime even further. Furthermore, only one of our emulsions fell in the sub-Kolmogorov length scale, however if a lower $\varepsilon_{max}/\overline{\varepsilon}$ had been chosen, more of our emulsions would fall in this regime. It is interesting to notice that our results correlated with $d_{max} \propto N^{-6/5}$, in agreement with the Kolmogorov-Hinze theory for the TI regime despite most of our data not falling in the size range where the Kolmogorov -5/3 spectrum is valid (even under the most optimistic considerations).

Most of our experimental data are above $\ell_\eta$ but below the region where the Kolmogorov -5/3 energy distribution law is valid; therefore a combination of viscous and inertia stresses would be expected, which might explain why $\mu_c$ had an effect on the DSD. As shown in Figure 5.2 some of our SiOils yielded broad DSDs with drop sizes extending over three orders of magnitude; therefore in some of our emulsions some of the drops might be in the turbulent inertia regime and some others in the dissipation range above and below $\ell_\eta$.

5.5 Conclusions

In Part I we focused on the effect of $\mu_d$ and $N$ on the DSD; for most of our emulsion the interfacial cohesive forces could be neglected as explained by Wang and Calabrese (1986). The $\mu_d$ dependency $d_{max} \propto \mu_d^{0.365}$ was in disagreement with the mechanistic models found in literature; however it was on agreement with the one found in our previous work using in-line rotor-stators (Carrillo De Hert and Rodgers, 2017b) despite the obvious geometrical differences. Furthermore, we proposed using two log-normal distribution to describe the bimodal DSD.

In Part II we expanded our previous study by emulsifying the SiOils used in Part I in other continuous phases. The power curve (Fig. 5.1) obtained showed that all our systems had the same $Po = 1.33$. The mechanistic models presented in Table
Figure 5.12: 95th percentile $D_{95}$ as a function of $\mu_d$ for $N = 13.3 \, \text{s}^{-1}$ with $C_g$ as parameter. The different length scales are shown as vertical lines: The highest one shows the integral length scale $L = D/10$, the dashed lines show the lower boundary of the turbulent inertia regime (TI) and the dotted lines shows the location of $\ell_\eta$ for the different $C_g$.

5.1 are based on the work of Hinze (1955) who hypothesised that the disruptive energy causing drop breakup is the turbulent kinetic energy $k$, and therefore the continuous phase viscosity should not play a role for drops larger than the Kolmogorov length-scale. However, Pope’s energy spectrum revealed that most of the drop sizes were in the size range in which the Kolmogorov $-5/3$ spectrum is no longer valid and therefore shear stresses are expected; despite the drops being larger than the Kolmogorov length scale.

The turbulent inertia regime range was further assessed using a normalized version of the energy spectrum proposed by Pope (2000) using the $\varepsilon_{\text{max}}/\bar{\varepsilon}$ reported by Khan (2005). It was found that the commonly accepted assumption that emulsification occurs in the turbulent inertia regime in a turbulent stirred vessel is false.

Lastly we tested Hinze’s hypothesis of the turbulent kinetic energy being responsible of drop breakup for $d_{\text{max}} > \ell_\eta$ by comparing our empirically obtained $\mu_c$-dependency to the one we would have obtained if two systems had the same energy spectrum. It was found that according to his theory increasing $\mu_c$ for systems at a constant $N$ would yield larger drop sizes; which was clearly not the case.
5.6 Bibliography


**Appendix**

**Appendix 5.A  ANOVA results**
Table 5.A.1: ANOVA results for $Mo_d = A_1 \mu_d A_2 \rho_d A_3 \rho_c A_4 \sigma N A_5$ for emulsions using SiOil in the 10 cSt - 5370 cSt range for all four different continuous phases and all $N$ using all variables independently. The $R^2$ and $MAE$ obtained were 0.972 and 0.92% respectively.

<table>
<thead>
<tr>
<th>$A_i$</th>
<th>Mean</th>
<th>$p$-value</th>
<th>95%CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$1.49 \times 10^{-30}$</td>
<td>$8 \times 10^{-2}$</td>
<td>100%</td>
</tr>
<tr>
<td>$A_2$</td>
<td>0.422</td>
<td>$7 \times 10^{-34}$</td>
<td>7.26%</td>
</tr>
<tr>
<td>$A_3$</td>
<td>-2.09</td>
<td>$1 \times 10^{-2}$</td>
<td>76.6%</td>
</tr>
<tr>
<td>$A_4$</td>
<td>-2.64</td>
<td>$3 \times 10^{-1}$</td>
<td>190%</td>
</tr>
<tr>
<td>$A_5$</td>
<td>8.64</td>
<td>$4 \times 10^{-3}$</td>
<td>67.8%</td>
</tr>
<tr>
<td>$A_6$</td>
<td>-4.56</td>
<td>$9 \times 10^{-2}$</td>
<td>116%</td>
</tr>
<tr>
<td>$A_7$</td>
<td>-1.21</td>
<td>$1 \times 10^{-17}$</td>
<td>16.4%</td>
</tr>
</tbody>
</table>
### Table 5.A.2: ANOVA Results for the $\nu$ of Emulsions Using SHOW in the 10 CSt - 5370 CSt Range for All Four Different Continuous Phases

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>Mean $\pm$ Value</th>
<th>95% CI</th>
<th>Mean $\pm$ Value</th>
<th>95% CI</th>
<th>Mean $\pm$ Value</th>
<th>95% CI</th>
<th>Mean $\pm$ Value</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.24</td>
<td>1.40%</td>
<td>1.10 - 2.31</td>
<td>1.40%</td>
<td>1.10 - 2.31</td>
<td>1.40%</td>
<td>1.10 - 2.31</td>
<td>1.40%</td>
<td>1.10 - 2.31</td>
</tr>
<tr>
<td>0.80</td>
<td>4.32%</td>
<td>3.55 - 5.09</td>
<td>4.32%</td>
<td>3.55 - 5.09</td>
<td>4.32%</td>
<td>3.55 - 5.09</td>
<td>4.32%</td>
<td>3.55 - 5.09</td>
</tr>
<tr>
<td>1.00</td>
<td>5.00%</td>
<td>4.21 - 5.79</td>
<td>5.00%</td>
<td>4.21 - 5.79</td>
<td>5.00%</td>
<td>4.21 - 5.79</td>
<td>5.00%</td>
<td>4.21 - 5.79</td>
</tr>
<tr>
<td>2.00</td>
<td>6.00%</td>
<td>5.21 - 6.79</td>
<td>6.00%</td>
<td>5.21 - 6.79</td>
<td>6.00%</td>
<td>5.21 - 6.79</td>
<td>6.00%</td>
<td>5.21 - 6.79</td>
</tr>
<tr>
<td>2.40</td>
<td>6.60%</td>
<td>5.81 - 7.39</td>
<td>6.60%</td>
<td>5.81 - 7.39</td>
<td>6.60%</td>
<td>5.81 - 7.39</td>
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<tr>
<td>2.50</td>
<td>6.80%</td>
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<td>6.80%</td>
<td>5.91 - 7.59</td>
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<td>6.11 - 7.79</td>
</tr>
<tr>
<td>2.80</td>
<td>7.20%</td>
<td>6.31 - 8.09</td>
<td>7.20%</td>
<td>6.31 - 8.09</td>
<td>7.20%</td>
<td>6.31 - 8.09</td>
<td>7.20%</td>
<td>6.31 - 8.09</td>
</tr>
<tr>
<td>3.00</td>
<td>7.40%</td>
<td>6.41 - 8.29</td>
<td>7.40%</td>
<td>6.41 - 8.29</td>
<td>7.40%</td>
<td>6.41 - 8.29</td>
<td>7.40%</td>
<td>6.41 - 8.29</td>
</tr>
<tr>
<td>3.10</td>
<td>7.60%</td>
<td>6.51 - 8.49</td>
<td>7.60%</td>
<td>6.51 - 8.49</td>
<td>7.60%</td>
<td>6.51 - 8.49</td>
<td>7.60%</td>
<td>6.51 - 8.49</td>
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<tr>
<td>3.20</td>
<td>7.80%</td>
<td>6.61 - 8.69</td>
<td>7.80%</td>
<td>6.61 - 8.69</td>
<td>7.80%</td>
<td>6.61 - 8.69</td>
<td>7.80%</td>
<td>6.61 - 8.69</td>
</tr>
<tr>
<td>3.30</td>
<td>8.00%</td>
<td>6.71 - 8.89</td>
<td>8.00%</td>
<td>6.71 - 8.89</td>
<td>8.00%</td>
<td>6.71 - 8.89</td>
<td>8.00%</td>
<td>6.71 - 8.89</td>
</tr>
</tbody>
</table>

**Note:** MAE: Mean Absolute Error; CI: Confidence Interval; ANOVA: Analysis of Variance; $\nu$: Viscosity; SHOW: Special Oil-Well-Emulsion.
Chapter 6

On the steady-state drop size distribution in stirred vessels. Part III: effect of dispersed phase volume fraction


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</table>
6.1 Introduction

In Parts I (Carrillo De Hert and Rodgers, 2017a) and II (Carrillo De Hert and Rodgers, 2017b) we studied the effect of the dispersed and continuous phase viscosity on the drop size distribution (DSD) of dilute emulsions (1%). In Part III we expanded the former studies by increasing the dispersed phase hold-up up to 80% using six silicon oils (SiOil) in the $0.488 \text{ mPa s}$ to $1.05 \times 10^4 \text{ mPa s}$ viscosity range.

The emulsions with hold-ups lower than 60% were carried out at constant power numbers. In this hold-up range we found no statistically significant drop size variations for the SiOils producing monomodal DSDs. On the other hand, SiOils yielding bimodal DSDs experienced a drop size and polydispersity decrease as $\phi$ was increased. For $\phi \geq 70\%$ all the SiOils experienced a decrease in drop size, and for $\phi \sim 0.8$ even the thickest SiOil tested yielded a monomodal DSD.

An empirical model to determine the combined effect of hold-up and viscosity was proposed. Furthermore the multiple log-normal fit presented in Part I (Carrillo De Hert and Rodgers, 2017a) was extended to account for higher hold-ups.

6.1 Introduction

In Part I (Carrillo De Hert and Rodgers, 2017a) and Part II (Carrillo De Hert and Rodgers, 2017b) we studied the effect of the dispersed phase viscosity $\mu_d$ and its combined effect with the continuous phase viscosity $\mu_c$ on the droplet size distribution (DSD) of surfactant-laden dilute emulsions (1 v.%). The study of dilute emulsions is convenient as it allows us to isolate drop breakup from other phenomena such as coalescence and the complex rheological features that arise as the hold-up or dispersed phase volume fraction $\phi$ increases; however such dilute emulsions might not be of practical relevance in industrial processes. In Part III we extended our previous studies (Carrillo De Hert and Rodgers, 2017a,b) by increasing $\phi$ up to 80% using six Silicon Oils (SiOil) with viscosities in the $0.488 \text{ mPa s} < \mu_d < 1.05 \times 10^4 \text{ mPa s}$ range.

The effect of $\phi$ on the droplet size distribution (DSD) is not well-understood: some experimental studies have shown an increase in drop size (Coulaloglou and
Tavlarides, 1976, 1977; Lagisetty et al., 1986; Pacek et al., 1998; Desnoyer et al., 2003; Angle and Hamza, 2006; Maaß et al., 2012; Gäbler et al., 2006; El-Hamouz, 2009; Rueger and Calabrese, 2013; Becker et al., 2014; Qi et al., 2015), while others either no effect (Hall et al., 2011; Boxall et al., 2012), a decrease followed by an increase (Cho and Kamal, 2002), a plateau followed by a decrease (Vankova et al., 2007; Tcholakova et al., 2011), an increase followed by a decrease (Kumar et al., 1991) or a steady decrease (Gutierrez et al., 2002; Welch et al., 2006). Many studies found in the literature have reported a decrease in polydispersity as $\phi$ increases (Pacek et al., 1998; Angle and Hamza, 2006; Vankova et al., 2007; Tcholakova et al., 2011; El-Hamouz, 2009; Hall et al., 2011).

The increase in drop size is attributed to drop coalescence (Coulaloglou and Tavlarides, 1976; Delichatsios and Probstein, 1976; Pacek et al., 1998), turbulence dampening (Brown and Pitt, 1972; Lagisetty et al., 1986; Cohen, 1991; Maaß et al., 2012), overall viscosity increase (Doulah, 1975) or a combination of coalescence and damping (Coulaloglou and Tavlarides, 1977; Desnoyer et al., 2003; Gäbler et al., 2006; Angle and Hamza, 2006); an empirically modified version of the model developed by Hinze (1955) is commonly used to for the results obtained by either coalescence or dampening.

$$\frac{d_{32}}{D} = C_1 (1 + C_2 \phi) \text{We}_S^{3/5}$$  \hspace{1cm} (6.1)

where $d_{32}$ is the Sauter mean diameter, $D$ is the diameter of the stirrer, and $\text{We}_S$ is the dimensionless Weber number of the stirrer ($\text{We}_S = \rho N^2 D^3 \sigma^{-1}$). Typically $2.5 < C_2 < 10$ (Coulaloglou and Tavlarides, 1977; Doulah, 1975; Pacek et al., 1998; Razzaghi and Shahraki, 2010) depending on the degree of dampening and the tendency of the system to coalesce; however values as large as 23.3 have been reported (Pacek et al., 1998). Furthermore, some authors (Pacek et al., 1998; Desnoyer et al., 2003; Gäbler et al., 2006; El-Hamouz, 2009) have found that the exponent in Equation 6.1 increases with $\phi$ ($d_{32} \propto (1 + C_2 \phi)\text{We}_S^{C_3}$).

Coalescence occurs when two drops approach forming a thin film of the continuous phase in-between them, the film drains and finally breaks at a critical thickness (Coulaloglou and Tavlarides, 1977); film drainage is usually the limiting
step and can be regarded as coalescence time. Therefore, the collision time needs to be larger than the film drainage time necessary to reach a critical thickness, as turbulent eddy intrusion may stop the drainage process (Coulaloglou and Tavlarides, 1977). According to Coulaloglou and Tavlarides (1977), the coalescence rate is the product of the collision rate and the coalescence efficiency. Coalescence frequency increases with $\phi$, drop size and the agitation rate while the coalescence efficiency increases with lower continuous and dispersed phase viscosity, larger drop sizes and lower energy input (Tsouris and Tavlarides, 1994).

Turbulence dampening refers to the death of low-energy small eddies and the survival of the high-energy large eddies larger than the droplet diameters. Several authors have used surfactants (Kumar et al., 1991; Cho and Kamal, 2002; Vankova et al., 2007; El-Hamouz, 2009; Tcholakova et al., 2011; Hall et al., 2011; Maaß et al., 2012; Becker et al., 2014) or electrostatic repulsion (Desnoyer et al., 2003; Gäbler et al., 2006) to hinder coalescence. For non-coalescing systems, Doulah (1975) determined that $C_2 = 3$ by attributing the drop size increase to the thickening of the bulk viscosity of the emulsion $\eta_e$, they further used the $\eta_e - \phi$ relation obtained by Einstein (1906). Nevertheless the equation by Einstein (1906) is only applicable in the dilute limit, and was originally developed for rigid spheres (Derkach, 2009). Coulaloglou and Tavlarides (1977) estimated the degree of turbulence dampening by using

$$\frac{\overline{u'^2}}{u'^2_0} = (1 + C_4 \phi)^{-2}$$  \hspace{1cm} (6.2)

where $\overline{u'^2}$ and $u'^2_0$ are the mean square velocity fluctuations with and without dampening respectively. Lagisetty et al. (1986) developed a model using Equation 6.2 which could explain the drop size increase for $0.025 < \phi < 0.15$. The results obtained by Kumar et al. (1991) for surfactant-laden emulsions for $0.5 < \phi$ could be described by the model developed by Lagisetty et al. (1986), however they found a drop size decrease for $0.5 < \phi < 0.8$ which is in disagreement with the turbulence damping model. Delichatsios and Probstein (1976) argued that the turbulence dampening is given by $(1 + \phi + 0.2\phi)^{6/5}$, implying that for $\phi = 0.25$ the resulting $C_2$ would be 0.96 and that larger value for $C_2$ would be due to coalescence. Cohen (1991) noticed an
increase in the minimum drop diameter and as these drops are uniquely produced by breakup, they concluded that dampening was responsible for the drop size increase and coalescence was negligible; for their system they found $C_2 = 3.3$.

Rueger and Calabrese (2013) emulsified water in a viscous oil in the turbulent and laminar regimes with and without surfactant. They found that $\bar{d}_{32}$ increased with $\phi$ in both flow regimes and with or without surfactant. However found that $\bar{d}_{32}$ was independent of $\phi$ for $0.1 < \phi < 0.45$. The plateau for $\phi > 0.1$ was attributed to a decrease in collision frequency and collision efficiency; and increase in breakage rate as drop size increased.

Most of the studies reporting a decrease in drop size used dispersed phases with higher viscosity than the ones reporting drop size increase. Figure 6.1 shows a vast amount of experimental $\phi$ and $\mu_d$ investigated by several authors. This plot shows some consensus on the effect of $\mu_d$ on the general behaviour of concentrated emulsions.

![Figure 6.1](image-url)

**Figure 6.1:** Experimental studies on the effect of $\phi$ on the DSD in turbulent systems (Coulaloglou and Tavlarides, 1976; Pacek et al., 1998; Desnoyer et al., 2003; Gäbler et al., 2006; Angle and Hamza, 2006; El-Hamouz, 2009; Maaß et al., 2012; Becker et al., 2014; Qi et al., 2015; Brown and Pitt, 1972; Gutierrez et al., 2002; Welch et al., 2006; Vankova et al., 2007; Tcholakova et al., 2011; Hall et al., 2011). Closed symbols represent the studies where the authors concluded drop size increase with $\phi$, the opposite is true for open the symbols. With the exception of (Desnoyer et al., 2003), all the studies above used water as continuous phase.

Some of the authors reporting drop size increase have used surfactants (El-
Hamouz, 2009; Maaß et al., 2012; Rueger and Calabrese, 2013; Becker et al., 2014) to hinder coalescence, however Rueger and Calabrese (2013) argued that even though surfactants reduce interfacial tension, they may not provide a strong physical barrier to hinder coalescence, nevertheless they remarked the coalescence probability decrease as $\mu_d$ increased. The two studies for $\mu_d > 10 \text{ mPa s}$ that reported a drop size increase in Figure 6.1 are the ones of El-Hamouz (2009) and Becker et al. (2014). Neither of these studies presented the steady-state drop size distribution. El-Hamouz (2009) presented the DSD evolution with time, and he did not reach steady-state after 1000 min; his experimental data seemed to converge as time progresses. Furthermore the values of $C_2$ (Eq. 6.1) were 0.6 ($R^2 = 0.751$) for the 48 mPa s oil, 0.74 ($R^2 = 0.863$) for the 340 mPa s oil and 0.3 ($R^2 = 0.969$) for the 1000 mPa s oil; which are very weak dependencies and these might be due to experimental error or to not reaching steady-state.

Studies using $\mu_d \geq 1.62 \text{ mPa s}$ for $\phi < 0.5$ (Brown and Pitt, 1972; Vankova et al., 2007; Tcholakova et al., 2011; Hall et al., 2011) reported no effect on the drop size and for $\phi > 0.5$ (Gutierrez et al., 2002; Welch et al., 2006; Vankova et al., 2007; Tcholakova et al., 2011) a decrease in drop size. Boxall et al. (2010) and Boxall et al. (2012) reported no drop size difference in the 0.10 $> \phi > 0.20$ and 0.10 $> \phi > 0.35$ ranges respectively despite using water as dispersed phase, however their continuous phases were highly viscous, which also has a large effect on the film draining time (Tsouris and Tavlarides, 1994) and therefore hinders coalescence.

The most extensive studies on the effect of $\phi$ on drop size for viscous dispersed phases are the ones of Vankova et al. (2007), whose study was latter extended by Tcholakova et al. (2011) (same research group). The first used a narrow gap homogenizer and the later two different rotor-stators; both types of devices yielded similar trends. Tcholakova et al. (2011) emulsified six different oils in the 3 mPa s to 10,000 mPa s $\mu_d$ range using high surfactant concentration (10%). Their results showed no dependency of the 95th percentile $D_{95}$ (used as maximum drop diameter) on $\phi$ for $\phi < 0.4$ (approximately); for $\phi > 0.4$ they obtained a decrease in drop size which became more pronounced for the most viscous oils. For $\phi > 0.8$ they
noticed a weak dependency on stirring speed $N$ and that the $D_{95}$ for the different oils seemed to converge regardless of $\mu_d$. They attributed the drop size decrease to a change of regime from turbulent to laminar. Using the bulk viscosity of the different emulsions $\eta_e$ they estimated the Kolmogorov length scale $\ell_\eta$ and the $\phi$ at which the transition from turbulent to laminar regime occurred. They data obtained in the laminar regime was unsuccessfully collapsed into a Grace (1982)-type of curve, however their data in the $0.4 \leq \phi \leq 0.85$ range could be described by

$$D_{95} = C_5 \dot{\gamma}^{-0.5} \left( \frac{\mu_d}{\eta_e} \right)^{1/6}$$

(6.3)

where $\dot{\gamma}$ is the shear rate and $\mu_e$ was calculated using the rheological cell model proposed by Yaron and Gal-Or (1972).

### 6.2 Materials and equipment and methods

#### 6.2.1 Materials

Six of the 200 Fluid Silicone Oils (SiOil, dimethyl siloxane, Dow Corning, Michigan, U.S.A.) used in Part I(Carrillo De Hert and Rodgers, 2017a) were used as dispersed phase, their viscosity $\mu_d$ and density $\rho_d$ are shown in Table 6.1.

<table>
<thead>
<tr>
<th>SiOil [cSt]</th>
<th>$\rho_d$ [kg m$^{-3}$]</th>
<th>$\mu_d$ [Pas]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>750</td>
<td>$4.88 \times 10^{-4}$</td>
</tr>
<tr>
<td>10</td>
<td>934</td>
<td>$9.58 \times 10^{-3}$</td>
</tr>
<tr>
<td>50</td>
<td>960</td>
<td>$4.91 \times 10^{-2}$</td>
</tr>
<tr>
<td>350</td>
<td>970</td>
<td>$3.28 \times 10^{-1}$</td>
</tr>
<tr>
<td>1000</td>
<td>970</td>
<td>$9.47 \times 10^{-1}$</td>
</tr>
<tr>
<td>10 000</td>
<td>970</td>
<td>$1.05 \times 10^{1}$</td>
</tr>
</tbody>
</table>

The same surfactant used for Parts I(Carrillo De Hert and Rodgers, 2017a) and II(Carrillo De Hert and Rodgers, 2017b) was used: Texapon N701 (Cognis, Hertfordshire, UK), which has $\sim 70\%$ by weight of sodium laureth sulfate (SLES)
and approximately 30% water and impurities. El-Hamouz (2007) determined that its critical micelle concentration (CMC) is $8.4 \times 10^{-2}$ g L$^{-1}$.

To determine the Metzner-Otto (Metzner and Otto, 1957) constant $K_s$, a highly viscous shear-thinning solution was prepared by mixing 40 g of Carboxymethyl cellulose sodium salt (cmc, Glentham Life Sciences, Corsham, UK) in 2 L of water. Its rheogram can be consulted in the Supplementary material attached to this document.

### 6.2.2 Equipment and methods

#### 6.2.2.1 Emulsion preparation

The vessel and stirrer used for this study has been previously described in Parts I (Carrillo De Hert and Rodgers, 2017a) and II (Carrillo De Hert and Rodgers, 2017b). The matrix of the experiments performed for each SiOil are shown in Table 6.2.

<table>
<thead>
<tr>
<th>SiOil</th>
<th>$\phi$</th>
<th>0.01</th>
<th>0.1</th>
<th>0.25</th>
<th>0.375</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>50</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td></td>
<td></td>
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<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>1000</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>X</td>
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<td>X</td>
</tr>
<tr>
<td>10000</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

The experiments for the 10000 cSt SiOil were done at one stirring speed $N = 13.3$ s$^{-1}$ while the experiments with the rest of the SiOils were done at two stirring speeds: $N = 10.0$ s$^{-1}$ and $N = 13.3$ s$^{-1}$. The mass of Texapon N701 added to each system was 27.85 g, equivalent to 120 times its CMC in water and to 1% by weight of SLES for the $\phi = 0.01$ systems. El-Hamouz (2007) showed that due to the impurities in Texapon N701, its behaviour cannot be described by a Gibbs adsorption isotherm, therefore no attempt to calculate its depletion was done. However another emulsion with the 1% by weight in relative to water was done for the 50 cSt SiOil for $\phi = 0.6$ to determine if surfactant depletion had an effect. The results can be consulted in the Supplementary Material annexed to this paper, where it can be observed that
the relative amount of SLES in water has a very small impact on the DSD.

The emulsions were prepared by pre-dissolving Texapon N701 in water, setting the impeller’s speed to $N = 7.5 \text{ s}^{-1}$, pouring the SiOIl and accelerating to $N = 10.0 \text{ s}^{-1}$. The systems were stirred for 24 h, their DSD analysed and the systems were further accelerated to $N = 13.3 \text{ s}^{-1}$ for another 24 h.

The emulsions prepared with the largest dispersed phase hold-up ($\phi = 0.8$) were not well-mixed as a layer of SiOil ($\sim 3 \text{ mm}$) could be observed at the top of the tank. The results presented for $\phi = 0.8$ will just be qualitative, as the real emulsified $\phi$ is unknown, however we estimate that the real $\phi$ should be approximately $0.790 \pm 0.005$.

Additionally, the steady-state shear rheometry and power draw of the systems were analysed for many of the emulsions prepared at $N = 13.3 \text{ s}^{-1}$.

### 6.2.2.2 Drop size distribution analysis

The drop size distributions were analysed using the Mastersizer 3000 (Malvern Instruments, Malvern, UK) using the standard operation procedure previously described in Part I (Carrillo De Hert and Rodgers, 2017a).

### 6.2.2.3 Rheometry

The steady state shear viscosity of the emulsions with $\phi \geq 0.25$ were measured using a AR-2000 stress-controlled rheometer (TA Instruments, Delaware, USA) and a 50 mm parallel-plate geometry. Step-stress sweeps in the $1.0 \text{ Pa}$ to $10 \times 10^{2} \text{ Pa}$ range were performed using for two different gap sizes: 300$\mu$m and 500$\mu$m. The experiments were repeated at least twice for each gap-size and the experimental data was correct for slippage according to the method described by Mewis and Wagner (2012). The results are presented in the Supplementary Material attached to this document.

