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An empirical equation for shear viscosity of shear thickening fluids

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Abstract

Quantitative modelling of the rheology of non-Newtonian fluids requires significant empirical input due to very complex behaviour of the bulk fluid as a result of particle-scale physics of fluids. The existing rheology models are mainly limited to certain fluid dynamics conditions such as shear rate, shear stress, etc. Adopting Doolittle's free volume theory approach, we have proposed an empirical equation to describe the relative free volume-dependent viscosity, the shear stress-dependent viscosity, the shear rate-dependent viscosity, and the dimensionless Péclet number-dependent relative viscosity of shear thickening fluids. The proposed formulae predict all rheologically different behaving Newtonian, intermediate shear thinning, shear thickening and extreme shear thinning regimes of shear-thickening fluids. The proposed formulae have been validated against the experimental rheological data of various shear thickening fluids over a range of pH, volume fraction, electrolyte concentration, temperature, and magnetic field. The results suggest that the predicted threshold material parameters of shear thickening fluids help to quantitatively evaluate the effect of vary-

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ing physico-chemical conditions on the rheology of shear thickening fluids. We simulated the flow of a shear thickening fluid, modelled using proposed shear rate-dependent equation, in a 2D staggered porous medium. We observed bimodal distribution of pore-scale shear rate, shear viscosity and velocity in a porous medium.

keywords: Colloidal suspension, Non-Newtonian fluid, Shear thickening fluid, Direct numerical simulation, OpenFOAM, Pore-scale simulation

1. Introduction

The suspension shear-thickening behaviour (*i.e.* increase in the shear viscosity with an increase in the shear stress/rate showed by colloidal/non-colloidal suspension) [1] has wide applications starting from cement [2], woven fabrics [3], chocolates [4], cornstarch [5] to ceramics [6]. The shear-thickening fluids are excellent for shock-absorption due to their high elastic modulus and high dissipation energy [6, 7]. Smart materials are being developed such as magnetorheological shear thickening fluids [8] which act as actuating fluids to maintain variable flow rate or force transfer scenario in many engineering applications such as artificial joints and breaks [7, 9].

Mixing colloidal particles or polymers (*i.e.* solute) in a solvent (*e.g.* water) leads to an increase in the viscosity of the solution, and further increase in the concentration of solute/colloids makes fluid behave like a non-Newtonian fluid. At lower stress, shear thickening fluids show Newtonian behaviour [6]. The fluid shows shear-thinning characteristics once critical stress exceeds, *i.e.* viscosity of the fluid drops with an increase in stress. The fluid can flow under weak stress and still be able to behave like a gel at rest. The viscosity of the fluid suddenly rises once it reaches critical stress at higher stresses [6]. This behaviour of a fluid is defined as shear thickening, which mostly depends on properties of solute/colloids (shape and size of molecules, volume fraction, etc.) and solvents (viscosity, deformation etc.) [6, 7, 10, 11]. Figure 1 shows the typical rheological behaviour of a shear thickening fluid under varying shear stress or shear rate. The typical shear thickening behavior can also be observed at low temperatures (*i.e.* temperature $> -40^{\circ}C$) [12].

Interparticle and intermolecular contact forces and hydrodynamic forces significantly contribute towards shear thickening of the suspension in the fluid [10, 13–17], the external or internal forces in solution cause displace-

29 ment of suspended colloid particles/solute. The force transmits from one
 30 colloid particle/solute molecule to the neighbouring colloid particle/solute
 31 molecule through intervening fluid. The hydrodynamic interaction between
 32 colloid particles/solute and solvent disturb local flow field of all colloids par-
 33 ticles/solute molecules [17, 18]. We note that the intervening fluid (solvent)
 34 acts as a lubricant between neighbouring colloids particles/solutes [1, 11].
 35 Hydrophobic or hydrophilic properties of the colloidal particles/polymer
 36 molecules along with hydrodynamic interaction between colloid/solute and
 37 solvent determines the relative motion of the particles and effectiveness of
 38 the solvent to act as a lubricant. The electrostatics [19, 20] and van der
 39 Waals forces play a significant role in maintaining the viscosity of the solu-
 40 tion [1, 7, 10]. Interparticle forces are dominant at lower stresses; on the
 41 contrary, hydrodynamic forces play a vital role at high stresses. Alteration
 42 of particles surface chemistry, ionic strength, shape and size affect the inter-
 43 particle or intermolecular forces, thus viscosity of the solution. The shear
 44 induced particle migration and shear banding also affect the shear thinning
 45 or thickening of the fluid [5].

46 Although many empirical models have been developed to characterise
 47 shear thinning behaviour of non-Newtonian fluids [18], a single equation
 48 which could completely characterise rheological behaviour of shear thicken-
 49 ing fluids (See Fig. 1) is meagre. Previously, Gopalakrishnan and Zukoski
 50 [21] proposed an empirical equation for the shear viscosity based on ther-
 51 modynamics and hydrodynamic interaction of shear thickening fluids. The
 52 constitutive relation proposed by Wyart and Cates [22] for shear thicken-
 53 ing suspension is well accepted constitutive model for shear thickening
 54 suspension. Galindo-Rosales *et al.* [23, 24] developed shear rate-dependent
 55 branch of equations based on Cross model [25] to capture first shear thin-
 56 ning, shear thickening and second shear thinning region of shear thickening

Figure 1: Typical rheological behaviour of a shear thickening fluid under varying relative free volume or shear stress or shear rate. (a) Shear rate - stress relationship, and (b) viscosity as a function of shear stress or shear rate. Typical shear thickening fluid shows Newtonian, shear thinning, shear thickening and second shear thinning regimes. We note that the image is representative and not to scale.

57 fluids. Recently, Steller and Iwko [26] proposed an empirical shear stress-
 58 dependent and shear-rate dependent model for the non-Newtonian fluids
 59 based on free volume theory. Steller-Iwko multi-model rheological equa-
 60 tion [26] captures the complicated viscosity curve of non-Newtonian flu-
 61 ids. Steller-Iwko [26] modified an empirical equation developed by Doolit-
 62 tle [27] to relate viscosity of the fluid with shear stress and shear rate.
 63 Free volume theory proposed by [27] is being extensively used to explain
 64 temperature-dependent viscosity variation observed in an amorphous poly-
 65 mer and glass-forming liquids. Williams-Landel-Ferry (WLF) equation [28]
 66 developed based on free volume theory of Doolittle [27] has been employed
 67 to model time temperature-dependent rheology of polymeric solutions (*e.g.*
 68 polystyrene melts [29], supra-macromolecular polymers [30]).

