INKJET PRINTED DROPS AND THREE-DIMENSIONAL CERAMIC STRUCTURES

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Doctor of Philosophy

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SCHOOL OF MATERIALS
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Abstract

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Doctor of Philosophy ---The University of Manchester

Inkjet Printed Drops and Three-dimensional Ceramic Structures

Inkjet printing is a versatile manufacturing method with applications beyond its traditional application in graphics and text printing, particularly in structural and functional materials. This thesis aims to enhance the understanding of DOD inkjet printing processes by investigating the behaviour of solvent mixtures and nanoparticle suspensions to identify the key parameters affecting drop ejection, drying and stacking processes.

Drop ejection and flight were investigated with two modes of inkjet printheads, using a range of fluids formulated from solvent mixtures and characterised by the dimensionless number $Z = (\rho \gamma a)^{1/2}/\eta$, where $\rho$, $\gamma$ and $\eta$ are the fluid density, surface tension and dynamic viscosity respectively and $a$ is the diameter of the printer nozzle. The printable range was found to be $1.17 \leq Z \leq 36.76$ for a 10 pl (21.5 μm diameter) shear-mode Dimatix printhead. However, with an 80 μm diameter squeeze-mode MicroFab printhead, the range was found to be narrower with $4.02 \leq Z \leq 16.2$. However, both printheads were found to show a printable range of Weber number with $0.4 < We < 20$. Weber number is determined by the drop velocity and hence the actuating pulse. When designing inks for future printing work, not only the fluid properties, but also the pulse voltages need to be considered.

The drop stacking and solidification processes of drops containing nano ZrO$_2$ particles were investigated to enhance the understanding of drop drying and drop/drop interactions. In-situ synchrotron X-ray radiography provides a promising method to track the time-evolved solid segregation within printed drops during drying. Both the initial contact angle and substrate temperature during printing strongly influence the drying process and the final dried deposit shape. The drops were first pinned and then there was a slight sliding of the three-phase contact line. Drops were deformed by the stacking of overprinted drops when printed on Kapton tapes and silicon wafer surfaces, but not on glass slides due to the small contact angle of water on glass slides. Crack-like defects were found at the edge of the final dried stacking structures.

The coffee stain effects within a single inkjet printed droplet and the 3D structures before and after sintering were investigated to find out the influence of ink properties, printing parameters and substrate temperature on inkjet printed structures. It was found coffee staining was more obvious at high substrate temperatures. When adding 25 vol% ethylene glycol (EG) or 5 wt% polyethylene glycol (PEG), the coffee stain effect is reduced or eliminated under room temperature drying.

X-ray tomography has been demonstrated as a valuable tool for the characterization of 3D printed objects and defects that form during their manufacture. Defects were characterised as microvoids or large-scale crack-like defects. The majority of the microvoids revealed are associated with mechanisms and processes within a single drop, e.g. segregation during dryings such as the formation of coffee stains or coffee rings. The size or distribution of microvoids can be controlled by changing the ink formulation, with higher PEG content inks showing lower concentrations of microvoids.
Declaration

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Dedication

To my parents and my parents-in-law,

To my husband Ruizhi Pei,

To my son Dongda Pei
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First of all, I would like to express my sincere gratitude to my supervisor, Professor Brian Derby, for his supervision and support on my Ph.D. research. His patience and encouragement help me go through tough times. His enthusiasm and motivation on scientific research always impress me and give me a deep and long-term influence on my determination of being a researcher. Beyond his invaluable supervision, he provided me a creative atmosphere, inspiration, and motivation for the research in the laboratories.

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I would like to thank my parents, parents-in-law and my brother for their everlasting love and the continuous and invaluable support during my Ph.D. period. Especially, my thanks go to my parents-in-law for taking good care of my son.

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Poster presentations

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7. Yuanyuan Liu, Robert Bradley and Brian Derby, Characterization of Defects in 3D Inkjet Printed Zirconia Structures by High-resolution X-ray Tomography, School of Materials Postgraduate Research Conference, University of Manchester, UK, 7th May 2014.
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CHAPTER 1 Introduction

1.1 Background

In recent years, there has been growing interest in using inkjet printing as a low-cost manufacturing method with applications in areas of structural and functional materials manufacture, such as ceramic fabrication, biomaterials and tissue engineering scaffolds, functional polymers and devices [1]. There has also been an increasing number of publications on the use of inkjet printing in ceramic fabrication [2]–[7]. There is no need for molds or dies for 3D inkjet printing ceramic objects. Fabrication of green bodies can be achieved by printing second and subsequent layers on top of pre-printed layers dried in air under ambient laboratory conditions. Compared to other additive manufacturing methods such as fused deposition modeling, selective laser sintering and stereolithography, inkjet printing allows the manufacture of multifunctional 3D ceramic objects by depositing different materials on the same layer [8].

Figure 1-1 shows a framework for the process of inkjet printing 3D objects. After slicing, the designed model will become digital signals, which control the printhead to jet an ink droplet or not at a given location. A line of printed droplets forms a printed line, while several printed lines coalesce to become a printed layer. The stacking of several layers forms a 3D object.

Figure 1-1 A research framework for inkjet printing 3D structures.
To obtain a desired 3D inkjet printed ceramic structure, it is necessary to satisfy a number of requirements [9]. These are:

1) To form regular drops, stable ceramic suspensions with defined fluid properties need to be passed through a droplet generator.
2) To create desired 2-D features, suspensions need to be delivered onto a substrate or a previously printed layer, with drops in sufficient proximity to each other to allow adjacent droplets to interact and coalesce.
3) The printed ceramic ink must undergo a phase transition to a solid deposit.
4) To produce 3-D structures, the deposition and drying/solidification processes need to be repeated on a layer of pre-deposited and dried material.

To generate accurate and repeatable droplets passed through a drop-on-demand (DOD) droplet printhead, the ink properties need to be adjusted to the printable range of the printhead. Simulations to predict the printable range of fluid properties for DOD printheads and experimental data have been reported using a characteristic dimensionless number, \( Z = \left( \frac{\rho \gamma}{\eta} \right)^{1/2} \), where \( \rho \), \( \gamma \) and \( \eta \) are the fluid density, surface tension and dynamic viscosity respectively, and \( a \) is the diameter of the printer nozzle [10]–[18]. However, there is no consensus on the applicability of a defined \( Z \) number for printable ink formulations for inkjet printing. It is not known whether there is a universal \( Z \) number range for inkjet printability or whether the range varies with different actuating pulses and different modes of printhead actuation. Ink printability and printable range need to be further investigated and compared among different modes of DOD printheads.

3D printing of ceramic parts occurs by the interaction and coalescence of liquid droplets, which then dry to form a solid object. The interaction of droplets and the drop drying process, which can influence both internal and external defects, are clearly important in determining the quality, accuracy and properties of a printed 3D object. A comprehension of how single droplets dry and stack together is important for understanding how 3D structures are built. During drying, particles may segregate to the edge of the droplet, resulting in non-uniform deposition (known as the “coffee stain” or “coffee ring effect” [19]), and associated defect formation. Optical coherence tomography and confocal optical microscopy have both been used to track particle motion and density distributions within drying drops [19]–[21].
However, only large viewable particles could be detected. These methods are not suitable for studying dense nanoparticle suspensions. The drying process of dense nanoparticle suspensions is not fully understood due to a lack of detailed information about the particle segregation process during droplet drying. It is also not clear whether defects form between or within the dried drops during the stacking process. Droplet drying and interaction processes need to be studied in real-time to help understand and control coffee stain formation and the formation of inkjet printed 3D structures.

To produce well-defined objects by inkjet printing, it is necessary to control the coffee stain phenomenon and to produce homogeneous uniform dried drops. There are already a number of procedures proposed to reduce the coffee stain effect [22]–[27], mainly using solvent mixtures and adjusting the drying temperature. Solvent mixtures have been used to suppress coffee staining by driving an opposing fluid flow generated using temperature or concentration gradient driven surface tension gradients (Marangoni convection) [28]–[30]. However, the influence of substrate temperature is not uniformly accepted as a controlling mechanism [31]. Thus, more study is needed to investigate methods of reducing the coffee stain and check the influence of substrate temperature. In addition, accurate characterisation of the internal structures of inkjet printed 3D objects is important to evaluate and predict the performance of inkjet printed objects and help to optimise their printing parameters and composition design.

1.2 Thesis objectives

The main thesis objective is to further understand the fundamentals of the mechanisms of inkjet printing and inkjet printing ceramic structures. Therefore, all the work carried out in this thesis is related to the study of ink droplets and 3D structures. The ink printability range, droplet drying and interaction processes and inkjet printed 3D structures are investigated.

1.3 Thesis outline

The structure of the thesis is as follows.
Chapter 1 introduces the background and motivation of the research. The thesis outline is also summarized.

Chapter 2 reviews the fundamentals of inkjet-printing technology, current understanding of inkjet printing processes and inkjet printing ceramic nanoparticle suspensions.

Chapter 3 describes the experimental materials and approaches used in the study. These include: experimental materials, ink formation methods, inkjet printheads, inkjet printers chosen, characterization methods and related analysis techniques.

Chapter 4 focuses on the influence of Z number and pulse voltage on ink printability for two different modes of printheads. The prepared fluids comprised: distilled water, a mixture of distilled water and ethylene glycol (EG), pure EG, pure diethylene glycol (DEG) and pure glycerol. These were chosen to study the printable range of fluid properties and help understand the printing parameters’ influence on the printing results. All the inks were firstly printed using a Pixdro LP50 printer equipped with a 10 pl Dimatix shear-mode piezoelectric printhead to generate droplets. The printable Z number range was investigated by comparing the generated droplet conditions of different inks with different inkjet printing parameters. These inks were also printed with an 80 μm squeeze-mode MicroFab printhead to make a comparison of the difference of printable Z range and suitable printing waveform for different printhead styles. These results informed the required ink properties and inkjet printing parameters for inkjet printing ceramic nanoparticle suspensions.

Chapter 5 focuses on the study of the drying and stacking mechanisms of inkjet printed nanoparticle suspensions on different substrates under different substrate temperatures. ZrO\textsubscript{2} powders were chosen as the model materials to study inkjet printing nanoparticle suspensions in this study. Three substrates of different contact angles with the inks were applied. The generated drops were printed on three different substrates of different contact angle at different substrate temperatures. The printed drops were studied using ultra-fast in-situ synchrotron X-ray 2D projections to record the dynamic drying and stacking processes.

Chapter 6 focuses on methods to reduce the coffee stain and characterisation the internal structures of the green body and sintering bodies using micro X-ray
computed tomography (microXCT). Small molecule EG and big molecular polyethylene glycol (PEG) additions to the ink as well as different substrate temperatures were used to investigate the use of solvent mixtures on reducing the coffee stain phenomenon with nanoparticle suspension. 3D green bodies and sintered structures were detected by the microXCT to image the internal structures without destruction.

Chapter 7 summarizes the main results and conclusion of the thesis, along with the inspirations obtained from current studies and the outlook for further research.
CHAPTER 2 Literature Review

This review focuses on the inkjet printing technique, inkjet printing process and ceramic suspensions. The first part introduces inkjet-printing technology and describes the development of piezoelectric drop-on-demand (DOD) inkjet printing. The second part presents a review of the current understanding of ink properties, printing parameters and nozzle geometries that influence drop ejection and flight during the printing process. The third part gives a brief review of the mechanisms of drop impact and spreading on substrates. The fourth part reviews the drying and solidification processes and characterization methods. The final part reviews inkjet printing ceramic suspensions, sintered inkjet printed bodies and X-ray tomography technology in detail.

2.1 Inkjet printing technology

Inkjet printing is a non-impact printing (NIP) technology. The concept of inkjet printing can be traced back to the 18th century when Jean-Antonie Nollet [32] carried out research on the effect of static electricity on a stream of droplets in 1749 and demonstrated the deflection of charged drops. The controlled positioning of individual drops of ink is the technology that underpins inkjet printing.

During inkjet printing, drops of ink in a size range of 1-100 picoliters (pl) [11] are produced and positioned such that the printing pattern is made directly on the substrate. After more than two and a half centuries development, inkjet printing now has been used widely not only in the publishing and graphics industries, but also to fabricate a range of functional devices, including displays, ceramic components, sensors, electronics components, and tissue engineering scaffolds [11].

As summarised in Figure 2-1, there are two families of droplet generation technologies used for inkjet printing, known as continuous inkjet (CIJ) printing and drop-on-demand (DOD) inkjet printing. Both of these methods can be used to generate drops with diameters in the range of 10-150 μm [11]. These two major technologies can be further sub-divided into categories, as shown in Figure 2-1. The working principles of these most commonly used inkjet printing technologies will be reviewed in the following sections.
2.1.1 Continuous inkjet printing

CIJ printing typically forms drops of diameter around 100 μm [11]. It has major commercial applications for marking and coding of products. It is also commonly applied to product packaging. The root of this technology can be derived from the 19th century, when William Thomson (Lord Rayleigh) published a Siphon Recorder patent in 1867 [34]. In this patent, an automatic receiving or recording instrument for electrical telegraphers was described. The first practical commercial device using CIJ printing was introduced in 1951, when Siemens used a droplet-based printing system to plot machine output traces replacing a galvanometer driven pen stylus [35].

CIJ printing generates drops by using a high-pressure pump to force fluid through a nozzle, creating a continuous stream of ink droplets via the Plateau-Rayleigh instability [36], as shown in shown in Figure 2-2a. The drops are electrically charged on generation. Drop flight is controlled by electrostatic deflector plates to direct their arrival at desired locations on a substrate. Only a small fraction of the droplets formed are used to print an image, while the majority of the ink will be recycled.
Figure 2-2 Graphical illustrations of the major commonly used principles behind different inkjet printing technologies: a) CIJ printing; b) thermal DOD inkjet printing and c) piezoelectric DOD inkjet printing. Adapted from Derby [11].

2.1.2 Drop-on-demand inkjet printing

In DOD inkjet printing, a drop is generated only when needed by producing a pressure pulse in a chamber filled with ink that is located behind the printing nozzle. Before drop generation, the printhead (the droplet generator) or the substrate is moved to the desired location. Subsequently, the drop will be generated and deposited in a precisely defined position.

DOD inkjet printing generates drops only when required for printing, saving raw materials and reducing the printing steps. As a consequence DOD inkjet printing is more material efficient with lower waste generation during drop production and placement than CIJ printing. In addition, DOD inkjet printing can produce smaller drop sizes and has better drop placement accuracy and fewer restrictions for the printed liquid comparing to CIJ inkjet printing [37]. Based on the mechanism used for generating the pressure pulse, DOD inkjet printing technologies can be divided into two major systems: thermal DOD inkjet printing (shown in Figure 2-2b) and piezoelectric DOD inkjet printing (shown in Figure 2-2c).

2.1.2.1 Thermal DOD inkjet printing

In 1977, Ichiro Endo described the principle of thermal DOD inkjet printing [37]. For thermal DOD inkjet printing (shown in Figure 2-2b), a micro-heater is applied to the ink in a reservoir immediately behind the printing nozzle, thus vaporizing a small amount of the ink producing a localised vapour pocket or bubble. Once the heat is
removed, the vapour condenses and the bubble rapidly collapses. The pressure pulse that is generated by the formation, expansion and collapse of the bubble, propagates towards the nozzle leading to droplet generation and ejection. After a drop is generated, the heater is ready to create another bubble to repeat the printing process.

In thermal DOD inkjet printing, the ink is ejected without any other mechanical movements. There is no particular requirement for the printhead, allowing thermal inkjet printers to be made at low cost. Thermal DOD inkjet printing is commonly used in desktop inkjet printers. However, thermal DOD inkjet printing has a vapour bubble formed by locally boiling the liquid ink. The vapour bubble generates enough kinetic energy to push a fluid droplet out of the nozzle. Thus, the solvent of thermal printing ink is basically restricted to water [37].

2.1.2.2 Piezoelectric DOD inkjet printing

1) Operating principle of piezoelectric DOD inkjet printing

In piezoelectric DOD inkjet printing (shown in Figure 2-2c), the operating principle is the generation of pressure waves in a fluid-filled channel behind an orifice. The pressure pulse is produced by the mechanical actuation of the chamber walls [38]. When a pulse voltage is applied, the piezoelectric material changes shape and generates a pressure pulse in the ink. This pressure pulse forces a droplet of ink out of the nozzle. At the end of orifice, the ink is normally retained by surface tension at the fluid/air interface. Hence the action of the pressure wave is to overcome the surface tension and eject the ink from the orifice. Above some critical value of this pressure, determined by the rheological properties of the ink and the mechanical properties and dimensions of the channel and orifice, the protruding ink will pinch off under surface tension to form a droplet [39].

After technical development of more than half a century, piezoelectric DOD inkjet printheads have been further developed and can be divided into four different drop formation modes (squeeze mode, shear mode, bend mode and push mode), as shown in Figure 2-3.
Figure 2-3 Schematics of different design modes for piezoelectric DOD inkjet printheads: a) squeeze mode; b) shear mode; c) bend mode and d) push mode. Adapted from Cummins and Desmulliez [40].

The first squeeze-mode printhead (Figure 2-3a) was patented by Zoltan in 1972 [41]. When a voltage applied in squeeze mode printheads, the piezoelectric electrodes will contract, squeezing the ink chamber and finally force a droplet out of the nozzle [40]. The squeeze-mode MicroFab prinheads, produced by MicroFab Technologies, Inc., have had widespread use and have attracted considerable interest in materials fabrication research [42]–[44]. The shear-mode printhead (Figure 2-3b) was invented by Fischbeck and Wright in 1986 [45]. In the shear mode, a voltage is applied to the piezoelectric electrodes causing the shear deformation to deform the upper part of the channels. This deformation is mirrored in the lower part of the channel forcing the channel into a chevron shape. Finally, a droplet is ejected by flexing of the channel [40]. This kind of prinheads is mainly produced and sold by Xaar and Fujifilm Dimatix. The bend-mode printhead (Figure 2-3c) was patented in the 1970s [46], [47]. The droplet is ejected by bending of the ink chamber wall. Bend-mode
printheads have been sold by Kyocera, Tektronix, Epson and Xerox [40]. The push-mode printhead (also named bump-mode printhead) was described by Howkins in 1984 [48], as shown in Figure 2-3d. A droplet is ejected by the piezoelectric rod expansion. Push mode printheads have been further developed by Epson, Trident, Hitachi and Brother [40]. In this project, the printability of inks using the squeeze-mode MicroFab printheads and shear-mode Dimatix printheads was investigated in detail.

2) Advantages of piezoelectric DOD inkjet printing

As an additive manufacturing technology, piezoelectric DOD inkjet printing has improved manufacturing capabilities when comparing with other current fabrication methods. The major advantages are as follows:

a) High quality of product

Piezoelectric DOD inkjet printing is a precision printing tool and comes out with a product with lower failure rate than other methods [49].

b) More productivity and flexibility

Piezoelectric DOD inkjet printing requires no dies or tools and produces objects directly from design file data. This reduces product lead times and allows greater productivity and flexibility in manufacture. Piezoelectric DOD inkjet printers can be used to print small-scale production runs of products in various patterns and colours. The digital models can be easily designed and changed, which allows faster prototyping and personalization. Comparing to fused deposition modeling, selective laser sintering and stereolithography, piezoelectric DOD inkjet printing makes it possible to manufacture multifunctional 3D ceramic objects by depositing different materials on the same layer [8].

c) Environmentally friendly and safe

As a drop-on-demand additive process, piezoelectric DOD inkjet printing generates a smaller amount of the waste in the printing processes than other materials fabrication methods [50]. The minimal materials loss of piezoelectric DOD inkjet printing makes it an environmentally friendly method. In addition, piezoelectric DOD inkjet
printing is a non-contact printing method with low noise during printing [51]. Thus, this technology can be quite friendly and safer for human beings.

**d) Wider variety of inks**

Although more expensive to manufacture, due to the piezoelectric material (usually lead zirconium titanate PZT) used for the printheads, piezoelectric DOD inkjet printing allows a wider variety of inks than thermal inkjet because there is no requirement for a volatile component. CIJ inkjet printing is not used for non-graphics applications because of the risk of contamination, which always occurs during the recirculation process of inks [52]. Thus, this study has used piezoelectric DOD printheads throughout.

**3) Application of piezoelectric DOD inkjet printing**

Piezoelectric DOD inkjet printing is mostly used for large-scale graphics printers in preference to thermal DOD. In addition, the high precision and the ability to deposit materials only when necessary have made piezoelectric DOD inkjet printing attractive as a manufacturing tool for scientific research for functional materials fabrication. Recently, there have been an increasing number of publications reporting the use of piezoelectric DOD inkjet printing as a materials fabrication tool. It has been applied to flexible electronics [1], plastic electronic devices [53], metals [54], tissue engineering [55]–[57], ceramic component manufacture [2], [3], carbon materials and sensors [38], [58]. This project mainly focused on the application of DOD inkjet in printing ceramic nanoparticle suspensions.

**2.2 Inkjet printing drop ejection and flight**

There are five stages of the DOD inkjet printing process: drop ejection, drop flight, drop impact, drop spreading and drop solidification [59]. A key aspect of inkjet printing is the generation and flight of individual droplets. The drop ejection and flight processes have fascinated scientists for many years. Figure 2-4 presents an example of a sequence optical images showing the formation of drops from an inkjet printer and the consequent formation of a trail of satellite drops following the principal drop. Hoath et al. [60] explained the drop ejection and flight processes using a schematic diagram as shown in Figure 2-5a. Drop ejection involves the
ejection of a column of liquid and the subsequent generation of a drop with an attached ligament of liquid extending to the printer nozzle. This ligament ruptures and the subsequent drop morphology depends on both the properties of the drop and the ligament. During drop flight, the ligament may retract into the drop or it may destabilise into a train of satellite drops. Hoath et al. [60] also presented a model for the length evolution of the ligament (also named as “tail” or “filament”) with time during the drop ejection process (shown in Figure 2-5b).

Figure 2-4 Fast optical images showing inkjet printing droplet evolution as a function of time. The polystyrene droplet remains attached to the nozzle through a persistent filament. Detachment occurs by formation of a pinch point after 200 $\mu$s and formation of secondary satellite droplets after 240 $\mu$s. Adapted from De Gans et al. [61].

Figure 2-5 a) A schematic diagram for an ink jet depicting ligament length (shown by the braces in each case) at various times: (I) near emergence, (II) stretching, (III) break-up, (IV) maximum ligament length, (V) tail recoiling, (VI) satellite formation (if any), (VII) final length state D, and (VIII) downstream drift of final length state D. b) A model for the ligament length attached to the main drop showing its evolution with time after emergence, for a main drop speed of about 6 m/s at 1 mm distance. The ligament length at break-up is $L_b$ and the final main drop diameter is $D$; between these states the ligament length remaining attached to the main drop is represented by a Gaussian shape. Adapted from Hoath et al. [60].
As shown in Figure 2-5a, a persistent ink ligament is formed and attaches the droplets to the nozzle in the early stages of drop formation. The ligament can be sustained for several hundreds of microseconds as shown in Figure 2-5b. Here, the ligament has broken into small fragments, which tended to form smaller “satellites”, as shown in Figure 2-5a. This model was also been confirmed in many reports from other inkjet printing researchers [18], [61]–[64]. If the ink contains particles, such as ceramic powder suspensions, it is believed that the particles can act as nuclei for ligament rupture and satellite formation. The satellites with lower velocities, mass and momentum will deposit after the major drop and will hit a substrate in different, random and undesired locations. Satellite drops introduce noise into a printed pattern accompanied by printing defects.

Although it is possible to correct some faults with satellite droplets, satellite droplets are undesirable in most applications and various approaches, which have been suggested for their reduction or elimination [65]. Xu et al. [66] found increasing the cell concentration has suppressed the formation of satellite droplets due to the increased viscous and elastic effects and a decreased capillary effect. Hoath et al. [67] suggested that adding polymers to the ink, e.g. aqueous solutions of PEDOT: PSS (1:2.5 by weight), can completely suppress satellites by influencing the rheology of the ligament, which is significant for many printing applications.

In addition to the presence or absence of satellites, the performance of the droplet ejection process can also be characterised by the droplet velocity, volume, consistency, shape and directionality [40]. All these performance parameters are affected by factors such as the ink physical properties, nozzle geometry and waveform design [18], [68]–[74]. The effects of these factors have been the subject of many computational [75], [76] and experimental [77], [78] studies.

### 2.2.1 Ink properties required for drop ejection and flight

Inkjet printing has used a range of materials as inks for the fabrication of devices. A printable ink needs to meet some specific property requirements determined by the physics and fluid mechanics of the drop generation process [37], [79]. The key ink property requirement is the ability to generate stable and uniform size droplets [59]. In order to improve printability, the droplet formation behaviour of inks with various
physical properties must be determined [68]. The three most important ink physical properties that influence drop formation behaviour are the viscosity, density, and surface tension of the printing ink [18]. These properties determine the ink printability, such as the generated drop size, drop shape, substrate wetting and the presence or absence of satellites [40]. The ink property requirements for drop-on-demand (DOD) mode inkjet printing are low viscosity, high surface tension and preferably Newtonian behaviour to ensure good inkjet printability [80]. The ink viscosity must be low enough to enable the ink reservoir to refill in a time within 100 μs of the drop ejection out of the nozzle by the transient pressure pulse [40]. The ink surface tension must be sufficiently high to prevent unwanted dripping from the nozzle and also low enough to enable the ejected droplet to break away from the nozzle [40]. The ink viscosity is generally considered to be more important than the ink surface tension for determining ink printability [38]. Low viscosities usually lead to satellite formation and residual pressure wave interaction between succeeding droplets. In contrast, high viscosities cause energy dissipation and hinder the formation of droplets [68]. In general, it is believed that ink properties should be controlled with a viscosity range of approximately 0.5-40 mPa·S and a surface tension range of 20-70 mN/m [80], [81].