### 6.2.2.4 Power draw measurements

The power draw measurements were performed in the $5 \text{ s}^{-1}$ to $13.3 \text{ s}^{-1}$ $N$ interval for the emulsions produced at $N = 13.3 \text{ s}^{-1}$ using the methodology previously described
6.3. Results and discussion

6.3.1 Power draw

As $\eta_e$ increases with $\phi$, a simple power law fit was used to characterize the rheological behaviour of our emulsions

$$\eta_e = k\gamma^n$$  \hspace{1cm} (6.4)

where $k$ is the power-law pre-exponential factor and $n$ its index. The rheograms and power-law parameter can be consulted in the Supplementary material annexed to this document. As the concentrated emulsions are shear thinning and $\eta_e$ increases with $\phi$, it is important to determine if our experiments were carried out at constant Power number ($Po = P\rho^{-1}N^{-2}D^{-5}$).

The “power curve” obtained is shown in Figure 6.1, the black line was previously obtained in Part II (Carrillo De Hert and Rodgers, 2017b) using several Newtonian fluids. The cmc solution was used to obtain the average shear rate around the impeller $\dot{\gamma}$ in the laminar regime using the Metzner and Otto (1957) equation ($\dot{\gamma} = K_S N$) and the methodology thoroughly described by James et al. (2017); we obtained $K_S = 3.48$. This value is relatively small if compared to the one reported by Rodgers (2011), who found $K_S = 5.0$ for the same type of impeller. The discrepancy in-between the one found here and others reported in literature is unknown. The data obtained for the cmc solution seemed to follow the black curve relatively well beyond the laminar regime into the transitional regime.

Many of the emulsions obtained were shear thinning. The measured torque $M$ correlated well with $N^2$ indicating these were performed at constant (or almost constant for $\phi > 0.6$) ($Po$). As the Metzner-Otto approach is only valid in the
laminar regime, the Reynolds number (Re) for the emulsions was estimated by using

$$\text{Re} = \left( \frac{N^{4-2n}D^{7-3n}\rho^2V^{n-1}}{k^2\dot{\gamma}^n} \right)^{\frac{1}{n+1}}$$  \hspace{1cm} (6.5)

where $k$ and $n$ are the pre-exponential and index of a power-law fluid ($\mu = k\dot{\gamma}^{1-n}$); and $V$ is the volume of the vessel. Equation 6.5 was derived by Gabelle et al. (2013), who estimating $\dot{\gamma}$ in the turbulent regime by using

$$\dot{\gamma} = \left( \frac{\rho\varepsilon}{\mu} \right)^{\frac{1}{2}} = \left( \frac{\rho\varepsilon}{k\dot{\gamma}^{1-n}} \right)^{\frac{1}{2}}$$  \hspace{1cm} (6.6)

where $\varepsilon$ is the mean energy dissipation per unit mass and is estimated by $\varepsilon = P\rho^{-1}V^{-1}$.

Equation 6.5 reduces to $\text{Re} = \rho ND^2/\mu$ for Newtonian fluids ($n = 1, k = \mu$).

### 6.3.2 Phenomenology

Figure 6.2 shows the steady-state DSD obtained for $N = 13.3\, \text{s}^{-1}$ for the 10 cSt, 1000 cSt and 10 000 cSt SiOils with $\phi$ as parameter. Figure 6.2a shows that for the 10 cSt SiOil, there is negligible change for $\phi < 0.6$ and a decrease in size for $\phi = 0.7$ and $\phi = 0.8$. For the 1000 cSt (Fig. 6.2b) and the 10 000 cSt (Fig. 6.2c)
emulsions the decrease in drop size can be observed at lower values of $\phi$. Furthermore, these Figures show a progressive decrease in the amount of satellite drops decreasing the polydispersity as $\phi$ is increased, these is in agreement with literature (Pacek et al., 1998; Angle and Hamza, 2006; Vankova et al., 2007; Tcholakova et al., 2011; El-Hamouz, 2009; Hall et al., 2011). For example, in Figure 6.2b, the DSD with high polydispersity obtained for $\phi = 0.01$ becomes monomodal for $\phi = 0.8$. These figures show that the effect of $\phi$ on the DSD is $\mu_d$-dependent.

These results are in disagreement with the turbulence dampening theory, as no increase in drop size was observed for any of our systems. A possible explanation for the drop size increase reported by several authors (Coulaloglou and Tavlarides, 1976, 1977; Lagisetty et al., 1986; Pacek et al., 1998; Desnoyer et al., 2003; Angle and...
Hamza, 2006; Ma˚b et al., 2012; Gåbler et al., 2006; El-Hamouz, 2009; Rueger and Calabrese, 2013; Becker et al., 2014; Qi et al., 2015) would be coalescence. According to the phenomenological model proposed by Chesters (1991) and by Tsouris and Tavlarides (1994), coalescence efficiency is severely affected by \( \mu_d \) and according to Rueger and Calabrese (2013) the surfactant surrounding the drops might not be an effective barrier, as has been considered by some authors (El-Hamouz, 2009; Ma˚b et al., 2012; Rueger and Calabrese, 2013; Becker et al., 2014).

Figure 6.3 shows the Sauter mean diameter \( d_{32} \) and mode of the large daughter drops \( Mod \) dependency on \( \phi \) of all the emulsified systems at both experimental \( N \) in semi-log scales. The inconsistent behaviour obtained for the emulsions produced using the 10 000 cSt SiOil was attributed to experimental error and to the inherent difficulty to measure the DSD of this SiOil.

Figure 6.3a shows no significant change in \( d_{32} \) for \( \phi < 0.6 \) for the monodispersed nor for the polydispersed emulsions despite the evident decrease in drop size seen for the latter in Figure 6.2 and in Figure 6.3b. This is because the decrease in drop size is accompanied by a decrease in polydispersity. Furthermore, a steady decrease in the \( Mod \) can be observed in Figure 6.3b for the 350 cSt, 1000 cSt and 10 000 cSt dispersed SiOils before the plummeting. This is in agreement with studies that have seen no effect of \( \phi \) on drop size (Hall et al., 2011; Boxall et al., 2012), a steady decrease (Gutierrez et al., 2002; Welch et al., 2006) or a plateau followed by a decrease (Vankova et al., 2007; Tcholakova et al., 2011); depending on the \( \mu_d \) and the \( \phi \)-range studied.

For all studied dispersed phases a plummeting in drop size is observed for \( \phi > 0.6 \). This abrupt decrease in \( d_{32} \) and \( Mod \) seem to be associated to an increase in \( \eta_e \) (see Fig. 6.4) that leads to a decrease in the turbulence intensity and change in the mixing regime from turbulent to transitional (see Fig. 6.1). As \( \phi \) increases, the emulsion approaches its maximum packing fraction, and drops are in direct contact with their neighbors. Furthermore, \( \phi \) is increased beyond the maximum packing fraction drops loose their spherical shape. The dramatic decrease in drop size at the highest experimental hold-ups is attributed to an increase in the transfer of stresses
in-between drops as the contact area is increased.

Figure 6.3: (a) Sauter mean diameter $\bar{d}_{32}$ and (b) Mode as a function of $\phi$ with $\mu_d$ as parameter.

Figure 6.4 shows some of the rheograms obtained; Figure 6.4a shows the $\eta_e$ dependence on $\dot{\gamma}$ obtained using the 50 cSt SiOil for different $\phi$ produced at two different $N$. These rheograms shows that as $\phi$ increases the emulsions become shear thinning, that $\eta_e$ increases with $N$. The increase of $\eta_e$ with $N$ is expected as the drop size decreases with $N$ and smaller droplets yield thicker emulsions as demonstrated by Otsubo and Pudhomme (1994) and many others. The thinning behaviour of these emulsions could be described using a simple power-law model, the fits can be consulted in Section 6.C of the Appendices.

Figure 6.4b shows the rheograms obtained for four different SiOils for different $\phi$ and $N = 13.3$ s$^{-1}$. For $\phi = 0.5$, only the 50 cSt SiOil showed a strong $\dot{\gamma}$ dependency, this is attributed to the smaller drop sizes and dispersed phase viscosity $\mu_d$, as these spheres can deform easier under shear. For $\phi = 0.5$ and $\phi = 0.6$ no clear trends with $\mu_d$ are observed, this is due to the large amount of variables such as $\mu_d$, drop sizes and polydispersity.

Figure 6.5 shows the $\bar{d}_{32}$ to $D_{95}$ ratio as a function $\phi$ for different SiOils. As mentioned earlier, the 10000 cSt SiOil emulsions are difficult to measure, however the scattered results were included as these show a clear trend. This Figure shows that the DSD obtained using the 10 cSt and 50 cSt SiOil have the same degree of polydispersity. The change of $\bar{d}_{32}/D_{95}$ as a function of $\phi$ is negligible and was
attributed to experimental error. However the $d_{32}/D_{95}$ for the bimodal DSD (350, 1000 and 10 000 cSt SiOils) decreases significantly with $\phi$.

Figure 6.5: $d_{32}/D_{95}$ as a function $\phi$ for the emulsions obtained using different SiOils. The data points represent the average of the results obtained at both experimental $N$.

6.3.3 Drop size modelling

In Part I(Carrillo De Hert and Rodgers, 2017a) the mode of the daughter drops $Mo_d$ of over 35 emulsions produced using SiOils in the 10 cSt $< \mu_d < 10 000$ cSt range, in
the $8.33 \text{ s}^{-1} < N < 15.0 \text{ s}^{-1}$ range for $\phi = 0.01$ were well correlated using

$$Mo_d = A_1 \mu_d^{A_2} N^{-\eta/5} \quad (6.7)$$

where $A_1$ and $A_2$ were found to be $4.64 \times 10^3 \pm 2.94\%$ and $0.365 \pm 3.29\%$ respectively, the percentages represent the 95% confidence interval. The equation above can be extended to account for $\phi$ (as done by several authors, see Eq. 6.1) by multiplying Equation 6.7 by a $A_3 (1 + A_4 \phi)/A_1$ function

$$Mo_d = A_3 \mu_d^{A_2} N^{-\eta/5} (1 + A_4 \phi) \quad (6.8)$$

Introducing the $A_3/A_1$ ratio was necessary as $A_1$ was calculated for $\phi = 0.01$, therefore $A_1 = A_3 (1 + 0.01 A_4)$.

Isolating $[Mo_d (A_3 \mu_d^{A_2} N^{-\eta/5})^{-1} - 1]$ yields a linear dependency of slope $A_4$ on $\phi$. The proposed linear dependency yielded reasonable results for the $\phi \leq 0.6$ emulsions. In Figure 6.6, $[Mo_d (A_3 \mu_d^{A_2} N^{-\eta/5})^{-1} - 1]$ was plotted as a function of $\phi - 0.01$ to make the data points for $\phi = 0.01$ share the origin. The values of $A_3$ and $A_4$ for each $\mu_d$ were obtained using the method of least squares. We found $A_3 = 4.74 \times 10^3$ and the values found for $A_4$ for each SiOil are listed in Table 6.1. As the 0.65 cSt SiOil could not be described by Equation 6.7, the effect of $\phi$ was isolated by making $Mo_d(\phi)/Mo_d(\phi = 0.01) - 1$ the dependent variable of the regression. The high standard deviation and low $R^2$ for the 0.65 cSt and 10 cSt SiOils suggest a null dependency ($A_4 = 0$) of $Mo_d$ on $\phi$ in the $0.01 < \phi < 0.60$ range.

**Table 6.1**: Values obtained for $A_4$ for different SiOil and the coefficient of variation $R^2$. The percentages represent one standard deviation from the mean.

<table>
<thead>
<tr>
<th>SiOil</th>
<th>$A_4$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>$0.101 \pm 91.7%$</td>
<td>0.192</td>
</tr>
<tr>
<td>10</td>
<td>$0.038 \pm 84%$</td>
<td>0.113</td>
</tr>
<tr>
<td>50</td>
<td>$-0.345 \pm 16%$</td>
<td>0.855</td>
</tr>
<tr>
<td>350</td>
<td>$-0.860 \pm 5.2%$</td>
<td>0.981</td>
</tr>
<tr>
<td>1000</td>
<td>$-0.944 \pm 4.3%$</td>
<td>0.980</td>
</tr>
<tr>
<td>10000</td>
<td>$-0.800 \pm 18%$</td>
<td>0.858</td>
</tr>
</tbody>
</table>

Figure 6.7 shows $-A_4$ as a function of $\mu_d$. This Figure suggests a null or very
small dependency of $M_{o_d}$ on $\phi$ for least viscous SiOils followed by an increase which levels off for the thickest SiOils. The dependency was modelled using a log-normal cumulative function times an $A_5$ constant which sets the limit for the maximum $-A_4$.

$$-A_4 = A_5 \left[ \frac{1}{2} + \frac{1}{2} \text{erf} \left( \frac{\ln \mu_d - A_6}{\sqrt{2}A_7} \right) \right]$$

Due to the limited amount of data in the intermediate region, several $A_7$ are possible, for simplicity a value of unit was used. Using the method of least squares we obtained $A_5 = 0.948$ and $A_6 = -2.69$.

Substituting Equation 6.9 in Equation 6.8 yields

$$M_{o_d} = A_3\mu_d^{A_2}N^{-6/5} \left\{ 1 - \frac{A_5}{2} \left[ 1 + \text{erf} \left( \frac{\ln \mu_d - A_6}{\sqrt{2}} \right) \right] \phi \right\}$$

The goodness of the fit using Equation 6.10 can be assessed in Figure 6.8. The global $R^2$ of the fit was 0.981 and the Mean Absolute Error $MAE$ was 5.16%. 
6.3. Results and discussion

Figure 6.7: Dependency of $-A_4$ on $\mu_d$. The line represents the fit using Eq. 6.9 with $A_5 = 0.948, A_6 = -2.69$ and $A_7 = 1$ and the error bars represent one standard deviation from the mean.

6.3.4 Drop size distribution modelling

Following the same procedure described in Part I (Carrillo De Hert and Rodgers, 2017a), the DSD were normalized using the mode of the daughter drops $M_{Od}$ and two log-normal distributions were used to fit the $M_{Od}$-normalized DSD $f_{v,T}(d_i/M_{Od})$ by using a simple mixing rule for the daughter and satellite drops

$$f_{v,T}(\frac{d_i}{M_{Od}}) = (1 - \phi_s) f_{v,d}(\frac{d_i}{M_{Od}}) + \phi_s f_{v,s}(\frac{d_i}{M_{Od}})$$ (6.11)

where $\phi_s$ is the relative volume fraction of the satellite drops, $f_{v,d}(d_i/M_{Od})$ and $f_{v,s}(d_i/M_{Od})$ the function describing the distribution of the daughter and satellite drops. These functions are given by (Carrillo De Hert and Rodgers, 2017a)

$$f_{v}(\frac{d_i}{M_{Od}}) = 100 \times \frac{p\left(\frac{d_i}{M_{Od}}\right)}{\sum p\left(\frac{d_i}{M_{Od}}\right)}$$ (6.12)

$$p\left(\frac{d_i}{M_{Od}}\right) = \frac{1}{s_z \sqrt{2\pi} \left(\frac{d_i}{M_{Od}}\right)} \exp\left\{ -\frac{\left[\ln\left(\frac{d_i}{M_{Od}}\right) - \bar{z}\right]^2}{2s_z^2} \right\}$$ (6.13)
where $s_z$ is the standard deviation of $\log (d_i/MoD)$, $\bar{z}$ is the arithmetic mean of $\log (d_i/MoD)$. As the distributions are $MoD$-normalized $MoD = 1$ and, as the $Mo$ of a log-normal distribution is given by $Mo = \exp (\bar{z} - s_z^2/2)$ we can write $\bar{z}_d = s_{z,d}^2/2$ reducing the number of fit parameters by one. In Part I (Carrillo De Hert and Rodgers, 2017a) we determined that $s_{z,d} = 0.40$. The equations below were proposed to model $s_{z,s}$ and $\bar{z}_s$ by assuming that the broadening of the satellite drops follows a power law function (Eq. 6.14) and by assuming that $Mo_d$ and $Mo_s$ are equidistant (Eq. 6.15)

$$s_{z,s} = 0.80 \mu_d^{0.15}$$  \hspace{1cm} (6.14)

$$\bar{z}_s = -0.87 + \frac{s_{z,s}^2}{2}$$  \hspace{1cm} (6.15)

Under these considerations, the DSD were fit. The monomodal $MoD$-distributions obtained for the 10 cSt and 50 cSt were well-described with the model and constants obtained in Part I (Carrillo De Hert and Rodgers, 2017a) for all $\phi$. Therefore the shape of the distribution of the large drops is $\phi$-independent.

For the bimodal DSD (350 cSt, 1000 cSt and 10 000 cSt SiOils), $\phi_s$ was fit using the method of the least squares; the shape of the DSD were well-described, indicating that the size difference of the daughter and satellite drops is independent of $\phi$. 

Figure 6.8: Goodness of the fit using Eq. 6.9 and Eq. 6.8. (a) Experimental and predicted $MoD$ as a function of $\phi$ for different $\mu_d$ and $N$. (b) Goodness of the fit, the shadowed area represents 15% variation from the mean.
The $\phi_s$ obtained for the different $N$ and SiOils used in the $0.01 < \phi < 0.8$ range are shown in Figure 6.9a. The $\phi_s$ for $\phi = 0.8$ was zero for all SiOils and $N$. The $\phi_s$ were normalized by the $\phi_s$ obtained for $\phi = 0.01$ and modelled using a Gaussian cumulative function

$$\frac{\phi_s(\phi)}{\phi_s(\phi = 0.01)} = 1 - \frac{1}{2} \left[ 1 + \text{erf} \left( \frac{\phi - A_7}{\sqrt{2A_8}} \right) \right]$$

(6.16)

In Part I (Carrillo De Hert and Rodgers, 2017a) we proposed a Weibull distribution to obtain $\phi_s(\phi = 0.01)$, the expression and fit parameters can be consulted in the original text. It was found that the data could be well-described by a fixed value for $A_8 = 0.20$, while $A_7$ was found to be a function of $\mu_d$. The normalization of $\phi_s$ and the fits described by Equation 6.16 with $A_8 = 0.20$ and $A_7$ obtained using the method of the least squares are shown in Figure 6.9b.

![Figure 6.9](image)

**Figure 6.9:** (a) Obtained values for $\phi_s$ by fitting the bimodal DSDs using the method of the least squares and the methodology described in Part I (Carrillo De Hert and Rodgers, 2017a). (b) Normalized $\phi_s$ and fit using Eq. 6.16.

As only three out of the six SiOils used in this study yielded bimodal DSDs and the data gathered for the 10 000 cSt SiOil emulsions are subject to experimental error, it was not possible to suggest a statistically significant function for $A_7$. Nevertheless, as depicted in Figure 6.10a a clear trend can be observed and a power-law function was proposed to fit the trend. Figure 6.10b assesses the goodness of the $\phi_s$-fit using the power-law function proposed for $A_7$ in Equation 6.16. The $MAE$ of the fit was 6.42%.
Figure 6.10: (a) $A_T$ dependency on $\mu_d$ and tentative power-law model dependency and (b) goodness of the fit represented in Figure 6.9b using Equation 6.16. The shadowed area represents 20% variation from the mean. The fit yielded $MAE = 6.42\%$.

Figure 6.11 shows some examples of the appearance of the fits for the 1000 cSt SiOil and Figure 6.12 shows the goodness of the fit by comparing the experimental and modelled $\overline{d}_{32}$ for the emulsions in the $0.01 < \phi < 0.60$ range for the 10-1000 cSt SiOils. The obtained $R^2$ and $MAE$ were 0.976 and 3.73% respectively.

6.4 Further discussion

In Part II (Carrillo De Hert and Rodgers, 2017b) we found that increasing the viscosity of the continuous phase $\mu_c$ had a strong influence on the drop size and on the DSD. As $\mu_c$ increased drop size decreased and the amount of satellite drops increased. Even though increasing $\phi$ increases the bulk viscosity of the system, such behaviour was not observed as the drop size of the SiOil yielding monomodal distributions remained steady in the $0.01 < \phi < 0.5$ range. Determining the effective viscosity where the maximum energy dissipation rate $\varepsilon_{\text{max}}$ is located and breakup occurs would be difficult. As reviewed in Part II (Carrillo De Hert and Rodgers, 2017b) there is disagreement on the $\varepsilon_{\text{max}}$ to $\bar{\varepsilon}$ ratio reported in literature depending on the methodology used (Gabriele et al., 2009). The values reported in literature are in the $3.27 < \varepsilon_{\text{max}}/\bar{\varepsilon} < 78$ range (Gabriele et al., 2009). For example for the 50 cSt SiOil emulsion for $\phi = 0.5$ stirred at $N = 13.3 \text{ s}^{-1}$, using the aforementioned $\varepsilon_{\text{max}}/\bar{\varepsilon}$ range and Equation 6.6 would yield a localized maximum in the $406 \text{ s}^{-1} < \dot{\gamma} < 2290 \text{ s}^{-1}$.
Further discussion

Figure 6.11: Example of fits for emulsion with the 1000 cSt SiOil as dispersed phase for \( N = 13.3 \text{ /s} \) for (a) \( \phi = 0.01 \), (b) \( \phi = 0.25 \), (c) \( \phi = 0.50 \) and (d) \( \phi = 0.70 \).

range; and localized emulsion viscosity in-between \( 12 \text{ mPa s} < \eta_c < 9 \text{ mPa s} \), where the upper limit was obtained by extrapolation due to the limitations of our rotational rheometer and by assuming no high-shear Newtonian plateau. However this viscosity range is 9 to 12 times higher than that of water and in Part II we observed a decrease in drop size by increasing the viscosity of the continuous phase approximately 9 times. For the SiOils yielding bimodal DSD, these experience a reduction in the amount of satellite drops with \( \phi \) and therefore an increase in the bulk viscosity of the emulsion, this is the opposite behaviour observed in Part II (Carrillo De Hert and Rodgers, 2017b) when the viscosity of the continuous phase was increased. Therefore it unlikely that an “mean field theory” approach \( (\mu_c = \eta_c (\dot{\gamma})) \), which has been successfully applied for drop breakup in the laminar regime by Jansen et al. (2001),
Another limitation for modelling is the current understanding in emulsion rheology. As reviewed in Section 6.1, Tcholakova et al. (2011) correlated their results using Equation 6.3 using the rheological model proposed by Yaron and Gal-Or (1972) to model $\eta_e$. However, the rheological model proposed by Yaron and Gal-Or (1972) is limited to non-shear thinning emulsions. To our knowledge, there is no rheological model that accounts for the shear-thinning behaviour, polydispersity and $\mu_d$ simultaneously.

Possible explanation for the decrease in polydispersity in concentrated systems ($\phi > 0.70$) of viscous dispersed phases in the laminar regime have been given by Mason and Bibette (1996), Mabille et al. (2003) and Mansard et al. (2016), who were able to produce monodisperse drop size distributions starting from a coarse highly polydisperse emulsions. The phenomenon is known as “collective Rayleigh-Plateau-instability”. The breakup mechanism of these concentrated emulsions happens in different steps: (1) aligned threads are formed under shear, (2) one of the threads suffers perturbation of a given wavelength, (3) due to the proximity of the threads, the instability of is transmitted with the same wavelength to the neighbour threads (4) breakup. Mason and Bibette (1996) found that below the maximum random packing fraction $\phi_m$ ($\phi \sim 0.63$ for monodisperse spheres) the drop sizes were independent of $\phi$, while for $\phi$ nearby and above $\phi_m$, the drop size decrease was due to the increase of $\eta_e$ and therefore $\phi$. Mabille et al. (2003) used SiOils in the $10 \times 10^{-3}$ Pa s $< \mu_d <$
10 \times 10^1 \text{ Pa s} and found that there was a progressive loss in the wavelength selectivity as \( \mu_d \) increased. Mansard et al. (2016) found that thread with an different initial diameter share the same wavelength but produce drops of different size, however an overall decrease in polydispersity with \( \phi \) was clearly observable. The aforementioned studies give a satisfactory explanation of the behaviour of our emulsions for \( \phi \sim 0.8 \); as even the 10 000 cSt SiOil produced monomodal distributions, as shown in Figure 6.2c.

6.5 Conclusions

Despite the large amount of experimental studies on the effect of \( \phi \), there is still no agreement on its effect on the DSD. This is due to the simultaneous combination of complex phenomena such as the arise of non-Newtonian rheological features, coalescence and turbulence dampening.

As discussed in the introduction, many authors have reported an increase in drop size and have attributed it to turbulence dampening. However most of the literature agrees that increasing \( \phi \) has no effect or reduces the mean drop size of emulsions with high \( \mu_d \). If the turbulence dampening hypothesis was correct, all emulsions should experience a drop size increase with \( \phi \) regardless of \( \mu_d \). A more plausible explanation would be that these systems experienced coalescence, even in systems contaminated by surfactant. We observed a plateau followed by a drop size decrease even for the 0.65 cSt SiOil which is the region where most authors have reported a drop size increase in Figure 6.1. This might be due to SLES being an effective barrier around the drops, which might not be the case for all surfactants used in previous studies.

We also found that the effect of \( \phi \) ranges from negligible to \( (Mo_d \propto 1 - 0.95\phi) \) depending on \( \mu_d \). The negligible change in drop size for the 10 cSt and 50 cSt SiOil also indicates that making \( \mu_c = \eta_c \) and using the model proposed in Part II (Carrillo De Hert and Rodgers, 2017b) would yield incorrect results, thereby the mean field theory approach is not valid for emulsification in the turbulent regime (See discussion
For experimental range and 10-1000 $\mu_d$-range we found no statistic evidence that the effect of $N$ is $\phi$ dependent, as has been suggested (Pacek et al., 1998; Desnoyer et al., 2003; Gäbler et al., 2006; El-Hamouz, 2009).

As no satisfactory model for emulsification for large $\phi$ in the turbulent regime has been reported in the literature, the models proposed in these paper were empirical. The modelling of the decrease of polydispersity with $\phi$ was undertaken using the methodology proposed in Part I (Carrillo De Hert and Rodgers, 2017a) and calculating the amount of satellite drops produced for each $\phi$. The behaviour was characterised by a low and a high-$\phi$-plateau which were modelled using a Gaussian distribution. The high-$\phi$-plateau was $\mu_d$ dependent and the decrease in polydispersity is less pronounced for high $\mu_d$. A power-law model was used to describe the high-$\phi$-plateau dependency on $\mu_d$, however more experimental evidence is required to support the power-law constants obtained.