69 Free volume theory assumes that the viscosity of the fluid depends on
 70 the free space available for molecules to move in a total volume. The rela-
 71 tive free-space available for molecules or particles depends on the stresses
 72 generated in the fluids [27]. Adopting Doolittle approach, the interlink
 73 between relative free space, viscosity and stress can be established to em-
 74 pirically define viscosity as a function of the relative free volume of shear
 75 thickening fluids.

76 The absence of a single rheological equation, which could characterise all
 77 regimes of shear thickening fluids (see Fig 1) and could be utilised for pore-
 78 scale fluid flow numerical simulation, motivated us to develop an empirical
 79 equation based on free volume theory that models rheological character-
 80 istics of shear thickening fluids using measurable parameters and identify
 81 threshold parameters of shear thickening fluid. We propose an empirical
 82 equation that relates the shear viscosity of shear thickening fluid with a rela-
 83 tive free volume. The proposed free volume-based equation is then utilised
 84 to develop a shear stress-dependent rheological equation and shear rate-

85 dependent rheological equation for shear thickening fluids. The proposed
 86 equations are validated against experimental data. Further, we simulate
 87 the flow of shear thickening fluid, using the proposed equation, through a
 88 2D micromodel porous medium.

89 2. Mathematical Formulations

90 The shear viscosity of non-Newtonian fluids can be defined using consti-
 91 tutive equation of generalised Newtonian fluids (GNF) [31, 32]. The
 92 shear stress-dependent viscosity functions ($\eta(\tau)$) define viscosity as a func-
 93 tion of the magnitude of deviatoric stress tensor (*i.e.* $\boldsymbol{\tau} = 2\eta(\tau)\mathbf{D}$)
 94 [26, 33–35]. The shear rate-dependent viscosity function ($\eta(\dot{\gamma})$) defines
 95 viscosity as a function of second invariant of rate-of-deformation tensor
 96 (*i.e.* $\boldsymbol{\tau} = 2\eta(\dot{\gamma})\mathbf{D}$) [31, 32]. Here, the magnitude of shear stress is
 97 $|\tau| = \sqrt{\frac{\boldsymbol{\tau}:\boldsymbol{\tau}}{2}}$ [33], the magnitude of shear-rate is $|\dot{\gamma}| = \sqrt{\frac{\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}}}{2}}$ [32],
 98 $\mathbf{D} = \frac{1}{2}\dot{\boldsymbol{\gamma}} = \frac{1}{2}(\nabla\mathbf{u} + (\nabla\mathbf{u})^T)$, and $\mathbf{u}$ is velocity vector. Most of the GNF
 99 model equations are empirical equations and have their limitations [31, 32].
 100 Amongst commonly used GNF equations (*i.e.* Power-law, Bingham, Her-
 101 schel–Bulkley, Carreau, Cross [31, 32]) in the literature, Cross equation [25]
 102 is considered to be deduced from physical basis (*i.e.* the rate kinetics of
 103 rupture and formation of linkage between the particles of the polymers)
 104 [23–25]

105 The shear stress-dependent Meter model equation (Eq. 1) [33, 36] is
 106 a logistic equation which describes S-shape type curve (*i.e.* Newtonian
 107 plateau at high and low shear values and slope at intermediate shear values)
 108 of many shear-thinning fluids.

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + \left(\frac{\tau}{\tau_p}\right)^{\alpha-1}} \quad (1)$$

here, η [Pa·s] is the shear viscosity; η_0 [Pa·s] is the zero shear viscosity of the Newtonian region of fluid; η_∞ [Pa·s] is the infinite shear viscosity. α is a Meter model exponent which represents the slope. τ_p is the threshold shear stress at which viscosity value is $\frac{\eta_0 + \eta_\infty}{2}$.

We modified the equation proposed by Meter as follows that captures the typical viscosity curve of the shear thickening fluid over a range of shear stress values (see Fig 1). We note that the proposed equation follows the similar type of approach as adopted by Galindo-Rosales *et al.* [23, 24],

$$\eta = \eta_{min} + \frac{\eta_0 - \eta_{min}}{1 + \left(\frac{\tau}{\tau_p}\right)^{m_s}} + \frac{(\eta_{max} - \eta_{min}) \left(\frac{\tau}{\tau_{d1}}\right)^{n_s}}{\left(1 + \left(\frac{\tau}{\tau_{d2}}\right)^{n_s}\right)^{S_s}} \quad (2)$$

here, η [Pa·s] is the shear viscosity; η_0 [Pa·s] is the zero shear viscosity of the Newtonian region of fluid (region 1); η_{min} [Pa·s] is the minimum viscosity of the intermediate shear thinning region (region 2) of fluid (*i.e.* minimum shear viscosity); η_{max} [Pa·s] is the maximum viscosity of the shear thickening region of fluid (*i.e.* maximum shear viscosity). m_s is an exponent which represents slope of the intermediate shear thinning region of fluid (region 2). n_s is an exponent which represents slope of the shear thickening region of fluid; S_s is an exponent which represents slope of the extreme shear thinning region of fluid (region 4). τ_p [Pa] is the shear stress at which viscosity of the solution drops to $\frac{\eta_0 + \eta_{min}}{2}$ in the intermediate shear thinning region (region 2). τ_{d1} [Pa] and τ_{d2} [Pa] are shear stresses at which viscosity of the solution drops to intermediate values between η_{min} and η_{max} in the shear thickening region (region 3). The viscosity at τ_{d1} is $\eta_{min} + \frac{\eta_0 - \eta_{min}}{1 + \left(\frac{\tau_{d1}}{\tau_p}\right)^{m_s}} + \frac{(\eta_{max} - \eta_{min})}{\left(1 + \left(\frac{\tau_{d1}}{\tau_{d2}}\right)^{n_s}\right)^{S_s}}$ and the viscosity at τ_{d2} is

131 $\eta_{min} + \frac{\eta_0 - \eta_{min}}{1 + \left(\frac{\tau_{d2}}{\tau_P}\right)^{m_s}} + \frac{(\eta_{max} - \eta_{min}) \left(\frac{\tau_{d2}}{\tau_{d1}}\right)^{n_s}}{2S_s}$. Fig. 1b shows rheological
 132 material parameters of the shear stress-dependent viscosity.