Several studies have been conducted on the jetting behaviour of inks with various viscosities and surface tensions [82], [83]. The behaviour of drop formation from inks with different properties has been assessed mainly using three dimensionless numbers. They are the Reynolds number ($Re$), Weber number ($We$) and $Z$ number ($Z$) [9], [11]. $Re$ represents the ratio of inertial to viscous forces as shown in Equation 2-1. $We$ represents a balance between inertial and capillary forces [84] as shown in Equation 2-2. $Z$ number is the inverse of Ohnesorge number ($Oh$, [85]) as shown in Equation 2-3:

$$Re = \frac{v_pa}{\eta}$$  \hspace{1cm} (2-1)

$$We = \frac{v^2_p a}{\gamma}$$  \hspace{1cm} (2-2)

$$Z = \frac{1}{Oh} = \frac{Re}{\sqrt{We}} = \frac{(\gamma_p a)^{1/2}}{\eta}$$  \hspace{1cm} (2-3)
where \( \rho, \eta, \) and \( \gamma \) are the density, dynamic viscosity and surface tension of the fluid, respectively. \( v \) is the fluid (drop) velocity, and \( a \) is a characteristic length. (The critical length for inkjet printing is sometime taken as the diameter of the printing nozzle [9], [11], [37], [84] or by other workers, the radius [10], [18], [68]; in this project it is fixed as the nozzle diameter).

Fromm carried out the earliest significant work in modeling the mechanisms of drop generation during inkjet printing and suggested \( Z > 2 \) for stable drop formation [10]. Reis and Derby [86] proposed that there is a range of \( Z \), with \( 1 < Z < 10 \), for stable drop generation using numerical simulation. They predicted that viscous dissipation prevents drop ejection when \( Z < 1 \), while satellite drops form together with the primary drop when \( Z > 10 \).

The \( Z \) number is independent of the velocity of the drop \( (v) \). However, there are further factors related to drop velocity that influence drop formation. In order to eject a droplet from a printhead, a minimum energy is needed to overcome the barrier from the surface tension \( (\gamma) \) and Laplace pressure [9]. The velocity of the drop that leaves the nozzle is bounded by a minimum velocity because a minimum pressure is necessary to overcome the pressure generated by surface tension at the nozzle \( P_s \), as shown in Equation 2-4. The pressure to overcome the surface tension is generated by droplet inertia, which gives a typical pressure of \( P_i \), as shown in Equation 2-5.

\[
P_s \approx \frac{4\gamma}{a} \tag{2-4}
\]

\[
P_i \approx \rho v^2 \tag{2-5}
\]

where \( \gamma \) is the liquid-air interface surface tension, \( a \) is the nozzle diameter, \( \rho \) is the droplet density, and \( v \) is the droplet velocity.

Thus, a minimum velocity \( (v_{min}) \) is required to meet the minimum energy for drop ejection. This is shown in Equation 2-6, ignoring the friction in the nozzle [37]. The measured velocity is somewhat lower than the predicted minimum velocity, but the order of magnitude of Equation 2-6 is correct [37].

\[
v_{min} \approx \left( \frac{4\gamma}{\rho a} \right)^{1/2} \tag{2-6}
\]
Equation 2-2 and Equation 2-6 can be used to predict a minimum value of the Weber number (see Equation 2-7) for inkjet printing [11].

\[ We = \frac{v^2 \rho a}{\gamma} \geq \frac{v_{\text{min}}^2 \rho a}{\gamma} \approx 4 \quad (2-7) \]

In addition to the requirements for drop formation, a printable ink is also limited by factors related to the impact of the droplet on a substrate. If the drop velocity is above the threshold of splashing, unwanted droplets will be produced during printing. Stow and Hadfield [87] proposed an empirical threshold for the onset of splashing as shown in Equation 2-8:

\[ We^{1/2} Re^{1/4} > f(R) \quad (2-8) \]

where \( f(R) \) is a function of surface roughness. Further research confirmed the \( f(R) \approx 50 \) for substrates with the flat and smooth surface [88].

Based on research data in printable fluid for DOD inkjet printing, Derby [11] proposed a map to define fluid properties suitable for DOD inkjet printing by axes of Reynolds and Weber numbers as shown in Figure 2-6.

Figure 2-6 A map showing the fluid properties suitable for DOD inkjet printing within a parameter space defined by axes of the Reynolds and Weber numbers. Adapted from Derby [11]. Note that Figure 4 in the paper [11] contains an editorial factor of 10 error in the Re axis, and the version shown in this revised figure has been kindly confirmed as correct by Prof. Derby. The displayed Weber number and Reynolds number ranges have also been adjusted.
As shown in Figure 2-6, accurate and repeatable drops are generated within a parameter space defined by the Reynolds and Weber numbers and hence by the physical and rheological properties of the ink [11]. If the ink is too viscous or the surface tension is too high, it is difficult to impart sufficient energy for drop formation. However, if the ink is too fluid and the surface tension is low, there is a tendency to form a train of satellites behind an initial main drop. The predicted regime of printability of \(1 < Z < 10\) shown in Figure 2-6 has been confirmed by other reports [8]. The map provides a useful guide for fluid properties selection [89]. However, Jang et al. [18] printed a range of fluids and studied the single droplet formability, positional accuracy, and maximum allowable jetting frequency. They proposed that the printable range as \(4 \leq Z \leq 14\). Tai et al. proved single droplets could be jetted for \(\frac{2}{3} < Z < 50\) [90]. Kim and Baek [16] simulated the drop-formation dynamics of Newtonian fluids and generated a printability range of \(1 \leq Z \leq 14\). All the reports above have mainly used squeeze-mode printheads, e.g. MicroFab printhead. Recently, Hill et al. [91] studied the printability of a 10 pl shear-mode Dimatix printhead by printing a series of \(\alpha\)-terpineol-based inks using a single trapezoidal pulse waveform. They proposed the printable range is \(3 \leq Z \leq 24\) and \(We < 35\) after comparing the deposit pattern of generated droplets on glass slides. However, they have not given the detail information about the droplet evaluation process. Thus, it is not known whether there is a universal \(Z\) number range for inkjet printability or whether the range varies with different actuating pulses and different modes of printhead actuation.

### 2.2.2 Waveform parameters required for drop ejection and flight

When the inkjet printing environment and the inks are chosen, the main parameter that influences drop behaviour is the driving waveform designed for drop generation. The driving waveform parameters (such as the waveform shape, amplitude, and frequency) can significantly alter jetting behaviour in addition to the fluid properties [68]. Optimal waveform design can be used to generate droplets with diameters an order of magnitude less than that of the nozzle [92]. The desired size of the droplets depends on the specific application. Larger droplet sizes result in quicker printing for large area applications, whereas small droplet sizes are ideal for applications where high spatial resolution and small dimensions are required but are more susceptible to
deflection by air currents. Incorrect design of the waveform can result in a range of undesirable phenomena such as wetting and puddle formation on the nozzle plate, which can prevent ejection or satellite droplet formation resulting in imprecise drop deposition and poor print quality. Many studies have undertaken to understand how the droplet formation process is related to piezoelectric actuation of the printhead. However, their results of these are often printhead-specific [74], [92], [93]. Bogy and Talke [75] proposed that sufficient pressure is generated at the nozzle by the constructive interference of the acoustic waves inside the printhead tube. The jetting mechanism involved the generation of pressure waves against the ink surface tension, allowing a small droplet to be ejected from the nozzle. The final droplet velocity and volume increased with the pulse amplitude [94]. Reis et al. [39] found that the ejected drop volume scales with the Ohnesorge number and with the displacement of the actuation used to initiate drop ejection. The acoustic response of the printhead affects the waveform design. Because of the effect of acoustic resonances, the speed of sound in the fluid is also important in controlling printed drop characteristics [95].

2.2.3 Nozzle geometries required for drop ejection and flight

Smaller nozzle diameters can produce droplets with lower volumes. Current commercial inkjet prinheads produce droplets with volumes in the range of 1-100 pl. Small drop volumes lead to smaller minimum feature sizes. However, the energy required for a smaller droplet to break away from the nozzle increases due to increased capillary forces [40]. Smaller droplets are also decelerated more quickly by air resistance, requiring that the gap between the printhead and substrate be reduced [78], [96]. The volatile components of the ink at the nozzle may evaporate if the nozzles are idle. This can lead to a higher viscosity of the ink at the nozzle compared to that in the reservoir. This disparity can lead to clogging of the nozzle or a shift in the properties required for droplet formation and ejection. This is referred to as the “first drop problem” [78], [97], [98]. Thus, regular cleaning of the nozzles and capping of the printhead when not needed are essential to ensure consistent wetting of the nozzles to solve this clogging problem.
2.3 Inkjet printing drop impact and spreading

A drop generated by the printhead has kinetic energy $E_c$ during drop flight, which is related to the drop velocity as shown in Equation 2-9.

$$E_c = \frac{2}{3} \pi \rho r^3 v^2$$

where $\rho$, $r$, $v$ are the ink density, drop radius and velocity, respectively.

For most applications of DOD inkjet printing, the next step after drop generation is drop deposition on a selected substrate. Drop deposition involves drop impact and spreading on the substrate. The drop kinetic energy $E_c$ is partially dissipated by viscous forces during impact, which normally has a duration < 1 μs. The rest of the drop kinetic energy is converted into the increased surface energy required for drop spreading on the substrate, which occurs over a longer time scale of 0.1-1 ms [40]. The equilibrium diameter of a drop on a substrate is determined by the surface energy balance between the drop and the substrate [99], [100]. When the drop kinetic energy is large, the drop may overshoot this diameter on impact. The deposited drop diameter then oscillates and becomes stable once the energy is fully dissipated by viscous processes [40]. The wetting of a liquid drop on a solid substrate is usually described using a contact angle as shown in Figure 2-7. The contact angle is related to the surface energy and the relationship is calculated by Young’s equation as shown in Equation 2-10.

$$\cos \theta = \frac{(\gamma_{SA} - \gamma_{SL})}{\gamma_{LA}}$$

where $\theta$ is the contact angle, $\gamma_{SA}$ is the solid surface free energy, $\gamma_{LA}$ is the liquid surface free energy and $\gamma_{SL}$ is the solid/liquid interfacial free energy. For a liquid
drop, the surface tension (surface force per unit length) and the surface energy density (surface energy per unit area) are identical.

Nearly all the literature data on the spreading of impacting drops is for mm-sized drops [101]. These big drops have much larger Weber and Reynolds numbers than inkjet printed drops. Also, the kinetic energy of the drop is more important. However, inkjet printed drops are considerably smaller than 1 mm and hence the influence of the kinetic energy of drop is negligible, and capillarity forces influence the spreading. Schiaffino and Sonin [102] demonstrated that the Weber number indicates the dominant force of the spreading process. The drop is pushed radially outwards by the impact induced pressure gradients at a high Weber number. However, the drop spreading is driven by interfacial capillary force at a low Weber number. Because inkjet printed drops are very small, the influence of gravity forces is negligible compared to surface tension. Hence, the spreading factor $\beta^*$ of the drip is a function of only the contact angle $\theta$ of the drop on the substrate [37]. Assuming that the ejected drop volume is unchanged during flight, the final equilibrium spread drop will form a footprint, which is determined by its initial volume and the equilibrium contact angle ($\theta_{eqm}$). The drop spreading factor ($\beta_{eqm}^*$) can be defined as the ratio of the drop diameter as a sphere ($d_{eqm}$) and the diameter of the equilibrium spread drop ($d_0$) on the substrate surface [103], as shown in the Equation 2-11.

$$
\beta_{eqm}^* = \frac{d_{eqm}}{d_0} = \left[\frac{4 \sin \theta_{eqm}}{(1-\cos \theta_{eqm})^2(2+\cos \theta_{eqm})}\right]^{\frac{1}{3}}
$$

(2-11)

2.4 Inkjet printing drop solidification

After impact and spreading on the substrate, the inkjet printed drop becomes a sessile drop and begins to solidify on the substrate. The sessile drop solidification process has attracted great interest for scientific research because it is a key process step to allow uniform and desirable solid features after printing. For nanoparticle suspensions, the drop solidification involves both drop solvent evaporation and particle transport and deposition.
2.4.1 Modes of drop solvent evaporation

Sadek et al. [104] proposed three modes of sessile drop drying under a fixed environment with controlled temperature, air velocity, and humidity.

1) The constant contact radius (CCR) mode (shown in Figure 2–8a):

The contact radius between the liquid and the substrate remains constant during evaporation, but the contact angle diminishes (Figure 2-8a). This situation is expected for a droplet with an initial contact angle smaller than 90° [21], [105].

2) The constant contact angle (CCA) mode (shown in Figure 2–8b):

The contact angle remains constant, and the shape of the droplet remains spherical throughout evaporation, whereas both volume and contact radius decrease (Figure 2-8b). This is expected for an ideal system including pure liquid and equilibrium state at the interface, which is often the case of a droplet with a contact angle bigger than 90° [21], [105].

3) A mix of these two modes:

The third mode is a mix of CCR and CCA modes. One mode may switch to the other at any time during evaporation [106]. Alternatively, both contact angle and contact radius may decrease together [107], which often occurs during the final stages of evaporation of a droplet.
The duration of each mode may be influenced by droplet composition and surface properties (microstructure, thermal conductivity, and chemical heterogeneity). For example, when a spherical droplet is deposited on a flat surface, the evaporation rate is slower compared to a free droplet where no substrate limits the evaporation rate. For a sufficiently small drop, its shape could be considered to a spherical cap of a fixed base radius of $R$ (as shown in Figure 2-9). Deegan et al. [108] considered the influence of the free surface on evaporation and proposed that the evaporation flux could be calculated using Equation 2-12:

$$J(r,t) \propto (R - r)^{2\theta - \pi - 2\theta}$$  \hspace{1cm} (2-12)

The presence of the surface reduces the space into which vapour can diffuse and thus reduces the evaporation rate. When the substrate is taken into account, the change in droplet volume can be expressed as a function of time using Equation 2-13 [109]:

$$-\rho \frac{dV}{dt} = 4\pi R_S D_V (c_S - c_\infty) f(\theta)$$  \hspace{1cm} (2-13)

where $\rho$ is the density of the drop liquid, $V$ is the drop volume, $t$ is the evaporation time, $R_S$ is the radius of the initial spherical droplet before impact on the substrate, $D_V$ the diffusion coefficient of vapour in air, $c_S$ is the vapour concentration at the droplet surface, $c_\infty$ is the vapour concentration at an infinite distance from the droplet surface, $f(\theta)$ the function of the contact angle of the droplet. Different authors have proposed polynomial expression of $f(\theta)$ [109]–[111], and this is fully described in Erbil’s review [112].
From Equation 2-13, it is clear that the contact angle between drop and substrate has a significant influence on the drop evaporation process. Depending on the contact angle, the substrate surface can be divided into four kinds for the study of evaporation. These are hydrophilic surface ($\theta < 45^\circ$), transition surface ($45^\circ \leq \theta \leq 90^\circ$), hydrophobic surface ($90^\circ < \theta < 140^\circ$) and ultra-hydrophobic surface [21]. The drop evaporates faster on hydrophilic surfaces [21].

2.4.2 Particle transport during drop solidification on different substrates

The transport mechanisms for particles in suspension during evaporation of the droplet have been widely investigated with the sessile droplet method [104]. There are various forces that affect the particles suspended in the droplets, such as gravity, buoyancy effects, Brownian motion and van der Waal interactions between either the particles or the particle and the substrate [113]–[115]. These forces result in different particle transport mechanisms [21], [29], [116]–[118]. Sadek et al. [104] considered the five most important physical particle transport mechanisms and gave a schematic mode as shown in Figure 2-10. They are Evaporation flux, Deegan flow, Marangoni flow, Gravity (or density driven flow) and Brownian motion.

![Schematic representation of particle transport mechanisms](image)

Figure 2-10 Schematic representation of particle transport mechanisms occurring inside a sessile drop. Adapted from Sadek et al. [104].

1) Evaporation flux:

As reviewed in the last section of solvent evaporation, the outward solvent evaporation flux induces an inward particle diffusional flux. The diffusion coefficients of particles are estimated using Stokes–Einstein’s equation (as shown in Equation 2-14). The diffusion coefficient depends on the internal liquid criteria such
as solution viscosity, particle radius, and temperature. Thus, for the same viscosity and temperature, the bigger particles are mainly located at the surface than the centre.

\[ D_{sol} = \frac{k_B T}{6\pi \eta \tau_p} \]  

(2-14)

where \( k_B \) is the Boltzmann’s constant (1.38 × 10^{-23} J/K), \( T \) is the temperature, \( \eta \) is the dynamic viscosity, and \( r_p \) the particle radius.

2) Deegan flow:

Deegan flow (also known as “outward capillary flow”) is an outward radial flow which appears to compensate for the faster evaporation of the thin liquid layer formed on the contact line of the sessile droplet [119]. It results in an accumulation of solutes by capillary action from the centre to the contact line, forming a solid deposit at the droplet periphery known as a “coffee ring.” This will be reviewed in detail in the following section.

3) Marangoni flow:

At the liquid-air interface, fluctuations in temperature and solute concentration generate a gradient of surface tension and usually result in Marangoni instability [104]. Convection rolls occur inside the droplet, dragging solutes along the surface to the centre. Deegan and Marangoni flows are the two most significant factors occurring in the droplet evaporation than other forces [117], [120]. Marangoni flow is known to counterbalance the Deegan flow by inducing solute circulation towards the droplet centre rather than the edge [22] and leading to a skin formation at the droplet surface due to weak diffusion [116], [121]. This phenomenon has been widely investigated by experimental and numerical analysis [22], [116], [117], [122], [123]. Its importance can be estimated using a dimensionless Marangoni number (\( Ma \)) named after Italian scientist Carlo Marangoni using the following Equation 2-15.

\[ Ma = -\frac{\left(\frac{dy}{dT}\right)_L L \Delta T}{\eta \alpha} \]  

(2-15)

where \( \gamma \) is the surface tension, \( T \) is the temperature, \( L \) is a characteristic length, \( \Delta T \) is the temperature difference, \( \eta \) is the dynamic viscosity and \( \alpha \) is the thermal diffusivity.
4) Gravity:

A few authors have studied the influence of the gravity during the evaporation of a single droplet [124]–[126]. For droplets larger than about 1 mm, the gravitational forces can contribute to droplet deformation. Additional to the other flows taking place inside the droplet, gravity can influence the solute segregation and thus the final deposit. Gravity should be considered when the droplet radius $R$ is larger than the capillary length $l_c$ (calculated using Equation 2-16). However, for DOD inkjet printing the dimensionless Bond number ($B_0$ as shown in Equation 2-17) is usually in range of 0.00038 to 0.01 and the gravitational forces can be neglected.

$$ l_c = \sqrt{\frac{\gamma}{g \rho}} \tag{2-16} $$

$$ B_0 = \frac{R^2}{l_c^2} = \frac{g \rho R^2}{\gamma} \tag{2-17} $$

where $\gamma$ is the liquid-air interface surface tension, $g$ the gravitational acceleration and $\rho$ is the drop density.

5) Brownian motion:

Brownian motion produces random movements of particles in suspension and may influence particle movement inside the droplet. Such random movement results from interactions between the particles and the liquid molecules, driven by temperature. The Brownian motion should be taken into account when the droplet liquid is made up of sub-micron particles in suspension. The Brownian flow was mentioned by Marín et al. [127] in the investigation of the fluid dynamics during the evaporation of a sessile droplet. The authors reported different particle deposition layouts according to the flow rate. When the evaporation rate is slow, solutes have time to arrange by Brownian motion and form an ordered phase. However, during rapid evaporation solutes are jammed into a disordered phase. Brownian motion is often neglected in evaporating systems, because its influence is widely regarded as weaker compared to other transport mechanisms [29].
2.4.3 Coffee stain or coffee ring

The drying of a sessile drop containing a nanoparticle suspension drop typically leaves the solute as a non-uniform deposit or stain on the substrate closely aligned to the edge or contact line. The non-uniform features within a single inkjet printed droplet are mainly caused by a phenomenon known as a “coffee stain” or “coffee ring” [119]. A coffee stain is a segregation pattern left after a particle-laden drop solidification. It is a phenomenon quite similar to the ring-like deposit along the perimeter of a spill of coffee, where nearly all the particles inside the drop will be carried to the edge as a result of internal flow during the drying process. A schematic of the coffee stain formation process is shown in Figure 2-11. However, the full description of the coffee stain phenomena related to evaporation induced deposition remains a scientific challenge [19].

![Figure 2-11 Images of a drying simulation using Brownian dynamics (only the solid particles are shown). Adapted from Breinlinger and Kraft [123].](image)

2.4.3.1 Coffee stains formation mechanism

Coffee stain formation was first modelled by Deegan et al. with their work published in Nature in 1997 [119]. They proposed a mechanism in which the contact line of the liquid was pinned by the deposition of solute from the suspension. This contact line was pinned due to the liquid adjacent to the contact line evaporating more rapidly with the presence of a large dry surface than that of the drop centre. If the contact line is pinned, it cannot retract as the solvent evaporates from the drop close to the contact line. This solvent is replaced by a radial flow from the drop centre. This radial flow transports fresh particles to deposit at the original contact line. A coffee stain (or coffee ring) forms after complete evaporation. In addition, Deegan et al. [108] proposed that two conditions must be fulfilled are contact line pinning and evaporation from the edge of the drop. The relaxation of either of these conditions can lead to uniform drop structure [108]. Fukai et al. [128] investigated the droplet
evaporation process and concluded that the pinning time or the receding distance are important factors to determine the shape and dimension of the final dried deposit.

However, Hu and Larson [22] showed the formation of the coffee-ring also needs the suppression of Marangoni flow caused by the latent heat of evaporation. Breinlinger and Kraft [123] presented a finite element model using a continuum advection–diffusion approach to track the particle concentration within a drop to predict coffee stain formation. While a gradient in surface tension was neglected by Widjaja and Harris [129], it was considered by Bhardwaj et al. [130], both leading to a good agreement with experimental findings. Manukyan et al. [21] found that both the initial contact angle and the pinning of the contact line played an important role in the flow direction and final dried drop shape. They proposed the contact line pinning, initial contact angle, and skin formation together influence the final dried shape of the sessile polymer drop.

Breinlinger and Kraft [123] summarised the most important parameters favouring ring structures to be: a pinned contact line, high particle concentration, small drop size and the presence of Marangoni flow. Lim et al. [131] also described the drop drying process using a model shown in Figure 2-12. The pinned contact line, outward convective flow and Marangoni flow were mainly concerned. Several experiments have confirmed that the pinning strength of the contact line depends on the drop fluid properties [22], [29], [132]. In addition, substrate temperature [22] and surfactant concentration [25] influence the Marangoni flow. Chon et al. [133] have studied the effect of ink viscosity and particle size on the printing pattern by varying particle loads and sizes at constant volume concentration. They found that coffee stain formation strongly depends on the nanoparticle size. The drops of smaller particles and higher viscosities were found likely to fully cover the substrate whereas drops of larger particles and smaller viscosities tended to form coffee stains.
2.4.3.2 Methods to suppress the coffee stains

As a non-uniform feature, the coffee stain effect must be controlled and eliminated to achieve successfully printed structures. There are several methods that have been investigated to reduce the coffee stain effect by controlling key parameters such as the contact angle of the droplet [134], the characteristic of the solutes [29], and the nature of the solvents or the drying environment [29], [117]. Sun et al. [135] reviewed three strategies used to suppress the coffee stains.

1) Decreasing the Deegan flow (outward capillary flow)

Yunker et al. predicted that changing the suspended particles from a spherical to ellipsoidal shape could restrain the radial flow and suppress the formation of a coffee-ring [24], [26]. Shen et al. [136] investigated the influence of a counter flow driven by diffusion and outward convection within the drop and proposed the existence of a minimal droplet size below which diffusion exceeds outward convection, and hence particles do not significantly accumulate at the edge of the drop. Shen et al. [136] confirmed that there was a critical minimal droplet size \( D_c \) as shown in Figure 2-13 top row, at which the \( \tau_{evaporation} = \tau_{diffusion} \). Below the critical droplet size, the solvent evaporation will be smaller than the particles diffusion to the edge. Thus, the coffee ring will be eliminated. Their experimental
data also well agreed with the simulations of Breinlinger and Kraft as shown in Figure 2-13 bottom row [123].

<table>
<thead>
<tr>
<th>Droplet Size (µm)</th>
<th>Coffee Ring</th>
<th>No Coffee Ring</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 µm</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>3 µm</td>
<td>![Image]</td>
<td>![Image]</td>
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<td>6 µm</td>
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<td>20 µm</td>
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</tr>
<tr>
<td>50 µm</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

Figure 2-13 Ring-shaped deposits develop above a critical diameter $D_c$. Comparison of the experiment (top row) and simulation (bottom row). Adapted from Shen et al. [136] and Breinlinger and Kraft [123].

2) Increasing Marangoni flows ($Ma$)

Several papers have investigated methods to facilitate Marangoni flow during droplet evaporation, opposing the radial Deegan flow and thus provide a uniform deposit after drying more desirable for inkjet printing [137]. The most common method is using solvent mixtures. Using an appropriate mixture of solvents with different values of surface tension and vapour pressure, it is possible to generate gradients in solvent concentration caused by the different rates of evaporation and these lead to gradients in surface tension. Park and Moon [120] eliminated coffee stains by using two different drying control agents-diethylene glycol (DEG) and formamide (FA). These solvent mixtures have high boiling temperature and low surface tension. When added to other solvents, e.g. water, they slow down the drying process and introduce surface tension gradients. If the surface tension of the edge of the drop is lower than that of the centre, this will result in an inward Marangoni flow. This drives particles flow back to the centre of the drop and reduce the probability of coffee stain formation. Derby’s group [30] used ethanol and polyethylene glycol (PEG) mixed with water to reduce the coffee stain effect, and they found adding 10 wt% polyethylene glycol to 10 vol% ZrO$_2$ particle suspensions can suppress the coffee stain. Still et al. [25] found adding a small ionic surfactant sodium dodecyl sulfate (SDS) to aqueous colloidal systems also increases the Marangoni flow. They proposed that the surfactant was transported to the drop edge by the outward
capillary flow. The increase in surfactant concentration reduces the edge surface tension, increasing the Marangoni flow and preventing the particles precipitating at the edge. Their results were also in agreement with other researches [27].

3) **Controlling the movement of the contact lines between air-liquid-solid**

Contact line pinning on the substrate is a necessary condition for coffee stain formation. The coffee stain formation could be controlled if the contact line is not pinned and can migrate while the drop is drying. The properties of the contact line are related to the wetting properties such as the advancing and receding contact angles, which play an important role in the final pattern of solute deposit [138], [139]. Thus, the movement of the contact line could be controlled by choosing or modifying the substrate wetting property and contact angle.