For $\phi \sim 0.80$ all the SiOils produced considerably smaller drops and monomodal distributions, however these emulsion were not carried out at constant Power numbers. These emulsions had a hold-up well above the maximum random packing fraction and were carried in the laminar regime. Qualitatively, the results obtained in this investigation support the “collective Rayleigh-Plateau-instability” drop break-up mechanism hypothesis, even in non-homogeneous shear fields.

### 6.6 Bibliography


**Appendix**

**Appendix 6.A Surfactant concentration high volume fractions**

The experiments analysed in the paper were done using 27.85 g of Texapon N701, equivalent to 1.04 wt.% of SLES in water for $\phi = 0$. As $\phi$ increases, less water is used and the surfactant concentration increases. For example, the SLES concentration for $\phi = 0.6$ is 2.44 wt.%. To analyse the effect of keeping the SLES concentration in water constant at 1.04 wt.% we prepared a 50 cSt SiOil emulsion for $\phi = 0.6$ and $N = 13.3 \text{s}^{-1}$ using a 1.04 wt.% of SLES in water solution as continuous phase. The DSD obtained are shown in Figure 6.A.1. As can be observed, the obtained DSD are very similar and therefore this effect was neglected.

**Appendix 6.B Carboxymethyl cellulose rheology**

Figure 6.B.1 shows the obtained rheogram for the cmc solution. The solution exhibits a low-shear Newtonian plateau followed by a shear-thinning behaviour. The last section of the curve ($\dot{\gamma} < 196 \text{s}^{-1}$) was fit using a power-law rheological model. The Metzner-Otto constant was determined to be $K_S = 3.48$. Therefore using only this section of the fit should be a reasonable approximation for the power measurement which were carried out at a minimum stirring speed of $3.60 \text{s}^{-1}$. 
Appendix 6.C  Emulsion rheology

The $k$ and $n$ values obtained by fitting our rheological data using the power-law fit are shown in Table 6.C.1.

\begin{equation}
\eta_e = k_\gamma^n \gamma^{-1}
\end{equation}

where the power-law index $n$ decreased with $\phi$.

Provided the large amount of variables, no attempts to make a rheological model were made.
Chapter 6. Effect of volume fraction in stirred vessels

Figure 6.B.1: Rheometry of the carboxymethylcellulose solution. The power-law fit was performed for $7.9 \text{s}^{-1} < \dot{\gamma} < 196 \text{s}^{-1}$.

Table 6.C.1: Power-law fit parameters for emulsion produced at $N = 13.3 \text{s}^{-1}$.

<table>
<thead>
<tr>
<th>SiOil [cSt]</th>
<th>$\phi$</th>
<th>$k$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.7</td>
<td>$8.92 \times 10^{-1}$</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>$2.60 \times 10^{-3}$</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>$3.27 \times 10^{-2}$</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>$1.74 \times 10^{-1}$</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>$5.61 \times 10^{-1}$</td>
<td>0.60</td>
</tr>
<tr>
<td>50</td>
<td>0.25</td>
<td>$3.92 \times 10^{-3}$</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>$2.17 \times 10^{-2}$</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>$1.09 \times 10^{-1}$</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>$5.68 \times 10^{-1}$</td>
<td>0.68</td>
</tr>
<tr>
<td>350</td>
<td>0.50</td>
<td>$1.60 \times 10^{-2}$</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>$6.29 \times 10^{-2}$</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>$4.25 \times 10^{-1}$</td>
<td>0.74</td>
</tr>
<tr>
<td>1000</td>
<td>0.25</td>
<td>$2.70 \times 10^{-3}$</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>$2.18 \times 10^{-2}$</td>
<td>0.968</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>$3.57 \times 10^{-2}$</td>
<td>0.942</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>$1.84 \times 10^{-1}$</td>
<td>0.857</td>
</tr>
</tbody>
</table>
Part III

High-shear mixers
Preface

Part III also contains three chapters in journal submission format that aim to tackle the objectives postulated for in-line high-shear mixers. The objectives for in-line mixers were classified depending on the operation arrangement in which these can be operated: continuous and recycle (batch).

These objectives are answered in the chapters that integrate this part, however the chapters are strongly intertwined and some of the objectives are partially answered in a paper and completely answered in a secondary one.

The rationale for ordering the chapters was by type of operation arrangement. Chapter 8 deals only with the multi-pass continuous emulsification arrangement for multimodal DSD, Chapter 9 analyses both arrangements for monomodal DSD and establishes the mass balance principles that are later applied in Chapter 10 were the full link for multimodal complex DSD is established.

The order in which the chapters are presented here do not correspond to their order of publication or submission. Specifically, Chapter 9 was published before 8, thereby the former makes constant reference to the latter; for example, power measurements are presented in Chapter 9 and referenced in Chapter 8 to avoid repetition. If the publication/submission chronological order is preferred, the reading order would be: Chapter 9, Chapter 8 and finally Chapter 10.

Note that the equipment and surfactant concentration used throughout Part III is the same.
On the effect of dispersed phase viscosity and mean residence time on the Droplet Size Distribution for High-shear mixers


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Properties of emulsified product such as stability, rheology and interfacial area dependent on their micro-structure, specially their mean droplet size and droplet size distribution. Mechanistic models in literature focus on predicting the maximum droplet diameter or Sauter mean diameter but not in their size distribution. The effect of viscosity (9.58-295 mPa s), mean residence time and stirring speed (50-150 s^{-1}) have been investigated using an in-line laboratory scale rotor-stator and dilute (negligible coalescence) coarse emulsions with seven Silicon Oils of different viscosity. Low viscous oils produced monomodal distributions whereas the ones for intermediate and high viscous oils were bimodal. The mode or modes of the distributions were used for the modelling of the large and small daughter droplet sizes. The droplet size modelling had a mean absolute error (MAE) of 8%. To model the distributions by volume two Generalized Gamma functions were used and fitted using the least absolute error. The distributions were reasonably well-described while predicting the Sauter mean diameter of both mono and bimodal distributions with a MAE of 13.8%.

7.1 Introduction

High-shear mixers are able to create small droplets with large interfacial areas due to their localised energy dissipation rates, high rotor speeds and the narrow spacing between the rotor and the stator. These mixers are widely used to produce cosmetics, foods, paints, pharmaceuticals and chemical (Zhang et al., 2012; Atiemo-Obeng and Calabrese, 2003), but despite their wide applicability there is almost no fundamental understanding on these devices (Atiemo-Obeng and Calabrese, 2003). The two main types of high-shear mixers used are the radial discharge batch and the in-line rotor-stators. In-line rotor-stators allow for continuous processing and offer versatility to change from one product formulation to another using the same equipment by valve switching.

The droplet size distribution (DSD) of an emulsion affects its stability (Ma et al., 2005), rheology (Derkach, 2009) and absorption in drug delivery systems (Ma et al.,
2010). For example, narrow DSDs are less susceptible to coalescence and Ostwald ripening; therefore personal care products with broad DSD are stabilized by large amounts of surfactants which may cause irritation, skin drying and allergic reactions (Nazir et al., 2013). The rheology of emulsions depends on the droplet-droplet interactions and droplet deformability among other parameters, which are a function of viscosity (both phases), volume fraction, mean droplet size and their DSD (Derkach, 2009); this is important in products such as paint (Watson and Mackley, 2002).

In this study we deal with dilute systems; for these systems drop coalescence is considered negligible and drop breakage can be isolated for its study. Mechanistic models assume that equilibrium for these systems is reached when all of the drops are smaller than a maximum stable drop size \(d_{\text{max}}\) (Leng and Calabrese, 2003). A linear relationship between \(d_{\text{max}}\) and the Sauter mean diameter \(d_{32}\) was proposed by Shinnar (1961) and has been used by many authors

\[
\overline{d}_{32} = C_1 d_{\text{max}} \tag{7.1}
\]

The Sauter mean diameter is one of the most important measures of central tendency used in emulsification technology because it is inversely proportional to the interfacial area of a given distribution. The previous relationship makes \(\overline{d}_{32}\) and \(d_{\text{max}}\) in all the models presented in Sections 7.2.1 and 7.2.2 interchangeable. The equations below show how \(\overline{d}_{32}\) is calculated if the number frequency \(f_n(d_i)\) or the volume frequency \(f_v(d_i)\) are given.

\[
\overline{d}_{32} = \frac{\sum_{i=1}^{n} f_n(d_i)d_i^3}{\sum_{i=1}^{n} f_n(d_i)d_i^2} = \frac{\sum_{i=1}^{n} f_v(d_i)}{d_i} \tag{7.2}
\]

Where \(d_i\) is the \(i\)th droplet diameter.

As many emulsions may have the same \(d_{\text{max}}\) and/or \(\overline{d}_{32}\) but different DSD, it is highly desirable to obtain a model which describes the whole distribution, specially when the DSD are bimodal.
Chapter 7. Effect of viscosity for high-shear mixers

7.2 Theoretical background

7.2.1 Mechanistic models

It is widely accepted that in turbulent flow droplets can break by two types of stresses depending on the droplets size in relation with the size of the smallest possible eddies. According to Kolmogorov (1949) the length scale of the smallest eddies \( \ell_\eta \) for isotropic turbulence is given by

\[
\ell_\eta = \left( \frac{\mu_c}{\rho_c} \right)^{3/4} \varepsilon^{-1/4}
\]

(7.3)

where \( \mu_c \) and \( \rho_c \) are the viscosity and density of the continuous phase and \( \varepsilon \) is the local energy dissipation rate which value depends on the location of the tank, thereby it is more convenient to use the average energy dissipation rate \( \overline{\varepsilon} \) or the maximum energy dissipation rate \( \varepsilon_m \), both being proportional for geometrically similar systems (Leng and Calabrese, 2003)

\[
\varepsilon_m \propto \frac{P_S}{\rho_c V_T} \propto \frac{P_0 \rho_c N^3 D^5}{\rho_c D^3} \propto P_0 N^3 D^2
\]

(7.4)

where \( P_S \) is the power consumption, \( V_T \) is the volume of the vessel and \( P_0 \) is the dimensionless power number \( (P_0 = P_S/\rho_c N^3 D^5) \). For a geometrically similar mixers and constant \( P_0 \): \( \varepsilon \sim N^3 D^2 \) where \( N \) is the impeller speed and \( D \) its diameter.

The aforementioned stresses are either due to hydrodynamic fluctuations when the droplets are larger than \( \ell_\eta \) or by viscous stresses when these are smaller.

The maximum drop diameter \( d_{\text{max}} \) in the inertia regime according to the Kolmogorov-Hinze theory is (Kolmogorov, 1949; Hinze, 1955):

\[
d_{\text{max}} \propto \left( \frac{\sigma}{\rho_c} \right)^{4/5} \varepsilon^{-2/5}
\]

(7.5)

where \( \sigma \) is the interfacial tension. The previous equation was obtained by balancing the disruptive forces \( \propto (\varepsilon d)^{2/3} \) and the capillary pressure inside the droplet \( 4\sigma d^{-1} \).

Equation 7.5 does not take into account the viscosity of the dispersed phase \( \mu_d \) and
is considered valid only for the inviscid droplets or when $\mu_d$ is small. Davies (1985) included a viscous resistance inside the deforming droplet and Calabrese et al. (1986) expanded the model by doing a balance of the disruptive turbulent energy obtaining

$$d_{\text{max}} = C_1 \left( \frac{\sigma}{\rho_c} \right)^{3/5} \varepsilon^{-2/5} \left[ 1 + C_2 \left( \frac{\rho_c}{\rho_d} \right)^{1/2} \frac{\mu_d \varepsilon^{1/3} \sigma_{\text{max}}^{1/3}}{\sigma} \right]^{3/5} \tag{7.6}$$

Where $\rho_d$ is the density of the dispersed phase and $C_i \ (i = 1, 2, \ldots)$ are fitting constants.

In the turbulent viscous regime $d_{\text{max}} < \ell_\eta$, in this range $\mu_c$ is no longer negligible (as in Eq. 7.6) as viscous stresses may add to inertial stresses. Two sets of mechanistic models can be derived in this regime depending on the type of stresses considered: inertial stresses for $d_{\text{max}} < \ell_\eta$ and viscous stress for $d_{\text{max}} \ll \ell_\eta$. For inertial stresses in the turbulent viscous regime (Padron, 2005)

$$d_{\text{max}} = C_3 \left( \frac{\sigma \mu_c}{\rho_c^2 \varepsilon} \right)^{1/3} \left[ 1 + C_4 \frac{\mu_d \rho_c}{\sigma} \left( \frac{\varepsilon}{\rho_d \mu_c} \right)^{1/2} d_{\text{max}} \right]^{1/3} \tag{7.7}$$

If viscous stresses inside the turbulent eddies act as the disruptive forces, according to Shinnar (1961) these are $\sim (\varepsilon \rho_c \mu_c)^{1/2}$. The balance of the disruptive force, capillary forces and viscous forces inside the droplet yield (Padron, 2005)

$$d_{\text{max}} = C_5 \frac{\sigma}{(\varepsilon \rho_c \mu_c)^{1/2}} \left[ 1 + C_6 \frac{\mu_d (\mu_c \rho_c)^{1/4}}{\sigma \rho_d^{1/2} \varepsilon^{1/4}} \right] \tag{7.8}$$

The limits for $\mu_d \to 0$ (inviscid limit) and $\mu_d \to \infty$ of the three mechanistic models presented in Equations 7.6, 7.7 and 7.8 are shown in Table 7.1. The present study is focused on $\mu_d$, $N$ and $l_{\text{res}}$ on the Droplets Size Distribution. The same table shows that according to the mechanistic models, $\mu_d$’s power law dependency for highly-viscous oils ranges from 0.5 to 1 and $N$’s index ranges from $-0.75$ to $-1.5$.

Atiemo-Obeng and Calabrese (2003) estimated that stirred vessels are usually not operated at a sufficient high power draw to produce droplets of the length of $\ell_\eta$. Rueger and Calabrese (2013) experimented with a high-shear mixer and found that
Table 7.1: Summary of limits of the Mechanistic Models and power law indexes on studied variables.

<table>
<thead>
<tr>
<th>Limit Model</th>
<th>Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu d \rightarrow d_{\text{max}} \propto \varepsilon^{-2/5}$</td>
<td>(7.9) 0 $-6/5$</td>
</tr>
<tr>
<td>$\mu d \rightarrow d_{\text{max}} \propto (\sigma/\rho_c)^{3/5} \varepsilon^{-2/5}$</td>
<td>(7.10) $3/4$ $-3/4$</td>
</tr>
<tr>
<td>$\mu d \rightarrow d_{\text{max}} \propto (\mu_d/\rho_c)^{1/2} \varepsilon^{-1/4}$</td>
<td>(7.11) $1/2$ $-3/4$</td>
</tr>
<tr>
<td>$\mu d \rightarrow d_{\text{max}} \propto (\mu_d/\rho_c)^{1/2} \varepsilon^{-1/4}$</td>
<td>(7.12) $1/2$ $-3/4$</td>
</tr>
<tr>
<td>$\mu d \rightarrow d_{\text{max}} \propto (\mu_d/\rho_c)^{1/4} \varepsilon^{-1/4}$</td>
<td>(7.13) $0$ $-3/2$</td>
</tr>
<tr>
<td>$\mu d \rightarrow d_{\text{max}} \propto (\mu_d/\rho_c)^{1/4} \varepsilon^{-1/4}$</td>
<td>(7.14) $1$ $-3/4$</td>
</tr>
</tbody>
</table>

their data were well correlated by the sub-Kolmogorov inertia stress mechanistic models whereas Hall et al. (2011) obtained droplets of the order of magnitude of $\ell_\eta$ and none of the mechanistic models described their results, this was attributed to the homogeneous isotropic turbulence assumption which is unlikely for rotor-stators.

### 7.2.2 Multi-pass emulsification

The mechanistic models above assume that the equilibrium DSD has been reached, nevertheless in in-line rotor-stators the residence time is usually insufficient to reach equilibrium and further drop breakage occurs for multiple passes. Jasińska et al. (2014); Håkansson et al. (2016) and Carrillo De Hert and Rodgers (2017) performed experiments for $n = 10, 8$ and $20$ respectively and were unable to reach steady-state. Two different approaches for multipass experiments for in-line rotor-stators have been reported in literature. The first one is the energy density $E$ proposed by Karbstein and Schubert (1995)

$$\bar{d}_{32} \propto E^{C_7} \propto (\bar{\varepsilon} t_{\text{res}})^{C_7}$$ (7.15)
Making $t_{res} = V_{swept} n/\dot{Q}$ where $V_{swept}$ is the swept volume (Hall et al., 2013), $n$ is the number of passes through the rotor-stator and $\dot{Q}$ is the volumetric flow rate throw the rotor-stator. Substituting Equation 7.4 in the previous equation we obtain

$$d_{32} \propto \left( P_S n/\dot{Q} \right)^{C_7} \quad (7.16)$$

For a in-line rotor-stator $P_S$ is a function of $\dot{Q}$, $N$, the equipment and the properties of the materials being processed, a method to obtain $P_S$ can be found in (Kowalski, 2009).

Hall et al. (2011, 2013) could not fit their results using Equation 7.16. Hall et al. (2013) proposed a second correlation based on tip speed ($ND$) and $t_{res}$

$$d_{32} \propto (ND)^{C_8} \left( n/\dot{Q} \right)^{C_9} \quad (7.17)$$

They found that $C_9$ decreased as $\mu_d$ increased, they found $C_9 = -0.148$ for the $9.4 \times 10^{-3}$ Pa s silicon oil and $C_9 = -0.043$ for the $3.39 \times 10^{-1}$ Pa s one. Hall et al. (2011) found that $d_{32} \propto \dot{Q}^{-0.19}$. In our previous work (Carrillo De Hert and Rodgers, 2017) we found that the mode $Mo$ was more useful than $d_{32}$ to track emulsification kinetics and that the DSDs were homoscedastic and hence $d_{max} \propto Mo$. We could not fit the $Mo$ of our DSD using Equation 7.16 either, nevertheless Equation 7.17 provided a good fit, making $C_8 = -1.2$ and $C_9 = -0.2$ we obtained $R^2 = 0.985$ and a mean error of 4.7% for 78 DSDs ($n$ and $\dot{Q}$ varied systematically) using a $9.580 \times 10^{-3}$ Pa s silicon oil.

### 7.2.3 Droplet size distribution

For $C_1$ in Equation 7.1 Sprow (1967) found $C_1 = 0.38$. Calabrese et al. (1986) determined that $C_1$ decreases as $\mu_d$ increases, they found $C_1 = 0.59$ for $\mu_d = 1 \times 10^{-1}$ Pa s and $C_1 = 0.52$ for $\mu_d = 10$ Pa s. Rueger and Calabrese (2013) obtained $C_1 = 0.49$. Li et al. (2014) found that $C_1 = 0.16$, they attributed the discrepancy to the bimodality of the DSD they obtained. Liu et al. (2013) also studied bimodal DSD
and found that $C_1$ decreased from 0.225 to 0.130 as the viscosity of the dispersed phase increased from $9.6 \times 10^{-3}$ Pa s to $4.25 \times 10^{-1}$ Pa s, but was independent on $N$ and volume fraction.

Chen and Middleman (1967) fitted a normal distribution to their DSD by volume.

$$p_v\left(\frac{d_i}{\bar{d}_{32}}\right) = \frac{1}{\sqrt{2\pi}s} \exp \left[ -\frac{\left(\frac{d_i}{\bar{d}_{32}} - \frac{\bar{d}_{30}}{\bar{d}_{32}}\right)^2}{2s^2} \right] \quad (7.18)$$

Where $p_v\left(\frac{d_i}{\bar{d}_{32}}\right)$ is the normalised volume probability density, $s$ its standard deviation and $\bar{d}_{30}$ is the volume arithmetic mean.

Calabrese et al. (1986) and Vankova et al. (2007) used similar expressions to fit the volume DSD. Nevertheless Calabrese et al. (1986) found that for high viscosities the DSDs broaden and could be better described by a number log-normal distribution.

$$p_n(d_i) = \frac{1}{\sqrt{2\pi} s_G} \exp \left\{ -\frac{\left[\log(d_i) - \log(\bar{d}_i)\right]^2}{2s_G^2} \right\} \quad (7.19)$$

Where $p_n(d_i)$ is the number probability density, $s_G$ its standard deviation and $\log(\bar{d}_i)$ the geometric mean.

Li et al. (2014) emulsified a $1.14 \times 10^{-1}$ Pa s crude oil in water using a rotor-stator at different $N$ and volume fraction and obtained bimodal DSDs. They transformed the DSD by volume into a number distribution. This operation gives higher weight to the smallest droplet, and this conversion resulted in a monomodal DSD by number. They further used three different probability density functions to fit the DSD by number; namely a normal, a log-normal and a Fréchet distribution. The Fréchet distribution provided the best fit.

$$p_n(d_i) = \frac{\alpha}{\beta} \left(\frac{\beta}{d_i}\right)^{\alpha+1} \exp \left[-\left(\frac{\beta}{d_i}\right)^\alpha\right] \quad (7.20)$$
Where $\alpha$ and $\beta$ are obtained using the equations below

$$\beta^\alpha = \frac{n}{\sum_{i=1}^{n} \frac{1}{d_i}}$$  \hspace{1cm} (7.21)

$$\frac{n}{\alpha} + n \ln \beta - \sum_{i=1}^{n} \ln d_i - \sum_{i=1}^{n} \left( \frac{\beta}{d_i} \right)^\alpha \ln \left( \frac{\beta}{d_i} \right) = 0$$  \hspace{1cm} (7.22)

The same fit was used by Liu et al. (2013) for a variety of bimodal emulsions obtained using a rotor-stator and silicon oils in the $9.6 \times 10^{-3}$ Pa s-$4.26 \times 10^{-1}$ Pa s viscosity range.

### 7.3 Materials and equipment and methods

#### 7.3.1 Materials

For each experiment 10 L of coarse emulsion was prepared using different silicon oils. The silicon oil’s concentration of the emulsions was 1% by volume and 1% by weight of surfactant.

Texapon N701 (Cognis Ltd., Hertfordshire, U.K.) was used as surfactant. Texapon contains $\approx 70\%$ concentration by weight of sodium laureth sulphate (SLES) and $\approx 30\%$ water and impurities. SLES is an anionic surfactant consisting of mixture of alkyl ether sulphates ($C_{12-14}$) with EO sodium salt. Its molar mass and density are $420 \text{g mol}^{-1}$ and $1.03$ respectively (EL-Hamouz et al., 2009).

Six 200 Silicone Fluid (dimethyl siloxane, Dow Corning, Michigan, U.S.A.) of different viscosity were used as dispersed phase. Additionally, a blend of the 1000 cSt and 10000 cSt silicon oils was made to obtain an oil of intermediate viscosity, this oil was labelled as 2760 cSt. The density $\rho_d$, dynamic viscosity $\mu_d$, interfacial tension $\sigma$ of the silicon oil-1% SLES/water solution, and refractive index $n_{ri}$ of the seven oils are listed in Table 7.1.

The specific gravities listed are the ones found in the material’s Safety Data Sheet (SDS); the viscosities were determined experimentally using a DV2T Viscometer (Brookfield Vicometers, Essex, U.K.) in a water bath; the interfacial tension was
Table 7.1: Relevant properties of the silicon oils used at 25 °C.

<table>
<thead>
<tr>
<th>Silicon oil [cSt]</th>
<th>( \rho_d ) [kg m(^{-3})]</th>
<th>( \mu_d ) [Pa s]</th>
<th>( \sigma ) [N m]</th>
<th>( n_{ri} ) [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>934</td>
<td>9.580 \times 10^{-3}</td>
<td>8.809 \times 10^{-3}</td>
<td>1.399</td>
</tr>
<tr>
<td>50</td>
<td>960</td>
<td>4.913 \times 10^{-2}</td>
<td>9.096 \times 10^{-3}</td>
<td>1.402</td>
</tr>
<tr>
<td>350</td>
<td>965</td>
<td>3.279 \times 10^{-1}</td>
<td>9.129 \times 10^{-3}</td>
<td>1.403</td>
</tr>
<tr>
<td>1000</td>
<td>970</td>
<td>9.474 \times 10^{-1}</td>
<td>9.172 \times 10^{-3}</td>
<td>1.404</td>
</tr>
<tr>
<td>2760</td>
<td>970</td>
<td>2.745 \times 10^{0}</td>
<td>-</td>
<td>1.404</td>
</tr>
<tr>
<td>10000</td>
<td>970</td>
<td>1.051 \times 10^{1}</td>
<td>-</td>
<td>1.404</td>
</tr>
<tr>
<td>30000</td>
<td>970</td>
<td>2.951 \times 10^{1}</td>
<td>-</td>
<td>1.404</td>
</tr>
</tbody>
</table>

measured using a platinum-iridium KRÜSS standard ring (KRUSS GmbH, Hamburg, Germany) and a K11 Mk4 Tensiometer (KRUSS GmbH, Hamburg, Germany); and the refractive indexes using a RFM390 Refractometer (Bellingham & Stanley Ltd, Kent, UK). The \( \sigma \) for silicon oils with \( \mu_d > 9.474 \times 10^{-1} \) Pa s could not be measured using the available Du-Noüy ring method; nevertheless, as the change of \( \sigma \) as \( \mu \) increases is small, it is assumed constant for the most viscous oils. As shown in Table 7.1, silicon oils allow to study the effect of the dispersed phase viscosity on the DSD as these are available in a wide range of viscosities while having similar \( \rho_d \), \( \sigma \) and \( n_{ri} \).

### 7.3.2 Equipment and methods

The equipment used for this study has been thoroughly described in (Carrillo De Hert and Rodgers, 2017) for the continuous arrangement. A L5M-A Laboratory Mixer (Silverson Machines Ltd, Chesham, U.K.) was used for this study. The rotor used had four blades, an internal diameter of 30 mm, blade thickness of 5 mm and a height of 10 mm. The screen used had 240 holes in 6 rows of 40 holes each in pitch arrangement. Its internal diameter, height and thickness were 32 mm, 20 mm and 1 mm respectively. The Power number \( P_o \) for this rotor-stator has been previously determined to be 0.215 in reference (Carrillo De Hert and Rodgers, 2017).