133 3. Free-Volume Theory

134 Most of the non-Newtonian fluid solutions are mixture of solute or
 135 colloidal particles (*e.g.* cornstarch, xanthan-gum) in a solvent (*e.g.* wa-
 136 ter). Note that colloids (*e.g.* silica nano-particles) are phase separated
 137 and insoluble molecules in the solution, whereas solute (*e.g.* polymers)
 138 dissolve in the solvent. The small molecular size of the solvent in the solu-
 139 tion helps solvent to act as a lubricant between solute/colloid molecules of
 140 larger size. The shear thinning or shear thickening behaviour observed in
 141 the non-Newtonian fluids depend highly on the thickness of the solvent's
 142 lubricant layer between solute/colloid particles molecules [6, 11, 37]. In-
 143 teraction between solute or colloid molecules is relatively frictionless (*i.e.*
 144 in equilibrium) at lower stress [6], and this may be the reason for New-
 145 tonian behaviour at a lower shear rate or shear stress (as in Region 1,
 146 Fig 1). An increase in the stress decreases frictionless interaction between
 147 solute/colloids molecules [1, 6, 15]; and solvent effectively acts as a lubri-
 148 cant between solute/colloids molecules. Solvent, being a lubricant, resists
 149 direct interaction between solute/colloids molecules. The viscous nature of
 150 the solvent streamlines solute/colloids molecules and increases the efficient
 151 transport of a solute/colloids in the solvent [6, 10]. The flow of a solvent
 152 is mostly laminar between solute/colloids molecules. This causes a drop
 153 in viscosity of a solution with an increase in shear stress (see Region 2 in
 154 Fig 1). Effectiveness of a solvent to act as a lubricant ceases at sufficiently
 155 higher shear stresses. Coagulation of solute/colloids molecules forms hydro
 156 cluster [6, 10, 11, 37, 38] in the solution due to direct contact between so-

157 lute/colloids molecules. The viscosity of the fluid increases abruptly at high
 158 stresses due to the larger size of the coagulated hydro cluster (see Region
 159 3 in Fig 1). However, at very high shear stresses direct contact between
 160 coagulated solute/colloids molecules breaks [39]. This leads to smaller size
 161 hydro clusters and separated solute/colloids molecules which decrease the
 162 viscosity of the solution (see Region 4 in Fig 1). The viscosity of the fluid
 163 could also decrease due to rupture or erosion of the hydro-clusters or parti-
 164 cles. The presence of artefact in the suspension may lead to the slipping of
 165 the particles if the colloidal suspension is solid-like. This may cause shear
 166 thinning at high shear values. We note that hydrodynamic and interparticle
 167 (intermolecular) interactions between solute/colloids and solvent strongly
 168 affect the relative free volume of solute/colloids and solvent and, in turn,
 169 viscosity of the solution is changed.

170 Macleod (1923) [40] was first to postulate that the viscosity of a fluid
 171 is influenced by the free space available for molecules to move in a total
 172 volume. He suggested that crowding of more molecules in small space
 173 will increase the viscosity of the fluid as it will increase the cohesive force
 174 between molecules and decrease the required time for molecules to move
 175 out of contact. The free space theory proposed by Macleod was further
 176 developed by Doolittle [27] in which he defined free-space in a liquid as
 177 space arises due to liquid's total thermal expansion without phase change.
 178 Doolittle defined relative free space as in Eq. 3,

$$\frac{V_f}{V_0} = \frac{V - V_0}{V_0} \quad (3)$$

179 Where $\frac{V_f}{V_0}$ is a relative free space for a single substance; V_f is a volume
 180 of free space per gram at any temperature; V_0 is a volume of one gram of
 181 liquid extrapolated to absolute zero temperature without change of phase;
 182 V is a volume of one gram of liquid at any temperature. Doolittle [27]

183 proposed an empirical equation to relate the viscosity of the solution with
 184 the free volume space as in Eq. 4,

$$\eta = A e^{\left(\frac{B}{V_f/V_0}\right)} \quad (4)$$

185 Here, A and B are material constants for a single substance. Although
 186 Doolittle validated Eq. 4 for the temperature-dependent decrease in vis-
 187 cosity of a Newtonian fluid, he noted that pressure and temperature could
 188 change relative free space in the liquid. Although Doolittle equation (*i.e.*
 189 Eq. 4) can not define rheology of shear thickening fluids, we could extend
 190 the free volume theory of Doolittle to model rheology of non-Newtonian
 191 fluids, specifically shear thickening fluids.

192 3.1. Relative free-volume dependent viscosity

193 Extending Doolittle free volume theory [27], we propose an empirical
 194 equation (Eq. 5) that relates the relative free volume (f) with the shear
 195 viscosity (η) of shear thickening fluids. We assume that (a) relative free
 196 volume of the solution changes due to hydrodynamic and inter molecular
 197 (or particle) forces; (b) fluid flow and deformation, thermal variation, ex-
 198 ternal and internal pressure, molecular movement due to chemical reactions
 199 generate these hydrodynamic and inter molecular (or particle) forces in a
 200 solution; (c) the change in relative free volume is proportional to the local
 201 stresses (shear, normal, or thermal); (d) V_f is free volume at any stress, V_0
 202 is volume of liquid at a zero stress and absolute zero temperature without
 203 phase change, V is volume of liquid at any stress, and the relative free

204 volume is $f = \frac{V-V_0}{V_0} = \frac{V_f}{V_0}$. Eq. 5 has the following form similar to Eq. 2:

$$\eta = \eta_{min} + \frac{\eta_0 - \eta_{min}}{1 + \left(\frac{f}{f_p}\right)^{m_f}} + \frac{(\eta_{max} - \eta_{min}) \left(\frac{f}{f_{d1}}\right)^{n_f}}{\left(1 + \left(\frac{f}{f_{d2}}\right)^{n_f}\right)^{S_f}} \quad (5)$$

205 here, f_p is a relative free volume of the fluid at which viscosity of the
 206 solution drops to $\frac{\eta_0 + \eta_{min}}{2}$ in the intermediate shear thinning region (region
 207 2); m_f is an exponent which represents slope of the intermediate shear
 208 thinning region of fluid (region 2). n_f is an exponent which represents slope
 209 of the shear thickening region of fluid; S_f is an exponent which represents
 210 slope of the extreme shear thinning region of fluid (region 4). f_{d1} and f_{d2}
 211 are relative free volumes of fluid at which viscosity of the solution drops to
 212 an intermediate value between η_{min} and η_{max} in the shear thickening region
 213 (region 3). The viscosity at f_{d1} is $\eta_{min} + \frac{\eta_0 - \eta_{min}}{1 + \left(\frac{f_{d1}}{f_p}\right)^{m_f}} + \frac{(\eta_{max} - \eta_{min})}{\left(1 + \left(\frac{f_{d1}}{f_{d2}}\right)^{n_f}\right)^{S_f}}$
 214 and the viscosity at f_{d2} is $\eta_{min} + \frac{\eta_0 - \eta_{min}}{1 + \left(\frac{f_{d2}}{f_p}\right)^{m_f}} + \frac{(\eta_{max} - \eta_{min}) \left(\frac{f_{d2}}{f_{d1}}\right)^{n_f}}{2^{S_f}}$.
 215 Fig. 1b shows rheological material parameters of a relative free volume-
 216 dependent viscosity.