Li et al. [138] found the coffee stain always appears on substrates of small contact angle, but concentrated dots were obtained on substrates of large contact angle. The shape change along the contact line provides a powerful capillary force to move the particle back to the centre and finally obtain a uniform structure. This phenomenon has also been applied to printing 3D microstructures under magnetic guiding by Wang et al. [140]. Eral and his colleagues [141] have suppressed coffee stains non-invasively by applied alternating voltage electrowetting. This method shakes the contact line by alternatively increasing and decreasing the contact angle, effectively depinning the contact line as the droplet evaporates. Furthermore, with appropriate choice of excitation frequency, internal flow fields can be generated counteracting the capillary flow increasing the efficiency of the suppression. In this project, various hydrophilic substrates such as silicon wafers, glass slides, and Kapton (polyimide) tapes were employed. Their wetting properties were significantly different on each substrate.

4) **Controlling the substrate temperature**

In addition, some researchers proposed that the coffee stain can be reduced by controlling the substrate temperature [58], [142]. Dou et al. [30] studied the coffee staining of ZrO$_2$ inks on glass slides held at different temperatures. They found that the coffee stain is suppressed with increasing substrate temperature. Ta et al. [143] studied the effect of the laser diameter, laser power density and exposure time on the
fluid flows, evaporation time and resultant distribution of suspended nanoparticles in evaporating droplets. Due to the laser heating the drop and increasing the temperature, laser-induced flows drive the particles to move and settle down in any chosen area with a selective pattern size. The uniform pattern was achieved by manipulating the laser diameter or exposure time, which has potential significance for inkjet printing that requires uniform structures.

However, in other research, increasing the substrate temperature was found to have little influence on coffee stain formation [31], [108] and may even increase the coffee stain driving force [144]. Soltman and Subramanian [31] proposed that when the substrate is heated, the heat transfer to the thinner pinned edge of the drop will cause it to rise in temperature more swiftly than the centre of the drop, increasing the evaporation rate at the edge more than in the centre of the drop. Hence, an increase in the radial flow to the edge of the drop is required. On the contrary, when the substrate temperature goes down, the coffee staining would be reduced or eliminated by decreasing evaporation rate at the edges more than that in the drop centre (see Figure 2-14). However, the shortcoming of their analysis is that they ignored the Marangoni effect.

![Cross section and 3D projection from an optical profilometer of single drops printed at the noted temperatures. Adapted from Soltman and Subramanian [31].](image-url)
2.4.4 Drop coalescence

There are still further operations that define as well as constrain the inkjet printing process. These mainly concern drop/substrate interaction and drop solidification. Unlike traditional graphics printing, which uses isolated droplets to produce images, materials inkjet printing requires the formation of continuous features through the overlap of droplets [11]. Each two overlapping drops will tend to coalesce, and a train of drops’ overlap and coalescence will finally form a printed line. There is already some research in inkjet printing drop coalescence. Different drop coalescence conditions can lead to different printed features [31] as shown in Figure 2-15.

![Drop spacing decreases](image)

Figure 2-15 Examples of principal printed line behaviours: (a) individual drops, (b) scalloped, (c) uniform, (d) bulging, and (e) stacked coins. Drop spacing decreases from left to right. Adapted from Soltman and Subramanian [31].

The uniform structure can be obtained when drop spacing decreases to appropriate drop spacing as shown in Figure 2-15c. Derby [9] proposed that it is the interaction between adjacent liquid drops and the consequent influence of surface tension that leads to the uniform surface when drop overlap is allowed before solidification with
suitable drop spacing. However, when drop spacing decreases further below a threshold, a bulge will appear, as shown in Figure 2-15d and a “stacked coins” structure will occur when evaporation is faster than the drop arrival rate (see Figure 2-15e).

For most inkjet printing materials applications, the final solidification of a single line needs to be a stable and uniform bead as shown in Figure 2-15c. Smith et al. [145] proposed a model of the bead width as a function of initial droplet diameter ($d_0$), droplet spacing ($p$), bead width ($w$), and contact angle ($\theta$) (as shown in Figure 2-16). The relationship is explained using Equation 2-18, which assumes conservation of volume [103], [145].

\[
w = \sqrt{2\pi d_0^3 / \left(3 p (\theta / \sin^2 \theta - \cos \theta / \sin \theta)\right)}
\]  

(2-18)

where $w$ is the bead width, $d_0$ is the initial droplet diameter, $p$ is the droplet spacing and $\theta$ is the contact angle.
Assuming that the contact line of an individual droplet is pinned and cannot retract, the minimum width of the bead is equal to the initial spherical cap diameter ($w = d_{\text{cap}}$) on the substrate. This diameter has been calculated using Equation 2-19 according to Van Dam [146].

\[ w = d_{\text{cap}} = \frac{2d_0}{(\tan(\theta/2) \ast (3 + \tan^2(\theta/2)))^{1/3}} \]  

(2-19)

Substituting this into Equation 2-18 for $w$ and rearranging, the following Equation 2-20 is obtained for the maximum droplet spacing $p_{\text{max}}$ with:

\[ p_{\text{max}} = \pi d_0 (\tan(\theta/2) \ast (3 + \tan^2(\theta/2)))^{2/3}/(6 \theta /\sin^2 \theta - 6 \cos \theta /\sin \theta) \]  

(2-20)

2.4.5 Drop stacking

All the above work has focussed on drop behaviour on smooth solid substrates. However, for 3D printing, only the first layer is printed on a smooth, flat solid substrate. The following layers will all be printed on a pre-printed surface, which will be rough and may be porous. Thus, the drop solidification mechanisms on a pre-printed porous surface is also an important issue especially for inkjet printing 3D ceramic structures.

Dou and Derby [23], [30] are the pioneers of exploring the coffee ring formation on the porous substrate. They found that the substrate surface morphology has significate influence on coffee staining formation. Drying on porous substrate can be modelled as a combination of fluid removal by evaporation combined with an additional capillary draining into the porous media. They also assumed that the transport of fluid into the powder beds was controlled by the pore size and described the details of the fluxes on the porous substrate [23] (as shown in Figure 2-17). Thus, it is possible for a drop to show no coffee ring when printing on a smooth solid substrate, but to show coffee ring when printing onto a pre-printed layer of dried zirconia powder.
Dou and Derby [23] proposed that the presence of a coffee stain during drying on a porous substrate is influenced by the relative magnitudes of the evaporation fluxes \( J_1 \) and draining fluxes \( J_2 \). They also modelled these fluxes by assuming no interaction between evaporation and draining fluxes and used a constant evaporation rate as shown in Equation 2-21. An important difference between the two solvent removal routes is that the draining flux does not change the composition of the fluid and hence cannot introduce a Marangoni effect, whereas the evaporation flux may.

\[
\frac{\rho}{d} 
\frac{dh}{dt} = -\rho \frac{1}{r} \frac{\partial}{\partial r} (r \rho v) - J_1(r,t) \sqrt{1 + \left( \frac{\partial h}{\partial r} \right)^2} - J_2(r,t) \tag{2-21}
\]

where \( J_1 \) and \( J_2 \) are the evaporation and draining fluxes, respectively.

### 2.4.6 Methods to characterize drop solidification

#### 2.4.6.1 Traditional methods to characterize drop solidification

Bodiguel et al. [147], Pouillard et al. [148], Marin et al. [127] and Nikolov et al. [149] have visualized the particle accumulation by using interferometric methods and horizontal imaging. Kang et al. [150], Jaijus and Singh [151] applied particle image velocimetry (PIV) to visualize the flow direction in sessile drops of water or ethanol-
water mixtures. Hu and Larson [22] thought local experimental observations inside the droplet usually limited to a qualitative description of the particle flow toward the edge, or to the visualization of the velocity field. Kajiya et al. [152] were the first to report quantitative data based on fluorescence intensity measurements inside a droplet of a polymer solution. They were able to measure the concentration as a function of time and space, and their results allowed a direct and quantitative visualization of the solute accumulation near the edge. However, as pointed out by these authors, such experiments ask for simultaneous investigations of the velocity field since the concentration field is coupled to the flow inside the droplet. These experiments integrate the concentration along the droplet thickness, which is the usual assumption made in the theoretical approach [153]. When recirculation flows are important, the use of this assumption is questionable, and there is a clear need for three-dimensional measurements directly inside a droplet.

Bodiguel and Leng [19] have investigated the drying kinetics inside a sessile droplet laden with a colloidal sol of silica nanoparticles using fast two-colour confocal microscopy imaging. Weon and Je [20] also investigated the spreading and drying behaviour with pure and colloidal droplets using optical and confocal microscopies. Manukyan et al. [21] have imaged internal flows in a drying sessile polymer dispersion drop on hydrophilic and hydrophobic surfaces using Spectral Radar Optical Coherence Tomography (SR-OCT). For turbid and barely transparent liquids, OCT is an excellent imaging method. It offers an easier and practical method compared to conventional confocal microscopy visualization. It also allows observation of the cross-sectional area of the standing liquid without disturbing the process. The OCT method allows visualization of the flow circulation directions in sessile polymer dispersion droplets on hydrophobic and hydrophilic surfaces. However, OCT is based on optical light source, and only large viewable particles could be detected. It is not suitable for studying nanoparticle suspensions.

2.4.6.2 In-situ synchrotron X-ray radiographic imaging

Current methods of drop visualisation using stroboscopic imaging or ultra-high speed video are limited to resolving the external shape of the drop and do not provide information concerning the distribution of particles within the drop. X-ray radiographic imaging has been successfully applied to investigate the rapid structural
evolution inside non-transparent materials such as metals [154] or high-speed dynamic process with a great detail [155]. Taking advantage of X-ray’s suitable wavelengths for the purpose, good penetration and attenuation capability, the fast synchrotron radiography was chosen to study re-distribution of suspended ceramic particles within inkjet droplet during their solidification in this project.

1) Basic physics of X-ray radiography

Considering an X-ray beam (intensity of $I_0$) incidents on an object, it will be attenuated (absorbed or scattered) and result in a transmitted X-ray beam with an intensity of $I$, as shown in Figure 2-18. There are four dominant interaction mechanisms of X-rays with matter. They are photoelectric effect, Compton scattering, coherent scattering and pair production [156]. The dominant interaction mechanism in low energy range (below 100 keV) is the photoelectric effect [157].

![Figure 2-18 A schematic diagram of X-ray dominant interaction mechanisms.](image)

Albert Einstein first described the photoelectric effect in 1905. When the X-ray photon has energy greater than the binding energy of an electron, the entire X-ray photon energy can be absorbed. The kinetic energy of the electron of the inner shell will be increased, and it will be liberated from the atom. The vacancy left by the free electron will be filled by outer shell electrons, with simultaneous energy radiation, known as characteristic fluorescence. Tightly bound electrons in materials with a higher atomic number are more likely to be involved in this photoelectric absorption due to the closer binding energies to that of X-ray photons. The X-ray attenuation coefficient $\mu$ is related to the X-ray photon energy of the incident beam $E$, the atomic
number Z of the elements that compose the material and the density of the investigated material ρ, as shown in Figure 2-19.

![Figure 2-19 Causes of attenuation: λ is the wavelength, Z is the atomic number and ρ is the mass density. Adapted from Thorsten M Buzug [158].](image)

The mass attenuation coefficient (μ∗) sharply depends on E and Z [159] (described using Equation 2-22). For mixtures and compounds, the value could be calculated using the Equation 2-23 [160].

\[
\mu^* = \frac{\mu}{\rho} = K \frac{Z^4}{E^3} \quad (2-22)
\]

\[
\mu^* = \frac{\mu}{\rho} = \sum_i w_i \left( \frac{\mu}{\rho} \right)_i \quad (2-23)
\]

Where K is a constant, E is the photon energy, ρ is the density, and Z is the atomic number of investigated material. Such an equation implies that, for any given photon energy, μ is proportional to ρ and \(Z^4\). \(w_i\) is the proportion of investigated material within compounds.

According to the Beer-Lambert Law (attenuation law), the X-ray absorbance is calculated using the Equation 2-24. For a fixed material, the molecule N is constant. Material concentration c can be equated with mass density by \(c = \frac{\rho}{N}\), while \(\varepsilon\) can be equated with the mass attenuation coefficient by \(\varepsilon = N\mu^*\). The measurable quantity \(\ln(I_0/I)\) is equal to the summation of the X-ray attenuation coefficients of the material.
at each point along the incident line. Thus, the beam intensity after traveling through a material is described using the Equation 2-25,

\[ A = \ln \frac{l_0}{I} = \varepsilon z c \]  

(2-24)

\[ I = I_0 e^{-\mu z} = I_0 e^{-\mu^*\rho z} = I_0 e^{-\int_{L} f(z)dz} = I_0 e^{-KZ^4\frac{\mu E}{\pi m^2}} \]  

(2-25)

where \( A \) is absorbance, \( f(z) \) is the X-ray attenuation coefficient at point \( z \), \( I \) is the transmitted X-ray beam intensity, \( l_0 \) is the incident X-ray beam intensity, \( \varepsilon \) is the molar absorptivity, \( c \) is the material concentration in solution, \( K \) is a constant, \( E \) is the photon energy, \( Z \) is the atomic number of investigated material, \( \mu^* \) is the mass attenuation coefficient, \( \rho \) is the density of the sample, \( \mu \) is the linear attenuation coefficient, and \( z \) is the sample path length (the sample thickness).

Thus, both the density (\( \rho \)) and the sample thickness (\( z \)) have an influence on the final X-ray intensity. In each 2D radiography image, the pixel greyscale value represents the flux of X-rays that passed through the sample and reached the detector. The density of the material controls absorption of the X-rays. Thus, the thicker the material, the fewer X-rays reach the detector. The goal is to find the solid material distribution change with time for different inks at different temperatures. The density \( \rho \) represents the material distribution. It is important to calculate the density change, and this needs to consider the influence of the thickness change of the droplets during drying.

2) Advantages of in-situ synchrotron X-ray radiographic imaging

There are some main advantages of X-ray beams generated by synchrotron sources over other characterization methods [161], [162]. First, the high flux from a synchrotron beamline enables experiments that record rapid dynamic processes with images of high signal/noise ratio. The X-ray beam intensity from a synchrotron light source is several orders of magnitude brighter than that generated by a laboratory X-ray source. This high flux of photons at synchrotron significantly reduces the time required for image collection and opens new possibilities for in-situ time-resolved experiments for the dynamic processes. Second, the synchrotron X-ray radiographic imaging is a non-destructive method suitable for dynamic process study. Third, this
beamline has a large working space, makes it suitable for setting up inkjet printing equipment inside.

### 2.5 Inkjet printing ceramic suspensions

#### 2.5.1 Ink components for inkjet printing ceramics

Inkjet printing is an attractive tool for the manufacture of ceramic components. Inkjet printing ceramics can be used to print ceramic suspensions directly onto a substrate drop by drop and then layer by layer, which will finally form the ceramic structures with the desired shape and composition distribution. For inkjet printing, ceramic inks are suspensions of ceramic powders mixed in different solvents, with the addition of a dispersant, surfactant, binder and other auxiliary materials.

##### 2.5.1.1 Different ceramic powders

There has been a growing number of research publications investigating the use of inkjet printing to fabricate different ceramic materials, such as ZrO$_2$ [163], TiO$_2$ [52], Al$_2$O$_3$ [165], CeO$_2$ [166], SnO$_2$ [167], [168], BaTiO$_3$ [169] as well as PZT [53]. Zhao et al. [163] have successfully created ZrO$_2$ powder into 3D shape by direct inkjet printing. In 2000, Evans’s group [52] printed 3D multilayer TiO$_2$ objects using a continuous inkjet printer. In 2008, Zhou et al. [169] successfully fabricated thick film ceramics through CIJ printing with two kinds of BaTiO$_3$ ceramic inks for continuous ink-jet printing synthesized by mechanical mixing and sol-gel methods. For ceramic suspensions, it is believed that the particle size distribution of the powder must be adjusted to obtain a ratio of 50 between the radius of the nozzle aperture and the maximum diameter of the powder to avoid the blocking of the nozzle [8]. Consequently, as the minimum aperture of the printheads is equal to 60 µm in this project, the maximum diameter of the ZrO$_2$ powders was adjusted by filtered to 2 µm with a mean diameter of 20-30 nm.

Zirconia (ZrO$_2$) ceramics show high-strength, high-fracture toughness and wear resistance over a wide temperature range, and has a versatile range of applications [170]. It has become an important ceramic material for a variety of applications including: orthopedic and dental applications [171], [172], electrolytes and electrochemical sensors [173], [174], gas and humidity sensors [175], [176], the.
electrolyte in fuel cells [177], catalysts [178], and optoelectrics [179]. In addition, the high attenuation difference between the ZrO$_2$ particles in suspension and the water-based solvent provides sufficient contrast to image the segregation of the ensemble solids (individual particle details could not be observed as they were beyond the detector resolution). Thus, ZrO$_2$ ceramic inks provide a good model material that allows us to capture the time evolution of segregation patterns within the drying solvent. Thus, due to these above important characteristics, high-purity nano ZrO$_2$ powders were chosen as the model materials to study inkjet printing nanoparticle suspensions in this study.

2.5.1.2 Solvent

Solvents of ceramic inks can be divided into organic and aqueous systems. However, those organic systems need some toxic substance, which causes severe irritation upon inhaling, clogs the nozzle and influence the stability of inkjet printing process. Water-based systems are preferred for environmental reasons and safety in production facilities. Thus, the solvents are usually chosen based on water or water-soluble organic solvents, such as alcohol, polyhydric alcohols and polysaccharides [52], [79]. The solvents are mainly used to disperse the ceramic powders, improve the stability of the ink, and ensure that the viscosity and surface tension of the ink remains stable during small changes in temperature.

2.5.1.3 Dispersant

Dispersants are typically soluble polymers, such as polyethylene glycol [23], [38], benzoic acid and its derivatives, polyacrylic acid and its copolymers. Those dispersants are added to make ceramic powders evenly distributed in the solvent, and avoid particle agglomeration or precipitation before printing.

2.5.1.4 Binder

Binders are always polymeric materials [180]. Their presence must not compromise the fluidity of the ink. After solvent evaporation, the binder gives strength to the printed ceramic body allowing it to be manipulated before sintering. Also, the increase in the molecular weight of the binder allows modification of the appropriate viscosity of the suspension [8].
2.5.1.5 *Surfactant*

Surfactants are also an important element in the ceramic ink formulation, and their function is to control the surface tension of the ink. The surfactant dosage is less than 3 wt% of the ink [180]. The addition of a surfactant to the ink allows influences the interaction and stacking of successive printed layers. The positive effect of the surfactant is to decrease the surface tension [8]. Surfactants were also well used for zirconia nanoparticle suspension research [30], [170].

2.5.1.6 *Other accessories*

Despite all the materials mentioned above, there are other materials needed for ceramic inks, such as pH regulators, drying control agents and preservatives [180]. The pH regulator is to improve the dispersion stability of the ceramic powders using ammonia and sulphate, etc. The chemicals that can help increase the drying rate of ink are ethanol and isopropanol. To decrease drying rates, ethylene glycol or glycerol can be added. In addition, some preservatives are also needed when there are risks of corrosion deterioration in the ink.

2.5.2 *Inkjet printing 3D ceramic structures*

Lejeune et al. [8] have printed PZT and TiO$_2$ suspensions as micro-pillar arrays on green ceramic sheets obtained by tape casting of organic PZT and TiO$_2$ suspensions using piezoelectric DOD inkjet printer with 52 and 60 µm nozzles from SPCTS. Green pillars were sintered at 1250 °C for PZT, leading to a shrinkage of 21%, and 1300 °C for TiO$_2$, leading to a shrinkage of 20%. Zhao et al. [163] have printed 3D ceramic pillars using a zirconia ink; pyrolysis was carried out in flowing air to remove the organic vehicle. A conservative heating schedule was used, namely: 60 °C/hr to 60 °C, 24 hr dwell, 5 °C/hr to 400 °C, 1hr dwell followed by furnace cooling. The zirconia was fired at 1450 °C for 2 hours in the air with a heating rate of 10 °C/min.

2.5.3 *Application for inkjet printing of zirconia nanoparticle suspensions*

Ceramic pillar arrays were first made by Mott et al. [7] using a drop-on-demand inkjet printer. A fine zirconia suspension in alcohol was used as the ink and passed directly through the nozzle. Zirconia/alumina thin films were printed using direct
DOD printing to form a functionally graded material (FGM) [4]. The point-by-point method of material addition and the freedom to create very intricate shapes categorise direct ceramic jet printing as a solid free forming pathway [181].

2.5.4 Methods to characterize 3D printed structures

2.5.4.1 Traditional methods to characterize 3D printed structures

Although inkjet printing has been successfully used for ceramic fabrication [9], there has been little study of the defects that form in a printed ceramic body. The properties of the ceramic ink, the printing parameters as well as the drying environment may all influence the final structure of the printed ceramic. Different kinds of defects may form in the printed structures, such as microscale holes and cracks, etc. The mechanisms for the formation of defects in printed ceramic structures have not been studied in detail. In order to understand how ink properties, printing parameters and sintering are related to the printed ceramic structures, appropriate characterization tools are needed to locate and identify both surface and internal structures. Currently, SEM can provide high-resolution images for characterising the outer surface of inkjet printed 3D structures. Serial cutting and intrinsically destructive sectioning, such as FIB nanotomography [182] and TEM, have been mostly used for investigating the internal structures. However, to expose a fresh surface these destructive methods may introduce defects. Therefore, it is necessary to measure the internal structures without any cutting or other pre-treatment when preparing the samples.

2.5.4.2 X-ray computed tomography

X-ray computed tomography (XCT) is a powerful non-destructive tool to investigate an object structure, [183] such as its dimensions, shape, the presence of internal defects, density, etc. [184], [185]. Computed tomography refers to the cross-sectional imaging of a sample from either transmission or reflection data, collected by illuminating the sample from different directions [186]. No special sample preparation is required using X-ray tomography. The recent developments of X-ray tomography towards higher spatial resolutions and faster scanning make it a suitable technique to evaluate ceramics’ quality and to test for defects, especially the internal defects, in the materials without any damage during the preparation of the 3D
samples. The following section covers some basic principles of the X-ray tomography technique.

1) **Principles of X-ray computed tomography**

There are three basic setups for X-ray tomography experiment: first generation scanner (parallel beam scanner), fan-beam scanner and cone-beam scanner [159]. Figure 2-20 shows principles of those three setups. All X-ray CT imaging systems are based on the same basic setup. A test sample is placed on a rotation stage between an X-ray source and a detector [187], [188]. The X-rays leave the beam source, pass through the sample and finally hit the detector. During a CT scan, the stage is continuously rotating so that a series of two dimension X-ray radiograph images are taken from different angles. These 2D images will be reconstructed into a 3D structure of the test objects. In this project, the cone beam scanners (as shown in Figure 2-20b) were used for characterising the internal structures of 3D printed objects.

![Image of X-ray tomography scanner](image-url)

**Figure 2-20** Principles of X-ray tomography scanner. Adapted from Richard Ketcham [189].

2) **The principle of 3D image reconstruction**

Fundamentally, tomographic imaging deals with reconstructing a 3D image from its 2D projections. In practical applications, the filtered back-projection algorithm (the inverse of Radon transform) is typically used for parallel beam reconstruction [190], whereas a Feldkamp algorithm is applied for cone-beam reconstruction [191]. When
the X-rays pass through the sample, the X-ray attenuation occurs as discussed before in the basic physics of X-ray radiography using in Equation 2-25. In the reconstructed 3D image, the pixel greyscale value represents X-rays intensity that passed through the sample and reached the detector. Thus, this reconstructed image can show the internal structures by different greyscale values.

3) **Volume rendering and image segmentation of 3D image reconstruction**

Volume rendering is a technique to visualize tomographic data three-dimensionally by adjusting the greyscale threshold [192]. Volume rendering is useful to separate structures with big threshold density difference. However, it is not enough for different structures with similar threshold density or quite small features. Thus, a manual or automatic image segmentation is needed to remove the unwanted structures from the image and label the small features with colors. In this project, the internal defects (microvoids and cracks) were separated out by adjusting the threshold of the greyscale value. These defects were also manually segmented and labeled with different colors.

4) **Advantages of X-ray tomography**

As a 3D high-resolution characterization technique, X-ray tomography has quite a number of advantages over traditional materials analysis techniques. The most obvious advantage of XCT is non-destructive testing of specimens. X-ray tomography does not damage the sample while measuring the structures of the specimens as it is a non-contact technique using X-ray transmission [187], [188]. As a non-destructive method, X-ray tomography has no requirement in preparing samples by cutting or polishing. Thus, 3D information can be obtained with the sample undamaged [183], [188]. The scans reveal all of the major features of the structure at a resolution comparable to that of optical microscopy. They also provide 3D information that cannot be obtained by other methods [193]. In addition, the sample can be tested by XCT under the actual working environment, such as under the influence of an applied load, or changing temperature for the *in-situ* tests [184].

5) **Application of X-ray tomography**

X-ray tomography can be applied to characterize a wide range of materials including biology and biomaterials [194], composite materials [195], energy materials [196],
geo-materials [197], metals [198], polymers [199], palaeontology [193], [200]. In addition, X-ray tomography has also been used as a powerful tool for characterising ceramic structures. In 2012, Meille et al. [201] used a laboratory in-situ X-ray tomography with a resolution of 6 μm per voxel to confirm the transition in mechanical behaviour. They have successfully observed large micro-cracks in the low relative porosity samples. Yan et al. [202] characterized the microstructures of multilayer ceramic capacitors before and after sintering through synchrotron X-ray nanotomography. They had also reconstructed and quantitatively analysed the 3D microstructures of the same sample. In addition, with the benefit of the ex-situ X-ray nano-tomography, they also had successfully tracked the morphology of the inner electrode changed by sintering. Vasic et al. [203] used X-ray computed microtomography as a complementary method for the characterization of activated porous ceramic preforms. Justice and Derby et al. [204] used dual-energy X-ray microtomography to make separate reconstructions of ZrO₂ particle-particle and voids distributions in metal matrix composite (MMC) by making measurements above and below the Zr K absorption edge. In summary, X-ray tomography has already become a unique and useful technology to characterize ceramic structures, particularly in studying the internal microstructures and the microstructural changes during sintering. To characterize and understand the defects present in the inkjet printed ceramic objects thoroughly, X-ray microtomography was applied to non-destructive measuring the internal defects.