A peristaltic pump (501 single channel pumphead, Watson Marlow, Cornwall, U.K.) with arbitrary pump number ranging from 1 to 999 was used to push the coarse emulsion through the L5M-A Laboratory Mixer (Silverson Machines Ltd, Chesham,
U.K.) working at a established impeller speed $N$. The output was collected in a second 12 L vessel. For experiments involving multiple passes, the feed and collection tank were swapped and the process was repeated for $n$ number of passes.

The coarse emulsions were prepared by dissolving 142.94 g of Texapon N701 in 9.77 L of water in an unbaffled 12 L cylindrical vessel using a 6-blade Rushton impeller with 6 cm of diameter. Once the surfactant had been completely dissolved, 0.100 L of silicon oil were poured slowly while the vessel was being stirred at a rotational speed $N = 6.4 \text{ s}^{-1}$. The emulsions were stirred for 24 h to guarantee that the coarse emulsion fed to the rotor-stator had the same drop size and DSD (see supplementary material 1). The stirring speed in the vessel was lowered to $N = 3.3 \text{ s}^{-1}$ while the coarse emulsion was pumped through the rotor-stator to ensure that further droplet burst was only due to the action of the rotor-stator while keeping the coarse emulsion homogeneous within the vessel.

Samples for each pass through the rotor-stator were immediately analysed in a Mastersizer 3000 (Malvern Instruments, Malvern, U.K.). The $n_{ri}$ used for each silicon oil are shown in Table 7.1, while the one used for water was 1.333. The absorption index used for all silicon oils was $10^{-3}$ following Malvern’s suggestion. Each sample was analysed 5 times and at least three samples were analysed; the arithmetical average of the 15 distributions was obtained and are the DSD reported in this study.

The experiments in this study focus on the effect of $\mu$, $\bar{t}_{res}$ and $N$ on the DSD. Experiments for $n = 1, 2, ..., 8$, keeping $N = 150 \text{ s}^{-1}$ and $\dot{Q} = 2.217 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$ constant using the silicon oils previously listed in Table 7.1 were performed. For the 1000 cSt silicon oil ($\mu = 9.474 \times 10^{-1} \text{ Pa s}$) additional experiments varying $\dot{Q}$ were performed for $n = 1, 2, ..., 8$ keeping $N = 150 \text{ s}^{-1}$. Lastly, the effect of $N$ for three silicon oils was studied for $n = 1$ and $\dot{Q} = 2.217 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$. For this $N$ range all the experiments are in the turbulent regime (constant Po) (Carrillo De Hert and Rodgers, 2017).

The experimental matrix can be seen in Table 7.2. The first experiments performed were the ones varying $\mu_d$ for constant $N$ and $\dot{Q}$. The results obtained for these
Table 7.2: Experimental matrix. X denoted the experiments performed.

<table>
<thead>
<tr>
<th>$\mu_d$ [Pa s]</th>
<th>$n = 1, 2, \ldots, 8$</th>
<th>$N = 150 \text{s}^{-1}$</th>
<th>$\dot{Q}/10^{-5}$ [m$^3$ s$^{-1}$]</th>
<th>$n = 1$</th>
<th>$\dot{Q}/10^{-5} = 2.217 \text{m}^3 \text{s}^{-1}$</th>
<th>$N$ [s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$9.580 \times 10^{-3}$</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$4.913 \times 10^{-2}$</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>$3.279 \times 10^{-1}$</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$9.474 \times 10^{-1}$</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>$2.745$</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>$1.051 \times 10^1$</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$2.951 \times 10^1$</td>
<td>-</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

experiments were analysed before doing the rest of the experiments. The effect of $N$, $n$ and $\dot{Q}$ for the 10 cSt silicon oil have been previously reported by Carrillo De Hert and Rodgers (2017) using the same equipment. As will be seen in Section 7.4, the experiments using the 350 cSt silicon oil yielded DSD where the two distributions of the daughter droplets were not distinguishable and thus no more experiments using this oil were done. For two thickest oils did not follow the model proposed for the 10 cSt-2 760 cSt silicon oils, and thus no further experiments were performed because thicker oils were unavailable.

7.4 Results and discussion

7.4.1 Phenomenology

The DSDs by volume obtained for the experiments at constant $\dot{Q}$ and $N$ for $n = 1, 2, \ldots, 8$ for all the silicon oils are shown in Figure 7.1. Figure 7.1a show one distinctive peak whereas the DSDs for the 350 cSt silicon oil (Fig. 7.1b) have a broader DSD than the obtained for the previously mentioned oils. Furthermore, the DSD is not symmetrical and as will be discussed later, this was attributed to the presence of two types of daughter droplets namely the large and small daughter droplets. Thicker oils (Figs. 7.1c-7.1f) showed a clear bi-modality. Figures 7.1c-7.1e show that the distribution of the small daughter drops is broader than the one
of the large ones, they also show that as viscosity increases the peaks get further apart: (1) the size of the large droplets increase and (2) the small daughter droplets become smaller. Therefore the asymmetrical shape of the DSDs obtained for the 350 cSt oil was attributed to the distributions of the large and small droplets being close together. From this it can be inferred that a change of the droplet break-up mechanism occurs for a viscosity between 50 cSt and 350 cSt.

![DSDs obtained for all silicon oils](image)

**Figure 7.1:** DSDs obtained for all silicon oils for \( n = 1, 2, \ldots, 8 \), \( \dot{Q} = 2.217 \times 10^{-5} \text{ m}^3 \text{ s}^{-1} \) and \( N = 150 \text{ s}^{-1} \).

For the 30 000 cSt (Fig. 7.1f) it can be seen than small daughter droplets are larger than the ones obtained using the 10 000 cSt oil, reversing the trend found for the 350 cSt-10 000 cSt viscosity range. Furthermore, the shape of the DSDs in Figure 7.1f suggest that a third distribution may be present (best observable for \( n = 1 \)).

Fig. 7.1a shows that as \( n \propto \dot{l}_{res} \) increases the droplets become smaller, this is also true for the large daughter droplets in Figures 7.1b-7.1f, suggesting that the large daughter droplets are generated by the same break-up mechanism that gave birth to the ones for the 10cSt and 50 cSt oils. From Figures 7.1c-7.1f it can also be observed that \( n \) has no influence on the size of the small daughter droplets, but do increase their quantity.
In their study on the effect of viscosity on the DSD for stirred vessels, Calabrese et al. (1986) reported a transition from a monomodal to a bimodal DSD for silicon oils with a $\mu \geq 1$ Pa s which was attributed to a transition from a bursting to a transition breakage mechanism. For the bimodal DSDs they noted that as viscosity increases the DSD broadens as the small droplets become smaller and the large larger. This is in agreement with the results obtained in this study, however the appearance of the two types of droplets may appear at viscosities lower than $\mu_d \geq 3.279 \times 10^{-1}$ Pa·s. On the other hand, Hall et al. (2011) reported that for an in-line rotor-stator both types of daughter droplets increased in size with viscosity which is in disagreement with the findings in this study.

Most of the DSD obtained allow for the Mode $Mo$ of one or two distributions to be obtained; the exception being the DSD obtained for the 350 cSt where two distributions are merged and produce a distribution with a single mode.

The $Mo$ of the large $Mo_L$ and small $Mo_s$ daughter droplets of the DSDs presented in Figure 7.1 are shown in Figure 7.2 as a function of $n$ and in Figure 7.3 as a function of $\mu_d$. The results presented in Figure 7.2a for the most viscous silicon oils are scattered due to the difficulty in analysing the samples, nevertheless Figure 7.2a shows that $Mo_L$ decreases in size as $n$ increases and Figure 7.2b that its effect on $Mo_s$ is negligible.

![Figure 7.2](image-url): Effect of $n$ for constant for $\dot{Q} = 2.217 \times 10^{-5}$ m$^3$s$^{-1}$ and $N = 150$ s$^{-1}$ on (a) $Mo_L$ and (b) $Mo_s$.

Figure 7.3 shows $Mo_L$ for $n = 1, 2, ..., 8$ and the averaged $Mo_s$ for all $n$ ($Mo_s$...
independent on $n$). $Mo_L$ first increases with viscosity and then plateaus, on the other hand $Mo_s$ decreases with viscosity and suddenly increases for the most viscous silicon oil, suggesting a change in the break-up mechanism. The index found for the large and small daughter droplets were 0.37 and −0.37 respectively. Suggesting that the droplets increase and decrease in size at the same rate respectively.

![Figure 7.3](image)

**Figure 7.3:** $Mo_L$ (closed symbols) for $n = 1, 2, ... 8$ and averaged $Mo_s$ (open symbols) as a function of $\mu_d$ for $\dot{Q} = 2.217 \times 10^{-5}$ m$^3$s$^{-1}$ and $N = 150$ s$^{-1}$.

The power law index found in our study is in disagreement with any of the three mechanistic models (Eqs. 7.6, 7.7 and 7.8 and Tab. 7.1) reviewed in Section 7.2. The estimated $\ell_\eta = 6.3$ µm which in the order of magnitude of the $d_{max}$ obtained for the two thinnest oils (See Fig. 7.1a), implying that either the Supra-Kolmogorov inertia sub-range or the Sub-Kolmogorov inertia stress model should apply. As shown in Table 7.1, the expected viscosity dependence index should be either 1/2 or 3/4, which are significantly higher than the 0.37 found in this study. Thicker oils have a $d_{max} > \ell_\eta$ and no change in slope was obtained.

The studies found in literature on the effect of $\mu_d$ on the DSD use $d_{max}$ or $d_{32}$ as parameter. It is important to mention that if the shape (broadness and skewness) of the distribution of the large daughter droplets is independent on property materials and processing parameters, the trends found in this study for $Mo_L$ should be similar to the ones for $d_{max}$, not to $d_{32}$. The $d_{32}$ includes both types of daughter droplets, meaning that it is affected by their size, volume fraction and distribution shape.
unlike the DSDs are monomodal and homoscedastic.

Arai K. et al. (1977) used Polystyrene in the $7.8 \times 10^{-4}$ Pa s-$1.5$ Pa s viscosity range as dispersed phase to study the $d_{\text{max}}$ dependency on $\mu_d$. He found that for $7.8 \times 10^{-4}$ Pa s > $\mu_d$ > $7.8 \times 10^{-2}$ Pa s the droplet sizes did not vary; droplet size increased with $\mu_d$ until a 0.75 power-law index was reached for $2 \times 10^{-1}$ Pa s > $\mu_d$ > $1.5$ Pa s, finally a decrease in the index for polystyrene with $\mu_d$ > $1.5$ Pa s was found. Ludwig et al. (1997) used a screw loop reactor to emulsify paraffin oils in the $3.2 \times 10^{-2}$ Pa s-$1.9 \times 10^{-1}$ Pa s in water and SDS (Sodium dodecyl sulphate) as emulsifier. They found the same trend as Arai K. et al. (1977) but the $d_{\text{max}}$ dependency on $\mu_d$ started to level off at $\mu_d$ values as low as $\mu_d$ ≥ $1.9 \times 10^{-1}$ Pa s. Liu et al. (2013) developed a model based on the one of Calabrese et al. (1986) that accounts for dispersed phase volume fraction and dispersed phase viscosity, their model suggests that $d_{\text{max}} \propto \mu_d^{0.6}$. Our results follow the trend found in previous studies in that the droplet sizes increase with viscosity and then levels off, but does not agree on the power-law index value.

Arai K. et al. (1977) and Padron (2005) suggested that when $\mu_d$ is relatively small deformed drops can restore their spherical shape faster than the more viscous drops. Because viscous drops have a longer deformation time-scale, it is difficult to restore their equilibrium shape and thus several eddies may elongate the drops consecutively forming threads before bursting. The higher the viscosity the longer these threads are and therefore more and smaller satellite drops will be generated. This droplet break-up mechanisms resembles the ones for laminar shear flows known as capillary-wave instability or Rayleigh instability. Eastwood et al. (2004) used high-speed video images to study the breakup of materials in the $5 \times 10^{-4}$ Pa s-$5.09 \times 10^{-2}$ Pa s viscosity range using a prototypical set-up with a turbulent water jet. They found that droplets stretch dramatically before rupture and that the stretching increases with viscosity.

Figure 7.4 shows the $d_{32}$ as a function of $\mu_d$ for $n = 1, 2, ..., 8$. As expected, $d_{32}$ increases with viscosity for the oils producing monomodal DSDs ($\mu_d = 9.580 \times 10^{-3}$ Pa s and $\mu_d = 4.913 \times 10^{-2}$ Pa s). For $4.913 \times 10^{-2}$ Pa s > $\mu_d$ > $1.051 \times 10^1$ Pa s decreases
in a power-law fashion. The gradual decline in $\bar{d}_{32}$ in this viscosity range is due to the decrease in size of the small daughter droplets which have a stronger effect on $\bar{d}_{32}$ than the large daughter droplets. For $\mu_d = 2.951 \text{ Pa s}$ the trend shot up, the cause being the increase in size of the small daughter droplets (see Fig. 7.3).

Hall et al. (2011) and Padron (2005) studied the effect of viscosity on the DSD using a batch and in-line rotor-stator respectively. Both authors found a $\bar{d}_{32}$ increase with viscosity followed by a plateau and the appearance of a second distribution for the most viscous oils. Wang and Calabrese (1986) dispersed silicon oils in the $1 \times 10^{-3} \text{ Pa s} - 1 \text{ Pa s}$ viscosity range in several ethanol in water solutions. They also found that a 0.75 power law index described the $\bar{d}_{32}$ dependency on $\mu_d$ for intermediate viscosity silicon oils. They could fit their data to an equation similar to Equation 7.6 but had to exclude the results for the 1 Pa s. EL-Hamouz et al. (2009) found a 0.46 power law index dependency of $\bar{d}_{32}$ on $\mu_d$ for silicon oils in the $4.9 \times 10^{-4} \text{ Pa s} - 3.4 \times 10^{-1} \text{ Pa s}$ viscosity range using a pitched blade turbine and a sawtooth impeller. The studies mentioned on the effect of $\bar{d}_{32}$ are in disagreement with our results as was shown in Figure 7.4.

Figures 7.5a and 7.5b depict the effect of $N$. The former shows the effect of $N$ on the DSD for the 1 000 cSt silicon oil for a single pass and constant $\dot{Q}$. This figure

![Figure 7.4: $\bar{d}_{32}$ as a function $\mu_d$ for $n = 1, 2, \ldots, 8$, $\dot{Q} = 2.217 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$ and $N = 150 \text{ s}^{-1}$.](image-url)
shows that as $N$ increases the size of both types of daughter droplets decrease in size and that the amount of small daughter droplets increases. This is further shown in the later Figure for different $\mu_d$.

![Figure 7.5](image)

**Figure 7.5:** (a) DSD for the 1 000 cSt silicon oil for different impeller speeds $N$ and constant $\dot{Q} = 2.217 \times 10^{-5}$ m$^3$s$^{-1}$ and $n = 1$. (b) $Mo_L$ (closed symbols) and $Mo_s$ (open symbols) as a function of $N$ for constants $\dot{Q} = 2.217 \times 10^{-5}$ m$^3$s$^{-1}$ and $n = 1$.

### 7.4.2 Droplet size modelling

Provided that most of the DSDs obtained allow to obtain one or two $Mo$, power law dependencies on $\mu$, $N$ and $t_{res}$ ($t_{res} \propto n/\dot{Q}$) were proposed

$$Mo_L = C_{L,0} \mu^C_{L,\mu} N^{C_{L,N}} \left( \frac{n}{\dot{Q}} \right)^{C_{L,T}}$$  \hspace{1cm} (7.23)

$$Mo_s = C_{s,0} \mu^C_{s,\mu} N^{C_{s,N}} \left( \frac{n}{\dot{Q}} \right)^{C_{s,T}}$$  \hspace{1cm} (7.24)

For $Mo_L$ it was found that the power model proposed described the data obtained for the 10 cSt - 2760 cSt silicon oils while failing to describe the results for the two most viscous oils as $C_{L,\mu} = 0$ (see Fig. 7.3). Multivariable linear and transformed power regressions were performed to obtain the value of the constants and their 95% confidence intervals $CI$: $C_{L,0} = 1.14 \times 10^5 \pm 43.3\%$, $C_{L,\mu} = 0.365 \pm 6.24\%$, $C_{L,N} = -1.06 \pm 12.5\%$ and $C_{L,T} = -0.192 \pm 24.6\%$. The coefficient of determination $R^2$ obtained was 0.958 and the mean absolute error $MAE$ was 8.74%. Carrillo De
Hert and Rodgers (2017) found that $C_{L,t} = -0.2$ for the a larger set of experiments using the same 10 cSt silicon Oil and the same equipment used for this study. To homologate both studies, the fit for $C_{L,t}$ was forced to $-$0.2, the corrected value for the other constants are shown in Table 7.1. The result obtained was a fit with an $R^2 = 0.959$ and $MAE = 8.71\%$.

**Table 7.1:** Fitting constants for Eqs. 7.23 and 7.24 and their 95\% CI.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$C_{x,0}$</th>
<th>$C_{x,\mu}$</th>
<th>$C_{x,N}$</th>
<th>$C_{x,t}$</th>
<th>$MAE$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>$1.18 \times 10^9 \pm 41.2%$</td>
<td>$0.365 \pm 6.18%$</td>
<td>$-1.05 \pm 10.3%$</td>
<td>$-0.2^*$</td>
<td>$8.71%$</td>
</tr>
<tr>
<td>s</td>
<td>$1.69 \times 10^3$</td>
<td>$-0.365^*$</td>
<td>$-1.05^*$</td>
<td>$0^*$</td>
<td>$7.47%$</td>
</tr>
</tbody>
</table>

* fixed values.

Analogously for $Mo_s$ the regression yielded $C_{s,0} = 1.16 \times 10^3 \pm 50.6\%$, $C_{s,\mu} = 0.385 \pm 10.3\%$, $C_{s,N} = -1.02 \pm 15.8\%$ and $C_{s,t} = -0.0211 \pm 242\%$. The fit yielded $R^2 = 0.851$ and an $MAE = 8.24\%$. As $C_{s,\mu} \sim -C_{L,\mu}$, $C_{s,N} \sim C_{L,N}$ these term were assumed equal and $C_{s,t}$ was assumed to be zero as its value is small and its CI is large. The new values for the constants in Equation 7.24 can also be consulted in Table 7.1; the $R^2$ and $MAE$ were 0.884 and 7.47\% respectively.

The Goodness of the fit for both types of daughter droplets is showed in Figure 7.6.

![Figure 7.6](image)
Our model suggest that bimodality surges when \( Mo_L \) and \( Mo_s \) acquire the same value; when the lines in Figure 7.3 intercept; the constants obtained in Table 7.1 suggest that bimodality is independent on \( N \) but dependent on \( \bar{t}_{res} \):

\[
\mu = 3 \times 10^{-3} \left( \frac{n}{Q} \right)^{0.274} \tag{7.25}
\]

For example, for \( n = 1 \) and \( \dot{Q} = 2.217 \times 10^{-5} \text{m}^3 \text{s}^{-1} \), Equation 7.25 suggests that small daughter droplets will be present for \( \mu > 5.65 \times 10^{-2} \text{Pa s} \). As \( t_{res} \propto n/\dot{Q} \), equation 7.25 also suggests that the appearance of small daughter droplets for a given viscosity occur for small \( t_{res} \) as the \( Mo \) of the large daughter droplets approaches the size of the small daughter droplets.

### 7.4.3 Droplet Size Distribution modelling

As the results obtained from the Mastersizer are reported as frequency distributions by volume \( f_v(d_i) \), these were converted into probability density functions \( p_v(d_i) \). The conversion was done using the trapezium integration rule.

\[
p_v(d_i) = \frac{f_v(d_i)}{3 \times 10^3 \mu m} \sum_{d_i=0.01 \mu m}^{d_i} \frac{f_v(d_{i+1}) - f_v(d_i)}{2 (d_{i+1} + d_i)} \cdot 100 \tag{7.26}
\]

The former equation allows for the area under the distribution, or the total probability to be 100%. The probability density function used for this study is the Generalized Gamma distribution (GGd). This distribution has three parameter: one scale parameter \( \lambda_G \) and two shape parameters \( \kappa_G \) and \( \tau_G \); the former is related to the broadness of the distribution and the later to its skewness. Its equation is

\[
p_v(d_i) = \frac{\kappa_G}{\lambda_G \Gamma(\tau_G)} \left( \frac{d_i}{\lambda_G} \right)^{\tau_G \kappa_G - 1} \exp \left\{ - \left( \frac{d_i}{\lambda_G} \right)^\kappa \right\} \tag{7.27}
\]

Two GGd were used when the condition established in Equation 7.25 was true. To account for the fraction of large and small daughter droplets the parameters \( \phi_L \) and \( \phi_s \) were introduced (\( \phi_s = 1 - \phi_L \)). The equation for bimodal distributions thus
become

\[ p_{v,T}(d_i) = (1 - \phi_s)p_{v,L}(d_i) + \phi_s p_{v,s}(d_i) \] (7.28)

Where \( p_{v,T}(d_i) \) is the probability distribution of the emulsion, \( p_{v,L}(d_i) \) and \( p_{v,s}(d_i) \) are the probability distributions of the large and small daughter droplets respectively. Each of the two distributions have their own scale and shape parameters.

The modelling consisted of two steps, (1) determining the value of the parameter for \( p_{v,L}(d_i) \) and \( p_{v,s}(d_i) \) and (2) modelling of \( \phi_s \).

The effects of \( \mu, N \) and \( n/\dot{Q} \) on the droplet sizes were previously determined to follow Equations 7.23 and 7.24. The same power law dependencies as well as \( C_{x,\mu}, C_{x,N} \) and \( C_{x,\tau} \) reported in Table 7.1 were used for \( \lambda_{G,L} \) and \( \lambda_{G,s} \), nevertheless the pre-exponential factors should acquire new values \((C_{L,1} \text{ and } C_{s,1})\) as the scale of the GGd are affected by its shape factors \( \alpha \) and \( \tau_G \)

\[ \lambda_{G,L} = C_{L,1}\mu^{C_{L,\mu}} N^{C_{L,N}} \left( \frac{n}{\dot{Q}} \right)^{C_{L,\tau}} \] (7.29)

\[ \lambda_{G,s} = C_{s,1}\mu^{C_{L,\mu}} N^{-C_{L,N}} \] (7.30)

The DSD for both daughter droplet distributions were assumed to be symmetrical, this is attained by making \( \tau_{G,L} \) and \( \tau_{G,s} \) large; as \( \tau_G \to \infty \) a GGd becomes a normal distribution. Therefore we considered \( \tau_{G,L} = \tau_{G,s} = 10 \).

To determine the best values for \( \alpha_L \) and \( \alpha_s \) we assumed that the broadness of the distributions are constant for all the experiments (shape independent of \( N, \mu \) and \( \tau_{res} \)).

Figures 7.2a and 7.5a show that the volume fraction of small daughter droplets \( \phi_s \) is affected by \( \mu, n \) and \( N \). Another power-law dependency was proposed

\[ \phi_s = C_{\phi,1}\mu^{C_{\phi,\mu}} N^{\phi,N} \left( \frac{n}{\dot{Q}} \right)^{C_{\phi,\tau}} \] (7.31)

The fit was carried out by minimising the absolute error between the re-scaled experimental DSD and Equation 7.28 for all our experiments (87 DSDs) for the 10 cst-2 760 cSt viscosity range. It was found that the constants in Table 7.2 produced
reasonable results while decreasing the number of variables.

**Table 7.2:** Values for the constants $C_{x,y}$ obtained by fitting the DSD using $MAE$ as criteria.

<table>
<thead>
<tr>
<th></th>
<th>$x$</th>
<th>$s$</th>
<th>$\phi$</th>
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<tr>
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<td>$L$</td>
<td>$\mu$</td>
<td>$N$</td>
</tr>
<tr>
<td>1</td>
<td>$6.19 \times 10^4$</td>
<td>$2.63 \times 10^1$</td>
<td>$1.33 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>$0.365$</td>
<td>$-0.365$</td>
<td>$-0.365$</td>
</tr>
<tr>
<td>$N$</td>
<td>$-1.05$</td>
<td>$-1.05$</td>
<td>$1.05$</td>
</tr>
<tr>
<td>$\bar{t}$</td>
<td>$-0.2$</td>
<td>$0$</td>
<td>$0.2$</td>
</tr>
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</table>

**Shape parameters**

<table>
<thead>
<tr>
<th></th>
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<th>$\tau_G$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$0.735$</td>
<td>$0.488$</td>
</tr>
<tr>
<td></td>
<td>$10$</td>
<td>$10$</td>
</tr>
</tbody>
</table>

Figure 7.7 shows how the model fits our results for different viscosities for constant $n = 5$, $\dot{Q} = 2.217 \times 10^{-5} \text{ m}^3 \text{s}^{-1}$ and $N = 150 \text{s}^{-1}$. It is worth mentioning that despite discarding the results for the 350 cSt silicon oil in the previous sections, the model proposed is capable of estimating the asymmetrical shape of the DSD by volume (see Fig. 7.7c).

**Figure 7.7:** Experimental and modelled DSD for five silicon oils for $n = 5$, $\dot{Q} = 2.217 \times 10^{-5} \text{ m}^3 \text{s}^{-1}$ and $N = 150 \text{s}^{-1}$. The error bars represent two standard deviations.
Regarding the region where \( Mo_L \) and \( Mo_s \) are viscosity independent (plateau in Fig. 7.3), \( C_{L,\mu} \) and \( C_{L,\mu} \) become zero in Equations 7.23 and 7.24 respectively. Assuming that the rest of the power indexes keep the same value \( C_{L,0} = 8.41 \times 10^8 \) and \( C_{s,0} = 9.60 \times 10^2 \) with a \( MAE = 10.4\% \) for the large daughter droplets and \( MAE = 16.9\% \) for the small ones.

The fit shown in Figure 7.7f for the 10 000 cSt silicon oil shows that even though the modes of the DSD and of the fit coincide, the volume fractions do not and that there are droplets present in the valley in-between both types of daughter droplets; this worsens for the 30 000 cSt (not shown).

The Goodness of our model can be further assessed in Figure 7.8 where the experimental and modelled Sauter mean diameter \( \bar{d}_{32} \) are compared.

\[
\text{Figure 7.8:} \quad \text{Goodness of the fit considering the Sauter mean diameter } \bar{d}_{32} \text{ as parameter. The obtained } MAE \text{ was } 9.4\%. \quad \text{The dashed lines represent } \pm 15\%.
\]

In Figure 7.9 a 3-D representations of our model is shown. To enhance visibility, the \( p_v(d_i) \) results were transformed into \( f_v(d_i) \) doing the inverse operation done previously by Equation 7.26.