217 3.2. Shear stress-dependent viscosity

218 The relative free volume in the liquid depends on the mobility of the
 219 molecules [26] (*i.e.* colloids or solutes and solvents). The size and shape
 220 of molecules, interaction amongst fluid molecules, spatial arrangement and
 221 intermolecular forces between molecules, and nature of bulk fluid flow deter-
 222 mines rheology of the fluid [6, 10, 11, 15]. An interaction amongst molecules
 223 (*i.e.* colloids, solute, solvent etc.) during fluid flow, thermal changes, and
 224 external/internal pressure generate stresses in the liquid. The relative free

space in the liquid changes under the influence of these stresses. We propose a non-linear empirical relationship between stresses in the liquid with a relative free volume as in Eq. 6,

$$f = \left(\frac{\tau}{\tau_0} \right)^m \quad (6)$$

Here, τ_0 [Pa] and m are material constants of the fluid. By substituting Eq. 6 in Eq. 5, we obtain the shear stress-dependent rheological model (Eq. 2) for a shear thickening fluid. The shear rate of the fluid will be as in Eq. 7

$$\dot{\gamma} = \frac{\tau}{\left(\eta_{min} + \frac{\eta_0 - \eta_{min}}{1 + \left(\frac{\tau}{\tau_p} \right)^{m_s}} + \frac{(\eta_{max} - \eta_{min}) \left(\frac{\tau}{\tau_{d1}} \right)^{n_s}}{\left(1 + \left(\frac{\tau}{\tau_{d2}} \right)^{n_s} \right)^{S_s}} \right)} \quad (7)$$

here, $\tau_p = \tau_0 (f_p)^{\frac{1}{m}}$, $\tau_{d1} = \tau_0 (f_{d1})^{\frac{1}{m}}$, $\tau_{d2} = \tau_0 (f_{d2})^{\frac{1}{m}}$, $m_s = m(m_f)$, and $n_s = m(n_f)$.

3.3. Shear rate-dependent viscosity

We note that the deformation of fluid under stresses alter the relative free volume of the fluid. We propose a non-linear [18] empirical relationship between shear rate with a relative free volume as in Eq. 8

$$f = \left(\frac{\dot{\gamma}}{\dot{\gamma}_0} \right)^n \quad (8)$$

Here, $\dot{\gamma}_0$ [s⁻¹] and n are material constants of the fluid. By substituting Eq. 8 in Eq. 5, we obtain a shear rate-dependent rheological model (Eq. 9)

for shear thickening fluids,

$$\eta = \eta_{min} + \frac{\eta_0 - \eta_{min}}{1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_p}\right)^{m_r}} + \frac{(\eta_{max} - \eta_{min}) \left(\frac{\dot{\gamma}}{\dot{\gamma}_{d1}}\right)^{n_r}}{\left(1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_{d2}}\right)^{n_r}\right)^{S_r}} \quad (9)$$

here, $\dot{\gamma}_p = \dot{\gamma}_0 (f_p)^{\frac{1}{n}}$, $\dot{\gamma}_{d1} = \dot{\gamma}_0 (f_{d1})^{\frac{1}{n}}$, $\dot{\gamma}_{d2} = \dot{\gamma}_0 (f_{d2})^{\frac{1}{n}}$, $m_r = n(m_f)$,
and $n_r = n(n_f)$; $\dot{\gamma}_p$ [s⁻¹] is a shear rate at which viscosity of the solution
drops to $\frac{\eta_0 + \eta_{min}}{2}$ in the intermediate shear thinning region (region 2). m_r
is an exponent which represents slope of the intermediate shear thinning
region of fluid (region 2). n_r is an exponent which represents slope of the
shear thickening region of fluid; S_r is an exponent which represents slope of
the extreme shear thinning region of fluid (region 4). $\dot{\gamma}_{d1}$ [s⁻¹] and $\dot{\gamma}_{d2}$ [s⁻¹]
are shear rate at which viscosity of the solution drops to an intermediate
values between η_{min} and η_{max} in the shear thickening region (region 3).
The viscosity at $\dot{\gamma}_{d1}$ is $\eta_{min} + \frac{\eta_0 - \eta_{min}}{1 + \left(\frac{\dot{\gamma}_{d1}}{\dot{\gamma}_p}\right)^{m_r}} + \frac{(\eta_{max} - \eta_{min})}{\left(1 + \left(\frac{\dot{\gamma}_{d1}}{\dot{\gamma}_{d2}}\right)^{n_r}\right)^{S_r}}$ and the
viscosity at $\dot{\gamma}_{d2}$ is $\eta_{min} + \frac{\eta_0 - \eta_{min}}{1 + \left(\frac{\dot{\gamma}_{d2}}{\dot{\gamma}_p}\right)^{m_r}} + \frac{(\eta_{max} - \eta_{min}) \left(\frac{\dot{\gamma}_{d2}}{\dot{\gamma}_{d1}}\right)^{n_r}}{2^{S_r}}$. Fig. 1b
shows rheological material parameters of a shear rate-dependent viscosity.