2.6 Summary

Inkjet printing has traditionally been used in the graphical and publishing industries. In recent years, it has been applied for material manufacturing due to the flexible and cheap nature and the low material wastage. However, challenges such as achieving stable droplet generation and elimination of coffee staining need to be addressed by improving the understanding of fluid behaviour throughout the various stages of inkjet printing. In addition, its application in ceramic fabrication using nanoparticle suspensions on various substrates requires further development. In-situ synchrotron X-ray radiographic imaging and X-ray computed tomography are two technology that can be used for investigating fast dynamic drying process and 3D internal structures, respectively.
CHAPTER 3 Experimental Materials and Methods

In this chapter, the experimental materials and approaches used in the study are introduced. The first part of this chapter presents the experimental materials and the formulations of the inks used in the study. The second part describes methods used to measure the important physical parameters needed to characterize ink behaviour. The third part describes the inkjet printheads, inkjet printers, substrates and heat treatment after printing used during the printing trials. The final part of the chapter focuses on the techniques used to characterize the printed materials and related analysis methods. Some figures and descriptions in this chapter are duplicated in the chapter 4-5 for ease of reference.

3.1 Ink preparation

3.1.1 Solvent based inks

To investigate the influence of Z number on ink printability, 11 solution-based inks were prepared with compositions selected to obtain a range of Z numbers from 0.05 to 36.76. Ink formulations included distilled water, solutions of distilled water and ethylene glycol, pure ethylene glycol (Sigma-Aldrich Company Ltd., Dorset, UK), pure diethylene glycol (Sigma-Aldrich Company Ltd., Dorset, UK) and pure glycerol (Sigma-Aldrich Company Ltd., Dorset, UK). Inks were either used in pure form or mixed to the desired composition in glass laboratory vessels. All the inks were filtered through a 0.45 μm filter (FIL5018, Scientific Laboratory Supplies Ltd., Nottingham, UK) before printing to ensure any impurity particles have been removed. These filters are 25 mm Whatman Puradisc syringe non-sterile filters with Polytetrafluoroethylene (PTFE) membrane and have 0.45 μm pore size.

3.1.2 Nanoparticle suspension inks

To investigate the coffee stain effect that may occur after drying of inkjet printed inks, a series of 6 inks containing nanoparticle suspensions were formulated for comparison. These inks were all prepared using 5 vol% nanoparticle ZrO₂ (particle
size 20-30 nm, purity 99.99%, PI-KEM Ltd., UK) and distilled water as the primary solvent. 1 wt% DISPEX A40 (Ciba Specialty Chemicals Inc., Basel, Switzerland) and 0.5 wt% DOLAPIX CE64 (Zshimmier & Schwarz, Lahnstein, Germany) were used as surfactants to effectively disperse the powders and achieve the minimum viscosity without significant sedimentation. Ethylene glycol (EG, Sigma-Aldrich Company Ltd., Dorset, UK) and polyethylene glycol (PEG, average MN CA. 1500, Sigma-Aldrich Company Ltd., Dorset, UK) were selected as solvent mixtures to study their effect on suppressing the coffee stain effect. All the components in the mixtures were ball milled for 24 hours to make uniform dispersed nanoparticle suspensions. These suspensions were filtered through 2 μm filters (SLAP02550, Millipore UK Ltd., Watford, UK) before printing to eliminate larger particles or agglomerates and to ensure that the nozzle was not blocked during the inkjet printing process. These filters are 25 mm syringe non-sterile filters with glass fiber membranes and have 2 μm pore size. An ink containing 5 wt% PEG was selected to investigate the inkjet printing drop drying and interaction processes in detail using in-situ synchrotron X-ray radiographic imaging.

### 3.2 Ink parameter measurements

All the prepared inks were also passed through filters (0.45 μm for pure solvent and 2 μm for nanoparticle suspensions) prior to characterization. 4 ml aliquots of the inks were extracted using an adjustable-volume pipette (5 ml Adjustable-Volume Pipettors, Fisher Scientific Ltd., Loughborough, UK) and weighed using a laboratory balance (ATX Series Analytical Laboratory Balance, Marsden Weighing Machine Group Ltd., Rotherham, UK). The mean densities of the inks were calculated from the measured volumes and weights. Ink viscosity was measured using a single head Hybrid Rheometer (Discovery Hybrid Rheometer, TA Instruments, New Castle, DE, USA). The surface tension and the contact angle of these inks on substrates were measured using a Drop Shape Analyzer (Krüss DSA 100, Krüss GmbH., Hamburg, Germany).
3.3 Inkjet printing method

Throughout this study, a number of inkjet printing systems were used including commercial equipment and home built systems. These printing devices each used commercial printheads, or droplet generators, as follows.

1) DMC-11610 Cartridge, a 10 pl Dimatix shear-mode printhead (Fujifilm Dimatix Inc., Santa Clara, CA, USA).
2) MicroFab MJ-AT-01-80-8MX, a squeeze-mode printhead of 80 µm internal diameter (MicroFab Technologies Inc., Plano, TX, USA).
3) MicroFab MJ-AT-01-60-8MX, a squeeze-mode printhead of 60 µm internal diameter (MicroFab Technologies Inc., Plano, TX, USA).

Printheads 1 and 2 were selected for printing the 11 solvent mixtures to study the influence of Z number on printability. Printhead 2 was also used to print the nanoparticle suspensions for drop drying and interaction experiments. Printhead 3 was chosen to investigate the inkjet printing coffee stain effect and 3D printed structures.

3.3.1 Dimatix printhead

An illustration of the 10 pl Dimatix cartridge structure is shown in Figure 3-1a. Each cartridge has 16 individually addressable nozzles with an orifice diameter of around 21.5 µm, with a nozzle to nozzle spacing of 254 µm. Figure 3-1b shows a schematic diagram of the actuator geometry used in the Dimatix printhead. A piezoelectric/Silicon (PZT/Si) Bimorph is bonded to the right angle tube. When a pulse voltage is applied, this bimorph deforms and generates a pressure pulse along the tube.
Figure 3-1 Schematic diagrams of Dimatix a) cartridge components and b) printhead. Adapted from the “Dimatix Recipes” [205].

Figure 3-2 shows a schematic of the processes that occur during the operation of the Dimatix printhead. The standard actuating pulse waveform can be divided into a series of stages [205].

1) Standby stage, the PZT/Si bimorph is slightly deformed prior to the initiation of the inkjet printing drive pulse.
2) Phase 1: a decrease in the actuation voltage causes PZT/Si bimorph to move upward and draw in the ink from the reservoir.
3) During phase 2, the voltage increases quickly to a high voltage, which drives the PZT/Si bimorph to deform and generate the initial droplet at the nozzle.
4) Finally, during phase 3 the droplet break-offs from the nozzle, and the PZT/Si bimorph returns to the standby position and prepares for the next drop generation cycle.
Figure 3-2 The schematic of the processes occur during the operation of the Dimatix printhead. Adapted from the “Dimatix Recipes” [205].

### 3.3.2 MicroFab printhead

The MicroFab prinheads used in this project (MJ-AT-01-60-8MX and MJ-AT-01-80-8MX) are piezoelectrical drop-on-demand squeeze-mode inkjet printheads and differ only in the nozzle diameter. Figure 3-3 shows a schematic image of the structure of a MicroFab printhead. A fluid fitting is bonded to the end of a glass tube, one end of which has been drawn to a capillary of internal diameter 60 μm or 80 μm. The glass tube is bonded to a radially poled annular piezoelectric (PZT) element at the centre. A blue and a red gauge wire are soldered to the outer electrode and the inner electrode, separately. The outer electrode is connected to the ground while the inner electrode receives the actuation voltage [206]. These wires are loosely twisted and placed together in a connector that matches the output cable of MicroFab’s JetDrive™ electronics box. The MicroFab’s JetDrive™ electronics box is connected to the computer and transfers the signal used to actuate the printhead.
The printhead is actuated by a waveform with voltage differentials applied to the inner and outer electrodes. The electric field is generated due to the voltage differentials. The piezoelectric actuator expands radially and contracts axially (or expands axially and contracts radially) when the electrical field is applied [206]. Figure 3-4 left shows the simple trapezoidal waveform used to actuate the printhead and generate a droplet. The actuation generates a pressure pulse in the fluid that leads to the ejection of a drop from the drawn capillary.

The process has been explained by Reis et al. [39], as shown in Figure 3-4 right and described as follows: a) a negative pressure wave is generated when an outwards
motion of the inner glass surface occurs; b) the pressure wave travels in the fluid along the glass tube producing a dilation acoustic wave to both the reservoir and the orifice; c) the expansion wave is reflected at the reservoir and becomes a compression wave, while the wave reflected from the nozzle is reflected as a dilation; d) the actuator closes when both reflected waves return to the centre generating a compressive pressure wave; e) if the dwell time is selected appropriately, the compression wave reflected from the reservoir will reinforce that generated by the piezoelectric actuator and f) finally ejects a droplet when the combined compression wave reaches the nozzle.

3.3.3 Pixdro LP50 inkjet printing system

To investigate ink printability, 11 solvent inks were printed using a Pixdro LP50 inkjet printer (Roth and Rau, Eindhoven, Netherlands) equipped with a 10 pl Dimatix cartridge, as shown in Figure 3-5.

![Figure 3-5 Pixdro LP50 (left) equipped with a 10 pl Dimatix printhead (right).](image)

All the inks were printed under an ink back pressure of -1.6 mbar with a relative humidity of 40% at 25 °C. To investigate the influence of pulse voltage on the ink behaviour, single trapezoidal pulse waveforms were designed to generate droplets. The echo voltage was fixed at 0 V, and the dwell voltage was in the range of 0-40 V (The maximum pulse voltage available for the Pixdro LP50-Dimatix system is 40 V). A snapshot of a waveform applied is shown in Figure 3-6. The rise time was set at 1 μs, the dwell time and fall time were both set at 3 μs, and the echo time was set to 0 μs. These parameters were chosen with the ethylene glycol as a test ink using 26 V dwell voltage and optimising pulse duration to achieve stable droplets.
The Pixdro-LP50 is equipped with a high-speed camera system and a flash LED for the stroboscopic imaging of printed droplets. Image analysis software (Dropview) is provided by the manufacturer and allows image capture of individual droplets and can be used to calculate the droplet volumes, positions, travel angles and travel velocities (shown in Figure 3-7). The parameters set for Dropview are also shown in Figure 3-7. The inks were all printed under the same jetting frequency of 1 kHz. At this jetting rate, the inks have consequent accelerations of several thousand g (g is the acceleration of gravity at the Earth’s surface and fluid shear rates > \(10^4\) s\(^{-1}\). [39])

The droplet images were captured by increasing the delay time of the fast imaging camera from 0 µs in steps of 10 µs until the droplet disappears from the screen. The LED duration was set to 2.5 µs to give the best contrast for the Dropview.
3.3.4 A custom inkjet printing system used for high-speed imaging of droplets

A static drop generating system coupled to an imaging system was constructed to visualize drop formation from an MJ-AT-01-80-8MX printhead (MicroFab Technologies Inc., Plano, TX, USA) as shown in Figure 3-8.

This drop generation system contained a pressure controller, a vacuum pump, a drive electronics module (JetDrive III, MicroFab), a laptop, a piezoelectric MicroFab printhead MJ-AT-01-80-8MX, a syringe reservoir, a light-emitting diode (LED), a heater, a camera, printing stage and heating stages. The reservoir was connected to the printhead by a tube, which utilizes capillary force to supply sufficient ink fluid, allowing continuous liquid column flow through the nozzle orifice. The reservoir is connected to a vacuum pump. The pump reduces the atmospheric pressure in the reservoir to prevent fluid from leaking through the orifice of the nozzle by gravity when not being actuated for printing. Thus, stable droplets can repeatedly be generated. The printhead was connected to a drive electronic board (JetDrive III, MicroFab), which were interfaced to a PC and controlled in a Lab VIEW™ (National Instruments, Austin, TX, USA) environment. The evolution of the droplets between the nozzle and the substrate can be observed and recorded using a CCD camera (ZEISS Axiocam ERc 5s, Carl Zeiss Ltd., Germany) using a flash LED for the stroboscopic imaging of printed droplets.
To investigate the drop drying and stacking processes, this lab-built platform was also installed on the I13-2 beamline (Diamond Light Source, UK) as shown in Figure 3-9. The drop watcher camera and associated LED were positioned at an angle of approximately 45° on the X-ray beam and detector direction. Considering an actual printing process, the appropriate distance between the printhead nozzle and the substrate for droplet formation was around 1.5 mm to avoid the influence of the air flow on the drop flying path. The printer was set to print with a dwell voltage of 90 V, an echo voltage of 0 V, a dwell time of 30 μs, rise time of 3 μs and fall time of 3 μs. All the inks were printed at a frequency of 3000 Hz.

![Setup of the printer at the beamline](image)

**3.3.5 MPP 1000 printing system**

To investigate the inkjet printing coffee stain effect and 3D structures, a laboratory inkjet printing platform MPP 1000 (Manchester Printing Platform version1000) was used. This printer was designed and constructed in the School of Materials, University of Manchester. It has a moveable x-y table (Micromech Systems, Braintree, UK) with a positional accuracy of 3 μm. The setup is equipped with a piezoelectrically actuated inkjet printhead of 60 μm in internal diameter (MJ-AT-01-
60-8MX, MicroFab Technologies Inc., Plano, TX, USA). The drive electronics (JetDrive III, MicroFab) were interfaced to a PC and controlled in a Lab VIEW™ (National Instruments, Austin, TX, USA) environment. Also, a LED stroboscopic illumination was used. The printer was set to print at a dwell voltage of 70 V and an echo voltage of 0 V. The dwell time, rise time and fall time were set to 35 µs, 3 µs and 3 µs respectively. All the inks were printed at a frequency of 1000 Hz. All the prepared inks were filtered through a filter of 2 µm before printing.

### 3.3.6 Substrates used

The droplet drying speed is related to the environment temperature, pressure, air flow speed, substrate temperature and droplet surface-area-to-volume ratio. The environment temperature, pressure and the air flow speed are constant parameters for experiments in the same environment. Then surface-area-to-volume ratio and substrate temperature are the key parameters to determine the droplet drying speed. For each ink, the surface-area-to-volume ratio is related to the contact angle of the ink with the substrate. Also, the substrate temperature is related to the heat treatment temperature of the substrate. To study the drop drying and stacking processes in detail, it is important to compare the drop drying processes on substrates with different contact angles at different substrate temperatures. Glass slides (Thermo Scientific Menzel GmbH & Co KG, Braunschweig, Germany), polished silicon wafers (IDB Technologie Ltd., Whitley, UK) and Kapton polyimide tape (VWR International Ltd., Lutterworth, UK) were chosen as the substrates in this study. These three kinds of substrates have different contact angles as shown in Figure 3-10. The ink wets the glass slide with a contact angle around 24°. The silicon wafer has a bigger contact angle around 36°, and the Kapton polyimide tape has the largest contact angle around 73°. Also, five substrate temperatures (room temperature, 45 °C, 60 °C, 75 °C and 90 °C) were investigated in this study.

![Figure 3-10](image-url). Images of contact angles from ZrO₂ suspensions on three different substrates: (a) glass slide; (b) silicon wafer and (c) Kapton polyimide.
Accurate and reproducible droplet positioning requires that the path of the droplets (the gap between the nozzle and the substrate) be perpendicular to the substrate. As a rule of thumb, the drop placement accuracy should be one tenth of the line width [40]. A big gap increases inaccuracy of droplet placement due to air currents, drop velocity variation, variation of nozzle behaviour over time and other factors [40]. Thus, the gaps were always around 1.5 mm to ensure the accuracy of deposition in this project.

### 3.3.7 Heat treatment

A horizontal dilatometer (Netzsch DIL 402C, Germany) was used to determine the sintering temperature for inkjet printed green bodies. Figure 3-11 shows a DIL curve of a 3D green body printed from 5 vol% ZrO₂ and 5 wt% PEG ink. As shown in Figure 3-11, there were three peaks due to the weight loss. The first peak around 130 °C was caused mainly by the water loss. The second peak around 317 °C was due to the loss of PEG from the ink formulation (autoignition temperature of PEG 1500 is 305 °C). The final main peak of 1203.5 °C was the sintering temperature of the 3D green body. Considering the 6-7 °C error between the set temperature and the real temperature of the high-temperature furnace, the printed ceramic samples were sintered in a furnace for heat treatment from room temperature, holding at 136 °C for 1 hour, 324 °C for 2 hours and 1210 °C for 4 hours. The heating and cooling rate were both 180 °C/h.

![Figure 3-11 The DIL test of a 3D inkjet printed green body from 5 vol% ZrO₂ and 5 wt% PEG ink.](image)
3.4 Characterization techniques and analysis methods

3.4.1 Calculations of the velocity and volume of printed drops during flight

To investigate the influence of the $Z$ number and pulse voltage on ink printability, the drop volume, the drop velocity and the presence or absence of satellites must be studied. Stroboscopic imaging was used to obtain representative images of the droplets. The images are analysed for ink jetablity and the presence of satellites. Average droplet volumes were measured using the droplet analysis module on the Pixdro LP50 Dropview system. Also, average droplet velocities were calculated by measuring droplet locations at different strobe time delays.

3.4.2 Calculations of the density during the drop drying process

To investigate the internal density change during drop drying processes, the Diamond Manchester Imaging Branchline (I13-2) was applied. I13-2 beamline has an energy range from 8-30 keV. X-rays energy was converted to visible pink light by a scintillator. Then the visible pink light is magnified and detected. The pink light beamline has high flux, which enables images of high signal/noise ratio to be recorded very quickly [207]. Therefore, rapid dynamic processes such as drop drying can be studied using this beamline.

3.4.2.1 Shape effect on the data for dome-shaped drops

The grayscale values of the images obtained from the *in-situ* synchrotron experiments were used to calculate the densities of the drops. However, the sample thickness has an influence on the final detected X-ray intensity, as the thickness is a function of position within the drop. Thus, the shape affects the grayscale value of the images. Figure 3-12 shows a simulation image of a projection for a single material ball using ImaSim. This is a simulation of a planar X-ray of 8-30 KeV source viewed through a ball of 2 cm diameter. From Figure 3-12, it is obvious that the ball shape has an influence on the X-ray absorption as the thickness changing together with the position. The absorption decreases from the centre to the edge of the ball while the thickness is decreasing.
3.4.2.2 Density calculation method for dome-shaped drops

1) For the same position, the drop $z$ distance and density $\rho$ are same:

In this experiment, the I13-2 pink beam has 14 different beam energy peaks together as shown in Figure 3-13. The beam energies, relative intensities and calculated absorption coefficients of the 14 pink beam energy peaks were shown in Table 3-1.
Table 3-1 The beam energies, relative intensities and calculated absorption coefficients of the 14 pink beam energy peaks.

<table>
<thead>
<tr>
<th>No.</th>
<th>Energy $E_j$ (KeV)</th>
<th>Relative intensity</th>
<th>Mass attenuation coefficient $\mu_j^* \rho z$</th>
<th>Percent $P_j$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.439999993</td>
<td>0.004208037</td>
<td>397.1568</td>
<td>0.4208</td>
</tr>
<tr>
<td>2</td>
<td>7.210005824</td>
<td>0.042131143</td>
<td>184.8493</td>
<td>4.2131</td>
</tr>
<tr>
<td>3</td>
<td>9.07999742</td>
<td>0.21853563</td>
<td>98.8349</td>
<td>21.8594</td>
</tr>
<tr>
<td>4</td>
<td>10.84997732</td>
<td>0.191346795</td>
<td>60.94299</td>
<td>19.1347</td>
</tr>
<tr>
<td>5</td>
<td>12.73002338</td>
<td>0.172307418</td>
<td>39.49133</td>
<td>17.2307</td>
</tr>
<tr>
<td>6</td>
<td>14.51001448</td>
<td>0.130792386</td>
<td>27.6812</td>
<td>13.0792</td>
</tr>
<tr>
<td>7</td>
<td>16.38001045</td>
<td>0.078811844</td>
<td>19.9182</td>
<td>7.8812</td>
</tr>
<tr>
<td>8</td>
<td>18.18001629</td>
<td>0.073718575</td>
<td>92.6374</td>
<td>7.3719</td>
</tr>
<tr>
<td>9</td>
<td>20.04000057</td>
<td>0.031540152</td>
<td>71.75041</td>
<td>3.154</td>
</tr>
<tr>
<td>10</td>
<td>21.8596231</td>
<td>0.027672317</td>
<td>57.12178</td>
<td>2.7672</td>
</tr>
<tr>
<td>11</td>
<td>23.71010171</td>
<td>0.011347217</td>
<td>46.15851</td>
<td>1.1347</td>
</tr>
<tr>
<td>12</td>
<td>25.5499959</td>
<td>0.008528309</td>
<td>37.94163</td>
<td>0.8528</td>
</tr>
<tr>
<td>13</td>
<td>27.38998657</td>
<td>0.00545768</td>
<td>31.61541</td>
<td>0.5458</td>
</tr>
<tr>
<td>14</td>
<td>29.24017097</td>
<td>0.003544565</td>
<td>26.63403</td>
<td>0.3545</td>
</tr>
</tbody>
</table>

Thus, according to the Beer-Lambert Law (or attenuation law), the beam intensity after traveling through a drop is described using Equation 3-1.

$$I_i = \sum_{j=1}^{14} I_{i,j} = \sum_{j=1}^{14} I_{0,j} e^{-\mu_j^* \rho z} \quad (3-1)$$

where $I_i$ is the emerging X-ray intensity at a chosen position and contains 14 different X-ray intensity of 14 different beam energies, $I_{0,j}$ is the incident X-ray intensity and also contains 14 different beam energies, $\mu_j^*$ is the mass attenuation coefficient of 14 different beam energies, $\rho$ is the density, and $z$ is the thickness of the sample.

For the experiment, the ink was mainly made of ZrO$_2$, PEG and deionized (DI) water. The value of $\mu_j^* \rho z$ could be calculated using:

$$\mu_j^* \rho z = V_z \mu_{ZrO_2,j}^* \rho_{ZrO_2} z + V_P \mu_{PEG,j}^* \rho_{PEG} z + V_z \mu_{H_2O,j}^* \rho_{H_2O} z \quad (3-2)$$

where $V$ is the volume percent of investigated material with a thickness $z$.

From Equation 2-22, $\mu^* \propto Z^4$. $Z_{ZrO_2} > Z_{PEG} > Z_{H_2O}$, then $\mu_{ZrO_2}^* \gg \mu_{PEG}^* \gg \mu_{H_2O}^*$. Thus, $\mu_j^* \rho z \approx V_z \mu_{ZrO_2,j}^* \rho_{ZrO_2} z$. To simplify the equation, in the later $\mu_j^*$ is $\mu_{ZrO_2,j}^*$.
and $\rho$ is $V_e \rho_{zr_0}^2. I_{0,j} = P_j I_0$. $P_j$ is shown in the Table 3-1. Thus, Equation 3-1 can be rewritten as the following equation:

$$I_i = I_0 \sum_{j=1}^{14} P_j e^{-K_j \rho z} = I_0 \sum_{j=1}^{14} P_j e^{-\mu_j \rho z}$$

(3-3)

2) For the different positions, the drop $z$ distance and density $\rho$ are different:

When focusing on different positions, the thickness $z$ and density $\rho$ are different. The drop was analyzed by slicing the spherical cap into different slices as shown in Figure 3-14a. The sliced layer was divided into several one-pixel wide concentric circles as shown in Figure 3-14b. Within each concentric circle, the density was considered to be a constant. The diameter of the slice was $2b = Np$, where $p$ was the distance of one pixel. Thus, the slice had $N$ pixels totally. $z_i = \sum_{x=1}^{n} L_{i,x}$. 