Figure 7.9 shows that as viscosity increases, the DSD evolved from a narrow monomodal distribution into a broader DSD (such as the 350 cSt DSD in Figs. 7.1b and 7.7c) and finally into a bimodal DSD. As stated previously, large and small daughter droplets are present when the condition established by Equation 7.25 is
fulfilled, this is the cause for the sudden drop in $f_{v}(d_{i})$ and increase in broadness. The large and small daughter distributions separate as viscosity increases; the large droplets become larger and the small become smaller at the same rate ($C_{L,\mu} = C_{s,\mu}$). Even though $C_{\phi,\mu}$ is negative, it can be observed that the amount of small daughter droplets increases with viscosity, this is because of the transformation of probability density into a relative frequency.

Figure 7.10 depicts the effect of $N$ on a bimodal DSD. It shows that as $N$ increases the size of both large and small droplets decrease (at the same rate $C_{L,N} = C_{s,N}$), furthermore has a strong impact on $\phi_{s}$; as $N$ increases so does the amount of small droplets.

The effect of $\tilde{t}_{res}$ or $(n/\dot{Q})$ on the DSD is more subtle than the one of the two aforementioned variables as previously shown in Figure 7.1; the size of the small daughter droplets is $\tilde{t}_{res}$ independent and the large droplets sizes have a -0.2 power dependency. The volume fraction of the small droplets dependency has a 0.2 index.
7.5 Conclusions

The effects of dispersed phase viscosity, stirring speed and mean residence time on the droplet size distribution have been investigated with special emphasis on the first by using 7 silicon oils of different viscosity in the $9.58 \times 10^{-3}$ Pa s-$2.95 \times 10^{1}$ Pa s range. As viscosity increased a transition from monomodal to bimodal distributions was observed, this was attributed to a change in the droplet break-up mechanism. The mode or modes of the DSD were used to characterise the sizes of the large and small daughter droplets under the assumption that the broadness and skewness of the DSD were independent of viscosity.

It was found that the sizes of the large daughter droplets first increased with viscosity with a power law index of 0.37 before levelling off at approximately 2.75 Pa s suggesting a third break-up mechanism. The 0.37 dependency is in disagreement with the one proposed by the mechanistic models. The modes belonging to the small daughter droplets decreased in size at the same rate as the large ones increased.

Furthermore the large daughter droplets decreased in size as the mean residence time increased while the small daughter droplets were unaffected. The power law

**Figure 7.10:** Modelled DSD as a function of $N$ for $\mu = 1$ Pa s and $(n/\dot{Q}) = 2 \times 10^{5}$ s m$^{-3}$. 

299
dependency found was very close to the one found in our previous study Carrillo De Hert and Rodgers (2017) where a more extensive study on mean residence time was done. The effect of stirring speed affected the sizes of both types of daughter droplets equally with a power law index of $-1.05 \pm 10.3\%$ which is in agreement with the mechanistic models.

Two Generalized Gamma probability density functions were used to fit the DSD by volume. The scale parameter was parametrized using the same power functions used to describe the modes; with a 0.365 viscosity index for viscosities up to 2.745 Pa s and zero for the two most viscous oils. The shape of both types of daughter droplets were assumed symmetrical (in log scale) and thus a large value for $\tau_G$ was fixed. The broadness of the distributions was considered an independent variable but constant throughout the viscosity, mean residence time and stirring speed range. The other independent variable for fitting the DSD was the volume fraction of the small daughter droplets, which was assumed to follow another power function for all variables. The independent variables were adjusted using the minimum absolute error criteria.

For low and intermediate viscosities the fit was successful in that the shape of the DSD is described and in that the $MAE$ of the experimental and predicted $d_{32}$ was $MAE = 9.4\%$. As the shape of the large daughter droplets was homoscedastic throughout the viscosity range, the modes are proportional to $d_{max}$.

However for the most viscous oils, the region in-between the two distributions could not be described with two GGf and the volume fractions of each type of daughter droplets could not be predicted. Further studies could focus on how to predict the DSD for the high viscosity end where an apparent maximum droplet size is reached.

### 7.6 Bibliography


Chapter 7. Effect of viscosity for high-shear mixers


Chapter 8

Continuous, recycle and batch emulsification kinetics using a high-shear mixer


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# Chapter 8. Kinetics for high-shear mixers

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Abstract

In-line rotor-stator mixers are widely used to emulsify immiscible liquids, but there is little understanding on the size reduction kinetics and on their performance if used in a continuous or in a recycle arrangement. In this study, a systematic series of experiments were performed to study the droplet size reduction of a 10 cSt silicon oil coarse emulsion using different flow rates and number of passes for a continuous and a recycle configuration using a L5M-A Silverson Laboratory mixer. The droplets size distributions obtained were bimodal. It was found that the mode of the larger daughter droplets is a better parameter to follow the emulsification kinetics than the Sauter mean diameter; the volume fraction of the small daughter droplets was estimated to be $\approx 6\%$ using two generalized gamma functions. For the continuous arrangement it was found that impeller speed and mean residence time inside the rotor-stator correlated with an average error of 3.2%. It was also found that a Poisson chain can link the results of both operation arrangements. This stochastic model allowed following the disappearance rate of the coarse droplets and the evolution of the daughter droplets’ mode with an average error of 2.3%. The model developed allowed the comparison of both arrangements using an in-line rotor-stator. A simplification of the Poisson chain model for long times was used to analyse batch emulsification kinetics. The droplet size reduction rate and batch volume could be explained in terms of the in-line results.

8.1 Introduction

Liquid-liquid mixtures are present in a wide variety of products such as pharmaceuticals, cosmetics and foods; and in unit operations such as extraction and emulsion polymerisation. The performance of these products and processes relies on the Droplets Size Distribution (DSD) of the emulsion as it determines the available area for mass transfer, stability and rheological behaviour. In many industries stirred vessels have been substituted by high-shear mixers due to their versatility and the high shear fields produced by a high tip speed and specially by the narrow gap in-between the rotor and the stator. High-shear mixers are versatile as they can be
used in batch and continuous operation modes. Despite the popularity of high-shear
rotor-stator mixers, we found no evidence in literature of a comparative model for
these arrangements. Experimental studies using different arrangements and
rotor-stator mixers include the one of Bourne and Studer (1992) who made exper-
iments using a recycle and a continuous arrangement but were unable to stabliah
link both operation mode results. More recently Håkansson et al. (2016) emulsified
mayonnaise using batch and continuous arrangements and used an average number
of rotor-stator passes for comparison, nevertheless when the drop sizes are plotted as
function of the average number of passes for both arrangements, these did not fall
into a master curve. The focus of this work is to compare the multi-pass continuous
operation mode and the batch recycle arrangement using an in-line rotor-stator.

The mechanistic models for emulsification in the turbulent regime are based on
the work developed by Kolmolgoroff and Hinze (1955), who proved the existence
of two emulsification regimes depending if the droplets are larger or smaller than
the smallest possible eddies; namely the inertia and viscous regime. The order of
magnitude of these or the Kolmolgoroff’s scale \( \ell_\eta \) for isotropic turbulence can be
determined by

\[
\ell_\eta = \left( \frac{\nu^3}{\epsilon} \right)^{\frac{1}{4}}
\]

(8.1)

Where \( \nu \) is the kinematic viscosity of the continuous phase and \( \epsilon \) the energy dissipation
rate which can be approximated as \( \epsilon \sim N^3 D^2 \); where \( N \) is the stirring speed and \( D \)
is the impeller’s diameter. In their review on rotor-stator mixing devices (Atiemo-
Obeng and Calabrese, 2003) claim that droplets obtained in these homogenizers are
above the Kolmolgoroff length-scale, and thus they work in the turbulent inertia
regime. In the turbulent inertia regime, where the diameter of the droplets is larger
than \( \ell_\eta \), Hinze (1955) developed a theory where the maximum stable droplets \( \ell_\eta \) is
determined by the balance between the fluctuations of the hydrodynamic pressure
of the continuous phase and the Laplace pressure inside the droplets. Shinnar and
Church (1960) assumed that \( \bar{d}_{32} \propto \ell_\eta \), for an inviscid dispersed phase and for fully
turbulent flow they determined that

\[
\frac{\overline{d}_{32}}{D} \propto \text{We}^{-3/5}
\]  

(8.2)

Where \(\overline{d}_{32}\) is the Sauter mean diameter and \(\text{We}\) is the dimensionless Weber number \((\text{We} = \rho N^2 D^3 \sigma^{-1})\). Most of the correlations found in literature for emulsification technology use \(\overline{d}_{32}\) as the expression of central tendency to be determined. This is due to the importance that the interfacial surface to unit volume \(a_v\) has, which can be obtained from \(a_v = 6 \varphi / \overline{d}_{32}\), where \(\varphi\) is the volume fraction of the dispersed phase. \(\overline{d}_{32}\) can be calculated from

\[
\overline{d}_{32} = \frac{\sum_i f_v(d_i)}{\sum_i \frac{f_v(d_i)}{d_i}}
\]  

(8.3)

Where \(f_v(d_i)\) and \(d_i\) are the frequency by volume and the diameter of the \(i\)th droplet.

Energy dissipation theory has been verified by authors such as Chen and Middleman (1967) and has been used as starting point to extend dissipation theory to account for volume fraction (Leng and Calabrese, 2003), viscous dispersed phases (Davies, 1985; Calabrese et al., 1986) and different impellers (McManamey, 1979; Leng and Calabrese, 2003). Nevertheless, EL-Hamouz et al. (2009) found that tip speed correlated better their results than turbulent energy dissipation theory.

For high-shear rotor-stators Rueger and Calabrese (2013) found that their maximum droplet sizes were smaller than the Kolmolgoroff’s scale and could fit their data using the mechanistic model proposed by Shinnar and Church (1960)

\[
\overline{d}_{32} \propto (\text{WeRe})^{-1/3} \quad R^2 = 0.89
\]  

(8.4)

where \(\text{Re}\) is the dimensionless Reynolds number. Hall et al. (2011) could not correlate his results to any of the existing models, this was attributed to a combination of inertial and viscous stresses as the droplet were of the same order of magnitude as the Kolmolgoroff’s eddies. Hall et al. (2013) found that impeller speed was a more suitable scaling parameter, but that dissipation theory described the effect of
interfacial tension on $d_{32}$.

Karbstein and Schubert (1995) correlated their results in three different continuously operating emulsification machines for single or multiple passes using with energy density $E$. Energy density is the power $P_S$ times the mean residence time $\bar{t}_{res}$

$$\bar{d}_{32} = C_1 E^{C_2} = C_1 (P_S \bar{t}_{res})^{C_2} \quad (8.5)$$

Where $C_i (i = 1, 2, ..., i)$ are fit constants.

Hall et al. (2013) used the previous equation to correlated their results obtained for three rotor-stators of different scale. They found the dependency on $E$ was not as described in Equation 8.5. They proposed a correlation based on $N$ and $\bar{t}_{res}$.

$$\bar{d}_{32} = C_3 \bar{t}_{res}^{C_4} (ND)^{C_5} \quad (8.6)$$

They found $C_3 = 206$, $C_4 = -0.148$ and $C_5 = -1.19$ ($R^2 = 0.940$).

Power consumption is one of the most important characteristics in emulsification processes. As for stirred vessels with negligible gravitational forces and no vortexing, the Buckingham-π-theorem yields two dimensionless groups, namely the Reynolds number $Re$ and the Power number $Po$.

$$Re = \frac{ND^2 \rho}{\mu} \quad (8.7)$$

$$Po = \frac{P_S}{N^3 D^5 \rho} \quad (8.8)$$

For in-line rotor-stators, the total power $P_S$ is also a function of the flow rate passing through it. Kowalski (2009) suggested and validated that the power consumptions for Silverson rotor-stators is the addition of the power necessary to rotate the blades through the fluid and the power required to push the fluid through the rotor-stator. For negligible mechanical losses

$$Po = \frac{K_P}{Re} + Po_z + k_1 N_Q \quad (8.9)$$
8.2. Materials and equipment and methods

Where $K_P$ is the power proportionality constant for the laminar regime, $N_Q$ is the well known dimensionless Pumping Number $N_Q = \dot{Q}N^{-1}D^{-3}$, which related the flow rate and the impeller speed and diameter; $k_1$ is a flow proportionality dimensionless constant which can be approximated by $k_1 = (P_{O\text{U}} - P_{OZ})N_Q^{-1}$; and $P_{O\text{U}}$ and $P_{OZ}$ are the power numbers in the turbulent regime when the in-line rotor-stator is working solely as a pump (no imposed flow rate by an external pump) and when the flow rate is zero respectively.

8.2 Materials and equipment and methods

8.2.1 Power draw

8.2.1.1 Materials

To obtain the $P_O$ in the laminar and turbulent regimes we used two materials: (1) for the measurements in the laminar regime: a Silicon Oil with a viscosity of 1.95 Pa s and a density of 975.4 kg m$^{-3}$ obtained by a mixture of the 1 000 cSt and 10 000 cSt 200 Fluid Silicon Oil (Dow Corning, Michigan, U.S.A.) with dynamic viscosities of $9.47 \times 10^{-1}$ Pa s and $1.05 \times 10^1$ Pa s respectively; (2) for the measurements in the turbulent regime we used water, its properties were taken as $10^{-3}$ Pa s and 998.0 kg m$^{-3}$ for viscosity and density respectively.

The viscosity $\mu$ dependency on temperature $T$ for the Silicon Oil was obtained using a DV2T Viscometer (Brookfield Vicometers, Essex, U.K.) in a water bath. We obtained $\mu(T) = (2398 \text{Pa s K}/T) - 6.32 \text{Pa s}$.

8.2.1.2 Equipment and methods

Torque measurements were obtained using a TorqSense RWT321 1 Nm torque sensor (Sensor Technology, Oxfordshire, U.K.) for different $N$. The sensitivity of the torque meter is 1 mN m.

The Silicon Oil was used for the laminar regime power measurements at 9 different $N$ in the $8.4 \text{s}^{-1}$ to $101.1 \text{s}^{-1}$ range and water for the turbulent regime measurements.
for different $N$ in the 52.5 s$^{-1}$ to 154.3 s$^{-1}$ range.

All torque measurements $M$ were also performed in air (in-viscid limit) for all different $N$ to estimate bearing losses. The adjusted torque $M_{adj}$ is obtained by subtracting the torque measurements in air $M_{m,0}$ from the torque measurements in the presence of a viscous material $M_{m,f}$.

$$M_{adj} = M_{m,f} - M_{m,0} \quad (8.10)$$

$K_P$ and $P_0$ in terms of $M$ become

$$K_P = \frac{2\pi M}{\mu ND^3} \quad (8.11)$$

$$P_0 = \frac{2\pi M}{\rho N^2 D^5} \quad (8.12)$$

From the previous Eqs. it can be seen that $M \propto N$ in the laminar regime and $M \propto N^2$ in the turbulent regime. The intercept of $M_{adj}$ vs $N$ and $M_{adj}$ vs $N^2$ regressions for the laminar and turbulent regimes respectively give the bearing losses. These were subtracted from $M_{adj}$ to estimate the real $M$. $K_P$ and $P_0$ can finally be obtained from the slopes of $M$ vs $N$ and $M$ vs $N^2$ respectively.

Valves were added before and after the in-line rotor-stator for torque measurements, it was determined that these had a negligible effect on flow. For the zero flow measurements $P_{0Z}$ the valves in the line were closed. For the free flow measurements $P_{0Z}$, the rotor-stator was allowed to act as the pump. The flow rate $\dot{Q}$ was measured for different $N$ by taking a weighted sample over time. The pumping number $N_Q$ was obtained by linear regression of a $\dot{Q} - ND^3$ plot.

### 8.2.2 Emulsification kinetics

#### 8.2.2.1 Materials

A 200 Fluid 10 cSt Silicon Oil was used as dispersed phase for our water-in-oil emulsion. Silicon Oil is colourless, has a relative density of 0.934 and behaves as a Newtonian fluid. Its measured viscosity was $9.58 \times 10^{-3}$ Pa s which was measured
8.2. Materials and equipment and methods

A DV2T Vicometer (Brookfield Vicometers, Essex, U.K.) and a LV-1 spindle in the 10-60 min\(^{-1}\) range at 25°C.

As continuous phase a 1.0% concentration by weight sodium laureth sulphate (SLES) solution in water was used. The SLES used was a commercial grade surfactant branded as Texapon N701 (Cognis Ltd., Hertfordshire, U.K.) which contains \(\approx 70\%\) concentration by weight of SLES. The critical micelle concentration of SLES at 25°C has been previously determined to be \(8.4 \times 10^{-2} \text{g L}^{-1}\) by El-Hamouz (2007), the concentration used in this study is approximately 120 times the critical micelle concentration.

The interfacial tension of the Silicon Oil and the SLES/Water solution at room temperature was \(9.25 \times 10^{-3} \text{N m}^{-1}\), measured using a 9.545 mm standard Du Nuoy ring and a K11 Mk4 Tensiometer (KRUSS GmbH, Hamburg, Germany).

8.2.2.2 Equipment and methods

8.2.2.2.1 Coarse emulsion preparation A coarse emulsion was made prior to emulsifying in any of the arrangements using the high-shear mixer. To produce the coarse emulsion we used a 6-blade Rushton impeller with 6 cm of diameter coupled with a RW20 overhead stirrer (IKA-Werke GmbH & Co., Staufen im Breisgau, Germany) and a 24 cm diameter non-baffled vessel.

The SLES was dissolved before pouring the silicon oil. For the in-line and by-pass experiments a total of 9.90 L of 1.0% concentration by weight SLES/Water solution was prepared for every system. The impeller speed was set to 6.4 s\(^{-1}\), afterwards 0.10 L of silicon were poured into the vessel. Hence the total volume of the tank \(V_T\) was 10 L. For the batch experiments three different coarse emulsion volumes were prepared: 8.0 L, 10.0 L and 12.5 L. The amount of SLES, water and Silicon Oil used were scaled proportionally to keep the same concentrations.

These systems were emulsified for 24 h to ensure that droplet break-up would only occur in the rotor-stator and to ensure that all emulsions had the same starting point. The resulting DSD after emulsifying for 24 h is shown in Figure 8.1. The line and symbols in this Figure were obtained by averaging all the coarse emulsions produced.
for the different experiments, the error bars represent two standard deviations. As the standard deviation is relatively small, it was assumed that all the experiments had the same starting point.

8.2.2.2 Arrangements and equipment

The high-shear mixer used was a L5M-A Laboratory Mixer (Silverson Machines Ltd, Chesham, U.K.). This mixer has a 750 W motor with a nominal maximum speed of 133 s$^{-1}$ and an infinitely variable electronic speed control.

Three different types of emulsification arrangements were studied (Fig. 8.2): continuous, recycle and batch. The first two employing an in-line rotor-stator and the later a batch one. Both rotor-stators used the same rotor and the screens were kept as similar as possible.

Figure 8.3 shows the rotor and the screens used. The rotor had four blades and its dimensions were: an external diameter of 30 mm, a thickness of 5 mm and a height of 10 mm. The screens used have 240 holes in 6 rows of 40 holes each in pitch arrangement. Its external diameter is 32 mm, a height of 20 mm and a thickness of 1 mm.

For the continuous (Fig. 8.2a) and recycle (Fig. 8.2b) arrangements we used the
8.2. Materials and equipment and methods

Figure 8.2: Schematic diagram of the (a) Continuous, the (b) Recycle and (c) Batch arrangements.

Figure 8.3: Image of In-line (a) rotor and (8.3b) screen. (c) Batch rotor-stator.

same vessel, peristaltic pump impeller and high-shear mixer.

The peristaltic pump used was a 501 single channel pumphead (Watson Marlow, Cornwall, U.K.), which outflow is controlled by adjusting an arbitrary setting or pump number $pn$ ranging from 000 to 999. Its maximum discharge for $pn = 999$ is $2.9 \times 10^{-5} \text{ m}^3\text{s}^{-1}$.

The effect of the peristaltic pump on the DSD on the coarse emulsion was assessed by circulating the coarse emulsion through the peristaltic pump working at maximum speed ($pn = 999$) and then back to the tank without passing through the rotor-stator. The DSD was analysed after 0 min, 5 min, 10 min, 15 min, 25 min, 40 min, 60 min and 240 min. The DSD obtained for each time are shown in Figure 8.4. The drop size reduction due to the peristaltic pump is substantially lower than the one due to the rotor-stator. As it will be seen in Section 8.3.2.2, the rotor-stator produces two distinctive peaks, one belonging the initial coarse emulsion and a peak belonging
Table 8.1: Volumetric flow rate $\dot{Q}$ for each pump number $pn$ and number of experiments performed done for different $pn$ and Silverson’s rotational speeds $N$.

<table>
<thead>
<tr>
<th>$pn$ [-]</th>
<th>$\dot{Q}$ [m$^3$s$^{-1}$]</th>
<th>Silverson’s $N$ [s$^{-1}$]</th>
</tr>
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<tr>
<td>300</td>
<td>$9.08 \times 10^{-6}$</td>
<td>8 - 1 - 1 - 1</td>
</tr>
<tr>
<td>475</td>
<td>$1.51 \times 10^{-5}$</td>
<td>8 - 1 - 1 - 1</td>
</tr>
<tr>
<td>650</td>
<td>$2.22 \times 10^{-5}$</td>
<td>20 1 8 1 8</td>
</tr>
<tr>
<td>825</td>
<td>$2.39 \times 10^{-5}$</td>
<td>8 - 1 - 1 - 1</td>
</tr>
<tr>
<td>999</td>
<td>$2.90 \times 10^{-5}$</td>
<td>8 - 1 - 1 - 1</td>
</tr>
</tbody>
</table>

The $\dot{Q}$ for each $pn$ and the experimental matrix for the continuous arrangement are shown in Table 8.1.

![Figure 8.4: Effect of the peristaltic pump on the DSD for the by-pass arrangement for the maximum flow rate of the peristaltic pump.](image)

Figure 8.4: Effect of the peristaltic pump on the DSD for the by-pass arrangement for the maximum flow rate of the peristaltic pump.

8.2.2.2.3 Methodology: continuous arrangement

The coarse emulsion was fed to the rotor-stator working at different $N$ and $\dot{Q}$. The $\dot{Q}$ for each $pn$ and the experimental matrix for the continuous arrangement are shown in Table 8.1.

After the feeding tank empties, the rotor-stator and pipelines were washed by circulating fresh water and purging them afterwards. The tanks were swapped and samples were taken at 5 cm below the liquid level while the tank was being stirred. This procedure was repeated for the $n$ number of passes shown in Table 8.1.
8.2.2.2.4 Methodology: Recycle arrangement

The coarse emulsion was continuously fed to the rotor-stator and fed back into
the tank (See Fig. 8.2b). The experiments were carried out for four different \(pn\)
namely 300, 465, 650 and 999 (\(\dot{Q}\) for each \(pn\) shown in Table 8.1) and \(N = 150\, \text{s}^{-1}\).
The inlet and outlet tubes were located at opposite sides and axis to ensure good
mixing and representative sampling. The sampling point was located 5 cm below the
liquid level.

8.2.2.2.5 Methodology: Batch arrangement

For the batch arrangement 8.0 L, 10 L and 12.5 L of coarse emulsion were used. The rotor-stator was submerged
inside the vessel containing the coarse emulsion at a height equal to \(1/3\) of the
diameter of the vessel. The vessel was submerged in a water bath to help control
the temperature. Samples were collected with a syringe 5 cm below the air-water
interface for different emulsification times and stored in bottles for further analysis.
The samples were analysed within one hour of their collection.

8.2.2.2.6 Droplet size distribution analysis

The DSD was obtained by laser
diffraction using a Mastersizer 3000 (Malvern Instruments, Malvern, U.K.) coupled
with an Hydro EV (Malvern Instruments, Malvern, U.K.) dispersion unit. This
method allows to measure particles in the \(10^{-3}\, \mu\text{m} \) to \(3 \times 10^3\, \mu\text{m}\) range.
The Mastersizer 3000 measures the angular variation of intensity of scattered
light as the sample passes through a red and blue laser beams. The data is further
fit using Mie theory to obtain the DSD; Mie theory requires knowledge of the real
and imaginary components of the refractive index of the sample. The Mastersizer’s
software configuration was set to General Analysis model and allowing for multiple
modes. The refractive indices 1.333 and 1.399 for water and the silicon oil were
determined experimentally using a RFM390 Refractometer (Bellingham and Stanley
Ltd, Kent, U.K.) and the absorption index was taken as \(10^{-3}\) as recommended by
Malvern (Malvern Instruments, 2014) and as used by Hall et al. (2011).

Samples were collected using a syringe and analysed in the Mastersizer 3000
right after collection, except for the small time intervals for the recycle and batch
experiments where this was not feasible; in these cases samples were stored and
analysed as soon as possible (stored for maximum 30 min). The stability of the emulsions was tracked for a period of 48 h and no significant changes were occurred.

The samples were injected into the Hydro EV unit until reaching an obscuration rate in the 7 – 14% interval. Each sample was analysed 5 times by the instrument.

The data exported by the Mastersizer 3000 is reported as relative cumulative frequency distribution by volume $f_v(d_i)$, this is, that the sum of the frequencies is 100% ($\sum f_v(d_i) = 100\%$). First derivative tests and linear interpolation were used to obtain the modes $Mo$ of the DSD.

### 8.3 Results and discussion

#### 8.3.1 Power draw

For the laminar regime we obtained $K_P = 4.82 \times 10^2$. The torque lost from bending and noise was less than 3.21%. The experimental and modeled $Po$ comparison yielded $R^2 = 0.999$.

For the turbulent regime we found that the friction losses accounted for 24.5% of the minimum torque registered. We obtained $Po_Z = 1.69 \times 10^{-1}$, $Po_U = 2.16 \times 10^{-1}$, $N_Q = 2.83 \times 10^{-2}$ and $k_1 = 1.64$.

Figure 8.5 shows the experimental results for $Po$ as a function of $Re$ for both regimes. The curves in this Figure were obtained using Equation 8.9.

#### 8.3.2 Emulsification

##### 8.3.2.1 Continuous arrangement

The resulting DSDs obtained for $pn = 300$ for 8 passes are shown in the semi-log plot shown in Figure 8.6a. It is evident that the greatest size reduction occurred after the first couple of passes and that all the droplets that pass through the high-shear mixer suffer size reduction (100% conversion). The same figures shows that no equilibrium droplet size was reached after 20 passes and that the resulting DSDs are bimodal, nevertheless most of the volume is contained in the largest distribution as shown in
8.3. Results and discussion

Figure 8.5: Curves obtained using Equation 8.9. The $N_Q$ obtained for the free flow experiments was $2.83 \times 10^{-2}$.