3.4. Péclet number-dependent relative viscosity

Stokes-Einstein-Sutherland equation (Eq. 10) defines diffusivity (D) of
the molecules/particles with a thermal energy $k_B T$ in a solvent of viscosity
 η_s [41, 42] as

$$D = \frac{k_B T}{6 \pi \eta_s a} \quad (10)$$

where, k_B [J/K] is the Boltzmann's constant, T [K] is the absolute
temperature, a [m] is the radius of the molecules/particles. Péclet number

(Pe), also known as dimensionless shear rate [41], relates the magnitude of thermal motion of molecules with a motion caused by shear. Péclet number as defined in Eq. 11 quantifies strength of the shear force compared to the Brownian forces in the fluid [41],

$$Pe = \frac{\dot{\gamma}}{\frac{D}{a^2}} = \frac{6 \pi \eta_s \dot{\gamma} a^3}{k_B T} \quad (11)$$

We obtain the dimensionless Péclet number-dependent relative viscosity of the shear thickening fluid (Eq. 12) by diving Eq. 9 over η_s and substituting Eq. 11 for the shear rate in Eq. 9,

$$\frac{\eta}{\eta_s} = \frac{\eta_{min}}{\eta_s} + \frac{\frac{\eta_0}{\eta_s} - \frac{\eta_{min}}{\eta_s}}{1 + \left(\frac{Pe}{Pe_p}\right)^{m_r}} + \frac{\left(\frac{\eta_{max}}{\eta_s} - \frac{\eta_{min}}{\eta_s}\right) \left(\frac{Pe}{Pe_{d1}}\right)^{n_r}}{\left(1 + \left(\frac{Pe}{Pe_{d2}}\right)^{n_r}\right)^{S_r}} \quad (12)$$

here, Pe_p is a Péclet number at which relative viscosity of the solution drops to $\frac{1}{2}(\frac{\eta_0}{\eta_s} + \frac{\eta_{min}}{\eta_s})$ in the intermediate shear thinning region (region 2). Pe_{d1} and Pe_{d2} are Péclet number at which relative viscosity of the solution drops to an intermediate values between $\frac{\eta_{min}}{\eta_s}$ and $\frac{\eta_{max}}{\eta_s}$ in the shear thickening region (region 3). $Pe \ll 1$ shows domination of Brownian motion in the fluid while $Pe \gg 1$ suggests that the microstructure is distorted by flow forces [41, 43]. Thus, arrangement of the molecules is highly dependent on Péclet number and by that viscosity of the fluid [43].

3.5. Conversion to an existing model

Eq. 2 converts to the shear stress-dependent Meter model (Eq. 1) [33, 36] by substituting $\eta_\infty = \eta_{min} = \eta_{max}$ and $m_s = \alpha - 1$. Similarly, Eq. 9 converts to the shear rate-dependent Cross model equation [25] (Eq. 13),

278 by substituting $\eta_\infty = \eta_{min} = \eta_{max}$ and $(\frac{1}{\dot{\gamma}_p})^{m_r} = C$.

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + C \dot{\gamma}^{m_r}} \quad (13)$$

279 This suggests that the free-volume theory based equations proposed
 280 in the present work capture the properties of an existing shear stress-
 281 dependent (Meter model) and shear rate-dependent rheological models (Cross
 282 model). Thus, free-volume theory based equation could be utilised to model
 283 purely shear-thinning rheology of the polymeric fluid along with rheology
 284 of the colloidal suspensions.

285 3.6. Numerical simulation

286 3.6.1. Governing equation for a shear rate-dependent rheological model

287 The laminar flow of an incompressible, single-phase shear thickening
 288 fluid through a void space is defined using governing continuity equation
 289 (Eq. 14) and momentum equation (Eq. 15):

$$\nabla \cdot \mathbf{u} = 0 \quad (14)$$

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla P + \nabla \cdot \boldsymbol{\tau} + \mathbf{f} \quad (15)$$

290 here, P is the pressure, $\mathbf{f}$ is any external body force, $\mathbf{u}$ is velocity vector,
 291 t is the time, and $\boldsymbol{\tau}$ is the stress tensor as defined in Eq. 16

$$\boldsymbol{\tau} = \eta(\dot{\gamma}) (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) \quad (16)$$

292 Where $\eta(\dot{\gamma})$ is the shear viscosity of a shear thickening fluid, which is
 293 a function of shear rate. The magnitude of the rate of strain tensor for
 294 shear-dominated flow is as follows

$$\dot{\gamma} = \sqrt{\frac{\dot{\gamma} : \dot{\gamma}}{2}} = \sqrt{2\mathbf{D} : \mathbf{D}} \quad (17)$$

295 here, $\dot{\boldsymbol{\gamma}} = (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)$ and $\mathbf{D} = \frac{1}{2} \dot{\boldsymbol{\gamma}}$

296 The shear viscosity $[\eta(\dot{\boldsymbol{\gamma}})]$ of a shear rate-dependent model is as defined
297 in Eq. 9.

298 3.6.2. Numerical domain, boundary condition and solver

299 We utilised finite volume method based OpenFOAM C++ libraries
300 [44, 45] for solving Eq. 14 and Eq. 15 in conjunction with a shear rate-
301 dependent model equation (Eq. 9). We simulated flow of a shear thickening
302 fluid through a 2D circular staggered micromodel porous medium over a
303 range of constant injection velocity (10^{-7} m/s - 0.1 m/s). The constant in-
304 jection velocity was applied at the right boundary. The numerical domain
305 had a uniform velocity of zero at the beginning of the simulation. The
306 no-slip condition was deployed at the boundary wall of the micromodel.
307 The snappyHexMesh module and blockMesh module of OpenFOAM were
308 employed to generate a fine hexagonal mesh in a porous media domain.

309 The PIMPLE algorithm with nOuterCorrectors of 5 was employed to
310 maintain stability and accuracy of shear thickening fluid flow simulations.
311 The Gauss linear uncorrected scheme of OpenFOAM was employed to dis-
312 cretise Laplacian term of governing equations. Gauss linear scheme was
313 used to discretise the gradient term and divergence term. The Gauss linear
314 scheme uses standard finite volume Gaussian integration. The time scheme
315 of the momentum equation was discretised using the second-order implicit
316 backward method. SmoothSolver with a Gauss-Seidel smoother was used to
317 determine velocity profile and Generalised Geometric-Algebraic Multi Grid
318 (GAMG) solver with diagonal incomplete-Cholesky (symmetric) smoother
319 was employed to estimate pressure field. The Courant number was main-
320 tained below 0.1 using time-step of 10^{-6} s. The convergence criteria were
321 set to 10^{-6} for both the velocity and pressure fields. We used Paraview

5.7.0 software to visualise and post process the shear thickening fluid flow simulation data.

4. Results and Discussion

4.1. Validation of the shear-stress dependent equation

We utilised rheological data of Cwalina *et al.* [46] and Laun [47] to validate the proposed shear stress-dependent model (Eq. 2). Cwalina *et al.* [46] investigated shear stress-dependent rheological characteristics of silica nanoparticles (diameter 520 nm) plus cubic aluminosilicate zeolites dispersed in a polyethylene glycol suspending fluid at colloidal volume fraction (ϕ) of 0.445, 0.518 and 0.507. Laun [47] scrutinized shear stress-dependent viscosity of a styrene-ethyl-acrylate-copolymer-latex of diameter 250 nm dispersed in the water over range of pH and NaCl concentration. We used Excel Solver-GRG nonlinear algorithm [48] to determine material parameters of the proposed rheological equations. The estimated material parameters of the shear thickening fluids of [46] and [47] are as given in Table 1.