Thus, according to Beer-Lambert Law or attenuation law, the beam intensity after traveling through the drop could be described using Equation 3-4:

$$I_{i,j} = I_0 \sum_{j=1}^{14} P_j e^{-\mu_j \rho z} = I_0 \sum_{j=1}^{14} P_j e^{-2\mu_j \sum_{x=1}^{n} L_{i,x} \rho_x}$$

(3-4)

The experimental data provides the raw beam intensity $I_0$ and $I_i$. $\mu_j$ is a constant for a fixed beam on a chosen material. Thus, $\rho z$ was defined $U_{i,j}$ as follows:

$$U_{i,j} = \rho z = 2 \sum_{x=1}^{n} L_{i,x} \rho_x$$

(3-5)
Based on Equation 3-4 and Equation 3-5, a function of $U_i$ can be defined:

$$f(U_i) = \frac{l_i}{l_0} - \sum_{j=1}^{14} P_j e^{-\mu_j U_i} = 0$$  \hspace{1cm} \text{(3-6)}$$

which gives the following derivative function:

$$f'(U_i) = \sum_{j=1}^{14} P_j \mu_j e^{-\mu_j U_i}$$  \hspace{1cm} \text{(3-7)}$$

According to the Newton-Raphson method $x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$, the $U_i$ was calculated using Equation 3-8.

$$U_i = U_{i-1} - \frac{f(U_{i-1})}{f'(U_{i-1})} = U_{i-1} - \frac{\frac{l_{i-1}}{l_0} \sum_{j=1}^{14} P_j e^{-\mu_j U_{i-1}}}{\sum_{j=1}^{14} P_j \mu_j e^{-\mu_j U_{i-1}}}$$  \hspace{1cm} \text{(3-8)}$$

From Figure 3-14 b, the $L_{l,x}$ can be calculated using Equation 3-9.

$$L_{l,x} = \begin{cases} 
0, & x < i \\
\sqrt{(R_x)^2 - (r_i)^2} - \sqrt{(R_x - p)^2 - (r_i)^2}, & x \geq i 
\end{cases}$$  \hspace{1cm} \text{(3-9)}$$

According to Equation 3-5, Equation 3-9 converted into a matrix equation (Equation 3-10) and the density along each slice was calculated using the linear equation (Equation 11).

$$\begin{bmatrix} 
L_{1,1} & L_{1,2} & \cdots & L_{1,n-1} & L_{1,n} \\
0 & L_{2,2} & \cdots & L_{2,n} \\
0 & 0 & \ddots & \ddots & \ddots \\
0 & 0 & \cdots & 0 & L_{n,n} 
\end{bmatrix} \begin{bmatrix} 
\rho_1 \\
\rho_2 \\
\rho_3 \\
\vdots \\
\rho_n 
\end{bmatrix} = \begin{bmatrix} 
U_1 \\
U_2 \\
U_3 \\
\vdots \\
U_n 
\end{bmatrix}$$  \hspace{1cm} \text{(3-10)}$$

$$\begin{bmatrix} 
\rho_1 \\
\rho_2 \\
\rho_3 \\
\vdots \\
\rho_n 
\end{bmatrix} = \frac{1}{2} \begin{bmatrix} 
L_{1,1} & L_{1,2} & \cdots & L_{1,n-1} & L_{1,n}^{-1} \\
0 & L_{2,2} & \cdots & L_{2,n} \\
0 & 0 & \ddots & \ddots & \ddots \\
0 & 0 & \cdots & 0 & L_{n,n}^{-1} 
\end{bmatrix} \begin{bmatrix} 
U_1 \\
U_2 \\
U_3 \\
\vdots \\
U_n 
\end{bmatrix}$$  \hspace{1cm} \text{(3-11)}$$

When $N$ is an odd number (setting $N = 2m-1$), the pixel centre is the centre of the circle (shown in Figure 3-15). The slice can be divided into $(N+1)/2 = m$ concentric circles. The density from the centre circle to the outside circles was named as $\rho_1$ to $\rho_m$. Then, $R_1 = p/2, R_2 = 3p/2, \ldots, R_m = (m-1/2)p$ and $n_1 = 0, n_2 = p, n_3 = 2p, \ldots, n_m = (m-1)p$. Thus, Equation 3-9 can be calculated as the following Equation 3-12 and
Matrix Equation 3-13. The experiment data gave the value of $U_1$, $U_2$, ..., $U_m$, the $p$ is calculated as one pixel, $m$ is calculated from the position. Thus, Equation 3-11 used to calculate the density $\rho_1$, $\rho_2$, ..., $\rho_m$ was converted as Equation 3-14 and Equation 3-15.

$$\begin{align*}
L_{iX} & = \begin{cases} 
0, & x < i \\
\sqrt{(xp - \frac{p}{2})^2 - (r_i)^2} - \sqrt{\left(\frac{3p}{2}\right)^2 - (r_i)^2}, & x \geq i
\end{cases} \\
\left[ \begin{array}{cccc}
1 & 0 & 0 & \cdots & 0 \\
-1 & 1 & 0 & \cdots & 0 \\
0 & -1 & 1 & \cdots & 0 \\
\vdots & \vdots & \ddots & \ddots & \vdots \\
0 & 0 & \cdots & -1 & 1
\end{array} \right] & = \begin{bmatrix} L_{i,1} \\
L_{i,2} \\
\vdots \\
L_{i,m} \end{bmatrix}, \quad x \geq i \\
\left[ \begin{array}{c}
\rho_1 \\
\rho_2 \\
\rho_3 \\
\vdots \\
\rho_m
\end{array} \right] & = \frac{1}{2} \begin{bmatrix}
p & \sqrt{5p} & \cdots & \sqrt{(2m-1)^2 - 4} & \sqrt{(2m-3)^2 - 4}p \\
0 & \frac{p}{2} & \cdots & \frac{(2m-1)^2 - 4}{p} & \frac{2m-3}{p} \\
\vdots & \vdots & \ddots & \ddots & \vdots \\
0 & 0 & \cdots & \frac{p}{2} & \frac{2m-3}{p}
\end{bmatrix}^{-1} \begin{bmatrix} U_1 \\
U_2 \\
U_3 \\
\vdots \\
U_m \end{bmatrix}
\end{align*}$$
When $N$ is an even number (setting $N = 2n$), the circle centre is the line to separate left and right (shown in Figure 3-16). Then, $R_1 = p$, $R_2 = 2p$, ..., $R_m = np$ and $r_1 = p/2$, $r_2 = 3p/2$, $r_3 = 5p/2$, $r_n = (n-1/2)p$. Thus, Equation 3-9 can be calculated as the following Equation 3-16 and Matrix Equation 3-17. The experiment data gave the value of $U_1$, $U_2$, ..., $U_n$, the $p$ is calculated as one pixel, $n$ is calculated from the position. Thus, Equation 3-11 used to calculate the density $\rho_1$, $\rho_2$, ..., $\rho_n$ was converted as Equation 3-18 and Equation 3-19.

![Figure 3-16 Image simulation of a top-view of the slice in Figure 3-14 a when a slice diameter is an even number.](image)

$$L_{i,x} = \begin{cases} 0, x < i \\ \sqrt{(xp)^2 - (r_i)^2} - \sqrt{(xp - p)^2 - (r_i)^2}, x \geq i \end{cases}, x:1 \rightarrow n, i:1 \rightarrow n$$ (3-16)

$$\begin{bmatrix} 1 & 0 & 0 & \cdots & 0 \\ -1 & 1 & 0 & \cdots & 0 \\ 0 & -1 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & -1 & 1 \end{bmatrix} \begin{bmatrix} \sqrt{(p)^2 - (r_i)^2} \\ \sqrt{(2p)^2 - (r_i)^2} \\ \vdots \\ \sqrt{(xp)^2 - (r_i)^2} \\ \vdots \\ \sqrt{(np)^2 - (r_i)^2} \end{bmatrix} = \begin{bmatrix} L_{i,1} \\ L_{i,2} \\ \vdots \\ L_{i,x} \\ \vdots \\ L_{i,n} \end{bmatrix}, x \geq i, x:1 \rightarrow n, i:1 \rightarrow n$$ (3-17)
### 3.4.2.3 Drop volume calculation

To investigate whether the drop density change varies with drop volume, the drop volume was also calculated. When a small drop spreads on a substrate, its shape is controlled by capillary forces, and it normally forms a dome shape as a spherical cap (as shown in Figure 3-17a). During the first drying stage, the drop will remain in a dome shape, until the top of the drop becomes flat as a spherical segment (as shown in Figure 3-17b). Finally, if a coffee stain forms, the drop will become a spherical segment with smaller spherical cap taken from the top centre (as shown in Figure 3-17c). The volume of a dome-shaped drop (spherical cap) is given by the equation of a spherical cap (as shown in Equation 3-20). The volume of the flat top drop (spherical segment) is given by the Equation 3-21. The volume of the coffee stain drop is given by the Equation 3-22.

![Figure 3-17 The drop volume calculation as a) spherical cap; b) spherical segment; c) coffee stain drop.](image)

\[
\rho_n = \frac{1}{2} \begin{bmatrix}
\sqrt{p_1} & \sqrt{(\sqrt{3} - \sqrt{7})p_2} & \ldots & \frac{\sqrt{4n^2 - 1} - \sqrt{(n-1)^2 - 1}}{2} p_n \\
0 & \sqrt{7} p_2 & \ldots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \ldots & \sqrt{2N - 1} p_n
\end{bmatrix}^{-1}
\begin{bmatrix}
U_1 \\
U_2 \\
U_3 \\
\vdots \\
U_n
\end{bmatrix}
\] (3-18)

\[
\rho_n = \frac{1}{2} \begin{bmatrix}
\sqrt{p_1} & \sqrt{(\sqrt{3} - \sqrt{7})p_2} & \ldots & \frac{\sqrt{N^2 - 1} - \sqrt{(N-2)^2 - 1}}{2} p_n \\
0 & \sqrt{7} p_2 & \ldots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \ldots & \sqrt{2N - 1} p_n
\end{bmatrix}^{-1}
\begin{bmatrix}
U_1 \\
U_2 \\
U_3 \\
\vdots \\
U_n
\end{bmatrix}
\] (3-19)

\[
V_{\text{cap}} = \frac{\pi h (3a^2 + h^2)}{6} \quad (3-20)
\]

\[
V_{\text{seg}} = \frac{\pi h (3a^2 + 3b^2 + h^2)}{6} \quad (3-21)
\]
\[ V_{\text{cof}} = \frac{\pi h(3a^2+3b^2+h^2)}{6} - \frac{\pi d(3c^2+d^2)}{6} \] (3-22)

3.4.3 Characterization of the defects of the printed structures before and after sintering

Inkjet printed 3D objects are constructed by the interaction of printed individual drops that dry to form the solid. Constructing a solid normally requires the deposition of drops, the merging of drops to form continuous lines, the interaction of lines to form solid sheets and the sequential printing of sheets to form the solid body. It is convenient to consider four classes of defects in printed ceramic structures, each of which is associated with steps in the building process.

1) Individual drop defects e.g. the coffee stain.
2) Line defects, mainly the result of missing drops during printing.
3) Surface defects e.g. caused by the overlap of adjacent printed lines.
4) Finally, the non-uniform stacking of layers can also influence on the volume defects.

The coffee stain and surface defects of the inkjet printing ceramic objects will be studied mainly using optical phase contrast microscopy (PCM, MicroXAM Phase Contrast Microscope, Phase Shift Inc., Tucson, AZ, USA) and scanning electron microscopy (SEM, Zeiss EVO60). The internal defects and 3D structures of the printed ceramics were characterized using high-resolution X-ray micro-tomography (ZEISS Xradia Versa 520, Carl Zeiss X-ray Microscopy Inc., Pleasanton, CA, USA) at Henry Moseley. The raw transmission 2D images from the micro-tomography experiments were reconstructed using a commercial image reconstruction software package (ZEISS XMReconstructor, Carl Zeiss X-ray Microscopy Inc., Pleasanton, CA, USA).

3.4.4 Software used for data analysis

To analyze the data generated in this study, a range of commercial image analysis and manipulation software packages were used.
CHAPTER 3  EXPERIMENTAL MATERIALS AND METHODS

3.4.4.1  Image J

A public domain software, Image J (Wayne Rasband, National Institutes of Health, USA), was used to analysis all the images obtained in this study and mainly used in dealing with the mask images for the data obtained during the Diamond synchrotron experiments. The process of masking the images is shown in Figure 3-18. First, all the images were cropped using Image J (shown in Figure 3-18a). 20 images were selected before drops emerged and were used to obtain an average intensity image as the background image (shown in Figure 3-18b). The raw images were all divided by the background image (shown in Figure 3-18c). Then, these divided images were binned with an X shrink factor of 2, and a Y shrink factor of 2 and a Z shrink factor of 1 using the Bin Method of Average. All the binned images were saved as 8-bit images. Then a mask for the drop was figured out by adjusting the threshold (shown in Figure 3-18d). Finally, the mask images were eroded (shown in Figure 3-18e) and dilated (shown in Figure 3-18f) to remove the noise component of the edge to create the final masks for the images.

Figure 3-18 The process of masking the images: (a) cropped raw image; (b) average background; (c) the divided picture; (d) the binned image and adjusted contrast to find the drop edge; (e) image after erosion; (f) mask image after dilating the image.
3.4.4.2 *Matlab*

The drop density during drying was analyzed from the radiographs by Matlab (The MathWorks, Inc., USA) using bespoke Matlab codes. The raw data of the XCT was performed using Matlab to reconstruction the 3D structures. The porosities of the scanned 3D structures were quantified using Matlab codes.

3.4.4.3 *Avizo*

All the XCT image processing and analysis were performed using Avizo 8.0 (FEI Visualization Sciences Group, Inc., Burlington, MA, USA) at the Henry Moseley X-ray Imaging Facility in University of Manchester. The microvoids and crack-like defects were segmented by Avizo 8.0.
CHAPTER 4 Influence of Z number and Pulse Voltage on Drop-on-Demand (DOD) Inkjet Printability

The following sections in Chapter 4 have been prepared as a manuscript for submission to the Langmuir. Some of the results have been given as an oral presentation at The 32nd International Conference on Digital Printing Technologies (NIP 2016), Manchester, United Kingdom, September 12-16, 2016.

The author has designed, prepared and performed the experiment, analysed the collected data, interpreted the results and wrote the first draft and the final version of this manuscript.
CHAPTER 4 Influence of Z number and Pulse Voltage on Drop-on-Demand (DOD) Inkjet Printability

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Abstract

The design of inks for drop-on-demand inkjet delivery is a key step in developing printable materials for functional applications. The key principle is that the ink is capable of producing stable single drops over a wide range of printing conditions. It is possible to define a dimensionless parameter space to identify a window of ink fluid physical properties and a process parameter (velocity) that enables appropriate design of printable inks. The dimensionless number Z, where $Z = 1/Oh$, the inverse Ohnesorge number, is a key indicator for drop formation in liquids and has been proposed as a metric for ink printability that is independent of velocity. Limiting bounds for Z define a minimum value that once exceeded leads to multiple drops or satellites. The velocity variable is has been conventionally presented in dimensionless form by the Weber number ($We$), which also shows bounds with minimum and maximum also defined by drop formation and satellite formation. Here we present experimental data obtained using two widely used inkjet droplet generators, with different actuation mechanisms, to demonstrate a window of printability defined by a combination of Z and We. The lower bound for Z is consistent with earlier work but with $Z > 5$ satellite formation is limited by a decrease in the maximum value of We to prevent satellite formation. Thus, inks with large values of Z have a reduced range of practical drop velocity. In addition, we show that lower values of Z produce drops with smaller variation in drop size with actuation voltage. These limiting values of Z and We can be used as a guide for ink design and formulation.

Key Words

Inkjet printing; Z number; Printability
4.1 Introduction

Inkjet printing forms a digital image by depositing patterns of droplets onto a substrate. There are two methods by which droplets are formed and patterned, namely continuous inkjet (CIJ) printing and drop-on-demand (DOD) inkjet printing [11]. In CIJ printing, a continuous stream of droplets is generated, but only a small amount of it is used for printing while the majority will be recycled. In DOD inkjet printing, drops are generated only when required by producing a pressure pulse in a chamber filled with inks [37]. Before drop generation, the inkjet printhead is moved to the desired location above the substrate (or the substrate is moved to the desired location under the printhead) to locate the drop in the desired position. DOD inkjet printing directly deposits materials on demand, which minimises the materials used in the process and reduces the printing steps. As a consequence, DOD inkjet printing generates lower waste materials during production with a smaller environmental footprint compared with CIJ printing.

DOD inkjet printing can be further divided into two major methods by which the pressure pulse required for drop ejection is generated: thermal DOD inkjet printing and piezoelectric DOD inkjet printing. In thermal DOD inkjet printing, a thin film micro-heater is present in a chamber close to the printing nozzle and this produces micro-bubbles by vaporizing a small volume of ink. The pressure pulse is generated by the formation, expansion and collapse of the bubble. The vapour bubble formation and collapse propagates a pressure wave through the fluid chamber to push a fluid droplet out of the nozzle. Thus, the solvent must possess a relatively low boiling temperature, this and other factors limit the base fluid to water [37]. In piezoelectric DOD inkjet printing, the pressure pulse for drop ejection is produced by the mechanical actuation of the chamber walls [38]. The piezoelectric material changes shape when a voltage is applied. This deformation generates a pressure pulse in a fluid chamber behind the printer nozzle forcing a droplet of ink from the nozzle. There are a number of different designs for the actuation mechanism in piezoelectric DOD inkjet printheads and these are grouped into different modes: squeeze mode, shear mode, bend mode and push mode [40].
Piezoelectric DOD inkjet printing has been applied in manufacturing structural and functional materials for a number of years [1], [3], [4], [8], [29], [39]. Despite this, there is no consensus as to how to predict the fluid properties and printing parameters that ensure stable and repeatable drop generation. A number of dimensionless groupings of physical constants can be used to represent the behaviour of liquid drops. The most commonly used are the Reynolds number (Re), Weber number (We) and Ohnesorge number (Oh) [9], [11]. Re is the ratio of inertial to viscous forces [84], as shown in Equation 2-1. We is a balance between inertial and capillary forces [84], as shown in Equation 2-2. Oh is a balance between the viscous and surface tension forces. Historically in the study of inkjet drop formation, Z number (the inverse of the Ohnesorge number as shown in Equation 4-3) has been used in many published reports on drop formation in DOD inkjet printing [10]–[15].

\[
Re = \frac{\nu a}{\eta} \tag{4-1}
\]

\[
We = \frac{\nu^2 pa}{\gamma} \tag{4-2}
\]

\[
Z = \frac{1}{Oh} = \frac{\sqrt{\nu pa}}{\eta} \tag{4-3}
\]

In the above equations, \( \rho, \eta, \) and \( \gamma \) are the density, dynamic viscosity, and surface tension of the fluid respectively, \( \nu \) is the velocity of the fluid (often taken as the drop velocity), and \( a \) is a characteristic length (in the literature this is usually the nozzle diameter which is around 21.5 \( \mu \)m for 10 pl Dimatix printheads).

Fromm carried out the earliest significant work in understanding the mechanisms of drop generation during inkjet printing and suggested that \( Z > 2 \) for stable drop formation [10]. Later, Reis and Derby [86] proposed that \( Z \) should be in the range of \( 1 < Z < 10 \) for stable drop generation using numerical simulation. They thought viscous dissipation prevents drop ejection when \( Z < 1 \), while satellite drops will form together with the primary drop when \( Z > 10 \). Derby [11] indicated that the predicted regime of printability of \( 1 < Z < 10 \) agreed with some literature data [8], [89]. However, Jang et al. [18] printed a range of fluids and studied the single droplet formability, positional accuracy, and maximum allowable jetting frequency. They proposed that the printable range was in the range of \( 4 \leq Z \leq 14 \). Tai et al. reported
that single droplets could be jetted for $\frac{2}{3} < Z < 50$ [90]. Kim and Baek [16] simulated the drop-formation dynamics for Newtonian fluids and predicted a printability range of $1 \leq Z \leq 14$. These results and a range of other experimental data are summarised in Table 4-1. As can be seen, there is no consensus on the applicability of a defined $Z$ number for printable ink formulation for inkjet printing.

Drop ejection is typically the result of the superposition of two or more consecutive waves that generate pressure pulses of sufficient magnitude to overcome viscous dissipation and the energy associated with forming a new surface. The propagation and reflection of acoustic pressure waves are a function of fluid properties, printhead design, and constituent materials. Hence, the desired superposition is typically achieved via adjustments to the electrical signals driving the piezoelectric actuator (frequency, voltage amplitude, and pulse duration) [39]. However, it is still not known whether the $Z$ range for printability varies with different actuating pulses.

Tsai et al. [14], [44] studied the effect of actuating pulse voltage on droplet formation of ethylene glycol, alcohol, DI water and a silver nanoparticle suspension using a 30 μm squeeze mode piezoelectric printhead with a bipolar pulse waveform. They found the workable pulse voltage range for single droplet formation is 23-29 V for DI water ($Z = 43.48$), 28-31 V for alcohol ($Z = 21.23$), 30-45 V for ethylene glycol ($Z = 2.99$) and 33-45 V for the silver nanoparticle suspension ($Z = 6.28$). Recently, Hill et al. [91] studied printability of a series of α-terpineol-based inks using a 10 pl Dimatix printhead by actuated by a single trapezoidal pulse waveform. They found a printable range of $3 \leq Z \leq 24$ and $We < 35$ after comparing the deposit pattern of droplets on glass slides. However, they did not give detailed information about the experimental procedure used.

The goal of this study is to further investigate the relationship between ink properties and drop-on-demand inkjet printability. A range of pulse voltages and printhead types are used to explore whether the printable $Z$ number range changes with actuating pulses and with different printhead designs. To best of my knowledge, all previous studies on printability reported in the literature have studied drop generation with a single printhead. Thus, it is difficult to compare the performance of inks between different printheads, because of uncertainties between different studies with different inks. This study presents an investigation of the influence of $Z$ number
and actuating pulse voltage on inkjet printability and drop generation for a range of fluids using two inkjet printheads with different actuation modes. They are a 10 pl shear-mode Dimatix printhead (DMC-11610, Fujifilm Dimatix, Santa Clara, CA, USA) and an 80 μm squeeze-mode MicroFab printhead (MJ-AT-01-80-8MX, MicroFab Technologies Inc., Plano, TX, USA). 11 model inks were made from solvent mixtures of ethylene glycol, diethylene glycol and distilled water. A range of actuating pulse voltages was studied.
### Table 4-1 A summary of the printable inks’ Z numbers obtained using drop-on-demand inkjet printheads in previous studies.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Nozzle manufacturer</th>
<th>Nozzle mode</th>
<th>Nozzle diameter (μm)</th>
<th>Inks⁴</th>
<th>Waveform type⁵</th>
<th>Z number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Link and Semiat [208]</td>
<td>Aprion</td>
<td>Push</td>
<td>30</td>
<td>Black dye ink</td>
<td>Trapezoidal</td>
<td>2.68</td>
</tr>
<tr>
<td>Dong et al. [78]</td>
<td>Trident</td>
<td>Push</td>
<td>53</td>
<td>GWI, GW, DI water</td>
<td>Single peak, Double peak</td>
<td>8.78, 12.6, 62.2</td>
</tr>
<tr>
<td>Choi et al. [43]</td>
<td>Self-designed</td>
<td>Push</td>
<td>100</td>
<td>GW</td>
<td>-</td>
<td>0.23-84.7</td>
</tr>
<tr>
<td>Rho et al. [209]</td>
<td>Dimatix</td>
<td>Shear</td>
<td>19</td>
<td>NP and pure solvents</td>
<td>-</td>
<td>0.55-36.7</td>
</tr>
<tr>
<td>Hill et al. [211]</td>
<td>Dimatix</td>
<td>Shear</td>
<td>21.5</td>
<td>α-terpineol-based inks</td>
<td>Trapezoidal</td>
<td>3-24</td>
</tr>
<tr>
<td>Liu et al. [68]</td>
<td>MicroFab</td>
<td>Squeeze</td>
<td>30</td>
<td>GW</td>
<td>Trapezoidal, Double, Bipolar</td>
<td>2.15-46</td>
</tr>
<tr>
<td>Tsai and Hwang [44]</td>
<td>MicroFab</td>
<td>Squeeze</td>
<td>30</td>
<td>EG, Alcohol</td>
<td>Bipolar</td>
<td>2.99, 21.23</td>
</tr>
<tr>
<td>Tsai et al. [14]</td>
<td>MicroFab</td>
<td>Squeeze</td>
<td>30</td>
<td>Silver nanoparticle suspension, DI water</td>
<td>Bipolar</td>
<td>6.28, 43.48</td>
</tr>
<tr>
<td>Wu et al. [17]</td>
<td>MicroFab</td>
<td>Squeeze</td>
<td>40</td>
<td>Computational fluid dynamics</td>
<td>Trapezoidal</td>
<td>17.39-53.7</td>
</tr>
<tr>
<td>Gan et al. [69]</td>
<td>MicroFab</td>
<td>Squeeze</td>
<td>50</td>
<td>PEDOT, DI water</td>
<td>Double W-shaped, Trapezoidal, Bipolar</td>
<td>1.98, 60.4</td>
</tr>
<tr>
<td>Jang et al. [18]</td>
<td>MicroFab</td>
<td>Squeeze</td>
<td>50</td>
<td>Mixtures of EG/DI, DEG et al.</td>
<td>Bipolar</td>
<td>4-14</td>
</tr>
<tr>
<td>Jo et al. [210]</td>
<td>MicroFab</td>
<td>Squeeze</td>
<td>50</td>
<td>GW</td>
<td>Trapezoidal</td>
<td>4.41-67</td>
</tr>
<tr>
<td>Shield et al. [83]</td>
<td>Self-designed</td>
<td>Squeeze</td>
<td>50</td>
<td>EG, DI water</td>
<td>Trapezoidal</td>
<td>18.4, 64</td>
</tr>
<tr>
<td>Son et al. [211]</td>
<td>MicroFab</td>
<td>Squeeze</td>
<td>50</td>
<td>DI water</td>
<td>Bipolar</td>
<td>58.80</td>
</tr>
<tr>
<td>Tai et al. [90]</td>
<td>MicroFab</td>
<td>Squeeze</td>
<td>50</td>
<td>GW</td>
<td>Trapezoidal</td>
<td>0.67-50</td>
</tr>
<tr>
<td>Bienia et al. [13]</td>
<td>Ceradrop</td>
<td>Squeeze</td>
<td>42, 52</td>
<td>Solvents, ceramic suspensions</td>
<td>Trapezoidal</td>
<td>1.27-16.69</td>
</tr>
<tr>
<td>Nallan et al. [12]</td>
<td>MicroFab</td>
<td>Squeeze</td>
<td>60</td>
<td>Solvent mixtures, gold nanoparticle suspensions</td>
<td>Bipolar</td>
<td>1-60</td>
</tr>
<tr>
<td>Szczech et al. [212]</td>
<td>MicroFab</td>
<td>Squeeze</td>
<td>60</td>
<td>Nanoparticle suspension</td>
<td>Bipolar</td>
<td>23.1-47.9</td>
</tr>
<tr>
<td>Perelaer et al. [213]</td>
<td>Micro drop</td>
<td>Squeeze</td>
<td>70</td>
<td>PT, PB</td>
<td>Trapezoidal</td>
<td>7.92-63.4</td>
</tr>
<tr>
<td>Seerden et al. [79]</td>
<td>Sanders Design International</td>
<td>Squeeze</td>
<td>70</td>
<td>Alumina/Paraffin suspension</td>
<td>Trapezoidal</td>
<td>2.56-17.75</td>
</tr>
<tr>
<td>Reis et al. [39]</td>
<td>Sanders Design International</td>
<td>Squeeze</td>
<td>75</td>
<td>Alumina/Paraffin suspension</td>
<td>Trapezoidal</td>
<td>1.48-12.7</td>
</tr>
<tr>
<td>de Gans et al. [28]</td>
<td>Micro drop</td>
<td>Squeeze</td>
<td>30-100</td>
<td>Polystyrene nanoparticle inks</td>
<td>Trapezoidal</td>
<td>21-91</td>
</tr>
<tr>
<td>Kim and Baeck [16]</td>
<td>MicroFab</td>
<td>Squeeze</td>
<td>2000</td>
<td>Computational fluid dynamics</td>
<td>Trapezoidal</td>
<td>1-14</td>
</tr>
<tr>
<td>Delrot et al. [214]</td>
<td>Self-designed</td>
<td>Thermal</td>
<td>100-300</td>
<td>Organic dye, GW</td>
<td>-</td>
<td>0.67-100</td>
</tr>
<tr>
<td>Esposito et al. [215]</td>
<td>HP Deskjet1000</td>
<td>Thermal</td>
<td>20</td>
<td>Nanoparticle suspension</td>
<td>-</td>
<td>6.73, 10.28</td>
</tr>
</tbody>
</table>

⁴DEG, EG, GW, GWI, NP, PB, PEDOT and PT denote diethylene glycol, ethylene glycol, glycerol–water mixture, glycerol–water–iso-propanol mixture, pre-crystallized NiO nanoparticle ink, polystyrene-buty1 acetate mixture, poly(3,4-ethylenedioxythiophene) and polystyrene-toluene mixture, respectively. Paraffin (wax) and PEDOT are non-Newtonian fluids.