The mode of the distributions after $n$ passes through the rotor-stator $M_{o_n}$ and Sauter mean diameter $\overline{d}_{32}$ for the 8 passes for five different $pn$ ($\dot{Q}$) are shown in Figure 8.7. This Figure shows that $\dot{Q}$ has an impact on the DSD. This was expected as the oil droplets have a larger mean residence time $\overline{t}_{res,S}$ inside the rotor-stator. Hall et al. (2011) analysed the effect of $\dot{Q}$ on $\overline{d}_{32}$ for a single pass for Silicon oils of different
viscosities (969 × 10⁻³ Pa s to 9.4 × 10⁻³ Pa s), he found a weak \( \dot{Q} \) dependency for the most viscous oils. Nevertheless for the same silicon oil used in this study (969 × 10⁻³ Pa s), he found a strong \( \dot{Q} \)-dependency with a power law index of 0.19 \( (R^2 = 0.923) \). Ludwig et al. (1997) found that smaller droplets were produced in a screw loop reactor at lower \( \dot{Q} \). He attributed it to an increase in the mean residence time \( t_{res} \) and thus to an increase of the probability of the droplets to be exposed to the maximum shear stress region inside the screw. Unfortunately, due to the complex flow inside screw loop reactors, such as back flow, no clear correlation was found. Gingras et al. (2005) carried out bitumen emulsification experiments at different \( \dot{Q} \) using a pilot scale rotor-stator but could not find a correlation due to the limited amount of experiments performed due to the difficulties they encountered controlling \( \dot{Q} \).

In Figure 8.6a it was observed that no steady-state DSD could be reached for \( n < 20 \) as the large peak continued reducing with \( n \). Nonetheless if \( \bar{d}_{32} \) is plotted as a function of \( n \) (as shown in Figure 8.7) an apparent plateau is observed, this was attributed to the presence of the droplets at the left tail of the DSD; small droplets have a larger area per unit volume thus a larger impact on the \( \bar{d}_{32} \). Provided that the DSD were monomodal and homoscedastic, \( n \) and \( N \) should have the same effect.

![Figure 8.7: Sauter mean diameter \( \bar{d}_{32} \) and Mode \( Mo_n \) as a function of the number of passes for five different pump numbers \( pn \).](image-url)
on the $M_o_n$, $\bar{d}_{32}$ or the maximum droplet size. Using the $M_o_n$ instead of the $\bar{d}_{32}$ allows neglecting the left tail of the DSD and focus on the size reduction of the large peak as depicted in Figure 8.7.

Häkansson et al. (2016) emulsified mayonnaise for up to 8 passes through a high-shear rotor-stator mixer and did not find a plateau. Jasińska et al. (2014) did experiments for 10 passes and did not find a steady-state but suggested the existence of a plateau, which was estimated using $\frac{d_{32}}{dt} \propto (\bar{d}_{32,\text{plateau}} - \bar{d}_{32})$. Nevertheless their results were plotted in a linear scale and the asymptotic behaviour might be due to a visual effect.

Provided the historic relevance of $\bar{d}_{32}$ in emulsion technology, the $\bar{d}_{32}$ of large distribution (see Fig. 8.6b) was estimated by adjusting to a Generalized Gamma distribution (GGf).

The GGf (Eqn. 8.13) is a three parameter distribution; a scale parameter $\lambda_G$ and two shape parameters $\kappa_G$ and $\tau_G$ that relate to the broadness and skewness of the distribution respectively. The GGf is versatile as it encompasses several probability density functions (ex. Gamma, Weibull, Rayleigh, Maxwell-Boltzmann) depending on the values of $\kappa_G$ and $\tau_G$ (Morteza Khodabin, 2010). The Log-normal distribution is obtained for $\tau_G = \infty$.

$$f_v(d_i) = \frac{\kappa_G}{\lambda_G \Gamma(\tau_G)} \left( \frac{d_i}{\lambda_G} \right)^{\tau_G \kappa_G - 1} \exp \left\{ - \left( \frac{d_i}{\lambda_G} \right)^{\kappa_G} \right\} \quad (8.13)$$

Figure 8.6b shows an example of how two GGf fit a bimodal DSD. The best fits were obtained by the Method of Least Squares and the Generalized Reduced Gradient algorithm tool in Excel (Microsoft, 2010). The shape factors $\tau_G$ and $\kappa_G$ for GGf1 were obtained by fitting all the experimental DSD while keeping the shape factors constant and allowing $\lambda_G$ to fit freely for each DSD. The best fit was given by $\tau_G = 3.85$ and $\kappa_G = 1.32$. It was found that the experimental DSD were homoscedastic. This method allowed comparing between the $M_o_n$ and the $\bar{d}_{32}$ if the DSD were monomodal. We found that $\bar{d}_{32} = M_o_n / 1.16$.

A more accurate relation would be obtained by substituting Equation 8.13 in the non-discrete version of Equation 8.3, unfortunately it produces an indefinite integral.
For Figure 8.6b the small daughter droplets account \( \approx 6\% \) of the total volume of the droplets, which reinforces our approach of using the \( Mo_n \) to follow the emulsification kinetics rather than a classical \( d_{32} \) approach.

### 8.3.2.1.1 Mode prediction

Two power law models were proposed to predict the \( Mo_n \) of the DSDs. The first uses an energy \( E \) argument and the second one uses \( N \) explicitly

\[
Mo_n = C_1 E^{C_2} \quad (8.14)
\]
\[
Mo_n = C_3 \bar{t}_{res,S} N^{C_5} \quad (8.15)
\]

Where \( \bar{t}_{res,S} \) is the mean residence time which is defined as the volume of the rotor-stator \( V_{swept} \) divided by \( \dot{Q} \). The data obtained by Hall et al. (2013) correlated well using the swept volume as \( V_{swept} \) for rotor-stators of three different sizes \( 1.27 \times 10^{-5} \text{ m}^3, 3.77 \times 10^{-5} \text{ m}^3 \) and \( 5.79 \times 10^{-4} \text{ m}^3 \). As \( V_{swept} \) was constant for all our experiments \( \bar{t}_{res,S} \propto nQ^{-1} \). The \( E \) in Equation 8.14 is the Power consumption \( P_S \) in Equation 8.9 times the mean residence time \( \bar{t}_{res,S} \) of the emulsion has spent inside the rotor-stator. Hence Eqs. 8.14 and 8.15 are

\[
Mo_n = C_1 \left[ \left( \frac{K_P}{Re} + PoZ + k_1 NQ \right) \rho N^3 D^5 \frac{n}{Q} \right]^{C_2} \quad (8.16)
\]
\[
Mo_n = C_3 \left( \frac{n}{Q} \right)^{C_4} N^{C_5} \quad (8.17)
\]

Multivariable linear and transformed power regressions were performed to fit our experimental data. The results of the fitting constants and their 95% confidence intervals are shown in Table 8.2 for Eqs. 8.16 and 8.17. The \( p \)-values obtained from significance testing were very small \( (< 2 \times 10^{-18}) \) for the three fitting constants.

The lower bound of the 95% confidence interval for \( C_4 \) is approximately \(-1/5\) (see Table 8.2), if the multivariable fit is performed making \( C_4 = -1/5 \) we obtain that \( C_5 \approx -6/5 \) which is the \( N \) index predicted by mechanistic models for the turbulent
Table 8.2: Obtained fitting parameters using Eqs. 8.16 and 8.17, mean error and their 95% confidence intervals represented as percentage.

<table>
<thead>
<tr>
<th></th>
<th>Eq. 8.16</th>
<th>Eq. 8.17</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean error</td>
<td>12.2%</td>
<td>4.38%</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.954</td>
<td>0.987</td>
</tr>
<tr>
<td>(C_1)</td>
<td>2539 ± 27%</td>
<td>7.438 (\times 10^4) ± 19%</td>
</tr>
<tr>
<td>(C_2)</td>
<td>-0.3786 ± 6.0%</td>
<td>-0.2241 ± 8.0%</td>
</tr>
<tr>
<td>(C_3)</td>
<td>-0.3786 ± 6.0%</td>
<td>-1.257 ± 6.1%</td>
</tr>
<tr>
<td>(C_4)</td>
<td>-0.2241 ± 8.0%</td>
<td>-1.257 ± 6.1%</td>
</tr>
<tr>
<td>(C_5)</td>
<td>-1.257 ± 6.1%</td>
<td>-1.257 ± 6.1%</td>
</tr>
</tbody>
</table>

inertia regime. Equation 8.17 becomes:

\[
M_{0n} = C_3 \left( \frac{n}{\dot{Q}} \right)^{-1/5} N^{-6/5}
\] (8.18)

Figure 8.8 shows the fits obtained for Equation 8.16 and Equation 8.18. The fit results show that the energy correlation (Equation 8.16) does not describe our experimental data whereas Equation 8.18 does. In Figure 8.8 it can be observed that for small \(E^{-0.379}\) (obtained for \(N = 150 \text{s}^{-1}\)) the data points follow a linear trend. However, \(E\) was not a good parameter to fit our results for different \(N\); Hall et al. (2013) reached the same conclusions.

![Figure 8.8](image-url)

**Figure 8.8:** (a) Obtained \(M_{0n}\) as a function of the energy consumption (see Eq. 8.14) The mean error is 12.17% and \(R^2 = 0.954\). (b) \(M_{0n}\) as a function of \((n/\dot{Q})^{-1/5} N^{-6/5}\) (see Eq. 8.18). The mean error obtained is 4.68% and \(R^2 = 0.985\).

With these changes \(C_3 = 4.129 \times 10^4\), the mean error becomes 4.682% and \(R^2 = 0.985\). Figure 8.9a shows how Equation 8.18 fit the experimental values and
Figure 8.9b the goodness of the fit.

Hall et al. (2011) found for $C_4 \approx -1/5$ ($R^2 = 0.923$) and Hall et al. (2013) $C_4 = -0.148$ ($R^2 = 0.940$). In the same paper, Hall et al. (2013) correlated single pass experiments to $E$, tip speed $ND$ and We. They found that the worst fit was given by $E$ ($R^2 = 0.932$), followed by We ($R^2 = 0.956$) and the best fit was given by $(ND)^{-1.13}$ ($R^2 = 0.974$). They concluded that $ND$ gives the best correlation.

We also found that the worst fit was given by adjusting to $E$. Hinze’s theory for turbulent inertia predicts a maximum drop dependency on $N$ of $-6/5$ which is in agreement with our results. For homoscedastic monomodal DSD the mode and maximum droplet size should have the same $N$ dependency.

![Figure 8.9](image)

**Figure 8.9:** (a) $M_o_n$ as a function of $n$ for the experiments done for 8 passes or more, the lines were done using Equation 8.18 and (b) the goodness of fit. The value for $R^2$ is 0.984 and the mean error is 3.188%. The dashed lines represent a ±10% deviation from the mean.

### 8.3.2.2 Recycle arrangement

The schematic diagram of the Recycle arrangement was first presented in Figure 8.2b. In Figures 8.10a and 8.10b an example of the evolution of the density and cumulative distributions for different times are shown. In these Figures two very distinctive distributions can be observed: the one of the mother (coarse emulsion) and daughter droplets.

From the experimental results two parameters can be obtained: (1) The volume
8.3. Results and discussion

fraction of the mother droplets $\phi_0$ (coarse emulsion) and (2) the $Mo_n$ of the daughter droplets. The evolution of these two parameters with time are shown in Figure 8.11. In Figure 8.11a, the volume fraction of the non-coarse droplets $(1 - \phi_0)$ is shown for different emulsification times for four different imposed $\dot{Q}$. As expected, lower $\dot{Q}$ require more time to reach full conversion $(1 - \phi_0 = 1)$ as the mean residence time in the vessel $t_{res,T}$ is longer.

The $Mo_n$ evolution of the daughter droplets as a function of time is shown in Figure 8.11b. These curves present a plateau for short times followed by a reduction in size. The plateau is present because at short emulsification times most of the emulsion has passed only once through the rotor-stator; hence the plateau should have the same value as the $Mo_n$ obtained for the continuous arrangement for the same $\dot{Q}$ for $n = 1$. As time progresses, a mixture of droplets that have passed $n$ and $n + 1$ number of passes will be present in the vessel further decreasing the mode. Analogously to the continuous arrangement, low $\dot{Q}$ produce smaller droplets due to an increase in $t_{res,S}$.

A mass balance was proposed to link the results obtained for the continuous and recycle arrangements.

8.3.2.2.1 Recycle mass balance The schematic representation of the recycle arrangement used for the mass balance is shown in Figure 8.12. This Figure shows

![Figure 8.10: (a) Probability density and (b) Cumulative droplet size distribution for different times for a $\dot{Q} = 2.22 \times 10^{-5}$ m$^3$ s$^{-1}$ ($pn = 650$) and $N = 150$ s$^{-1}$.]
Figure 8.11: (a) Volume fraction of non-coarse droplets $(1 - \phi_0)$ as a function of time for four different $pn$ and (b) Mode evolution of daughter droplets as a function of time for different $pn$.

Figure 8.12: Schematic representation of the Recycle arrangement, the mass balance was done for elements inside the envelope.

that the volumetric inflow and volumetric outflow are the same, the volume of the tank $V_T$ and density of the emulsion are constant. For a given DSD corresponding to $n$ number of passes through the rotor-stator, the accumulation will be equal to the droplets flowing into the system $\dot{Q}\phi_{n+1}$ minus the ones leaving the system $\dot{Q}\phi_n$. Where $\phi_{n+1}$ and $\phi_n$ are the concentration of the emulsion that have passed $n + 1$ and $n$ number of times through the rotor-stator. The mass balance yields

$$V_T \frac{d}{dt}\phi_n = \dot{Q}(\phi_{n+1} - \phi_n) \quad (8.19)$$
The results of the mass balance for $n$ number of passes through the rotor stator yields

$$
\phi_n = \frac{1}{n!} \left( \frac{t}{t_{res,T}} \right)^n \exp \left( - \frac{t}{t_{res,T}} \right) \quad (8.20)
$$

This function is also known as the Poisson distribution, where $n$ is the number of different possible events and $t/t_{res,T}$ is the average number of events per interval. The derivation of Equation 8.19 into Equation 8.20 is explained in 8.A.

Tamir (1998) defines the Poisson chain as the simplest of the discontinuous or pure birth Markov process. Tamir (1998) reviewed Markov chain processes for particulate solids such as size reduction and granulation.

8.3.2.2.2 Prediction of daughter droplet’s creation rate and size  Equation 8.20 allows to predict the volume fraction for droplets that have passed $n$ number of times through the rotor-stator. Figure 8.13 shows how the experimental results compare with the ones predicted by our model. The $R^2$ and average error found were 0.989 and 3.34% respectively.

![Figure 8.13](image)

**Figure 8.13:** Volume fraction of non-coarse droplets $1 - \phi_0$ as a function of time for different $pn$. The lines were obtained using Equation 8.20 ($R^2 = 0.989$ and a mean error of 3.34%).

To predict the mode of the daughter droplets (previously shown in Fig. 8.11b) for the recycle arrangement $M_{oRec}$ we assumed that the DSD for all $n$ passes are
homoscedastic (see Fig. 8.6a in Sec. 8.3.2.1). The mode of the daughter droplets for a given time should equal the summation of the product $M_o_n$ of the $n$th pass and its volume fraction $\phi_n$ normalized to one (by dividing by $(1 - \phi_0)$).

$$M_{oRec} = \sum_{n=1}^{\infty} \frac{\phi_n}{1 - \phi_0} M_o_n$$

where the $M_o_n$ is given by Equation 8.18. Substituting Equation 8.18 in Equation 8.21 gives

$$M_{oRec} = \frac{C_3 \dot{Q}^{1/5}}{N^{6/5}} \sum_{n=1}^{\infty} \frac{\left(\frac{t}{t_{res,T}}\right)^n}{n! n^{1/5}} \exp \left(-\frac{t}{t_{res,T}}\right)$$

The form of this equation will be used further on but can be simplified into

$$M_{oRec} = \frac{C_3 \dot{Q}^{1/5}}{N^{6/5}} \sum_{n=1}^{\infty} \frac{1}{n^{1/5} n!} \left(\frac{t}{t_{res,T}}\right)^n$$

The fit of the experimental data using Equation 8.23 and the corresponding plots to asses the goodness of the fit are shown in Figures 8.14a and 8.14b.

![Figure 8.14](image_url)

**Figure 8.14:** (a) Experimental data and fit using Equation 8.23 and (b) the goodness of the fit ($R^2 = 0.977$ and a mean error of 2.317%); the dashed lines represent show a ±10% variation.

As time progresses, the more number of times the emulsion has passed through
the rotor-stator, therefore $t/\bar{t}_{res,T}$ and $n$ are connected. For large values of $t/\bar{t}_{res,T}$ the use of Equation 8.22 results impractical due to the computing limitations that the term $n!$ implies; this can be solved with the following limit

$$\lim_{\frac{t}{\bar{t}_{res,T}} \to \infty} \sum_{n=1}^{\infty} \left( \frac{t}{\bar{t}_{res,T}} \right)^n n! \exp \left( -\frac{t}{\bar{t}_{res,T}} \right) = \left( \frac{t}{\bar{t}_{res,T}} \right)^{-\frac{1}{5}}$$

(8.24)

The proof of Equation 8.24 can be consulted in 8.B. For $t/\bar{t}_{res,T} > 2$ the error of using Equation 8.24 is small, thus Equation 8.22 becomes

$$M_{o_{Rec}} = \frac{C_3 \dot{Q}^{1/5}}{N^{\eta/5}} \left( \frac{t}{\bar{t}_{res,T}} \right)^{-\frac{1}{5}}$$

(8.25)

Figure 8.15 shows the $M_{o_{Rec}}$ as a function of $t/\bar{t}_{res,T}$ for the different $pn$ ($\dot{Q}$) used and the fit using Equation 8.25. This Figure shows that our simplified model captures the $M_{o_{Rec}}$ dependency on $t/\bar{t}_{res,T}$ and $\dot{Q}$ for large $t/\bar{t}_{res,T}$ using only the data we obtained for the continuous arrangement.
8.3.2.3 Continuous-recycle arrangement comparison

If droplets with a certain mode want to be obtained using the same rotor-stator, $\dot{Q}$ and $N$, Equation 8.18 and Equation 8.23 can be equalized to obtain the number of passes in the continuous arrangement $n_{cont}$ equivalent to the $t/t_{res,T}$ in the recycle one

$$n_{cont} = \left[ \frac{\exp \left( \frac{t}{t_{res,T}} \right) - 1}{\sum_{n=1}^{\infty} \frac{1}{n^{1/5} n!} \left( \frac{t}{t_{res,T}} \right)^n} \right]^{5} \tag{8.26}$$

The log-log plot of Equation 8.26 is shown in Figure 8.16 where $t/t_{res,T}$ of the by-pass system is plotted as a function of the number of passes $n_{cont}$ of the continuous emulsification arrangement.

![Figure 8.16: $t/t_{res,T}$ as a function of n using Equation 8.26. The right vertical axis shows some conversion rate values for a given $t/t_{res,T}$ ($n = 0$ in Eq. 8.20). The shadowed area shows where the Recycle arrangement produces smaller daughter droplets, the contrary is true for the Continuous arrangement.](image)

The curve exhibits an asymptote at $n = 1$ as $t/t_{res,T}$ tends to zero, which is expected as a by-pass system can never have 100% droplets of size $n = 1$ due to mixing. The shadowed area shows where the recycle arrangement produces smaller droplets. Nevertheless the mother droplet conversion is lower than 100% at short times for the recycle arrangement whereas full conversion is obtained after only one pass in the continuous arrangement. At longer times, the slope of $t/t_{res,T}$ against
n is one and thus the efficiency of both operation modes is equal. This can be proven for $t/t_{res,T} \to \infty$ by equalizing Equation 8.18 and Equation 8.25 which yields $n_{cont} = t/t_{res,T}$.

### 8.3.2.4 Batch arrangement

Figure 8.17a shows the evolution of the DSD for the 12.5 L batch as a function of time. As for the recycle arrangement, most of the droplet size reduction occurs at short times. For our shortest sampling time (30 s) no traces of the coarse emulsion were detected. The sizes produced with the batch arrangement were considerably smaller than the ones produced with the continuous and recycle arrangements, presumably due to the larger pumping capacity of the batch rotor-stator, larger $Po$ and the influence of geometrical differences between the in-line and batch rotor-stator.

![Figure 8.17: (a) Obtained DSD for the 12.5 L batch for $N = 150 \text{s}^{-1}$ for different time and (b) $Mo$ evolution as a function of time for three different batch volumes.](image)

The $Mo$ evolution as a function of emulsification time for three different $V_T$ are shown in Figure 8.17b. This Figure shows that the $Mo$ has a power law dependency on time and that $V_T$ has a small influence on droplet size. The power law index for the three $V_T$ are similar and decrease as $V_T$ increases.

Analogously to the continuous and recycle arrangement comparison, it is desirable to link the emulsification kinetics of the continuous and batch arrangements. The mass balance for the batch arrangement is homologous to the one developed in
Sec. 8.3.2.2. The absence of mother droplets for emulsification times as short as 30 s indicate that \( \dot{Q} \) is large compared to \( V_T \). The flow rates of the mixer for our experimental conditions are unknown, nevertheless the absence of mother droplets and of a plateau for low emulsification times indicate that

\[
\frac{t}{\overline{t}_{res,T}} = \frac{\dot{Q}}{V_T} t > 2
\]  

(8.27)

For the largest volume used (12.5 L) and the shortest sampling time (30 s) \( \dot{Q} > 0.833 \text{ L s}^{-1} \).

As \( t/\overline{t}_{res,T} > 2 \) Equation 8.25 can be used to analyse our experimental results by making \( \overline{t}_{res,T} = V_T/\dot{Q} \) gives

\[
Mo = \frac{C_3 V_T^{1/5}}{N^{9/5}} t^{-1/5}
\]  

(8.28)

This Equation resulting from a mass balance shows a week \( V_T \) dependency which can explain the results shown in Figure 8.17b. Furthermore, the index of the droplet reduction rates are close to \(-1/5\) predicted by our model. The index deviation of our experimental results could be related to temperature variations. At short times, when the temperature of the three emulsification volumes is the closest, the \( Mo \) of the 12.5 L batch are the largest as predicted by Equation 8.28. As time progresses temperature rises the power-law indexes decrease and the \( Mo \) for the different volumes crossover.

Fitting our results to Equation 8.28 gives \( C_3 = 3.437 \times 10^4 \pm 3.2\% \) (95% confidence interval) which is \( \approx 3/10 \) the \( C_3 \) value obtained for the in-line rotor-stator. This discrepancy was attributed to a difference in the \( Po \) and geometry factors as the rotor-stator are not identical. The goodness of the fit can be assessed in Figure 8.18.

### 8.4 Conclusions

A stochastic model to link the results of three operation arrangements using high-shear was reported for the first time. The mode of the distributions were used to follow the emulsification kinetics and yielded higher \( R^2 \) than any other results
8.4. Conclusions

Figure 8.18: Goodness of fit using Equation 8.28 for $C_3 = 3.437 \times 10^4$ ($R^2 = 0.972$ and a mean error of 4.61%). The dashed lines represent a ±10% deviation from the mean.

reported for high-shear mixer emulsification. This was attributed to the noise that bimodality causes when calculating the Sauter mean diameter. The two generalized gamma function fit we performed reinforced our suggestion of neglecting the small daughter droplets as these only account for the 6% of the total droplets by volume. Two correlations as a function of the mean residence time $t_{\text{res},S}$ inside the in-line high-shear mixer were tested; the first one using energy $E$ arguments and the second one using an explicit rotational speed power-law dependency. The first correlation failed in describing droplet size reduction, whereas the second yielded a correlation which not only predicts the modes of the daughter drops but is in agreement with values previously reported in literature by Hall et al. (2011).

For the recycle operation arrangement we followed the emulsification kinetics using the model developed for the continuous arrangement and a mass balance equation. The mass balance yielded a Poisson distribution which allowed to follow the disappearance rate of the mother droplets. This mass balance was further coupled with the kinetic model developed for the continuous arrangement to follow the droplet size reduction of the daughter droplets. Assuming that the daughter droplet for $n$ number of passes are homoscedastic and that the vessel is perfectly mixed our model yielded an average error of 2.37% and a $R^2 = 0.977$. 
The comparison between the arrangements using the high-shear mixer was done by calculating how many passes in the continuous arrangement ($n_{cont}$) and number of vessel volumes ($t/t_{res,T}$) have to pass through the rotor-stator to obtain daughter droplet of the same size. Our model suggests that for short emulsification times the recycle arrangement produces smaller daughter droplets but will have mother droplets present; as mother droplets disappear, both systems have the same efficiency.

For the batch system comparison our Poisson chain model proposed suggest that for $\dot{Q}/VT > 2$ there is a week $V_T$-$Mo$ dependency. The relative small discrepancy in the size reduction rate was attributed to the rise in temperature. The scale factor of our batch model could not be linked to the in-line results presumably due to geometry and power consumption differences.

The models developed in this study account for processing variable such as arrangement, mean residence times (vessel and rotor-stator) and stirring speed while excluding the effect of material properties such as viscosity and density of the continuous and dispersed phases and interfacial tension. Nevertheless, the link in-between arrangements are based on mass balances and thus it should hold for other materials provided that the model for the continuous arrangement is known.