Fig 2 and Fig 3 show good fit of the viscosity-shear stress data using Eq. 2 and shear rate-shear stress data using Eq. 7 with experimental measurements of Cwalina *et al.* [46] (ϕ : 0.445 - 0.518) and Laun [47] (pH: 5.1 - 7; NaCl Conc.: 0 - 1.14 g/L). The root means square error (RMSE) of the Eq. 2 and Eq. 7 with respect to the experimental data ranged from 5.4×10^{-4} to 1.6×10^{-2} in Fig 2 and Fig 3, respectively, which suggest statistically good fits of the shear stress-dependent equation with the experiment.

Eq. 2 could capture Newtonian, shear thinning and shear thickening region of the silica nanoparticles based shear thickening fluid of [46] at ϕ of 0.445. At $\phi = 0.507$, Eq. 2 could capture shear thinning, shear thickening and extreme shear thinning at high shear values (see Fig 2a and 2b) of

Figure 2: An experimental rheological data of a silica nanoparticles and cubic aluminosilicate zeolites -based shear thickening fluid of [46] over a range of volume fraction (ϕ) modelled using a proposed shear stress-dependent model. (a) shear viscosity as a function of shear stress modelled using shear stress-dependent equation (Eq. 2), and (b) shear rate as a function of shear stress modelled using shear stress dependent equation (Eq. 7). The material parameters are given in Table 1.

Table 1: Estimated material parameters for shear thickening silica nanoparticles-cubic aluminosilicate zeolites based fluid of [46] over range of volume fraction and shear thickening styrene-ethylacrylatecopolymer latex fluid of [47] over range of pH and NaCl concentration.

Parameter	Volume fraction (ϕ) [46]			pH of solution [47]				NaCl conc (g/L) [47]		
	0.445	0.507	0.518	5.1	5.7	6.2	7	0	0.287	1.14
η_0 [Pa.s]	1	3	5.4	0.787	11.84	83.408	200	120.2	50	0.2
η_{min} [Pa.s]	0.42	1	1	0.034	0.034	0.034	0.034	0.034	0.034	0.034
η_{max} [Pa.s]	2	12	4	0.72	0.260	0.170	0.09	0.15	0.23	0.52
τ_p [Pa]	0.1	0.024	0.026	0.05	0.033	0.029	0.04	0.02	0.02	0.304
τ_{d1} [Pa]	815	44	490	604.6	2567	6700	12847	8398	3476	1120
τ_{d2} [Pa]	393	146	445	939	3629	10196	21474	14000	3041	4621
m_s	1.37	0.5	1	1.344	2.02	2.3	2.1	2	1.9	2.845
n_s	1.4	1.04	1.29	1.389	1.462	1.354	1.3	1.804	1.172	0.969
S_s	1	1.85	1	1.261	1.194	1.255	1.004	1.347	0.9	2.005

the shear thickening fluid of [46]. Fig 3 shows that Eq. 2 correctly depicts the effects of the pH and NaCl concentration on the rheological behaviour of the styrene-ethyl-acrylate-copolymer-latex fluid. Charge on the particle and degree of dissociation change due to pH variation in the solution. Addition of NaCl-salt in the solution increases total ion concentration in the fluid. These parameters strongly affect intermolecular interactions (due to van der Waals and electrostatic forces) between colloids and solvents. The relative free volume in the solution changes due to the combined effect of these intermolecular interactions and hydrodynamic forces. Table 1 shows decrease in η_{max} and an increase in η_0 , τ_{d1} and τ_{d2} with an increase in the pH. On the contrary, Table 1 reports increase in η_{max} and decrease in τ_{d1} and τ_{d2} with an increase in the electrolyte (NaCl) concentration. We note that the proposed model predicted Newtonian viscosity (η_0) of [47] shear thickening fluid solution, which would not have been possible to identify by observation of the rheological data or graph. The predicted

364 minimum shear-thinning viscosity (η_{min}) of 0.034 Pa.s over a range of pH,
 365 and NaCl concentration of [47] indicate that varying hydrogen concentra-
 366 tion and ionic strength did not significantly affect the η_{min} of a latex fluid.
 367 This suggests that the proposed rheological equation helps to quantitatively
 368 correlate rheological behaviour of the shear thickening fluid under varying
 369 physiochemical conditions.

370 4.2. Validation of the shear-rate dependent equation

371 We utilised rheological data of Kalman *et al.* [49], Maus *et al.* [50]
 372 and Zhang *et al.* [51] to validate proposed shear rate-dependent model
 373 (Eq. 9). Kalman *et al.* [49] investigated shear rate-dependent rheological
 374 characteristics of monodisperse polymethylmethacrylate (PMMA) particles
 375 dispersed in polyethylene glycol fluid at colloidal volume fraction (ϕ) of
 376 0.40, 0.45, 0.48 and 0.49. Maus *et al.* [50] measured shear viscosity of the
 377 α,ω -Mg carboxylato-polyisoprene (MCPI) in decahydronaphthalene over a
 378 range of temperature (25 °C, 30 °C, 35 °C). Zhang *et al.* [51] scrutinized
 379 shear rate-dependent viscosity of carbonyl iron particles of 5 μ m mean
 380 size and fumed silica particles dispersed in ethylene glycol over a range of
 381 magnetic field (kA/m). The estimated material parameters of the shear
 382 thickening fluids of [49], [50], and [51] are as given in Table 2.

383 Fig 4, Fig 5 and Fig 6 show good fit of the viscosity-shear rate data
 384 using Eq. 9 with experimental measurements of Kalman *et al.* [49] (ϕ : 0.4
 385 - 0.49), Maus *et al.* (Temp: 25-35 °C) [50], and Zhang *et al.* [51] (Magnetic
 386 field: 0 - 300 kA/m). The root means square error (RMSE) of the Eq. 9
 387 with respect to the experimental data is ranged from 2×10^{-1} to 3×10^1 in
 388 Fig 4, Fig 5, and Fig 6 respectively, which suggests a statistically good fit
 389 of the shear rate-dependent equation with experiments.