⁵The waveforms for inkjet nozzles operated in different modes are a little bit different.
CHAPTER 4  STUDY OF INKJET PRINTABILITY

4.2 Experimental procedure

4.2.1 Experiment inks

To investigate the influence of fluid properties on ink printability, 11 solution based inks were prepared with compositions selected to obtain a range of $Z$ numbers from 0.05 to 36.76. Ink formulations included distilled water, solutions of distilled water and ethylene glycol, pure ethylene glycol (Sigma-Aldrich Company Ltd., Dorset, UK), pure diethylene glycol (Sigma-Aldrich Company Ltd., Dorset, UK) and pure glycerol (Sigma-Aldrich Company Ltd., Dorset, UK). Inks were either used in pure form or mixed to the desired composition in glass laboratory vessels. All the inks were filtered through a 0.45 μm PTFE syringe filter (Puradisc Whatman, Little Chalfont, UK). 4 ml aliquots of the inks were extracted using a 5 ml adjustable-volume pipette (Fisher Scientific Ltd., Loughborough, UK) and weighed using a laboratory balance (ATX, Marsden Weighing Machine Group Ltd., Rotherham, UK). The mean densities of the inks were calculated from the measured volumes and weights. Viscosity and surface tension were measured using a single head Hybrid Rheometer (Discovery Hybrid Rheometer, TA Instruments Inc., New Castle, DE, USA) and a Drop Shape Analyzer (Krüss DSA 100, Krüss GmbH, Hamburg, Germany), respectively.

4.2.2 Dimatix printhead experimental setup

All these inks are printed using Pixdro LP50 inkjet printer (Roth and Rau, Eindhoven, Netherlands) equipped with a 10 pl Dimatix cartridge, as shown in Figure 4-1.
All the inks were printed under an ink back pressure of -1.6 mbar with a relative humidity of 40% at 25 °C. To investigate the influence of pulse voltage on the ink behaviour, single trapezoidal pulse waveforms were designed to generate droplets. The echo voltage was fixed at 0 V, and the dwell voltage was in the range of 0-40 V (The maximum pulse voltage available for the Pixdro LP50-Dimatix system is 40 V). The rise time was set at 1 µs, the dwell time and fall time were both set at 3 µs, and the echo time was set to 0 µs. These parameters were chosen with the ethylene glycol as a test ink using 26 V dwell voltage and optimising pulse duration to achieve stable droplets.

The Pixdro-LP50 is equipped with a high-speed camera system and a flash LED for the stroboscopic imaging of printed droplets. Image analysis software (Dropview) is provided by the manufacturer and allows image capture of individual droplets and can be used to calculate the droplet volumes, positions, travel angles and travel velocities. The inks were all printed under the same jetting frequency of 1 kHz. The droplet images were captured by increasing the delay time of the fast imaging camera from 0 µs in steps of 10 µs until the droplet disappears from the screen. The LED duration was set to 2.5 µs to give the best contrast for the Dropview.

4.2.3 MicroFab printhead experimental setup

A static drop generating system coupled to an imaging system was constructed to visualize drop formation from an MJ-AT-01-80-8MX printhead (MicroFab Technologies Inc., Plano, TX, USA) as shown in Figure 4-2.
This drop generation system contained a pressure controller, a vacuum pump, a drive electronics module (JetDrive III, MicroFab), a laptop, a piezoelectric MicroFab printhead MJ-AT-01-80-8MX, a syringe reservoir, a light-emitting diode (LED), a heater, a camera, printing stage and heating stages. The reservoir was connected to the printhead by a tube. The reservoir is connected to a vacuum pump. The pump reduces the atmospheric pressure in the reservoir to prevent fluid from leaking through the orifice of the nozzle by gravity when not being actuated for printing. Thus, stable droplets can repeatedly be generated. The printhead was connected to a drive electronic board (JetDrive III, MicroFab), which were interfaced to a PC and controlled in a Lab VIEW™ (National Instruments, Austin, TX, USA) environment. The evolution of the droplets between the nozzle and the substrate can be observed and recorded using a CCD camera (ZEISS Axiocam ERc 5s, Carl Zeiss Ltd., Germany) using a flash LED for the stroboscopic imaging of printed droplets.

4.3 Results and discussion

4.3.1 Inks' physical properties and calculated Z numbers

The summary of the physical properties of the inks and their Z numbers are shown in Table 4-2.
CHAPTER 4  STUDY OF INKJET PRINTABILITY

Table 4-2 A summary of inks’ physical properties and calculated Z numbers in this work.

<table>
<thead>
<tr>
<th>Ink No.</th>
<th>Solvent type (volume fraction)</th>
<th>Density (g/ml)</th>
<th>Viscosity (mPa·s)</th>
<th>Surface tension (mN/m)</th>
<th>Z number-Dimatix 10 pl (Z&lt;sub&gt;21.5&lt;/sub&gt;)</th>
<th>Z number-MicroFab 80 μm (Z&lt;sub&gt;60&lt;/sub&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DI water</td>
<td>0.991</td>
<td>1.07</td>
<td>72.65</td>
<td>36.76</td>
<td>70.91</td>
</tr>
<tr>
<td>2</td>
<td>ethylene glycol (0.05) + water (0.95)</td>
<td>0.992</td>
<td>1.16</td>
<td>69.51</td>
<td>33.20</td>
<td>64.03</td>
</tr>
<tr>
<td>3</td>
<td>ethylene glycol (0.10) + water (0.90)</td>
<td>0.994</td>
<td>1.47</td>
<td>68.85</td>
<td>26.09</td>
<td>50.33</td>
</tr>
<tr>
<td>4</td>
<td>ethylene glycol (0.15) + water (0.85)</td>
<td>1.002</td>
<td>2.32</td>
<td>67.70</td>
<td>16.46</td>
<td>31.76</td>
</tr>
<tr>
<td>5</td>
<td>ethylene glycol (0.25) + water (0.75)</td>
<td>1.014</td>
<td>2.72</td>
<td>66.97</td>
<td>14.05</td>
<td>27.09</td>
</tr>
<tr>
<td>6</td>
<td>ethylene glycol (0.50) + water (0.50)</td>
<td>1.048</td>
<td>4.39</td>
<td>60.28</td>
<td>8.40</td>
<td>16.20</td>
</tr>
<tr>
<td>7</td>
<td>ethylene glycol (0.75) + water (0.25)</td>
<td>1.077</td>
<td>7.81</td>
<td>52.68</td>
<td>4.47</td>
<td>8.63</td>
</tr>
<tr>
<td>8</td>
<td>ethylene glycol (0.85) + water (0.15)</td>
<td>1.093</td>
<td>10.48</td>
<td>50.15</td>
<td>3.28</td>
<td>6.32</td>
</tr>
<tr>
<td>9</td>
<td>Ethylene glycol</td>
<td>1.105</td>
<td>15.78</td>
<td>45.51</td>
<td>2.08</td>
<td>4.02</td>
</tr>
<tr>
<td>10</td>
<td>Diethylene glycol</td>
<td>1.090</td>
<td>27.09</td>
<td>42.73</td>
<td>1.17</td>
<td>2.25</td>
</tr>
<tr>
<td>11</td>
<td>Glycerol</td>
<td>1.261</td>
<td>934.00</td>
<td>76.20</td>
<td>0.05</td>
<td>0.09</td>
</tr>
</tbody>
</table>

From the results in Table 4-2, it can be clearly seen that the density and viscosity increase while the surface tension decreases when increasing the ethylene glycol volume fraction in the ink mixture. These results in a decline of Z number value when the ethylene glycol volume fraction (vol%) increases in the ink mixture, as shown in Figure 4-3. Diethylene Glycol and Glycerol are also added for exploring the minimum Z number value for printable ranges. It was found that pure glycerol is not printable even when the maximum voltage applied to either printing system.

Figure 4-3 Plot of Z number against ethylene glycol volume fraction (vol%) using a 10 pl Dimatix printhead (Black triangle) and an 80 μm Dimatix printhead (Red dot).
4.3.2 Printability of inks using the Dimatix printhead

4.3.2.1 The influence of Z number and pulse voltage on the printability of inks using the Dimatix printhead

To investigate the effect of ink physical properties on the inkjet printing printability, images of drop formation, obtained from inks with a range of Z numbers, were compared using a constant pulse voltage of 23 V. Images were taken using an LED trigger delay after drop generation in the range of 30-120 μs (as shown in Figure 4-4). The ink 10 with Z = 1.17 is not printable using 23 V actuation. At this voltage it was found that inks with Z > 2 were printable, i.e. from inks 1-9 (pure EG through to pure water). Single droplets were formed with pure EG and their velocities increased when EG/water solutions were used with decreasing EG content. When Z number increases to Z > 8, satellite drops were formed. As the value of Z increases, with further reduction in the EG content, more satellites are formed. The velocity of the first main droplet first increases with increasing value of Z, reaching a maximum when Z = 14.05 at 25 vol% EG in the solution. The velocity then decreases as Z increases further as the EG content is reduced. There was no significant change in the volume of the first droplet as the composition of the ink (and hence Z) varied.
Figure 4-4 Images of drop formation for inks 1-9 with Z ranging from 2.08 to 36.76 at a constant pulse voltage of 23 V using a 10 pl Dimatix printhead.

Not only do the ink physical properties have an influence on the ink printability, but the printing environment and waveform parameters are also important for generating stable droplets. To make things simple, here all the inks were printed with a single pulse waveform with a constant rise, dwell and fall time, and a fixed printing temperature of 25 °C. The only parameter of the waveform that was varied in this study was the pulse amplitude (voltage).

Figure 4-5 shows images of drop formation for ink 7 printed using a range of pulse voltages with LED trigger delays of 30 μs to 120 μs. When the voltage is smaller than 16 V, no stable drops were generated. As the actuation voltage increases, the drops are generated with longer tails and larger volumes. A tail forms as the ligament
behind the initial ejected fluid ruptures. It retracts and joins the major droplet within 100 μs. The ligament first appears to form an additional drop at a pulse amplitude > 25 V. But it catches up the first main drop and is reabsorbed. However, when the amplitude > 28 V, the secondary drops remain a stable satellites trailing the primary leading drop. Moreover, when the pulse voltage is further increased, additional satellites are formed. The Figure 4-5 also shows that the droplets are formed with longer tails with increasing the pulse voltage. The first droplet velocity also increases with the pulse voltage. There appears to be a small increase in the diameter of the first droplet as the pulse voltage exceeds the initial threshold value. However, it does not show much when further increase with larger pulse voltages.

Figure 4-5 Images of drop formation for ink 7 (Z = 4.47) with actuating pulse voltages in the range of 16-30 V using a 10 pl Dimatix printhead.
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For a single trapezoidal input pulse, the voltage amplitude and its rate of variation (which is constant for a given assembly, temperature, and driver electronics), determines the magnitude of the volume change induced by the piezoelectric actuating elements in the fluid channels [39]. Since the piezoelectric displacement is proportional to the applied electric field, increasing voltage amplitude results in larger volume changes in the same amount of time (dictated by the time constant of the piezoelectric circuit), and hence bigger induced pressure waves and fluid accelerations [39]. Consequently, there is a minimum voltage required to eject a drop. Above this critical value, both the volume and velocity of the ejected droplets increase with voltage if all other parameters are kept constant [39]. Tsai et al. also found that there is a minimum pulse voltage for DI water [14]. Their group also reported that pulse voltage has an effect on the behaviour of alcohol and ethylene glycol inks [44].

4.3.2.2 The influence of Z number and pulse voltage on single droplet formation

From the analysis of the sequence of images formed at different LED trigger intervals, it is possible to determine the distance from the printer nozzle at which a single spherical drop is clearly formed. Figure 4-6 shows that the single droplet formation distance \( (D_s) \) increases with increasing pulse voltage for all the inks studied. For inks with \( Z < 14 \) printed using a constant pulse voltage, the single \( D_s \) decreases with increasing the \( Z \) value. However, for inks with \( Z > 14 \), the \( D_s \) has no obvious relationship with \( Z \) value.

![Figure 4-6](image_url)  
Figure 4-6 The calculated droplets distance from the nozzle to form a single droplet under different pulse voltages of different inks using a 10 pl Dimatix printhead.
4.3.2.3 *Z* number and pulse voltage influence on the velocity for Dimatix printhead

Both drop size and drop velocity define the footprint that a droplet makes after impact and spreading on a substrate [39]. Hence, there is a need to understand how parameters such as fluid density and viscosity interact with the piezoelectric actuation signal to define the size and velocity of the ejected droplet [39].

To investigate the velocity of the first main droplet, the droplet’s position and nozzle position were marked to measure the droplet’s distance from the nozzle with increasing LED strobe trigger delay time under different pulse voltages for the 10 printable inks (shown in Figure 4-7). All the inks show the same behaviour. The main droplet starts jetting out earlier and quicker with applied higher pulse voltages. The tails of the main droplet before breakoff from the nozzle also become longer with applied higher pulse voltages.

Figure 4-7 The calculated droplets distance from the nozzle with increasing LED strobe delay time under different pulse voltages of different inks using a 10 pl Dimatix printhead.

The mean velocities of the printed droplets were calculated by measuring the distance change between LED triggers delay from 60 μs to 120 μs. The main droplet velocity shows an approximately linear growth with increasing applied pulse voltages for all the inks studied, as shown in Figure 4-8a. All the inks have a critical
minimum printable voltage (V_min). When Z > 14, all the inks show a similar relationship between drop velocity and actuation voltage. However, for inks with Z < 14, each ink appears to show a different relation between velocity and the pulse voltage. The mean velocities for the single droplets are selected out (shown in Figure 4-8b). As shown in Figure 4-8b, all the inks start droplet ejection out at velocities around 1.3 m/s. When the velocity smaller than 4 m/s, single droplets are formed. Most inks could achieve single droplets with velocity around 5.4 m/s. The inks with Z = 4.47 and Z = 3.28 are even able to generate single droplets with velocity of 6.6 m/s and 6 m/s, respectively. Figure 4-8c shows the relationship between the drop velocity and the voltage above the critical minimum printable voltage (here named as V-V_min) for drop formation for all the inks studied. It is clear that a slope with ± 1 m/s error for velocity as a function of voltage above the critical voltage for drop formation. The velocities for single droplets were selected out and increasing with the V-V_min, as shown in Figure 4-8d.

Figure 4-8 a) The pulse voltage influences on the velocity for different inks; b) selected pulse voltage influences on the velocity of single droplets for different inks using a 10 pl Dimatix printhead; c) the velocity as a function of voltage above the critical voltage for drop formation: the closed symbols are single droplets and the open symbols are the droplets with satellites; d) the velocity as a function of voltage above the critical voltage for drop formation for single droplets of different inks.

When considering the influence of Z on the droplet velocity at a fixed pulse voltage, the data was replotted in Figure 4-9a. It is clear that the main droplet velocities show nearly linear growth with for inks with bigger Z number for the inks with Z < 14.

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However, the average main droplet velocities are similar for inks with $Z > 14$. The mean velocities for the single droplets are selected out (shown in Figure 4-9b). Bigger pulse voltages are needed for inks with smaller $Z$ number to form single droplets for those inks with $Z < 14$. However, for the inks with $Z > 14$, they all start printable around 13 V at velocities around 1.3 m/s.

Figure 4-9 a) The $Z$ number influences on the velocity for different inks; b) the $Z$ number influences on the single droplet velocity for different inks using a 10 pl Dimatix printhead. The closed symbols are single droplets and the open symbols are the droplets with satellites.

Thus, the printable velocity range can be defined between the black square and the purple triangle for single droplet formation as shown in Figure 4-10. The red dot curve also shows the velocities of the best printable single droplets with a short traveling distance for the satellites to join into the main droplet.

Figure 4-10 The $Z$ number influences on the velocity for different inks using a 10 pl Dimatix printhead.
4.3.2.4 The influence of Z number and pulse voltage on the droplet size with the Dimatix printhead

The mean size of the printed droplets was calculated by measuring the sizes of five droplets at 120 μs and taking their average. Figure 4-11a shows the relationship between the pulse voltage and droplet size for each of the inks. The X axis is voltage that the pulse voltage above the critical minimum voltage for drop formation (V-V_{min}). It is clear that the average droplet size increases monotonically with increasing pulse voltage for all the inks studied. For inks with Z > 14, the size-voltage relation appears to be very similar. This is comparable with the same velocity-voltage behaviour shown in Figure 4-8a. Figure 4-11b shows the relationship between the average velocity and the droplet size, again all inks with Z > 14 display similar behaviour.

When considering the influence of Z number on the droplet volume at a fixed pulse voltage, the data was transfer in Figure 4-12a. It is clear that the droplet volume also shows nearly linear growth with for inks with bigger Z number for the inks with Z < 14. However, the average droplet volumes are similar for inks with Z > 14. The mean volumes for the single droplets are selected out (shown in Figure 4-12b). Bigger pulse voltages are needed for inks with smaller Z number to form single droplets for those inks with Z < 14. However, for the inks with Z > 14, they all start printable around 13 V at volumes around 5 pl. Those trends are similar to that of the average droplet velocity shown in Figure 4-9. This result of shear-mode Dimatix
printhead is agreed with the result of Reis et al. [39]. They also found that drop velocity and volume exhibit a linear relation with pulse voltage for squeeze mode printhead.

Figure 4-12 Z number influences on the droplet volumes for different inks using a 10 pl Dimatix printhead: a) symbols represent different pulse voltages; b) symbols represent different V-V_{min}. The closed symbols are single droplets, and the open symbols are the droplets with satellites.

4.3.2.5 The relationship among Z number, pulse voltage and ink printability using Dimatix printhead

Figure 4-13 shows the relationship among Reynolds number, Weber number and ink printability by comparing the printability under different pulse voltages of the 10 printable inks shown in Table 4-2. The data superimposed on proposed printable range proposed by Derby [11]. It is clear that Derby’s earlier prediction is not consistent with the results presented here at high values of Z. The lower limit of Z = 1 is consistent with the data and, on referring to the compilation of published data collated in Table 4-1, this would also appear to be the minimum value for printability reported by other workers [12], [13], [16], [39], [69]. For inks in the range 1 < Z < 5 there appears to be another limit with We < 20 required to prevent satellite formation. As Z increases to larger numbers the critical We reduces to We = 5 at Z = 16.46 and remains at this value with inks 1-3.
Figure 4-13 A graph showing the relationship among Reynolds number, Weber number and inkjet printability by comparing the printability under different pulse voltages of 10 inks using a 10 pl Dimatix printhead shown in Table 4-2. The data superimposed on proposed printable range proposed by Derby [11]. The closed symbols are single droplets, and the open symbols are droplets with satellites.

Four pulse voltages were picked out to compare the influence of pulse voltage on ink printability, as shown in Figure 4-14. It is clear that at low pulse voltage of 15 V, only inks with $Z > 8$ are printable and has single droplets formation. With pulse voltage of 20 V, single droplets are formation for inks of $3.28 \leq Z \leq 14.05$ but satellites are formed for inks with $16.46 \leq Z \leq 36.76$. Further increasing the pulse voltage to 23 V, the printable range is $2.08 \leq Z \leq 8.4$ fitting well with the previous study of Derby [11] and Fromm [10]. However, when using pulse voltage of 26 V, the ink of $Z = 8.4$ already has satellites formation.
Figure 4-14 Graphs showing the relationship among Reynolds number, Weber number and inkjet printability by comparing the printability under selected pulse voltages of 10 inks using a 10 pl Dimatix printhead shown in Table 4-2. The data superimposed on proposed printable range proposed by Derby [11]. a) 15 V; b) 20 V; c) 23 V; d) 26 V.

Figure 4-15 shows the relationship among Z number, pulse voltage and inkjet printability by comparing the minimum printable voltages (Black squares), the best pulse voltages (Red dots) and satellites start formed voltages (Blue triangles) of 8 inks shown in Table 4-2. The data was fitted to 3 curves to find the trend of the print range (the area between the black line and the blue line) of different inks with Z ranging from 1.17 to 36.76 under different pulse voltages.
Figure 4-15 A graph showing the relationship among Z number, pulse voltage and inkjet printability by comparing the minimum printable voltages (Black squares), the best pulse voltages (Red dots) and satellites start formed voltages (Blue triangles) of 8 inks using a 10 pl Dimatix printhead shown in Table 4-2. The green line is for pulse voltage 20 V.

It is found that the printable voltage range nearly has a linear change when \( Z < 14 \) and becomes only slightly varying among inks with \( Z > 14 \). Accurate and stable drops without satellites could be formed using inks of \( Z > 4 \) under voltages lower than 20 V, but much higher voltages needed when printing inks of \( Z < 4 \). However, the differences between the minimum printable voltages and the satellites start formed voltages are quite similar to 7 V for almost all the inks considered except ink 7 with the difference of 11 V. The best pulse voltages have a relationship with the Z number similar to that of the satellites start formed voltages. The inks with high Z number (such as DI water) are also printable without satellites when using low voltages in the range of 13 V to 19 V.
4.3.3 Printability studies with the MicroFab printhead

4.3.3.1 The influence of print dwell time on the printability of inks using the MicroFab printhead

Reis et al. [39] found that the droplet velocity shows a more complicated and periodic behaviour with changing the pulse dwell time and that the periodic dependence is a function of the acoustic properties of the fluid-filled chamber in the droplet generator. The acoustic properties are a function of the fluid properties, printhead design, and constituent materials. Hence, each fluid with different physical properties may have specific optimum printing conditions where the desired superposition of the acoustic pressure waves is achieved. To optimise a suitable dwell time for the MicroFab printhead, different dwell times were compared with a constant print voltage of 60 V for ink 6-8. Figure 4-16a shows that for the ink 8 on increasing the dwell time from 7 μs to 29 μs, the drop velocity first increases and then decreases until jetting stops. The droplet velocity has a maximum as a function of the dwell time and also has two dwell time values with minimum velocities. This result is in agreement with the experiments of Reis et al. [39], [216]. They reported that in a simple tubular actuated piezoelectric printhead, the influence of dwell time is related to the time required for the initial pressure pulse, generated by the leading edge of the rectangular actuating signal, to travel from the actuated region to the ends of the fluid chamber and back to the initiation point, with appropriate phase shifts induced by the reflection conditions. It is clear that the time interval of this phenomenon is related to the acoustic wave speed of the fluid-filled chamber and its length. Commercial inkjet printheads are normally designed and operated such that further reflections of the pressure waves are damped to prevent unwanted interference that might result in variable drop size or velocity as the operating frequency of the printhead is changed. However, acoustic phenomena must be recognized and accounted for when developing ink-jet delivery systems with experimental fluids [39]. Comparing Figure 4-16 a, b and c, it can be seen that for the maximum velocity is generated at 14 μs, 16 μs and 12 μs for three different inks, respectively. In the following experiment, the dwell time is fixed at 14 μs for all the inks.
4.3.3.2 The influence of Z number on the printability of inks using the MicroFab printhead

To investigate the effect of ink physical properties on the inkjet printing printability, the images of drop formation for inks with different Z numbers were compared under a constant pulse voltage of 60 V using LED delay times from 25 μs to 400 μs (as shown in Figure 4-17). Ink 11 with $Z = 0.09$ and ink 10 with $Z = 2.25$ are not printable using the 80 μm MicroFab printhead. It was found that when printing under 60 V pulse amplitude, inks were only printable with stable droplets for ink 6-8 ($6.32 \leq Z \leq 16.2$). Ink 1-5 and ink 9 were jettable but the droplets were irregular, chaotic.
and difficult to observe. This agrees with results reported by other researches for squeeze-mode printheads [18], [86].

Figure 4-17 Images of drop formation for inks 6-8 with Z number ranging from 6.32 to 16.2 at a constant pulse voltage of 60 V using an 80 μm MicroFab printhead.

4.3.3.3 The influence of pulse voltage on the printability of inks using the MicroFab printhead

The images are obtained by a short pulse of light from a LED that is synchronized with the pulse generating the drop. By adjusting the delay between the actuation pulse and the pulse applied to the LED, the droplets are captured at different locations along the flight path. Figure 4-18 shows the droplet flight paths of ink 8 printed under different pulse voltages from 25 μs to 400 μs every 25 μs.
Figure 4-18 Images of drop formation for ink 8 (Z = 6.32) under pulse voltage at 40-90 V using an 80 μm MicroFab printhead.

From Figure 4-18a, the fluid interface is withdrawn from the equilibrium position indicating the arrival of the expansion wave at the orifice, as shown in the images at 25 μs. After the compression wave reaches the orifice, it causes the fluid to emerge as shown in the images at 50 μs. Another expansion wave reaching the orifice causes the fluid to pull back (as shown in the images at 75 μs and 100 μs) and to break off and leave the orifice (as shown in the images at 125 μs). The ejected fluid is pulled in a spherical drop by surface tension forces (as shown in the images at 150 μs).

When increasing the pulse voltage to 50 V, the ligament becomes longer and breaks into satellite drops (as shown in Figure 4-18b at 175 μs). These join up with the main droplet to form a single droplet (as shown in Figure 4-18b at 200 μs). Further increasing the pulse voltage, requires a longer time for the satellites to join into the main droplet (as shown in Figure 4-18c within 300 μs and Figure 4-18d more than 400 μs). On increasing the pulse voltage to larger values (as shown in Figure 4-18e and Figure 4-18f), the satellites are no longer able to catch up with the main droplets within the observable flight distance. This phenomenon agrees with the Dimatix
results reported earlier in this section on the effect of pulse voltage on droplet generation and behaviour in flight.