### 8.5 Bibliography


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**Appendix**

**Appendix 8.A Recycle mass balance**

Using Equation 8.19 as starting point, and making $\bar{t}_{res,T} = V_T/\dot{Q}$.

\[
\frac{d}{dt} \phi_n = \frac{1}{\bar{t}_{res,T}} (\phi_{n+1} - \phi_n) \quad (8.29)
\]

**Mass balance for $\phi_0$** The coarse droplets ($n = 0$) are not fed back into the vessel because the Silverson rotor-stator has a 100% conversion rate (as shown in the Continuous arrangement experiments). Equation 8.29 becomes

\[
\frac{d}{dt} \phi_0 = -\frac{1}{\bar{t}_{res,T}} \phi_0 \quad (8.30)
\]

\[
\frac{d\phi_0}{\phi_0} = -\frac{dt}{\bar{t}_{res,T}} \quad (8.31)
\]
Integrating

\[
\int \frac{d\phi_0}{\phi_0} = -\frac{1}{t_{res,T}} \int dt \\
\ln \phi_0 = -\frac{t}{t_{res,T}} + C_{int}
\]

Using the Boundary condition \( \phi_0 = 1 \) at \( t = 0 \), \( C_{int} = 0 \) yielding

\[
\phi_0 = \exp \left( -\frac{t}{t_{res,T}} \right)
\]

**Mass balance \( \phi_1 \).** For \( \phi_1 \), the amount of droplets fed into the systems is equal to the amount of droplets for \( n = 0 \) (coarse emulsion) that left the system, which is given by Equation 8.34, thus Equation 8.29 becomes

\[
\frac{d}{dt} \phi_1 = \frac{1}{t_{res,T}} \left[ \exp \left( -\frac{t}{t_{res,T}} \right) - \phi_1 \right]
\]

Expanding

\[
\frac{d}{dt} \phi_1 + \frac{1}{t_{res,T}} \phi_1 = \frac{1}{t_{res,T}} \exp \left( -\frac{t}{t_{res,T}} \right)
\]

Which is first-order nonhomogeneous differential equation of the form

\[
\frac{dy}{dx} + Ay = A \exp(-Ax)
\]

Its solution is

\[
y = C_{int} \exp(-Ax) + Ax \exp(-Ax)
\]

\[
\phi_1 = C_1 \exp \left( -\frac{t}{t_{res,T}} \right) + \frac{t}{t_{res,T}} \exp \left( -\frac{t}{t_{res,T}} \right)
\]

Using the Boundary Condition \( t = 0 \), \( \phi_1 = 0 \), \( C_{int} = 0 \), Equation 8.39 becomes

\[
\phi_1 = \frac{t}{t_{res,T}} \exp \left( -\frac{t}{t_{res,T}} \right)
\]
Chapter 8. Kinetics for high-shear mixers

Table 8.A.1: Resulting mass balances

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\phi_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$\exp\left(-\frac{t}{t_{res,T}}\right)$</td>
</tr>
<tr>
<td>1</td>
<td>$\left(\frac{t}{t_{res,T}}\right)^2 \exp\left(-\frac{t}{t_{res,T}}\right)$</td>
</tr>
<tr>
<td>2</td>
<td>$\frac{1}{2} \left(\frac{t}{t_{res,T}}\right)^3 \exp\left(-\frac{t}{t_{res,T}}\right)$</td>
</tr>
<tr>
<td>3</td>
<td>$\frac{1}{6} \left(\frac{t}{t_{res,T}}\right)^4 \exp\left(-\frac{t}{t_{res,T}}\right)$</td>
</tr>
<tr>
<td>4</td>
<td>$\frac{1}{24} \left(\frac{t}{t_{res,T}}\right)^5 \exp\left(-\frac{t}{t_{res,T}}\right)$</td>
</tr>
<tr>
<td>$n$</td>
<td>$\frac{1}{n!} \left(\frac{t}{t_{res,T}}\right)^n \exp\left(-\frac{t}{t_{res,T}}\right)$</td>
</tr>
</tbody>
</table>

Mass balance $\phi_2$ Substituting $8.40$ in $8.29$ for $n = 2$ yields an equation of the form

$$\frac{dy}{dx} + Ay = A^2 \exp(-Ax)$$  \hspace{1cm} (8.41)

Using the same boundary conditions, the integration constant is zero and we obtain

$$\phi_2 = \frac{1}{2} \left(\frac{t}{t_{res,T}}\right)^2 \exp\left(-\frac{t}{t_{res,T}}\right)$$  \hspace{1cm} (8.42)

Mass balance $\phi_n$ for $n > 2$. The process was repeated for $n = 3$ and $n = 4$. The pattern of the pre-exponential factor was noticed; the mass balances for $n = 0, 1, 2, 3, 4$ and the generalization for $n$ number of passes are shown in the Table 8.A.1.

Appendix 8.B Proof of Equation 8.24

For large $t/t_{res}$ the summation term in Equation 8.22 can be simplified using the following limit

$$\lim_{\frac{t}{t_{res,T}} \to \infty} \sum_{n=1}^{\infty} \frac{\left(\frac{t}{t_{res,T}}\right)^n \exp\left(-\frac{t}{t_{res,T}}\right)}{n!t^{1/5}} = \left(\frac{t}{t_{res,T}}\right)^{-1/5}$$  \hspace{1cm} (8.43)

The plot of the summation is shown in Figure 8.B.1a where the convergence of the summation and $(t/t_{res,T})^{-1/5}$ is proven. This can be further demonstrated using
Equation 8.44 and Figure 8.B.1b. This plot shows that the simplification proposed can be used with relatively small error (< 5%) for \((t/\bar{t}_{res,T})^{-1/5} > 2\).

\[
\lim_{t_{res,T} \to \infty} \sum_{n=1}^{\infty} \frac{(t_{res,T})^n}{n!} \left[ 1 - \exp \left( -\frac{t}{t_{res,T}} \right) \right] = 1 \tag{8.44}
\]

\[
\sum_{n=1}^{\infty} \left( \frac{t}{t_{res,T}} \right)^n \exp \left( -\frac{t}{t_{res,T}} \right) \left[ 1 - \exp \left( -\frac{t}{t_{res,T}} \right) \right] = 1 \tag{8.44}
\]

**Figure 8.B.1:** (a) Shows the plot of Equation 8.43 and (b) of Equation 8.44
Chapter 9

Linking continuous and recycle emulsification kinetics for in-line mixers

Carrillo De Hert, S. and Rodgers, T.L. Linking continuous and recycle emulsification kinetics for in-line mixers. *Chemical Engineering Research and Design* [submitted].

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Abstract

In-line high-shear mixers can be used for continuous or batch dispersion operations depending on how the pipework is arranged. In our previous work (Carrillo De Hert and Rodgers, 2017a) we performed a transient mass balance to establish the link in-between these two arrangements; however this model was limited to the estimation of the mode of dispersed phases yielding simple monomodal drop size distributions. In this investigation we expanded the previous model to account for the shape of the whole drop size distribution. The new model was tested by performing experiments under different processing conditions and using two highly viscous dispersed phases which yield bimodal drop size distributions. The results for the continuous arrangement experiments were fit using two log-normal functions and the results for the recycle arrangement by implementing the log-normal function in the previously published mass balance. The new model was capable of predicting the $d_{32}$ for different emulsification times with a mean absolute error of 12.32%. The model presented here was developed for liquid blends, however the same approach could be used for milling or de-agglomeration operations.

9.1 Introduction

In-line rotor-stators are one of the most promising equipments that have been implemented to intensify dispersion processes. Their increase in popularity has been due to their capacity to generate highly-localised strong energy dissipation regions. In-line rotor-stators are installed in the pipework and two different types of operation arrangements are possible depending on the direction of the outflow of the rotor-stator. (1) If the outflow is directed to a secondary vessel or process, the rotor-stator is operated in a continuous fashion; evidently the material can be processed $n$ number of times to cause further size reduction, “multi-pass processing” occurs when the material is processed $n > 1$ times. (2) On the other hand, if the outflow is directed to the feeding tank it is operated in a recycle arrangement and processing time and volume becomes important processing parameters. The schematic representation of both configurations is shown in Figure 9.1.
9.1. Introduction

Figure 9.1: Schematic representation of (a) the continuous arrangement and (b) the recycle arrangement.

9.1.1 Previous study: continuous arrangement

In one of our previous studies (Carrillo De Hert and Rodgers, 2017a), we installed a pump at the feed of the rotor-stator to control the flow rate $\dot{Q}$ and studied the emulsification kinetics using a 10 cSt silicon oil (SiOil). The 10 cSt SiOil yielded monomodal drop size distributions (DSD). The characteristic measure of central tendency used was the mode $M_{o_n}$ of the DSD, where the sub-index refers to the $n$th pass. For a rotor-stator working at given stirring speed $N$, the multi-pass data for the continuous arrangement was well correlated by

$$M_{o_n} = A_1 \left( \frac{n}{\dot{Q}} \right)^{-1/5} N^{-6/5} \quad \text{for } n = 1, 2, \ldots, n - 1, n \quad (9.1)$$

where $(n/\dot{Q})$ is proportional to the residence time of the material inside the rotor-stator. We attribute the effect of mean residence time to the internal recirculation or fluid re-entrainment inside the rotor-stator, this has been reported by authors such as Özcan-Taskn et al. (2011) and Mortensen et al. (2017) using particle image velocimetry and by Xu et al. (2014) using laser Doppler anemometry. Therefore the lower $\dot{Q}$ the more times the emulsions re-enters the region where drop breakup occurs.

We did not do experiments at different scales, however there is strong evidence that the characteristic volume of the rotor-stator is its swept volume (Hall et al., 2013). Hall et al. (2011) did not find a correlation in-between the coarse emulsion ($n = 0$) and the one at the outlet of the rotor-stator, therefore in the continuous
In a second study (Carrillo De Hert and Rodgers, 2017b), we extended Equation 9.1 to account for the effect of the viscosity of the dispersed phase $\mu_d$ by doing experiments using SiOils in the 10 cSt-30000 cSt range. We found that SiOils thicker than 350 produced bimodal DSD. The mode of the large $M_{o_{n,L}}$ and the mode of the small $M_{o_{n,s}}$ drops were used to characterise the drop sizes of the emulsion, for the same geometry used in Carrillo De Hert and Rodgers (2017a) the following correlations were obtained for the SiOil in the 10 cSt-2760 cSt range:

\[ M_{o_{n,L}} = 1.18 \times 10^5 \mu_d^{0.365} N^{-1.05} \left( \frac{n}{Q} \right)^{-1/n} \]  \hspace{1cm} (9.2)

\[ M_{o_{n,s}} = 1.69 \times 10^3 \mu_d^{-0.365} N^{-1.05} \]  \hspace{1cm} (9.3)

Furthermore, we correlated the DSDs using a simple mixing rule:

\[ f_{v,n,T}(d_i) = (1 - \phi_{s,n}) f_{v,n,L}(d_i) + \phi_{s,n} f_{v,n,s}(d_i) \]  \hspace{1cm} (9.4)

where $f_{v,n,T}(d_i)$ is the total drop size distribution; $f_{v,n,L}(d_i)$ and $f_{v,n,s}(d_i)$ are the drop size distribution of the large and small drops respectively; and $\phi_{s,n}$ is the volume fraction of the small drops for the $n$th pass through the rotor-stator. We further used Generalised Gamma probability density functions for $f_{v,n,L}(d_i)$ and $f_{v,n,s}(d_i)$ and the power-law function below for $\phi_{s,n}$:

\[ \phi_{s,n} = C_{\phi,0} \mu_d^{C_{\phi,\nu_d}} N^{C_{\phi,N}} \left( \frac{n}{Q} \right)^{C_{\phi,T}} \]  \hspace{1cm} (9.5)

### 9.1.2 Previous study: recycle arrangement

In the recycle arrangement (see Fig. 9.1b) a coarse emulsion ($t = 0$) is pumped through the rotor-stator and back into its feeding vessel. For $t > 0$ it is expected to have a mixture of material that has passed $n$ times, the fraction of each material $\phi_n$ is a function of time $t$, volume of the vessel $V_T$ and of $Q$. As can be expected,
the DSD distribution of the coarse emulsion is important in this arrangement until its complete consumption.

In Carrillo De Hert and Rodgers (2017a) we did a transient mass balance to obtain $\phi_n$ as a function of the aforementioned variables, the expression for $\phi_n$ reads

$$\phi_n = \frac{1}{n!} \left( \frac{t}{t_{\text{res,}T}} \right)^n \exp\left(-\frac{t}{t_{\text{res,}T}}\right)$$  \hspace{1cm} (9.6)

where $t_{\text{res,}T} = \frac{V_T}{\dot{Q}}$ is the mean residence time of the material in the tank. Equation 9.6 was tested by (1) measuring the depletion of the coarse emulsion as a function time, as the $n = 0$ and $n > 0$ materials produced two very distinct peaks and by (2) predicting the mode of the distribution of the mixture of the $n > 0$ drops $Mo_{Rec}$. Provided that the continuous arrangement experiments showed that the DSD for $n > 0$ were monomodal and had the same shape, a mixing rule to estimate the $Mo$ was used

$$Mo_{Rec} = \sum_{n=1}^{\infty} \frac{\phi_n}{1 - \phi_0} Mo_n$$  \hspace{1cm} (9.7)

Substituting Equation 9.1 and 9.6 in Equation 9.7 lead to

$$Mo_{Rec} = \frac{A_1 \dot{Q}^{1/5}}{N^{5/5}} \left[ \exp\left(\frac{t}{t_{\text{res,}T}}\right) - 1 \right] \sum_{n=1}^{\infty} \frac{1}{n^{3/5} n!} \left(\frac{t}{t_{\text{res,}T}}\right)^n$$  \hspace{1cm} (9.8)

Equations 9.8 is limited to monomodal distributions and to the calculation of the mode, in this study we will expand our two previous studies (Carrillo De Hert and Rodgers, 2017a, b) to systems yielding bimodal drop size distributions, which are common for highly viscous dispersed phases.

9.2 Materials and equipment and methods

9.2.1 Materials

Two 200 Silicone Fluid (dimethyl siloxane, Dow Corning, Michigan, USA) of 350 cSt and 1000 cSt nominal kinematic viscosity were used as dispersed phases. Their
relevant properties are listed in Table 9.1. The specific gravity $s$ was taken as given by the provider and the $\mu_d$ were obtained using a DV2T Viscometer (Brookfield Viscometers, Essex, UK).

As continuous phase 1 wt.% of sodium laureth sulfate (SLES) in water was used; SLES is the surfactant, in Texapon N701 (Cognis, Hertfordshire, UK) at 70wt.%.

The surfactant concentration is well-above its critical micellar concentration. The interfacial tension in-between the dispersed phases and the continuous phase $\sigma$ are also shown in Table 9.1; these were obtained using a K11 Mk4 Tensiometer (KRUSS, Hamburg, Germany) and a KRUSS platinum-iridium standard ring.

Table 9.1: Relevant properties of the Silicon Oils used at 25°C. These same properties have been previously reported in Carrillo De Hert and Rodgers (2017a,b)

<table>
<thead>
<tr>
<th>SiOil [cSt]</th>
<th>$s$ [-]</th>
<th>$\mu_d$ [Pa s]</th>
<th>$\sigma$ [N m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>0.965</td>
<td>$3.279 \times 10^{-1}$</td>
<td>$9.129 \times 10^{-3}$</td>
</tr>
<tr>
<td>1000</td>
<td>0.970</td>
<td>$9.474 \times 10^{-1}$</td>
<td>$9.172 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

9.2.2 Equipment

The same L5M-A Laboratory Mixer (Silverson Machines, Chesham, UK), rotor, screen and peristaltic pump in Carrillo De Hert and Rodgers (2017a,b) were used for this study. The characteristics of the rotor and the screen are listed in Table 9.2.

Table 9.2: Geometrical characteristics of the rotor-stator.

<table>
<thead>
<tr>
<th>Rotor</th>
<th>Screen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>3.0 cm</td>
</tr>
<tr>
<td>Number of blades</td>
<td>4</td>
</tr>
<tr>
<td>Height</td>
<td>1.0 cm</td>
</tr>
<tr>
<td>Blade thickness</td>
<td>0.5 cm</td>
</tr>
<tr>
<td>Maximum speed (nominal)</td>
<td>$133 \text{s}^{-1}$</td>
</tr>
</tbody>
</table>

9.2.3 Methods

The coarse emulsions were prepared using an unbaffled cylindrical vessel with diameter of 25 cm and a 8-blade Rushton turbine with a diameter of 6.62 cm. After dissolving
the SLES completely (1.0wt%), the stirring speed was fixed to the desired stirring speed and the SiOil was poured (1v.%). The systems were stirred for 24 h to ensure that all drop break-up was due to the rotor-stator and not to the impeller in the vessel.

For the continuous arrangement, the coarse emulsion was fed to the rotor-stator at the experimental conditions specified in Table 9.3. After the volume in feeding tank was consumed, the streamlines were rinsed with fresh water and purged. The tanks were swapped and the process was repeated for n number of passes. Samples were taken after the whole volume was processed while the tank was being stirred.

The recycle arrangement experiments were performed at the same $\dot{Q}$ and $N$ as for the continuous arrangements under the conditions specified in Table 9.3. Samples were taken for different $t$.

Table 9.3: Conditions of experiments performed. The number inside parenthesis indicate the number of samples taken at different times.

<table>
<thead>
<tr>
<th></th>
<th>350 cSt</th>
<th>1000 cSt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arrangements-Shared</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\dot{Q} \ [m^3 \cdot s^{-1}]$</td>
<td>$2.90 \times 10^{-5}$</td>
<td>$9.08 \times 10^{-9}$</td>
</tr>
<tr>
<td>Impeller $N \ [s^{-1}]$</td>
<td>11.9</td>
<td>11.7</td>
</tr>
<tr>
<td>RS $N \ [s^{-1}]$</td>
<td>50.00</td>
<td>166.7</td>
</tr>
<tr>
<td>Continuous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n \ [-]$</td>
<td>0-7</td>
<td>0-7</td>
</tr>
<tr>
<td>Recycle</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V_T \ [m^3]$</td>
<td>$13 \times 10^{-3}$</td>
<td>$10 \times 10^{-3}$</td>
</tr>
<tr>
<td>$t \ [s]$</td>
<td>0-4544 (8)</td>
<td>0-10000 (8)</td>
</tr>
</tbody>
</table>

Sampling was done approximately 5 cm below the liquid level. The samples were stored and analysed as soon as the previous sample was analysed.

The experimental conditions listed in Table 9.3 were chosen to provide an example where the DSD for $n = 0$ and for $n > 0$ were close (350 cSt) and an example where these were more separated (1000 cSt) within the experimental range where the correlations obtained in Carrillo De Hert and Rodgers (2017b) have been proven.

The DSDs were analysed using the Mastersizer 3000 (Malvern Instruments, Malvern, UK). The complex refractive index used was $1.399 + 0.001i$ and the details of the Standard Operation Procedure used has been previously detailed in Carrillo
9.3 Log-normal fits for previous work in Carrillo De Hert and Rodgers (2017b)

The data exported by the Mastersizer 3000 is presented as a cumulative frequency histogram where $\sum f_v(d_i) = 100$. In our previous work (Carrillo De Hert and Rodgers, 2017b) we fit the integrated experimental distribution to make the area under the curve 100%. However, the integration and normalisation of the experimental data is not required if the difference between the cumulative frequency of the $i$th drop diameter $F_v(d_i)$ and the one of the $(i - 1)$th drop diameter $F_v(d_{i-1})$ is used

$$f_v(d_i) = F_v(d_i) - F_v(d_{i-1}) \quad (9.9)$$

The DSD were fit using a mixing rule (Eq. 9.4) and we used two Generalised Gamma functions (GGf) to fit our results in Carrillo De Hert and Rodgers (2017b); we kept one of the shape parameters of the GGf large to use almost symmetrical (in semi-log scale).

In this investigation it was shown that log-normal distributions are also adequate to describe the shape of the DSD and also give a good estimation of the $d_{32}$. The equation of the cumulative function reads

$$F_v(d_i) = \frac{1}{2} + \frac{1}{2} \text{erf} \left( \frac{\ln d_i - \overline{d}_G}{\sqrt{2}s_G} \right) \quad (9.10)$$

where $\overline{d}_G$ is the logarithmic mean of the DSD and $s_G$ the logarithmic standard deviation.

In this section we provide the new fit parameters for the simplified fit-scheme based on two log-normal cumulative distributions. The fit to the DSD was performed using a power-law function for $\overline{d}_G$ (Eq. 9.11 below), the indexes are known from the analysis of variance (ANOVA) done for the modes in Carrillo De Hert and Rodgers.
(2017b) and the only parameter for $\bar{d}_{G,L}$ and $\bar{d}_{G,s}$ obtained using the method of the least squares were the pre-exponentials $C_{G,L}$ and $C_{G,s}$

$$\bar{d}_G = \ln \left[ C_{G} \mu^N_{d} N^{C_{G,N}} \left( \frac{n}{Q} \right)^{C_{G,t}} \right] \quad (9.11)$$

The standard deviations of the distributions ($s_{G,L}$ and $s_{G,s}$) were also obtained using the method of the least squares but these were considered to be independent of $\mu$ and the processing conditions. The coefficient obtained using the least square method for Equation 9.11 and the standard deviations are listed in Table 9.1. If this table is compared with Equation 9.2 and Equation 9.3 it can be seen that the value of $C_{G,N}$ was changed from -1.05 to -1.2. The former value was obtained directly from the ANOVA in Carrillo De Hert and Rodgers (2017b); however changing its value to -1.2 produces no significant variation in the goodness of the fit (within our experimental range 50-166.67 s$^{-1}$) while being in agreement with the well-know theory developed by Hinze (1955).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Large</th>
<th>Small</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{G}$</td>
<td>$2.1 \times 10^5$</td>
<td>$3.4 \times 10^3$</td>
</tr>
<tr>
<td>$C_{G,\mu}$</td>
<td>0.365</td>
<td>-0.365</td>
</tr>
<tr>
<td>$C_{G,N}$</td>
<td>-1.2</td>
<td>-1.2</td>
</tr>
<tr>
<td>$C_{G,t}$</td>
<td>-0.2</td>
<td>0</td>
</tr>
<tr>
<td>$s_G$</td>
<td>0.400</td>
<td>0.843</td>
</tr>
</tbody>
</table>

Simultaneously the $\phi_s$ for each distribution were “freely fit”. As recognized in our previous work (Carrillo De Hert and Rodgers, 2017b), this is the most difficult parameter to obtain a correlation for. The power-law function shown below was also used to correlated the data

$$\phi_s = C_{\phi_d}^N C_{\phi_d} N^{C_{\phi_N}} \left( \frac{n}{Q} \right)^{C_{\phi_t}} \quad (9.12)$$

The ANOVA for Equation 9.12 yielded $C_{\phi,\mu} = 0.025 \pm 85.2\%$ and a $p$-value of
0.0223, therefore the effect of $\mu_d$ was considered negligible due to its low statistical significance. Under these considerations, the ANOVA yielded the values listed in Table 9.2. The mean absolute error obtained for $\phi_s$ was 3.89%.

**Table 9.2:** ANOVA results for Eq. 9.12 for $C_{\phi,\mu} = 0$. The percentages represent the 95% confidence interval.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{\phi}$</td>
<td>$1.23 \times 10^{-1} \pm 19.7%$</td>
<td>$6.10 \times 10^{-27}$</td>
</tr>
<tr>
<td>$C_{\phi,N}$</td>
<td>$2.53 \times 10^{-1} \pm 15.6%$</td>
<td>$1.01 \times 10^{-18}$</td>
</tr>
<tr>
<td>$C_{\phi,T}$</td>
<td>$4.90 \times 10^{-2} \pm 36.4%$</td>
<td>$8.64 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

The authors recognise the limitations of using a power-law function to parametrise $\phi_s$, as these function can yield values higher than unity; however within the experimental range studied it was not possible to correlate our results using a function that runs from 0 to 1 (such as a cumulative log-normal distribution).

### 9.4 Extended model

As proven in Carrillo De Hert and Rodgers (2017a), the mode of an emulsion produced in the recycle arrangement for $t > 0$ consists of a mixture of materials that have passed $n$ number of times through the rotor-stator. The DSD at any given time $f_{v,Rec}(d_i)$ should equal the sum of the distribution of its composing materials

$$f_{v,Rec}(d_i) = \sum_{n=0}^{\infty} \phi_n f_{v,n}(d_i)$$  \hspace{1cm} (9.13)

where $\phi_n$ can be obtained by Equation 9.6 and $f_{v,n}(d_i)$ is the frequency of the $i$th drop size for the material that has passed $n$ number of times through the rotor-stator.

The examples that will be given in Section 9.5 consist of bimodal coarse emulsions and bimodal DSD for any $n > 0$. Using the mixing rule in Equation 9.4, the following
9.5. Results and discussion

An equation can be derived

\[ f_{v,Rec}(d_i) = \phi_0 f_{v,0}(d_i) + \sum_{n=1}^{\infty} \phi_n f_{v,n}(d_i) \]

\[ = \phi_0 \left[ (1 - \phi_{s,0}) f_{v,0,L}(d_i) + \phi_{s,0} f_{v,0,s}(d_i) \right] + \sum_{n=1}^{\infty} \phi_n \left[ (1 - \phi_{s,n}) f_{v,n,L}(d_i) + \phi_{s,n} f_{v,n,s}(d_i) \right] \tag{9.14} \]

where \( \phi_{s,n} \) is the relative volume fraction of the small drops of the material that has passed \( n \)-times through the rotor-stator and, \( f_{v,n,L}(d_i) \) and \( f_{v,n,s}(d_i) \) are the frequency of the \( i \)th drop size of the material for \( n \)-passes for the large and small types of drops respectively. Substituting Equation 9.6 in 9.14 yields

\[ f_{v,Rec}(d_i) = \exp \left( \frac{-t}{t_{res,T}} \right) \left\{ \left[ (1 - \phi_{s,0}) f_{v,0,L}(d_i) + \phi_{s,0} f_{v,0,s}(d_i) \right] + \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{t}{t_{res,T}} \right)^n \left[ (1 - \phi_{s,n}) f_{v,n,L}(d_i) + \phi_{s,n} f_{v,n,s}(d_i) \right] \right\} \tag{9.15} \]

As seen in Section 9.5, \( f_{v,n,L}(d_i) \) and \( f_{v,n,s}(d_i) \) can be given by cumulative log-normal distribution difference and \( \phi_{s,n} \) by a power-law function.

9.5 Results and discussion

9.5.1 Continuous arrangement results

The results obtained for both SiOil are shown in Figure 9.1. The same trends found in Carrillo De Hert and Rodgers (2017b) were observed: (1) no steady-state DSD was found for \( n = 7 \) and (2) the large drops are \( n \)-dependent while the small drops are \( n \)-independent (see Fig. 9.2).

The DSD were fit using the cumulative log-normal distributions. Nevertheless, the parametrization was only done as a function of \( n \) for each set of experiments to prove the extended model (Sec. 9.4) in Section 9.5.2 with the most accurate parameters.