390 Fig 4 illustrates that the Eq. 9 can encompass all four regions (New-
 391 tonian, intermediate shear thinning, shear thickening, and extreme shear

Figure 3: The experimental rheological data of styrene-ethyl-acrylate-copolymer-latex based shear thickening fluid of [47] over a range of pH and NaCl concentrations modelled using proposed shear stress-dependent model. (a) shear viscosity as a function of shear stress modelled using shear stress-dependent equation (Eq. 2), and (b) shear rate as a function of shear stress modelled using shear stress dependent equation (Eq. 7). The material parameters are given Table 1.

Figure 4: Shear viscosity of monodispersed polymethylmethacrylate (PMMA) particles based shear thickening fluid of [49] over a range of volume fraction (ϕ) modelled using the proposed shear rate-dependent equation (Eq. 9). The material parameters are given Table 2.

Figure 5: Shear viscosity of α, ω -Mg carboxylato-polyisoprene (MCPI)-based shear thickening fluid of [50] over a range of temperatures modelled using the proposed shear rate-dependent equation (Eq. 9). The material parameters are given Table 2.

Table 2: Estimated material parameters for the shear thickening PMMA particles-based fluid of [49] over a range of volume fraction, the MCPI fluid of [50] over a range of temperature, and the carbonyl iron and silica particles-based fluids of [51] over a range of magnetic field

Parameter	Volume fraction (ϕ) [49]				Temperature ($^{\circ}\text{C}$) [50]			Magnetic field (kA/m) [51]			
	0.49	0.48	0.45	0.40	25	30	35	0	100	200	300
η_0 [Pa.s]	437	143	292	146	477	239	140	20	300	500	800
η_{min} [Pa.s]	8.34	2.3	1	0.60	10	10	10	1.5	2.0	10	11
η_{max} [Pa.s]	293	42	10	1.82	1770	520	213	25	29	32	45
$\dot{\gamma}_p$ [s^{-1}]	0.00146	0.0044	0.0028	0.0065	0.9	1.8	5	2.2	0.7	1.8	1.5
$\dot{\gamma}_{d1}$ [s^{-1}]	0.3	1.8	4	10	3	5.5	11	961	522	415	420
$\dot{\gamma}_{d2}$ [s^{-1}]	0.3	1.82	3.61	10	7.8	11	18.52	1095	557	467	442
m_r	1.1	1.1	1	1.1	2.1	1.9	1.5	0.9	0.82	1.3	1.3
n_r	10.6	8.88	4.27	2.04	1.46	1.24	1.59	6.46	7.09	5.31	7.69
S_r	1.01	1.03	1.03	1.07	1.95	1.42	1.49	1.43	1.13	1.21	1.16

thinning) of the PMMA shear thickening fluid over a range of ϕ values. On the contrary, as depicted in Fig 5, intermediate shear-thinning region is absent in the rheological data of [50]. Yet, Eq. 9 is able to correctly capture Newtonian followed by shear thickening and extreme shear-thinning regions of the fluid over a range of temperature values. Further, Table 2 shows constant minimum viscosity (η_{min}) of the fluid at high shear rate values in the extreme shear thinning region. This suggests that η_{min} also represents the lowest limiting viscosity value of the extreme shear thinning region.

An increase in the ϕ of the particles in the solution increased η_{min} and η_{max} , and decreased $\dot{\gamma}_{d1}$ and $\dot{\gamma}_{d2}$ (see Table 2) of [49]. We note that $\dot{\gamma}_{d1}$ and $\dot{\gamma}_{d2}$ have approximately same values for given ϕ values of [49]. The slope (m_r) of the intermediate shear thinning region of [49] has same value of 1.1 over a range of ϕ , except for $\phi=0.45$. These results suggest that the shear rate-dependent rheological model helps predict threshold shear

Figure 6: Shear viscosity of carbonyl iron particles and fumed silica particles-based magnetorheological shear thickening fluid of [51] over a range magnetic field modelled using the proposed shear rate-dependent equation (Eq. 9). The material parameters are given in Table 2.

rate values ($\dot{\gamma}_p$, $\dot{\gamma}_{d1}$, and $\dot{\gamma}_{d2}$). As predicted, the rheological parameters of [50] show decrease in η_0 , η_{max} , m_r and increase in $\dot{\gamma}_{d1}$, $\dot{\gamma}_{d2}$, n_r with increase in the temperature of the shear thickening fluid. We note that increase in the temperature generates thermal stresses, which change the relative free volume in the solution. This leads to decrease in the viscosity of the solution with increase in the temperature. Increase in exposure of the magnetic field (0 - 300 kA/m) to the shear thickening fluid of [51] increased η_0 , η_{min} , η_{max} and decreased $\dot{\gamma}_{d1}$ and $\dot{\gamma}_{d2}$ (see Table 2 and Fig 6). The shear-rate dependent model (Eq. 9) could estimate η_{min} of the fluid.

These results suggest that the shear stress-dependent equation (Eq. 2)

Table 3: Estimated material parameters for a shear thickening superball silica fluid of [52] over a range of volume fraction

Parameters	Volume fraction (ϕ) [52]	
	0.24	0.28
η_0	1.98	2.6
$\frac{\eta_s}{\eta_{min}}$	1.96	2.53
$\frac{\eta_s}{\eta_{max}}$	2.02	2.72
Pe_p	800	700
Pe_{d1}	4×10^4	1.8×10^4
Pe_{d2}	4.1×10^4	2.1×10^4
m_r	2	1.5
n_r	1.5	1.1
S_r	1.01	1.03

and shear rate dependent equation (Eq. 9) capture highly non-linear rheological characteristics of the shear thickening fluid and predict threshold measurable parameters of shear thickening fluids such as threshold shear stress/rate.

4.3. Validation of the Péclet number-dependent equation

Fig 7 shows a perfect fit of the experimentally determined Péclet number-dependent relative viscosity of the superball silica fluid of [52] with Eq. 12. The material parameters are given in Table 3. Pe in Fig 7 corresponds to the shear rate of 10^0 s^{-1} to 10^3 s^{-1} . We note that Pe takes into account the size of the particle (see Eq. 11). The observed shear thickening behaviour of the fluid at $Pe > 10^3$ suggests a strong dependence of shear thickening on changes in the microstructural arrangement. The Pe_p , Pe_{d1} , Pe_{d2} values obtained using Eq. 12 could be considered as a threshold Pe which helps to modulate shear thinning and shear thickening behaviours in non-Newtonian fluid.

Figure 7: Comparison of the experimentally measured Péclet number-dependent relative viscosity of the superball silica at volume fraction of (a) $\phi = 0.24$, and (b) $\phi = 0.28$ of [52] with a proposed Péclet Number-dependent equation (Eq. 12).