4.3.3.4 The influence of Z number and pulse voltage on single droplet formation

Figure 4-19 shows that the single droplet formation distance increases with increasing pulse voltage for all the inks printable with the 80 μm MicroFab printhead. The ink becomes printable with a single droplet generated with a small tail at the lowest printable voltage. With increasing applied pulse voltage, the droplets are ejected with longer tails before breaking off from the nozzle. The tails break into small fragments that form smaller satellite droplets following the big main droplets. Some of the satellites can catch up and join with the main droplets during droplet flight. However, at larger applied voltages, the satellites cannot rejoin the main droplets. These stable satellites remain separated from the main droplets during flight, and even more satellites form with further increasing the voltage. This phenomenon agrees with those results reported earlier in this section with Dimatix printhead and other previous works [217].

![Graph showing the relationship between pulse voltage and droplet formation distance](image-url)

Figure 4-19 Droplets distance from the nozzle to form a single droplet under different pulse voltages for different inks using the 80 μm MicroFab printhead.
4.3.3.5 *Z number and pulse voltage influence on the velocity for MicroFab printhead*

To investigate the velocity of the first main droplet, the droplet’s position and nozzle position were marked to measure the droplet’s distance from the MicroFab nozzle, with increasing LED strobe trigger delay, for different pulse voltages with the printable inks (shown in Figure 4-20). All the inks show the same behaviour. The main droplet starts jetting out earlier and quicker with increased pulse voltages. The tails of the main droplet before breakoff from the nozzle also become longer.

![Graph showing droplets distance from the nozzle with increasing LED strobe delay time under different pulse voltage of different inks using an 80 μm MicroFab printhead.](image)

The mean velocities of the printed droplets were calculated by measuring the distance change between LED triggers delay from 200 μs to 400 μs. All the inks have a critical minimum printable voltage ($V_{min}$). Figure 4-21 shows the relationship between the drop velocity and the voltage above the critical minimum printable voltage (here named as $V-V_{min}$) for drop formation for all the inks studied. It is clear that the velocity increases with the $V-V_{min}$, but there is no similar slope as that of Dimatix printhead.
Figure 4.21 The relationship between the velocity and the voltage above the critical voltage for drop formation using an 80 μm MicroFab printhead. The closed symbols are single droplets, and the open symbols are droplets with satellites.

Figure 4.22 shows the influence of Z on the droplet velocity at different pulse voltages and V-V\textsubscript{min}. It is clear that the main droplet velocity increases with increased pulse voltage. There is an average minimum velocity for inks when printable, which is similar to the behaviour using Dimatix printhead, but with a smaller value around 0.7 m/s. However, the velocities for increased voltages decreases as Z increases from 6.32 to 8.63, and the droplet velocities are similar to ink of Z = 8.63 and Z = 16.2, which are different from those using Dimatix printhead.

Figure 4.22 a) The Z number influences on the velocity for different inks; b) The Z number influences on the single droplet velocity for different inks using an 80 μm MicroFab printhead. The closed symbols are single droplets, and the open symbols are the droplets with satellites.

Figure 4.23 shows the printable velocity of MicroFab printhead compared with the printable range of Dimatix as shown in Figure 4-10. It is obvious that these two
modes of printhead have different printable range. The printable range for MicroFab printhead is much smaller than that of Dimatix printhead.

4.3.3.6 The influence of Z number and pulse voltage on the droplet size with the MicroFab printhead

The mean size of the printed droplets was calculated by measuring the sizes of five droplets at 250 μs and taking their average. Figure 4-24a shows the relationship between the pulse voltage and droplet size for each of the inks. The X axis is a voltage that the pulse voltage above the critical minimum voltage for drop formation (V - V\text{min}). It is clear that the average droplet size increases monotonically with increasing pulse voltage for all the inks studied. Figure 4-24b shows the relationship between the velocity and the droplet volume for the printable inks. The droplet volume also increases with droplet velocity. This phenomenon agrees with those results reported earlier in this section with Dimatix printhead and other previous works [86]. However, the droplets with satellite forms when the velocity > 3 m/s and droplet size > 250 pl, which is smaller than reported in the other literature. The considering flight distance is limited to only 1 mm for satellites to join up with the

Figure 4-23 The printable range for different inks using an 80 μm MicroFab printhead. The closed symbols are single droplets, and the open symbols are droplets with satellites. The data superimposed on proposed printable range proposed above for Dimatix printhead.
main droplets. However, the distance is always much bigger, which gives more time for a satellite to join into the main droplet and forms a single droplet.

Figure 4-24 a) The pulse voltage influences on the droplet volume for different inks; b) The relationship between the droplet velocity and droplet volume for different inks using an 80 μm MicroFab printhead. The closed symbols are single droplets, and the open symbols are droplets with satellites.

When considering the influence of Z number on the droplet volume at a fixed pulse voltage, the data was transfer in Figure 4-25a. This result of shear-mode Dimatix printhead is agreed with the result of Reis et al. [39]. They also found that drop velocity and volume exhibit a linear relation with pulse voltage for squeeze mode printhead.

Figure 4-25 a) Z number influences on the droplet volumes for different inks; b) Z number influences on the single droplet volumes for different inks using an 80 μm MicroFab printhead. The closed symbols are single droplets, and the open symbols are droplets with satellites.
4.3.3.7 The relationship among Z number, pulse voltage and ink printability using MicroFab printhead

Figure 4-26 shows the relationship among Reynolds number, Weber number and inkjet printability by comparing the printability under different pulse voltages of the 10 printable inks shown in Table 4-2. The data superimposed on proposed printable range proposed by Derby [11]. It is clear that Derby’s earlier prediction agrees with the results presented here that the $Z < 10$ are printable. However, the $Z = 4.02$ is thought to be the limit for the 80 um MicroFab printhead, which more similar to results of Jang et al. [18]. For ink 8 with $Z = 6.32$, there appears to be another limit with $We < 20$ required to prevent satellite formation, which agrees with the above Dimatix result. However, the critical $We$ reduces to $We = 0.4$ and remains at this value with inks 7 and ink 8. Considering the pulse voltages, it is clear that at a low pulse voltage of 40 V, only inks with $Z = 6.32$ is printable and has single droplets formation. With pulse voltage of 50 V and 60 V, single droplets are formation for inks of $6.32 \leq Z \leq 16.2$. Satellites are formed for inks with $Z = 6.32$ when increased voltage to 70-90 V. However, for ink with $Z = 8.63$, single droplet forms even when using the max voltage of 90 V. For ink $Z = 16.02$, when using 70-90 V pulse voltage, the droplets are chaotic and hard to be recorded by the camera. For ink $Z = 4.02$, it is only printable with single droplet generated at 90 V.

![Graph](image)

Figure 4-26 A graph showing the relationship among Reynolds number, Weber number and inkjet printability by comparing the printability under different pulse voltages of ink 6-9 using an 80 μm MicroFab printhead. The data superimposed on proposed printable range proposed by Derby [11] and Jang et al. [18] (shown with the green lines of $4 \leq Z \leq 14$). The closed symbols are single droplets, and the open symbols are droplets with satellites.
4.3.4 Printability range comparison between MicroFab and Dimatix printheads

Comparing these two modes of printheads, it is clear that the ink ejection and flight processes are similar. The ink becomes printable with a single droplet generated with almost no tails at the lowest printable voltage. With increasing the applied pulse voltage, the droplets are ejected out with longer tails before breaking off from the nozzle. The tails break into small fragments that form smaller satellite droplets following the big main droplets. Some of the satellites can catch up and join with the main droplets during droplet flight. However, at larger applied voltages, the satellites cannot rejoin the main droplets. These stable satellites remain separated from the main droplets during flight, and even more satellites form with further increasing the voltage. However, the ink printabilities are different. The printable range is wider with $1.17 \leq Z \leq 36.76$ and $0.4 < We < 15$ for the 10 pl shear-mode Dimatix printhead. With a high voltage of $V > 20$ V, the printable range has a fixed range. For example, at 23 V the printability range is approximately $2 < Z < 10$, at 25 V approximately $1.5 < Z < 6$ and at 20 V $3 < Z < 15$. However, at a low voltage of $V < 20$ V, inks with $Z > 4$ are printable and no maximum limit as shown in Figure 4-15. For example, At 15 V the lower bound is $Z > 8$ with no satellites observed for all larger values of $Z$ investigated. Even DI water with $Z = 36.76$ is printable with single droplet formation at the voltage range of 13-19 V. However, the printable range for the 80 μm squeeze-mode MicroFab printhead is narrow to $4.02 \leq Z \leq 16.2$ and $0.4 < We < 20$.

Figure 4-27 shows the relationship among Reynolds number, Weber number and inkjet printability by comparing the ink printability of MicroFab printhead and Dimatix printhead. The data superimposed on proposed printable range proposed by Derby [11] and Nallan et al. [12]. The closed symbols are single droplets, and the open symbols are droplets with satellites. It is clear that both the data for the Dimatix printhead and the MicroFab printhead fixed in the printability range proposed by Nallan et al. [12]. Both the Dimatix and MicroFab printheads have a printability peak around $Z = 8$. The minimum printable $Z$ number is around 1. However, Nallan et al.’s range have a bigger range with smaller minimum limit and bigger satellite formation limit for Weber number. This is because in this work the slow droplets which two droplets shown in the same images are thought to be too slow for real
printing and considered as not suitable for the print situation, while they thought as printable with smaller Weber number. In addition, they considered a slight longer distance around 1.3 mm than the distance considered in this work within 1 mm. This will give more time for satellites to join up with the main droplet and have a single droplet formation with a bigger Weber number.

![Graph showing the relationship among Reynolds number, Weber number and inkjet printability](image)

**Figure 4-27** A graph showing the relationship among Reynolds number, Weber number and inkjet printability by comparing the ink printability of MicroFab printhead and Dimatix printhead. The data superimposed on proposed printable range proposed by Derby [11] and Nallan et al. [12]. The closed symbols are single droplets, and the open symbols are droplets with satellites.

### 4.4 Conclusions

The relationship among the print pulse voltage, the ink physical properties and the inkjet printability for two different modes of printheads have been investigated. It was found that both the print pulse voltage and Z number influence the inkjet printability of fluids for both printheads. For a given ink, it was found that there was a critical voltage to eject a droplet. Increasing the pulse voltage led to an increase in drop velocity for well-formed drops, until above a critical voltage satellites forms. Further increasing the pulse voltage leads to the formation of more satellites. With
the Dimatix printhead, Figure 4-15 shows that the range of pulse voltage for single drop formation remains constant for $Z > 14$ while for $Z < 14$ both the minimum voltage for drop ejection and the voltage at which satellites form increase in step with each other. Thus, it is obvious that the printable range for the $Z$ number is also a function of applied pulse voltage as shown in Figure 4-15. For example, at $25$ V the printability range is approximately $1.5 < Z < 6$. At $20$ V, the range is $3 < Z < 15$. However, the lower bound is $8 < Z$ with no satellites observed for all larger values of $Z$ investigated at $15$ V. However, with the MicroFab printhead the printability could be described by $4 < Z < 14$, which is in agreement with the results of Jang et al. [18] and a larger range than proposed by Derby and Reis [11], [86]. However, Derby used a slightly different squeeze-mode printhead (Sanders Design International) than the MicroFab used in this study.

It is reasonable that different research works on printable $Z$ number range are slightly different when they are using different pulse voltages or different printing systems. These results could give an explanation of the different $Z$ number range shown in different research published when they are using different printheads and pulse voltages. The printable range is wider with $1.17 \leq Z \leq 36.76$ and $0.4 < We < 20$ for the $10$ pl shear-mode Dimatix printhead. However, the printable range for the $80$ μm squeeze-mode MicroFab printhead is narrow to $4.02 \leq Z \leq 16.2$ and $0.4 < We < 20$. When designing the future printing work, not only the fluid properties need to be considered, but also the pulse voltages need to be adjusted as well.

In summary, the common factor from this work and other $Z$ number study is that the minimum $Z$ number is in the range of 1-4. However, the maximum $Z$ number is depended on the pulse voltage amplitude. For a fixed ink, the drop velocity increases with the pulse voltage and thus the Weber number increases, satellites forms when the Weber number reaches a critical number. From this work, when considering the travel distance is $1$ mm, the Weber number limit is around $20$.

4.5 Acknowledgement

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CHAPTER 5 *In-situ* High-speed Imaging of Inkjet Printing Nanoparticle Suspensions on the Drying and Stacking Process

The following sections in Chapter 5 have been prepared as a manuscript for submission to the Langmuir. Some of the results have been given as poster presentations at Gordon Research Conference on Ceramics, Solid State Studies in, Mount Holyoke College, Massachusetts, United State, July 30-August 5, 2016.

The author has designed, prepared and performed the experiment, analysed the collected data, interpreted the results and wrote the first draft and the final version of this manuscript.
Chapter 5 *In-situ* High-speed Imaging of Inkjet Printing Nanoparticle Suspensions on the Drying and Stacking Process

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**Abstract:**

Inkjet printing can be used to manufacture ceramic objects from particle suspensions. To use this 3D printing method, it is important to understand both the drop drying and stacking processes. During drying, particles may segregate to the edge of the drop, resulting in non-uniform deposition (a coffee stain), and associated defect formation. This process is not fully understood due to no detailed information about the particle segregation process during drop drying. It is also not clear whether there defects form between or within the dried drops during the stacking process. In this study, ZrO₂ inks were prepared and printed using a lab-built inkjet printer equipped with an 80 μm MicroFab printhead to generate drops on three different substrates held at different temperatures. The drying and stacking process were characterised using a time-resolved *in-situ* synchrotron X-ray radiography. This has shown that both the initial contact angle and substrate temperature during printing strongly influence the drying process and final dried deposit shape. 2D X-ray radiography images show that the drops were first pinned and then there was a slight sliding of the three-phase contact line. Mechanisms for the coffee stain formation were discussed. Bubbles and microvoids have been observed forming at the interface between two drops during stacking. The initially printed drops were deformed by the action of the second drops stacked above them during the drying process when printed on Kapton at room temperature. Crack-like defects were found at the edge of the final dried drops.

**Keywords:** *In-situ* synchrotron; Inkjet Printing; Drying; Stacking
5.1 Introduction

Inkjet printing allows the accurate placement of picoliter volumes of fluid on an arbitrary substrate [11]. In the past two decades, it has been developed as a ceramic processing method [2], [3], [7], [8], [163], [181]. Inkjet printing ceramic structures are built up layer-by-layer through the interaction and coalescence of sequentially printed droplets. After deposition, an individual printed droplet dries. The drying process of nanoparticle ceramic suspensions is a very complicated topic. Due to their complex chemical properties, nanoparticle ceramic suspensions can show unexpected drying phenomena and intriguing final structures. Fluid flow within the drying droplet can lead to the radial outward transport of particles in suspension to form a ringlike deposit (the coffee ring or coffee stain) rather than the desired uniform deposition [119]. It is generally agreed that the coffee ring forms when a drying droplet is pinned at the contact line and has a contact angle sufficiently small to generate a shallow gradient of the surface [20], [22], [89], [104], [105], [108], [119]. Because the line is pinned and cannot retract, the solvent is replenished by an outward flow of fluid in a drying droplet. This combination leads to greater proportionate solvent loss close to the contact line. There are already a number of procedures proposed to reduce the coffee stain effect [22]–[27], mainly using solvent mixtures or varying the substrate temperature. Solvent mixtures are believed to suppress coffee staining by driving an opposing fluid flow generated using temperature or concentration gradient driven surface tension gradients (Marangoni convection) [28]–[30]. However, the influence of substrate temperature is not uniformly accepted as a controlling mechanism [31]. This uncertainty is because the coffee stain formation mechanism cannot be fully understood without detailed information about the particle segregation process within the fluid during droplet drying.

High-speed optical imaging has been used to track the motion of droplets drying after printing on a transparent substrate, identifying particle segregation and characterising the droplet outer shape change [218]. Optical coherence tomography and confocal optical microscopy have both been used to track particle motion and density distributions within drying drops [19]–[21]. However, most systems studied have used relatively low particle volume fractions (< 0.1%) to allow the tracking of
individual particles. These prior researches have focussed on low concentration dispersions or polymer particles. Only large viewable particles could be detected, and thus these methods are not suitable for studying dense nanoparticle suspensions.

To the best of my knowledge, no prior works have been published on the real-time evolution of solid particle segregation in a ceramic ink during the droplet drying process. The real-time evolution of solid particle segregation is a key to understand the coffee stain formation mechanism. In addition, optical imaging is not capable of providing any details about the internal configuration of the solid particle ensembles in the drying ink droplets.

In-situ synchrotron X-ray radiography imaging has been successfully applied to investigate the change of internal structure in materials, particularly rapid structural evolution inside non-optical-transparent materials [154], [155], [219]. Taking advantage of the penetration and attenuation capabilities of X-rays, high photon flux synchrotron radiography was applied in this study to study the time-resolved evolution of droplet solidification (drying) and segregation of solid particles inside micrometre scale droplets produced by inkjet printing. The shape change and particle segregation of a ZrO$_2$ ink were investigated during the drying process, to better understand the evolution of dried drop shape and the presence or absence of a coffee stain. The real-time interaction of two droplets printed on top of each other after drying of the lower first droplet was also studied. Time-resolved in-situ synchrotron radiography can provide enhanced insight on particle distribution during droplet drying of a single print, and also during the coalescence of adjacent ink droplets. This information will facilitate better control of object manufacture through understanding the mechanisms of coffee stain and defect formation after printing.

### 5.2 Experimental procedure

#### 5.2.1 Ink preparation

Aqueous ZrO$_2$ ink was prepared with 5 vol% ZrO$_2$ (particle size 20-30 nm, purity 99.99%, PI-KEM Ltd., UK) and two different surfactants with 1 wt% DISPEX A40 (Ciba Specialty Chemicals Inc., Basel, Switzerland) and 0.5 wt% DOLAPIX CE64 (Zshimmier & Schwarz, Lahnstein, Germany). Polyethylene glycol (PEG, average
MN CA. 1500, Sigma-Aldrich Company Ltd., Dorset, UK) were selected as solvent mixtures to suppress the coffee stain effect. All the components in the mixtures were ball milled for 24 hours to make uniform dispersed nanoparticle suspensions. These suspensions were filtered through 2 μm filters (SLAP02550, Millipore UK Ltd., Watford, UK) before printing to eliminate larger particles or agglomerates and to ensure that the nozzle was not blocked during the inkjet printing process.

5.2.2  *In-situ* synchrotron experiment setup

An inkjet printer drop generator was installed on I13-2 beamline (Diamond Light Source, UK) for the experiments as shown in Figure 5-1. A relatively high flux polychromatic (pink) X-ray beam was used for the experiment. The printer was fixed on the I13-2 beamline sample stage. The drop watcher camera and associated LED were positioned at an angle of approximately 45° on the X-ray beam and detector direction.

An ink syringe was fixed vertically on a stage equipped with a piezoelectrically actuated inkjet printhead with an internal diameter of 80 μm (MJ-AT-01-80-8MX, MicroFab Technologies Inc., Plano, TX, USA) using a plastic holder. The printer also equipped with a drive electronic board (JetDrive III, MicroFab) interfaced to a PC and controlled in a Lab VIEW (National Instruments, Austin, TX, USA) environment. The printing waveform was fixed on a single pulsed waveform. The rise time, fall time and echo time are all 3 μs. Dwell time is 30 μs and dwell voltage is 90 V. Echo voltage and idle voltage are both 0 V. Droplets were generated at 3000
Hz using a small piezoelectric actuated inkjet printing droplet generator and deposited on temperature controlled printing substrates. Three different substrate materials (glass slides, silicon wafers and Kapton polyimide tape) and three substrate temperatures (room temperature, 45 °C and 60 °C) were investigated. All the substrates were cleaned thoroughly before carrying out the experiments; firstly, the substrates were washed by ultrasonication with deionized water and ethanol for 5 minutes, finally dried by a flow of nitrogen gas. Then these cleaned substrates were fixed on SEM stubs by two-sided adhesive tape and then put into the centre hole on the substrate heater platform.

The high difference in X-ray attenuation between the ZrO₂ particles in suspension and the water-based solvent provides sufficient contrast to image the segregation of the ensemble solids (individual particle details could not be observed as they were beyond the detector resolution) and allow us to capture the time evolution of segregation patterns within the drying drop. The water-based solvent was relatively transparent to the X-rays. However, using a pre-determined near field placement of the detector screen, appreciable refraction based 1st order phase contrast was achieved at the liquid-air interface, providing liquid drop shape details. Once a second drop was overprinted, similar evolution features plus the presence of any voids formed during overprinting were captured via fast imaging. Pco.dime camera combined with 5 × objective lens (total magnification 10 ×) enabled real-time imaging with about 2.2 × 2.2 mm² field of view and pixel size of approximately 1.1 µm. Images were taken at frame rates from 25 Hz to 500 Hz. This provided a good compromise for capturing fast dynamics and with a relatively high signal/noise ratio, without dominant dynamic blurring during exposures. It should be noted that the shape change of single printed droplets during drying (original diameter around 100 µm, drying within 1 second) could be detected. However, the resolution was not good enough to give consistent information of the density change inside a single droplet with 10 × total magnification. Thus, bigger drops were printed by overprinting 50-200 droplets using 3000 Hz printing frequency. All experiments were carried out in an air-conditioned environment at constant humidity (45% Rh) and temperature (22 °C).
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5.3 Results and discussion

5.3.1 Drop evaporation and drying mode

To control the final shape of inkjet printed drops using nanoparticle suspensions, it is important to understand the drying process of the printed drops on the substrate. In this experiment, the drying of 5 vol% ZrO\textsubscript{2} drops on Kapton polyimide tapes was mainly investigated. In these cases, the equilibrium contact angle of the ink on the substrate is about 73°, which means the maximum height of the spreading drop is around half of its diameter. As the concentration of ZrO\textsubscript{2} is only 5 vol%, it is assumed that the drop shape is not affected by the ZrO\textsubscript{2} nanoparticles content.

Figure 5-2 A schematic representation of a ZrO\textsubscript{2} drop with an initial radius of a, a height of h and a contact angle of θ drying on a solid substrate.

Figure 5-2 shows a schematic of the ZrO\textsubscript{2} drop drying process. Popov [111] proposed an evaporation model for a drying drop with a constant contact diameter, assuming transport control by atmospheric diffusion. The drop evaporation rate \( \frac{dV}{dt} \), drop volume and evaporation time \( t \) can be calculated as follows [109].

\[
\frac{dV}{dt} = \frac{4\pi a D_v (c_S - c_\infty) f(\theta)}{\rho}
\]  

(5-1)

\[
V = a^3 f(\theta)
\]  

(5-2)

\[
t = \frac{\pi \rho \theta_0 a^2}{16 D_v (c_S - c_\infty)} = \frac{\pi \rho \theta_0}{16 D_v (c_S - c_\infty) f(\theta)} V^2 \frac{4}{3}
\]  

(5-3)

where \( \rho \) is the density of the drop liquid (here is the water), \( V \) is the drop volume, \( t \) is the evaporation time, \( a \) is the radius of the initial spherical drop before impact on the substrate, \( D_v \) the diffusion coefficient of vapour in air, \( c_S \) is the vapour concentration.
at the drop surface, \( c_\infty \) is the vapour concentration at an infinite distance from the drop surface, \( f(\theta) \) the function of the contact angle of the drop. Different authors have proposed polynomial expression of \( f(\theta) \) [109], [110], [220], and this is fully described in Erbil’s review [112]. Here, \( f(\theta) = \frac{\pi(2 - 3 \cos \theta + \cos^3 \theta)}{3 \sin^3 \theta} \) as defined by Stringer and Derby [103].

For the main solvent of water, the diffusion coefficient of vapour in air (\( D_V \)) and density (\( \rho \)) can be calculated using the following equations.

\[
D_V = 21.6 \times 10^{-6} \times (1 + 0.0071T) \tag{5-4}
\]

\[
\rho = 1000 - 0.0067 \times (T - 3.98)^2 + 5.2 \times 10^{-7} \times (T - 3.98)^4 \tag{5-5}
\]

The value of \( c_S - c_\infty \) can be calculated using the following Equation 5-6 as also used in the supporting information of Shen et al. [136].

\[
c_S - c_\infty = \frac{M_w P_{vs}(1 - RH)}{R_g(273.15 + T)} \tag{5-6}
\]

where \( M_w \) is the molar mass of water (18.0152 g·mol\(^{-1}\)), \( P_{vs} \) is the saturation water vapor pressure (\( P_{vs} = 610.7 \times 10^{\frac{357}{237.15+T}} \)), \( T \) is the substrate temperature in degrees Celsius (°C), RH is the relative humidity level and \( R_g \) is the ideal gas constant (8.3144 J·mol\(^{-1}\)K\(^{-1}\)).

From Equation 5-3, it can be seen that the time scale of the drop evaporation is influenced by the drop contact angle with the substrate, substrate temperature, relative humidity and the drop diameter on the substrate. For drop drying with constant contact angle and environment condition, the temperature and relative humidity are constant and the drop evaporation time shows a linear increase with \( \sqrt{V} \). However, with a real drop, the drop diameter after fully dried is not as same as the initial diameter. The fully dried diameter is indeed the diameter of the ring at depinning [111]. Depinning is the detachment process of the liquid phase from the deposit ring, which has been observed experimentally in colloidal suspensions [221]. The time at which the detachment occurs and the ring stops growing, namely the depinning time (\( t_d \)), depends on the initial concentration of the solute [111]. Popov
also proposed that typical ratio of the depinning time \( t_d \) and the full evaporation time \( t_f \) are in range of 0.4-0.8.

5.3.2 Study of the drop drying process

5.3.2.1 Single droplet drying

A single droplet was printed and imaged (see Figure 5-3).

![Figure 5-3 Sequence of images of single droplet printed on Kapton.](image)

Figure 5-3 shows the drying process of a single droplet printed on Kapton at 60 °C. The droplet had an original diameter around 90 μm and dried within 11 s to be a dome droplet with a base diameter around 75 μm. The first image has an initial contact angle of approximately 88°. The droplet was firstly pinned at the edge with an angle around 88°. Then the droplet became smaller with the same contact angle within the first second. Finally, both the droplet size and the contact angle become smaller.