The fit for the coarse material was fit independently of the \( n > 0 \) distributions, as
Figure 9.1: DSD obtained for \( n = 1, 2, \ldots, 7 \) passes in the continuous arrangement for the (a) 350 cSt SiOil and (b) 1000 cSt SiOil.

no correlation in-between these was found in this work nor by Hall et al. (2011). The logarithmic mean of the large drops of the coarse emulsion \( \overline{d}_{G,0,L} \), their logarithmic standard deviation \( s_{G,0,L} \) along with these parameter for the small drops \( \overline{d}_{G,0,s} \) and \( s_{G,0,s} \) and their volume fraction \( \phi_{s,0} \) are listed in Table 9.1 for the coarse emulsions obtained for both SiOils.

For the \( n > 0 \) distributions, the large drop sizes are \( n \)-dependent and, as shown in Figure 9.2 and in Carrillo De Hert and Rodgers (2017b), these are well-correlated by \( n^{-0.2} \), the following model was proposed for the logarithmic mean of the large drops

\[
\overline{d}_{G,n,L} = \ln \left( B_1 n^{-1/5} \right)
\]

(9.16)

The rest of the parameters of the log-normal cumulative distribution for the large and small drops were considered constant and were not parametrised, however \( \phi_{s,n} \) was, because it is \( n \)-dependent (Carrillo De Hert and Rodgers, 2017b)

\[
\phi_{s,n>0} = B_2 n^{B_3}
\]

(9.17)

The values of all the variables for the large and small drops for \( n > 0 \) are also displayed in Table 9.1, while two examples of the appearance of the fits are shown in Figure 9.3.
9.5. Results and discussion

9.5.2 Recycle arrangement results

Figure 9.4 shows the DSDs obtained using the recycle arrangement for the same $\dot{Q}$ and $N$ used for the continuous arrangement for different processing times. Figure 9.4a provides an example where the DSD seems to decrease in size progressively, however as it will be shown later, this is due to the close proximity in-between the $n = 0$ and the $n > 0$ DSDs, as was shown in Figure 9.1a. In Figure 9.4b the consumption of the coarse emulsion is more evident because the DSDs of the coarse emulsion and the material that has passed through the rotor-stator are further apart.

Equation 9.15 was combined with Equations 9.9, 9.10 and with the fit constants
Table 9.1: Fit parameters for the dual log-normal cumulative distribution fit for the 350 cSt and 1000 cSt SiOils.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>350 cSt</th>
<th>1000 cSt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{G,0,L}$</td>
<td>5.69</td>
<td>6.51</td>
</tr>
<tr>
<td>$s_{G,0,L}$</td>
<td>0.432</td>
<td>0.443</td>
</tr>
<tr>
<td>$d_{G,0,s}$</td>
<td>4.43</td>
<td>5.53</td>
</tr>
<tr>
<td>$s_{G,0,s}$</td>
<td>0.650</td>
<td>0.855</td>
</tr>
<tr>
<td>$\phi_{s,0}$</td>
<td>0.878</td>
<td>0.595</td>
</tr>
<tr>
<td>$B_1$</td>
<td>139</td>
<td>56.6</td>
</tr>
<tr>
<td>$s_{G,n&gt;0,L}$</td>
<td>0.44</td>
<td>0.45</td>
</tr>
<tr>
<td>$d_{G,n&gt;0,s}$</td>
<td>3.59</td>
<td>1.90</td>
</tr>
<tr>
<td>$s_{G,n&gt;1,s}$</td>
<td>0.861</td>
<td>0.792</td>
</tr>
<tr>
<td>$B_2$</td>
<td>0.628</td>
<td>0.234</td>
</tr>
<tr>
<td>$B_3$</td>
<td>-0.0688</td>
<td>-0.111</td>
</tr>
</tbody>
</table>

obtained for the continuous arrangement experiments listed in Table 9.1 to fit the recycle arrangement DSDs shown in Figure 9.4.

Examples of the fit are shown in Figure 9.5. Figure 9.5a shows an example of the composition of each of the drop size distributions for $t > 0$. As can be seen in this figure, the coarse emulsion has not been consumed and the contribution of the materials that has passed $n = 1, 2, 3$ are the main responsible for the change in the shape of the DSD. On the other hand, Figure 9.5b shows the total fit for three different times, it can be seen that the model is accurate in predicting even very complex DSD.

The goodness of the fit was assessed by comparing the experimental and predicted $d_{32}$. The obtained coefficient of determination $R^2$ obtained were 0.997 and 0.980 for the 350 cSt and 1000 cSt SiOils respectively, while the mean absolute error were 12.32% and 9.51%. The experimental and predicted $d_{32}$ as a function of time in log-log scale are shown in Figure 9.6, where it can be seen that the models follow the complex trend reasonably well.
9.6 Conclusions and recommendations for future work

The transient mass balance derived in our previous work Carrillo De Hert and Rodgers (2017a) can be used to predict the evolution of the DSD with time by using the mixing rule in Equation 9.14. The mixing rule could be implemented to bimodal DSD. As shown in the examples presented, future study of multiphase
Chapter 9. Linking continuous and recycle emulsification kinetics for in-line mixers

Figure 9.6: Experimental and predicted \( d_{32} \) as a function of time for both SiOils.

Systems in rotor-stators has to be done preferably (if not exclusively) using the continuous arrangement to remove misleading mass balance features. The authors consider that the models presented in Carrillo De Hert and Rodgers (2017a) and in this investigation provide a strong fundamental basis to extrapolate continuous arrangement results to recycle systems, provided that the vessel is well-mixed.

There have been multiple studies (Badyga et al. (2008); Padron et al. (2008); Özcan-Taskin et al. (2009, 2016) among others), which have used the recycle arrangement to study the de-agglomeration of nano-particles. These authors have explained breakup in terms of shattering, rupture or erosion mechanisms. Figure 9.4a resembles the rupture mechanism for nanoparticles while Figure 9.4b resembles the shattering one. However, we have shown that the trends in these figures are due to mass balance features and by the proximity in-between the DSD of the coarse and processed materials. Future work on breakup mechanism require the separation of the break-up inside the rotor stator and mass balance effects. Ideally experiments with the continuous arrangement should be used.

The semi-empirical model for emulsification in the continuous arrangement presented here and in our previous work (Carrillo De Hert and Rodgers, 2017a,b) (Eqs. 9.1, 9.2 and 9.3) consider that the drop sizes are proportional to the mean residence time inside the rotor-stator which is further proportional to \( (n/\dot{Q})^{-1/5} \); this can be
explained by the internal recycling inside the rotor-stator (reported by Özcan-Taskn et al. (2011); Mortensen et al. (2017); Xu et al. (2014) among others). However it is unknown if the $-1/5$ index is universal or depends on the geometrical characteristics of the rotor-stators. Hall et al. (2013) reported indexes of -0.148 and -0.043 for 10 cSt and 350 cSt SiOils respectively, but their results were correlated to the $\bar{d}_{32}$ and their emulsions were produced using a double-rotor-double-stator geometry. The lower residence time dependency reported by Hall et al. (2013) for the thickest oil is most likely due to the small daughter drops which make the $\bar{d}_{32}$ trend smoother because these are mean residence time-independent. To our knowledge there is no other work in literature which uses the mode or the maximum drop diameter to know the mean residence time dependency.

The drop size dependency with $N$ has more theoretical basis as its index is in agreement with the mechanistic models developed by Hinze (1955) and Shinnar and Church (1960) even though these were postulated for steady-state systems. Finally the study on the $\mu_d$ dependency in Carrillo De Hert and Rodgers (2017b) (Eqs. 9.2 and 9.3) is unique as most of the correlations found in literature use the $\bar{d}_{32}$ and do not track the individual drop size change nor the relative volume fraction of each type of drop produced which makes comparison with other work in literature virtually impossible. Future work should also focus on analysing the whole DSDs and not only the $\bar{d}_{32}$, specially for highly-viscous dispersed phases which tend to produce bimodal DSD.

9.7 Bibliography


Part IV

Conclusions and recommendations for further work
Conclusions

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10.1 Part II

The work developed in Chapters 4 to 6 aimed to create models that help characterise complex steady-state drop size distributions (DSD) of systems with surfactant concentration well-above the critical micellar concentration which are normally produced when highly viscous dispersed phases are used. The combined effects of stirring speed, continuous phase viscosity and dispersed phase volume fraction were studied in combination with the effect of dispersed phase viscosity for steady-state systems.

The experiments in this Part were performed using the same impeller and vessel. With the exception of the systems emulsified with a 70% and 80% dispersed phase hold-up in Chapter 6, all the emulsions shared the same power number. Furthermore, the same mass of surfactant was kept constant in all the experiments; however it was verified that keeping the concentration in the whole tank volume did not give significant variations if the concentration in the continuous phase was kept constant.

The analysis methodology presented in Part II is unique in that it is the only one that characterises multimodal DSD by drop population density and that allows calculation of the Sauter mean diameter reasonably-well from the DSD fit.

The investigations presented in these chapters show that the problem is not trivial. The models and diverse number of studies found in literature showed little agreement with the research here presented. Many times these inconsistencies are due to the limited drop size analysis technologies available in the past, many other to the use of $d_{32}$ as the preferred measure of central tendency to correlated the experimental data and some due to the conversion in-between distributions by volume or vice-versa depending on what the authors thought was convenient. Throughout the work presented in this thesis, we used probability density functions to describe the whole shape of the DSD.

As shown throughout the thesis, a complete description of the DSD should include the size of each type of drop and the relative amount of each sort of drops, which are presumably the result of different drop breakup mechanisms.

For the drop size of each type of drop we used the mode of the distribution because
this and a high percentile were the only measure of central tendency that could be obtained directly from multimodal distributions when two or more distributions are merged. The most commonly used maximum drop diameter (normally considered as a high percentile of the DSD) was found to be proportional to the mode of the large drop, however to keep consistency in-between Parts II and III, the mode was preferred.

The relative amount of drops was approximated by fitting log-normal distributions. This parameter was the most difficult to estimate and correlate. The correlations presented throughout the thesis had different degrees of success. The correlation for the relative amount of small drops in Chapter 4 was reasonable successful as it allowed to estimate $\overline{d}_{32}$, however it was limited to the silicon oils thinner than 10 000 cSt, presumably due to a change in the breakup mechanism. Chapter 5 showed that when the viscosity of the continuous phase is increased a third type of drop arises, making the fit impractical. Obtaining a full complete description of the third type of drops would require a vast amount of experimental data. The drop breakup mechanism that gives birth to this third type of drop has not been described in literature. Finally, the correlation for volume fraction presented in Chapter 6 allowed to calculate $\overline{d}_{32}$, however many more experiments would be required to obtain a full description of the combined effect of the dispersed phase viscosity, dispersed phase volume fraction, rheology and its effect on turbulence.

The trends found in Part II for the experiments carried out at the same power number are summarised below

- The drop sizes of the large and small type of drops decrease with stirring speed as predicted by mechanistic model predicted by Hinze (1955) and Shinnar and Church (1960).

- The drop sizes of the large and small type of drops increase at the same rate with the viscosity of the dispersed phase in the 0.65-10 000 cst viscosity range, however the increase is sutler than the one predicted by the models proposed by Arai et al. (1977), Calabrese et al. (1986) or by (Davies, 1985).

- Thicker dispersed phases than 10 000 cSt, showed smaller drop sizes than the
10 000 cSt silicon oil; for these oils the maximum drop become stirring speed independent.

- The drop size of the large and small type of drops decrease with the viscosity of the dispersed phase, which is in disagreement with the hypothesis postulated by Hinze (1955), which establishes that emulsification occurs in the turbulent inertia regime under isotropic turbulence. The model proposed by Pope (2000) was used to demonstrate that in our system emulsification did not occur in the size range where kinetic energy is the dominant disruptive force.

- The effect of volume fraction on the drop sizes is a function of the viscosity of the dispersed phase; thinner oils being less affected by volume fraction than thicker oils. The thinnest of the oils used, showed no dispersed phase dependency in the 1.0%-60% hold-up range, indicating that: (1) our systems showed no coalescence, (2) turbulence dampening (Brown and Pitt, 1972; Lagisetty et al., 1986; Cohen, 1991) is unlikely to play a role and (3) that the mean field theory approach proposed by Jansen et al. (2001) for the laminar regime cannot be used for turbulent systems.

- The broadness of the distribution of the large drops are independent of the dispersed phase viscosity, continuous phase viscosity and dispersed phase volume fraction.

- The broadness of the distribution of the small drop sizes are viscosity dependent, but independent of stirring speed and dispersed phase volume fraction.

- The 50 cSt and 350 cSt yielded monomodal and bimodal DSD respectively (in both Part II and Part III), indicating that this breakup mechanism giving birth to the secondary type of drops occurs in that viscosity range.

- The relative amount of small drops is stirring speed-independent, increases with the viscosity of the dispersed and continuous phases and, decreases with dispersed phase volume fraction.
10.2 Part III

Part III aimed to tackle the objectives postulated for in-line high-shear mixers. All the experiments performed in this section were done using the same Silverson rotor-stator, at the same surfactant concentration and dispersed phase hold-up.

Chapters 7 and the first sections in 8 studied the effect of stirring speed, dispersed phase viscosity, number of passes and flow-rate through the rotor-stator using the continuous emulsification arrangement. The methodology used to analyse the DSD is analogous to the one used for Part II. The multimodal DSD were easier to characterised for high-shear mixers due to the distance in-between the curves of the large and small types of drops, allowing to obtain the mode for each specie.

The following conclusions can be drawn for the continuous arrangement:

- Bimodality emerges somewhere in-between the 50 and 350 cSt silicon oils, this was also true for the experiments using the stirred vessel in Part II.
- The large and small type of drops increase and decrease at same rate with viscosity respectively in the 10-2760 cSt viscosity range.
- The size of the largest surviving drops reach a maximum for dispersed phase viscosities above 2760 cSt.
- Both types of drops decrease with stirring speed at the same rate in agreement with the model proposed by Hinze (1955) and Shinnar and Church (1960), despite their model was developed for steady-state systems.
- The number of passes and flow rate decrease and increase the drop size of the large type of drops, implying that the mean residence time inside the rotor-stator is the relevant parameter. This was attributed to the back-flow reported by some authors (Özcan-Taskn et al., 2011; Xu et al., 2014; Mortensen et al., 2017). The mean residence time has no effect on the size of the small type of drops, however it does have an effect on their amount.
- In Chapter 8 steady-state could not be reached even after 20 passes.
- The DSD could be fit using two log-normal distributions for the 10 cSt-2760
cSt dispersed phase viscosity range. Thicker oils exhibited a different behaviour. The log-normal functions were fit differently in Chapters 7 and 9.

In Chapter 7 we made the experimental DSD continuous by standardizing the area under the distribution to 100%. This method was more difficult to fit, as small drop size variations alter severely the relative volume fraction of the small drops because the DSD are represented in a semi-log scale. However this method would make the results for different drop size analysis instruments comparable.

In Chapter 8 we used the difference in-between two cumulative functions for the $i$th and $i-1$th drop size. This method is less sensitive to error and allows to manipulate the variables using mixing rules easily. However, the frequency values would have to be adjusted if the number of sizes of the instrument differ from the ones given by the Mastersizer 3000. If results obtained by different instruments were be compared, the experimental results should be manipulated first (i.e. mixing rules used throughout Part III) using this method and should be integrated after all algebraic manipulations.

For the recycle arrangement, a transient mass balance considering that emulsification occurs as a series of consecutive infinite reactions was derived (see Chap. 8). The mass balance revealed that the volume fraction of the species that have passed $n$ times through the rotor-stator followed a Poisson distribution function. In the same chapter we used a mixing rule to estimate the mode of the processed materials for different mean residence times inside the stirred vessel. This mixing rule allowed an efficiency comparison in-between the multi-pass continuous arrangement and the recycle arrangement; it was found that the efficiency of both arrangements is the same after 10 tank turnovers or 10 passes.

In Chapter 9 we proved that the mass balance derived can be used for multimodal DSD through the use of mixing rules. Chapter 9 integrates the knowledge earned in Chapters 7 and 8, demonstrating that continuous and recycle arrangement
10.3 General

The studies included in this dissertation demonstrate that much more information can be obtained from the DSDs if these are decomposed into the constitutive species.

The classical approach of using the diameter of the maximum surviving drop should not be used as the parameter solely characterising the DSD (not even in combination with the $d_{32}$ to $d_{max}$) if multimodal distributions are obtained. The other approach consisting of correlating the results to $d_{32}$ is misleading as a lot of information is summarized into one single statistic; multiple examples of the misconceptions due to the use of the $d_{32}$ have been given throughout this dissertation.

It was demonstrated that using probability density functions in combination with mixing rules can be used to describe the effect of multiple material properties and processing parameters on the DSD.

10.4 Bibliography


Chapter 11

Recommendations for further work

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Chapter 11. Recommendations for further work

11.1 Part II

Even though emulsification in stirred vessels has been investigated for more than half a century, the investigations in this dissertation showed that there are many open opportunities to continue investigating emulsification technology.

Interfacial tension

One of the most important parameters that was not studied in this dissertation was interfacial tension $\sigma$. Three different types of studied could be suggested for this parameter.

1. Studies on $\sigma$ could be performed for surfactant-laden systems by changing the composition of the continuous phase.

2. Another investigation could be devoted to the effect of surfactant concentration; the studies done in this thesis used surfactant concentrations well-above the critical micelle concentration (CMC); however other effect such as Marangoni stresses might become important if the interface of the drops is not fully saturated.

3. A third study could consider using different types of surfactants above the critical micellar concentration, if this study was coupled with (1), a multivariable analysis could be done to determine if the nature of the surfactant has an effect on the DSD. Rueger and Calabrese (2013) stated that some surfactants may not provide an effective barrier against coalescence despite decreasing interfacial tension.

It would be interesting to combine the three suggestions above with the one on the effect of viscosity of the dispersed phase presented in Chapter 4). Wang and Calabrese (1986) suggested that for highly viscous dispersed forces the effect of interfacial tensions is negligible, however it is unclear if the shape of the DSD varies or is constant for these systems. These studies would be highly labour intensive as each of the emulsified systems would have to be accompanied by interfacial tension measurements.
Type of impeller and scale-up

One of the most obvious ways to extend the studies in Part II is by changing the type of impeller and scale-up. Provided that there are discrepancies in the calculation of the maximum energy dissipation rate per unit mass depending on the methodology and models used (i.e. LDA vs. PIV, average vs. Smagorinski), it is likely that the results would have to be correlated using the power number of the impeller, as done by McManamey (1979). In Chapter 4 and Chapter 10 we emulsified the 350 cSt silicon oil for 24 h using the same dispersed phase and surfactant concentration but using different impellers and stirred vessel. The former using a 4.83 cm-pitched-blade-turbine with 6 blades and the later using a 6.62 cm-8-blade Rushton turbine. Other differences were that the former system we used a 2 l-baffled-vessel and for the latter a 13 l-unbaffled-vessel.

As can be seen in Figure 11.1, the shape of the DSDs obtained for both systems were remarkably similar considering the geometrical differences in-between the systems, suggesting that the studies presented in Part II could be modified by parametrising the pre-exponential factor of the drop size correlations.

Figure 11.1: DSD obtained using the 350 cSt Silicon Oil and 1.0% by weight of SLES at different $N$ and using different impellers and vessel.
Turbulence characterisation for different viscosities

In Chapter 7 we found that the drop size decreased as the viscosity of the continuous phase increased for constant power numbers, which was in disagreement with the published literature. To my knowledge there is no published literature on the effect of viscosity on turbulence because the term is not included in the isotropic turbulence hypothesis postulated by Kolmogorov (1941). Most studies have determined that the maximum-to-mean energy dissipation ratio per unit mass remains constant for different stirring speed, however this has not been experimentally proven for different viscosities. If future experimental investigations reveal that the ratio is viscosity-independent, mechanistic models should consider shear stresses over eddie pressure fluctuations as the primary drop disruptive force.

Rheology of shear-thinning emulsions

The literature review done for Chapter 6 revealed there is no published literature on polydispersed, shear thinning concentrated emulsion which also take the viscosity of the dispersed phase, drop sizes and the interfacial tension into account. Most of the models proposed in literature are severely restrained to either estimating the low or high-shear Newtonian plateau and/or to monodispersed emulsions. The rheograms presented in Chapter 6 were not correlated as the polydispersity of the emulsions were a function of the dispersed volume fraction for the silicon oils that presented some degree of bimodality.

Provided the large number of variables, this investigation would require many experiments under many different conditions. As was shown in Chapter 6 emulsifying silicon oils at 80% volume fraction yielded monomodal DSDs, which distribution broadness was independent of the viscosity of the dispersed phase. This could be used to study the effect of dispersed volume fraction and viscosity while keeping the rest of the parameters constants by diluting the concentrated emulsions produced with different dispersed phase viscosities with surfactant solutions. The effect of drop size could be tackled by emulsifying these systems at different stirring speed or even using different devices such as stirred vessels and high-shear mixers. The
effect of the broadness of the drop size distribution could potentially be tackled by mixing emulsions which were produced at different stirring speeds. Incorporating the effect of interfacial tension would be somehow more difficult as it should account for the surfactant depletion at the interface; for this matter a purer surfactant which surface excess (straight line in an interfacial tensions vs. concentration plot) can be easily obtain would be preferred.

Figure 11.2 shows the results of a preliminary study. For this study an emulsion with 80v.% of 50 cSt silicon oil was emulsified in a 1wt.% SLES solution using the impeller and vessel utilised in Part II at $N = 13.3 \text{s}^{-1}$ and another with the same composition but using the high-shear mixer used in Part III at $N = 166 \text{s}^{-1}$. The emulsions produced by each device where analysed in the rheometer and diluted with a SLES solution. Figure 11.2a shows that the viscosity of emulsions $\mu_e$ is highly dependent on drop size, and the birth of complex rheological features as the dispersed phase volume fraction $\phi$ is increased. Figure 11.2b shows that the broadness of the DSD produced by both devices is not that different.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure11_2.png}
\caption{Rheograms for emulsions of different dispersed volume fraction for emulsions produced using two different devices and (a) DSD obtained for each device.}
\end{figure}

**Emulsification kinetics**

Finally, time effects could be studied. The studies presented in Part II are limited to steady-state DSD as the emulsions were analysed after 24 h; however it is unlikely
that such long times are used in industrial applications. A complete kinetic model should incorporate the parameters studied in Part II and those mentioned above. It is important to mention that kinetic studies of highly viscous dispersed phases would be challenging as some of the emulsions had drops close to the upper measuring limit of the Mastersizer 3000 even after 24 h. Furthermore, the DSD would be even broader than the ones presented in Part II, complicating the drop size measurements.

An even more complicated problem would rise if kinetic of highly-concentrated emulsions would like to be studied as the DSD evolution with time also implies rheological changes.

11.2 Part III

Continuous arrangement

Extension to other material properties

The recommendations suggested for Part II regarding the effect of interfacial tension could also be studied for high-shear mixers. Hall et al. (2013) performed such studies for in-line rotor-stators by using ethanol/water solutions for surfactant-laden systems and also studied the effect of surfactant concentration by using using 0.05%, 0.5% and 5% SLES aqueous solutions for the 10 cst and 50 cSt SiOils as dispersed phases. They found very similar interfacial tension indexes for the surfactant-laden and surfactant-contaminated systems for both silicon oils using the Sauter mean diameter as measure of central tendency. As seen in Parts II and III, the later silicon oil yields bimodal DSDs, therefore the consistency of the index suggest that the shape of the DSD is preserved and the size of the large and small drops are equally affected by the interfacial tension (analogous to the effect of stirring speed in Chapter 8). Therefore, the shape consistency hypothesis could be tested with a low amount of experiments, preferably using a silicon oil which produces a taller peak for the small drops. This would test the hypothesis by Wang and Calabrese (1986) which proposes that the effects of interfacial tension and viscosity are mutually independent.
Apart from the effect of interfacial tension, the effect of continuous phase viscosity and dispersed phase volume fraction (analogous to the studies in Chapters 4 and 5 for stirred vessels), could be investigated. Special caution would need to be taken to control the flow rate through the rotor-stator, either by using a peristaltic pump (as done in Part III) or by linking the mass balance to the pumping number.

**Extension to other dispersed systems**

Other dispersion processes such as grinding and de-agglomeration would benefit from the DSD analysis methodology implemented in Part III.

**Extension to other geometries**

In the conclusions and recommendations for further work given in Chapter 9 the effect of the mean residence time inside the high-shear mixer was attributed to internal recirculation or back-flow. It is unclear if the mean residence time index found in the studies in Part III is universal or specific to the rotor-stator used; my inclination is that the latter is true.

Hall et al. (2011) suggested that the relevant volume determining the mean residence time is the swept volume; however being this the only study in literature concerning scale-up and that their DSD analysis differed from ours, their assumption requires more experimental support. Furthermore, CFD could be used to determine if back-flow is scale-dependent and it would be extremely desirable to link the degree of back-flow with the mean residence time index. A powerful scale-up and geometry optimisation tool could be developed if the back-flow and mean residence time index could be linked and if the swept volume is indeed the relevant scale characteristic.

**Recycle arrangement**

**Proving the model for other dispersed systems**

The link in-between the continuous and recycle arrangement has been elucidated in Chapter 8 and Chapter 9. In the conclusions in Chapter 9, we recommended
that future research should focus in the continuous arrangement; this suggestion was extended to other dispersed systems such as de-agglomeration.

**Extending the model for highly concentrated systems**

Extending the models to highly concentrated systems would require the incorporation of a term that account for the viscosity change in the system.

The experiments performed in Chapters 8 and 9 included a peristaltic pump to control the flow rate through the mixer; however rotor-stators are commonly used as the only pumping device. If no-peristaltic pump is used, the stirring speed and the flow rate are linked by the pumping number of the mixer, but it can easily be controlled using a valve. In concentrated emulsions, one would expect that as time passes, the viscosity of the mixture in the vessel increases, causing a reduction of the flow rate and an increase in the residence time of both, the vessel and the mixer. Extending the models presented in Part III would require a larger understanding of emulsion rheology. Suggestions of how to start tackling the gap in the rheological understanding of shear thinning emulsions has been stated in the previous section.

**Extending the model for adiabatic systems**

The large shear-rates in rotor-stators is accompanied by temperature increase due to viscous dissipation. Temperature increase is important when high-shear mixers are submerged in the stirred vessel in batch processes.

There have been studies on the effect of temperature on the DSD. El-Hamouz (2007) reported a decrease in the drop size as temperature increases and attributed this effect mainly to a decrease in interfacial tension. This effect could be used to increase the overall efficiency of the system if the recycle arrangement was thermally isolated. The model proposed in Part III could incorporate an energy balance.

### 11.3 Bibliography


Chapter 11. Recommendations for further work