4.4. Pore-scale flow simulation

We simulated the flow of a PMMA particles-based fluid of [49] over a range of constant injection velocity (10^{-7} m/s - 0.1 m/s) in a circular staggered porous medium (domain size: 4.2 mm $\times$ 2.4 mm, circle diameter: 262 μ m, pore-throat size: 162 μ m, channel depth: 120 μ m, porosity: 0.7, see Fig 8). The material parameters of PMMA fluid used for simulation are as given in the Table 2.

Fig 8 shows spatial distribution along with the frequency of the shear rate, shear viscosity and velocity in the 2D porous medium. Fig 8d,e,f indicate that the field of shear rate, viscosity and velocity is non-uniformly distributed in the porous media domain. The bi-modal distribution in Fig 8a,d suggest that the shear rate profile at the micromodel boundary is different from the central part of the micromodel. The first tall peak in the fig 8d is shear rate distribution in the central part, and a small peak at high shear values is shear rate distribution at the boundary. Similar

447 to shear rate profile, bi-modal distribution observed in the shear viscosity
 448 profile in Fig 8e indicate variation in the distribution of viscosity in the
 449 central region and boundary region of the porous medium. Fig 8c imply
 450 that the PMMA fluid has higher velocity along the flow direction; further,
 451 there exists a no-flow region with a velocity lower than 10^{-5} m/s before
 452 and after circular blocks of the porous medium.

453 The average shear rate, the average shear viscosity, and the average
 454 velocity of the fluid flow in the porous medium for each simulation over
 455 a range of injection velocity are estimated using 'integrate variable' filter
 456 of the Paraview 5.7.0 software. Fig 9a compare the average shear rate of
 457 the porous medium with an average viscosity of the porous medium over a
 458 range of volume fraction and injection rate. Fig 9a depict shear thickening
 459 behaviour of the fluid in the porous medium similar to the rheological data.
 460 Note that the average values of shear rate and shear viscosity of the porous
 461 medium do not overlap with a rheological data of the PMMA fluid measured
 462 using a rheometer (i.e. as in Fig 4).

463 Fig 9b shows the non-linear relationship between average velocity and
 464 pressure gradient during the flow of PMMA based shear thickening fluid
 465 in the 2D staggered porous medium. Further, we can deduce from Fig 9b
 466 that with an increase in the volume fraction of the particle in the fluid
 467 increases the pressure requirements. The results of direct numerical sim-
 468 ulation indicate that the proposed shear rate dependent rheological model
 469 for shear thickening fluid can be utilised to gain pore-scale insight of shear
 470 thickening fluid flow. In future, we will use the proposed rheological model
 471 to numerically simulate two-phase shear thickening fluid flow using volume
 472 of fluid method, specifically to understand the shear thickening fluid flow
 473 behaviour while displacing Newtonian fluid at pore-scale.

Figure 8: Spatial distribution of a) shear rate (b) shear viscosity (c) velocity and frequency of d) shear rate e) shear viscosity f) velocity in the porous media domain during PMMA fluid ($\phi = 0.45$) flow at a constant injection velocity of 0.1 m/s.

Figure 9: (a) Average shear viscosity - average shear rate, and (b) average velocity - pressure gradient over a range of volume fraction (ϕ) obtained after simulated flow of PMAA shear thickening fluid of [49] through the 2D staggered porous medium over a range of constant injection rates.

474 5. Conclusions

475 The free volume theory proposed by Doolittle is protracted for a shear
476 thickening fluid. An empirical formula is proposed to relate the shear vis-
477 cosity of shear thickening fluid with a relative free volume of the fluid. The
478 stresses generated in the fluid due to intermolecular forces, hydrodynamic
479 forces, and thermal variation cause a change in the relative free volume.
480 The non-linear relationship between stresses and the relative free volume
481 is used to develop a shear stress-dependent rheological equation for shear
482 thickening fluids which captures different behaviours such as Newtonian, in-
483 termediate shear thinning, shear thickening, and the extreme shear-thinning
484 regime of a shear thickening fluid. An equation for the shear rate-dependent
485 viscosity is also formulated using a non-linear relationship between the shear
486 rate and the relative free volume. The proposed formulations convert to
487 the existing Meter model and Cross model. We note that the proposed rhe-
488 ological model equation are empirical generalised Newtonian fluid (GNF)
489 models similar to power-law, Carreau, Cross, Meter models.

490 The perfect fit of the experimental data of various shear thickening fluid
491 (silica nanoparticles, latex, PMMA particles, MCPI, carbonyl iron particles
492 based shear thickening fluid) with the shear stress-dependent equation and
493 the shear rate-dependent equation over a range of physicochemical prop-
494 erties (volume fraction, pH, NaCl concentration, temperature, magnetic
495 field) suggests that the proposed rheological formulations could be utilised
496 to evaluate rheological characteristics of the shear thickening fluid using
497 measurable parameters. The nine material parameters of the proposed
498 formulation help to quantitatively analyse the effect of varying physico-
499 chemical conditions on rheology of shear thickening fluids. The proposed
500 equation predicts critical viscosity parameters of shear thickening fluids
501 such as η_0 , η_{min} , η_{max} . The threshold shear stress parameters (τ_0 , τ_p ,

502 τ_{d1}, τ_{d2}), the threshold shear rate parameters ($\dot{\gamma}_0, \dot{\gamma}_p, \dot{\gamma}_{d1}, \dot{\gamma}_{d2}$) and the
503 threshold Péclet number parameters (Pe_p, Pe_{d1}, Pe_{d2}) of the proposed
504 equations are parameters that modulate the effective transmutation of rhe-
505 ological characteristics (*i.e.* from Newtonian to shear-thinning followed by
506 shear-thickening regime).

507 Numerical simulations of PMMA-based fluid (modelled using shear rate-
508 dependent equation) flow through 2D circular staggered porous medium
509 shows that the proposed shear rate dependent equation can be employed for
510 conducting shear thickening fluid flow studies. We observed shear thinning,
511 shear thickening followed by again shear thinning of the PMMA-based fluid
512 flow in 2D porous medium. The shear rate, shear viscosity and velocity in
513 2D porous medium has bimodal distribution, which indicate that the flow
514 behavior of the shear thickening fluid at boundary of porous medium is
515 different than in the central part of the porous medium. We will extend
516 this work a) to upscale pore-scale shear viscosity of the shear thickening
517 fluid to continuum scale and b) to simulate two phase shear thickening fluid
518 flow in a porous medium.

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527 **Conflict of interests**

528 The authors declare that they have no conflict of interest.

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