5.3.2.2 The influence of drop size on the drying process

As shown in Figure 5-3, single droplets can be imaged by time-resolved \textit{in-situ} synchrotron radiography. The shape change of a single printed droplet during drying (original diameter around 100 μm, drying within 1 second) can be detected. However, the droplet initially only covers 3062 pixels and after drying this reduces to 2072 pixels. Thus, the resolution was not good enough to give consistent information about the density change inside a single droplet during drying using 10
× total magnification. Thus, bigger drops were printed through printing several droplets at a fixed location, to investigate the drying process of inkjet printed nanopowder suspensions.

To examine how the drop size influences on the drying process, large drops were printed by triggering 50 droplets, 100 droplets or 200 droplets at one time using 3000 Hz printing frequency and then comparing their drying behaviour (shown in Figure 5-4).

![Figure 5-4](image)

Figure 5-4 Images showing shape change during drying of different drop sizes printed on Kapton at room temperature.

From Figure 5-4, it is found that with increasing the drop size, the trend in shape changes was similar for all three sizes. Thus, it is reasonable to study the droplet drying processes using bigger drops. All the drops were first pinned by the contact line and then the contact angle decreased while drying. Figure 5-5 shows the remaining percentages of drop diameter, height and volume during drying of drops printed on Kapton at room temperature of different drop sizes. It is clear that the drops undergo a step change in diameter indicating several pinning incidents. Figure 5-5a shows the first main depinning time ($t_d$) for drops formed from 50 droplets is 16 s and its full evaporation time ($t_f$) is 38 s. Thus, the ratio of $t_d/t_f$ is around 0.42, which agrees with the ratio range of 0.4-0.8 proposed by Popov [111]. Figure 5-5b shows the first main depinning time ($t_d$) for drops formed from 100 droplets is 21 s and the full evaporation time ($t_f$) is longer than 120 s. Thus, the ratio of $t_d/t_f$ is smaller than 0.18. Figure 5-5c shows the first main depinning time ($t_d$) for drops formed from 200 droplets is 35 s and the full evaporation time ($t_f$) is longer than 120 s.
s. Thus, the ratio of $t_d/t_f$ is smaller than 0.3. All subsequent studies used drops formed from 100 printed droplets unless otherwise stated.

Figure 5-5 Comparisons of the remaining percentages of drop diameter, height and volume during drying of drops printed on Kapton at room temperature of different drop sizes. a) 50 droplets; b) 100 droplets; c) 200 droplets.

### 5.3.2.3 The influence of substrate contact angle on the drying process

Three substrates have been chosen to investigate the effect of contact angle on the drying process. These were Kapton polyimide tape (referred to as Kapton) with a contact angle of 73°, a silicon wafer (referred to as silicon) with a contact angle of 36° and glass slides (referred to as glass) with a contact angle of 24°. Drops drying on three different substrates were compared (shown in Figure 5-6).

From Figure 5-6, it is clear that coffee stain formation occurs at room temperature when printed on silicon and glass, which have smaller contact angle than that on the Kapton tape. The sample on glass slides has an original contact angle around 30° and then spread to a lower contact angle. After 3 s, the diameter of the sample contact...
angle and height were all smaller, and the drop had dried as a coffee ring. The sample on the silicon shows a similar behaviour to that on the glass. It shows an original contact angle around 45° and spreads with a smaller contact angle and after 3.5 seconds the contact angle and height decrease at the same time, finally forming a coffee ring when fully dried. However, the coffee ring was smaller and higher on the silicon comparing to that on the glass slide. While the Kapton substrate has an original contact angle of 85° and without apparent surface shape change until after 8 seconds, the contact angle and height became smaller, but the diameter of the base does not change much. The glass and silicon substrates have smaller contact angles which make the drop spread wider and with much lower height than that of drops on Kapton. The nanoparticles were pinned at the small contact angle on the edge and had not enough time for traveling back before drying at the edge. Thus, a coffee stain forms after drying.

Figure 5-7 shows the remaining percentages of drop diameter, height and volume during drying of the drops printed at room temperature on different substrates. It is clear that the depinning time for drops drying on the Kapton (21 s) is much longer than that for on the silicon (6 s) and glass (8 s). Both the change rates of height and volume decrease from Kapton to glass.

![Figure 5-7](image)

Figure 5-7 Comparisons of the remaining percentages of drop diameter, height and volume during drying of 100 droplets printed at room temperature on different substrates. a) Kapton; b) silicon; c) glass.
5.3.2.4 The influence of substrate temperature on the drying process

In addition to the drop size and the substrate contact angle, the influence of substrate temperature on the drying process was studied. Three substrate temperatures (room temperature, 45 °C and 60 °C) were used in this experiment. The behaviour of the drops on Kapton at different substrate temperatures were compared (shown in Figure 5-8).

![Figure 5-8 Images of shape changes of 100 droplets during drying on Kapton at different substrate temperatures.](image)

From Figure 5-8, there were visible shape change differences among drop drying at different substrate temperatures. When the substrate temperature is higher, with a faster evaporation rate, drops exhibited shape changes from a dome to a coffee ring. Figure 5-9 shows the remaining percentages of drop diameter, height and volume during drying of drops printed on Kapton at different substrate temperatures. It is obvious that the rate of volume decrease rate is faster with increasing temperature. Also, the depinning time becomes shorter, and the height decreases more rapid when increasing the temperature.
Figure 5-9 Comparisons of the remaining percentages of drop diameter, height and volume during drying of 100 droplets printed on Kapton at different substrate temperatures: a) room temperature; b) 45 °C and c) 60 °C.

5.3.2.5 Density changes analysis during the drying process

To compare the density change with or without coffee stain formation, drops printed on Kapton at room temperature and at 45 °C were selected for comparison. The density change during drying was investigated from the radiographs using bespoke Matlab codes. Figure 5-10 and Figure 5-11 show images and computed reconstructions of density variations during drying of drops on Kapton at room temperature and 45 °C, respectively.
Figure 5-10 Images and computed reconstructions of density variations during drying of the 100 droplets triggered out at one time on Kapton at room temperature (From top to bottom are the X-ray images, Longitudinal section view, the cross-section views and density curves of those three positions marked on the longitudinal section view).
Figure 5-11 Images and computed reconstructions of density variations during drying of the 100 droplets triggered out at one time on Kapton at 45 °C (From top to bottom are the X-ray images, Longitudinal section view, the cross-section views and density curves of those three positions marked on the longitudinal section view).

The longitudinal section view of the 45 °C drying sequence in Figure 5-11 confirms the formation of a coffee stain during drying. This follows the schematic illustration of the process as proposed by Park and Moon and shown in the red square in Figure 5-12b [120]. The longitudinal section view of the room temperature drying sequence in Figure 5-10 is in agreement with the uniform structure drying model, as shown in the blue square in Figure 5-12a also proposed by Park and Moon [120].

Figure 5-12 Schematic cross-section view of the drop profiles for inks drying at two different temperatures. This data is compared with models proposed by Park and Moon [120]. a) The room temperature; b) 45 °C.
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However, there was a drop shape spreading at the beginning of the drying process in this case. Drops were first pinned, and the density of ink increases around the edge of the contact line during the first several seconds of the drying process (21 s for the room temperature drop shown in Figure 5-10 and 2 s for the 45 °C drop shown in Figure 5-11), while the shape changes were similar. Next, the particles travel to the edge and to the ink/air interface with a decrease in the height of the drop.

The drop dried at the room temperature has a uniform film shape at the surface and nearly uniform density inside. However, when increasing the temperature to 45 °C, more particles travel to and stay at the lower edge of the drop close to the contact line and form wider rings. It is quite likely that the temperature introduces a flow to bring the particles down to the substrate. In addition, at room temperature, the drop has a slower drying speed and gives particles more time for distribution, which could explain the dome shape rather than a coffee ring shape after drying.

From the cross-section views and the density curves at different heights of the 45 °C drying sequence shown in Figure 5-11, both the density of the edge and centre of the drop increase during drying. There is a ring at the edge with a growing width, and finally formed a ring shape. The results agree with the simulations of Crivoi and Duan’s [222] 3D model of the coffee ring effect. However, for the density curves at different heights in the room temperature drying sequence in Figure 5-10, there is only a narrow ring at the edge with a similar width for all the heights and the density in the centre are nearly uniform. Both the density of the edge and centre of the drop increase during drying, the height differences between the edge and the centre becomes bigger at the first 56 s and then decreases to uniform structures at the final drying stage.

5.3.3 Study of drop stacking process

Despite a perfectly smooth substrate, during 3D printing, the formal printed layers might give a rough surface before the next drop stacks on top. Thus, drops were printed on previously printed and dried drops to determine whether defects form between or within the dried drops during the stacking process. The influence of drop size, substrate contact angle and substrate temperatures on the stacking and the following drying processes were investigated.
5.3.3.1 The influence of drop size on the stacking and drying processes

To find out the impact of the drop size on the stacking and drying processes, drops formed from 50, 100 and 200 droplets were dried and the stacking and drying of a second printed drop on the original printed and dried drop were compared (shown in Figure 5-13). A significant difference observed in the second drop is the presence of air bubbles in the second drop after printing. In addition, the original drop was deformed by the action of the second drops stacked above them for all drop sizes printed on Kapton at room temperature. However, more bubbles were observed and more evident deformation was seen with increasing printed drop size. In addition, there were more defects present after drying, such as cracks at the edges of the drops or internal cracks and holes, inside the larger dried drops. The bubbles may be formed from the air inside the initially dried drop structures and along the roughness dried top surface. When a drop is printed on the dried layer, it may deform the dried drop and increase the pressure of any entrained air. This air can flow in two directions, either into the substrate or into the liquid to form a bubble. For smaller drops, there is less air entrained, and this can also travel from the bottom substrate to the fluid and finally come out of the stacking structures before the second print layer is dried. The larger amount of entrapped air that may transfer to the second drop may lead to the final cracks and voids seen in the larger drops after drying. In addition, with longer time, those small micro bubbles will have more time to combine into big bubbles and thus be imaged in the radiographs.

![Images of stacking and drying process of drops with different drop sizes printed on Kapton at room temperature.](image)

Figure 5-13 Images of stacking and drying process of drops with different drop sizes printed on Kapton at room temperature.
5.3.3.2 The influence of substrate contact angle on the stacking and drying processes

To investigate the influence of substrate contact angle on the stacking and drying processes, drops were printed on Kapton, silicon and glass substrates and dried before stacking a second drop on (shown in Figure 5-14). It is found that bubbles form in the second drop when stacking on the previously dried drops for the Kapton and silicon substrates deposited at room temperature drying conditions, but not on the glass. The initially printed drops were deformed by the action of the second drops stacked above them for drops printed on Kapton and silicon, but not for the glass. This is possibly due to the small contact angle. As discussed in the previous section, the small contact angle results in drops with a lower height. Thus, any air can more easily migrate to the edge of the drop and escape quickly. Any small micron bubbles escape rapidly. For any that remain, there is insufficient time to combine to form a bubble resolvable in the experiment.

![Figure 5-14 Images of stacking and drying process of 100 droplets printed on different substrates at room temperature.](image)

5.3.3.3 The influence of substrate temperature on the stacking and drying processes

To study the influence of substrate temperatures on the stacking and drying processes, drops were printed and stacked on Kapton at room temperature, 45 °C, and 60 °C. These were compared in Figure 5-15. In all cases, bubbles are seen to form, and the initial drop is deformed by the second printed drop. The larger bubbles may form because of the lower fluid viscosity allowing more rapid bubble coalescence.
### Figure 5-15 Images of stacking and drying process of 100 droplets printed on Kapton at different temperatures.
5.4 Conclusions

In overall, this experiment provides the first real-time in-situ visualisation of drop drying and drop/drop interactions during printing. The experimental data provides promising information of time-evolved solid segregation within printed drops during drying on three different substrates at three different substrate temperatures. The drop size has little influence on the drying process, other than the drying time becoming longer with increased drop size. The substrate contact angle and temperature have a significant impact on coffee stain formation. By testing the drop overprinting, information on drop/drop interactions can be obtained. Microvoids have been observed to form at the interface between two drops from air entrapment. Increasing the temperature makes the drops drying faster, and dried drops are more easily deformed on the substrate. Drops were deformed by the stacking drops when printed on Kapton and silicon at room temperature, but not on the glass slide due to the smaller contact angle. No deformation occurred in all cases at a higher substrate temperature of 45 °C. Evidence of a bubble formation inside or between the drops on deposition during the stacking and drying process were found from the image sequences.

5.5 Acknowledgement

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CHAPTER 6 Suppressing of Coffee Stain and Characterization of Defects in 3D Inkjet Printed Zirconia Structures by High-resolution X-ray Tomography

The following sections in Chapter 6 have been prepared as a manuscript for submission to the Journal of the American Ceramic Society. Some of the results have been given as an oral presentation at The American Ceramic Society on 39th International Conference and Expo on Advanced Ceramics and Composites, 25-30 January, 2015 in Florida, USA.

The author has designed, prepared and performed the experiment, analysed the collected data, interpreted the results and wrote the first draft and the final version of this manuscript.
Chapter 6 Suppressing of Coffee Stain and Characterization of Defects in 3D Inkjet Printed Zirconia Structures by High-resolution X-ray Tomography

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Abstract:

The aim of this study is to find out the influence of solvent mixtures, substrate temperature and printing drop spacing on inkjet printed structures. Inks containing ZrO₂ nanoparticle suspensions have been formulated to print droplets using a laboratory scale inkjet printer. Small molecule ethylene glycol (EG) and big molecular polyethylene glycol (PEG) additions to the ink as well as different substrate temperatures were used to investigate the use of solvent mixtures on reducing the coffee stain phenomenon with nanoparticle suspension. 3D green bodies were printed from different ink compositions using different drop spacings. Single inkjet printed droplets were characterized after drying using optical phase contrast microscopy (PCM) and scanning electron microscopy (SEM). High-resolution X-ray microtomography was used to characterize the defect population within 3D inkjet printed ZrO₂ structures before and after sintering.

When adding 25 vol% EG or 5 wt% PEG, the coffee stain is reduced or eliminated under room temperature drying. It was found coffee staining was more obvious at high substrate temperatures. X-ray tomography has been demonstrated as a valuable tool for the characterization of internal structures of 3D printed objects. The majority of the microvoid defects revealed are associated with drop segregation during dryings such as the formation of coffee stains or coffee rings. The largest crack-like defects have areas larger than a single drop and hence were likely to be formed by poor drop-drop coalescence. The defect density within printed structures appears to be independent of drop spacing as long as drop overlap occurs.

Keywords: X-ray tomography; Inkjet Printing; Coffee Stain; Satellites; Defects
6.1 Introduction

Inkjet printing allows the accurate placement of picolitre volumes of fluid on an arbitrary substrate \[11\]. It has major commercial applications in graphics output and other conventional printing operations \[9\]. Inkjet printing can also be used as a 3D printing method through the repeated overprinting of individual layers. Nowadays, there has been a growing interest in using inkjet printing as a manufacturing method with applications in areas of structural and functional material manufacture \[1\]. Inkjet printing has been developed as a ceramic processing method in the past decades \[4\]–\[7\], \[23\]. There are an increasing number of publications on the use of inkjet printing in ceramic component fabrication in recent years \[2\], \[3\]. At present, a significant number of ceramic materials, e.g. ZrO\(_2\) \[163\], TiO\(_2\) \[164\], BaTiO\(_3\) \[169\], PZT \[223\] and Al\(_2\)O\(_3\) \[165\] have been successfully used to produce stable ceramic suspensions for inkjet printing. However, there has been little or no study of the mechanisms that may lead to defect formation within an inkjet printed ceramic body. These defects may form as the consequence of processes, e.g. drying, within a single printed drop or else form as a consequence of interactions between printed drops. Thus, all aspects of the printing process have the potential to influence the final printed structure and imperfections in the process may lead to a range of defects from microvoids to larger crack-like defects.

Non-uniform features within a single inkjet printed droplet are believed to be mainly caused by a phenomenon known as a “coffee stain” or “coffee ring” \[119\]. A coffee stain is a phenomenon quite similar to the ring-like deposit along the perimeter of a spill of coffee, where nearly all the particles inside the liquid will be carried to the edge as a result of internal flow during the drying process. The coffee ring forms when a drying drop is pinned at the contact line and has a contact angle sufficiently small to generate a shallow gradient of the surface close to the edge of the drop. This combination leads to a greater solvent loss near the contact line than the centre. Because the line is pinned and cannot retract, the solvent is replenished by an outward flow of fluid in a drying drop. The outward flow continuously delivers particles in suspension to the drying contact line and results in a ring deposit after drying.
To improve the quality of 3D inkjet printed ceramic structures, it is important to suppress the formation of coffee stains during the drying of inkjet printed drops. There has been prior work reported on methods to reduce the coffee stain effect [23], [141], mainly using solvent mixtures or varying the substrate temperature. Solvent mixtures are believed to suppress coffee staining by driving an opposing fluid flow generated using temperature or concentration gradient driven surface tension gradients (Marangoni convection) [28]–[30]. The substrate temperature was also controlled to suppress the coffee stain in some research [30], [58], [142]. However, the influence of substrate temperature is not uniformly accepted as a controlling strategy [28], [31], [144], which needs further investigation.

3D objects are fabricated from patterns of printed drops. The coalescence of these drops to form a continuous structure is a key step in the fabrication of solid ceramic objects. For most ceramic printing applications, drop coalescence occurs before the drop has completely dried. The shape of the printed object, usually formed as a series of lines, is controlled by fluid flow processes between overlapping printed drops that are deposited at a fixed spacing. It is clear that drops must be spaced to allow overlap to promote coalescence and that there is also a critical upper bound to drop spacing to allow the formation of parallel sided lines [31]. However, if drops are printed too close together, defects can form due to a local flow instability [103], [224]. Thus, there is a limited range of appropriate drop spacing where a uniform structure can be obtained [9]. In addition to these two mechanisms that can lead to defects in printed ceramics, defects may form through other printing related mechanisms including missing droplets [49] and misplaced droplets [65], [67], [225]. To investigate the influence of drop spacing and ink properties on the 3D printed structures, an appropriate characterization tool is needed to locate and identify defects within printed objects.

Conventionally, defects in ceramic structures are identified on the original surface, or on a fracture surface during post-failure analysis, and are typically characterized using scanning electron microscopy (SEM). Internal features can be exposed and identified following serial cutting and sectioning originally through mechanical polishing. Recent developments allow sample sectioning through FIB nanotomography [182] and characterized using TEM. However, these approaches
are intrinsically destructive and can introduce additional defects. Thus, those methods do not give a true description of the defects present in ceramic structures.

X-ray computed tomography (CT) is an emerging technique that can be used to investigate the internal structure of an object non-destructively [183]–[185], [201]–[203]. The test sample is usually placed on a rotatable stage between an X-ray source and a detector [187], [188]. During a CT scan, the stage rotates so that a series of two dimension X-ray projections are taken from different angles. These projections can subsequently be reconstructed using appropriate algorithms to show the 3D internal structure of the object. Recent developments in X-ray CT have allowed submicron spatial resolutions to be achieved in the reconstructed images. This high resolution makes X-ray CT a suitable technique to identify defects and evaluate the internal structure of printed ceramics. Furthermore, no special sample preparation is required before testing using X-ray CT. Thus, defects and artefacts associated with sample preparation can be largely avoided. In this study, high spatial resolution X-ray microtomography was used to characterize internal defects within 3D inkjet printed ZrO\textsubscript{2} ceramic structures before and after sintering.

6.2 Experimental procedure

6.2.1 Materials and methods

Nanoparticle ZrO\textsubscript{2} (particle size 20-30 nm, purity 99.99%, PI-KEM Ltd., UK) was used as a model material with reasonably high X-ray absorbance to give good contrast with defects. ZrO\textsubscript{2} inks were prepared with 5 percent ZrO\textsubscript{2} powder volume content. 1 wt% DISPEX A40 (Ciba Specialty Chemicals Inc., Basel, Switzerland) and 0.5 wt% DOLAPIX CE 64 (Zshimmier & Schwarz, Lahnstein, Germany) were applied as the surfactants to achieve the minimum viscosity without significant sedimentation. Ethylene glycol (EG, Sigma-Aldrich Company Ltd., Dorset, UK) and polyethylene glycol (PEG, average MN CA. 1500, Sigma-Aldrich Company Ltd., Dorset, UK) were selected as solvent mixtures to study their effect on suppressing the coffee stain effect. All the samples were ball milled for 24 hours to make the uniform dispersed nanoparticle suspensions. These suspensions were filtered through 2 μm filters before printing to eliminate larger particles and ensure the nozzle did not
get blocked during the inkjet printing process. The experiment procedure and a diagram illustrating the inkjet printing deposition are shown in Figure 6-1.

As shown in Figure 6-1, ZrO₂ inks were printed using an in-house designed and built laboratory-scale inkjet printing platform MPP 1000 (Manchester Printing Platform 1000). This printer used an x-y table with a positional accuracy of 3 μm (Micromech Systems, Braintree, UK). The printer was equipped with a piezoelectrically actuated inkjet printhead of internal diameter 60 μm (MJ-ATP-01-60-8MX, MicroFab Technologies Inc., Plano, TX, USA). Also, a drive electronic (JetDrive III, MicroFab) was interfaced to a PC and controlled in a LabVIEW (National Instruments, Austin, TX, USA) environment. The printer was set to print at a dwell voltage of 70 V and an echo voltage of 0 V. The dwell time, rise time and fall time were set to 35 μs, 3 μs and 3 μs, respectively. All the inks were printed at a frequency of 1000 Hz.

To better understand the formation of 3D objects through the coalescence and drying of printed drops, experiments were carried out to produce isolated printed drops and
also to fabricate solid objects by printing arrays of overlapping drops. All printed arrays were fabricated in a square pattern with the drop spacing identical in the x- and y-directions; two drop spacings of 100 μm and 125 μm were used. 3D structures were produced by overprinting up to 500 layers. These 3D printed objects had a footprint on the surface of approximately 1 mm × 1 mm to allow high-resolution X-ray tomographic imaging. Thicker specimens show greater attenuation of the transmitted X-rays and cannot achieve the < 1 μm resolution required to image defects within the printed structure. The green bodies were sintered in a high-temperature furnace for heat treatment from room temperature to 1210 °C using the following temperature profile: holding at 136 °C for 1 hour, 324 °C for 2 hours and 1210 °C for 4 hours. The heating and cooling rate were both 180 °C/h.

6.2.2 Characterization of the defects

The possible defects in the printed ceramic structures were classified into four categories:

1) Defects within an individual drop. These are believed to be primarily generated by coffee stains and missing individual drops.
2) Line defects of an entire missing row of drops caused by a defective printing nozzle.
3) Planar defects formed when there is non-uniform overlapping of printed lines.
4) Larger-scale defects caused by non-uniform stacking of printed layers.

Optical phase contrast microscopy (PCM, MicroXAM Phase Contrast Microscope, Phase Shift Inc., Tucson, AZ, USA) and SEM (Zeiss EVO60, Carl Zeiss, Jena, Germany) were applied to characterize the single printed drops and surface defects on the inkjet printed ceramic objects. Internal defects and 3D structures of the printed ceramic parts were characterized using a high-resolution laboratory based X-ray micro-tomography system (ZEISS Xradia Versa 520, Carl Zeiss X-ray Microscopy Inc., Pleasanton, CA, USA). Tomographic scans were performed using a 20 × objective lens, giving a reconstructed voxel size of 0.51 μm. 2001 projections were taken over 360° with an exposure time of 30 s. The individual powder particles in the ceramic ink were significantly smaller than the voxel volume of the tomography data. The presence of microvoids and cracks in the tomographic data was assessed by a thresholding procedure, and a void was assigned if the image
density was below a critical level in a given voxel. Image reconstruction, thresholding, and manipulation were carried out using Avizo 8.0 (FEI Visualization Sciences Group, Inc., Burlington, MA, USA) and Avizo Fire software (FEI Visualization Sciences Group, Inc., Burlington, MA, USA).

6.3 Results and discussion

6.3.1 The effect of small molecule solvent mixture and substrate temperature on coffee stains

EG is a small molecule solvent with higher boiling point (197.3 °C) than that of water (100 °C). Also, EG has a lower vapour pressure at 20 °C (0.008 KPa) than that of water (2.3 KPa). The surface tension and viscosity of a water-ethylene glycol mixture change with the amount of ethylene glycol as shown in Figure 6-2. By adding more ethylene glycol, the mixture surface tension decreases, and viscosity increases.

![Figure 6-2 Viscosity and surface tension of ethylene glycol and DI water mixtures at room temperature.](image-url)

In order to investigate how the small molecule solvent mixture influences the coffee stain formation during the drying of single droplets, the fully dried morphologies of droplets printed from two inks (5 vol% ZrO₂ ink without EG and 5 vol% ZrO₂ ink
with 25 vol% EG) were characterized. Also, to study the influence of substrate temperature on coffee stain formation, inks were printed on substrates held at RT, 45 °C, 60 °C and 75 °C. In order to find how the addition of EG and substrate temperature influenced coffee staining within overprinted or stacked structures, the surface morphology of the deposit after 5 printing passes was studied. All the printed samples were characterized using SEM and are shown in Figure 6-3. It can be seen that the plan view of a single droplet of the 5 vol% ZrO\textsubscript{2} ink (Figure 6-3a) is very similar to that after 5 printing passes (Figure 6-3b), although at higher temperatures some of the 5-passes drops show the influence of a lack of register between passes. Adding EG (Figure 6-3c) resulted in larger droplets with extra satellite drops more prevalent. However, with the addition of 25 vol% EG, the droplets become dome-shaped at room temperature with no coffee staining, although coffee stains reappear with increasing substrate temperature.

![Figure 6-3 SEM images of droplets printed at different temperatures: a) 1 pass of ink with 0 vol% EG; b) 5 passes of ink with 0 vol% EG; c) 1 pass of ink with 25 vol% EG; d) 5 passes of ink with 25 vol% EG.](image-url)
PCM was used to measure the height of the printed drops and hence quantify the coffee stain effect. In Figure 6-4a and Figure 6-4b (5 vol% ZrO$_2$ ink without EG), the coffee stain effect became worse with increasing temperature for both 1 and 5 droplet passes. In Figure 6-4c, adding EG at room temperature (RT) resulted in dome-shaped droplets, which was a good consequence of a suppressing coffee stain effect. However, outside coffee rings observed when increasing temperature. After printing 5 passes, all samples remain dome-shaped in Figure 6-4d.

Figure 6-4 PCM images of droplets printed at different temperatures: a) 1 pass of ink with 0 vol% EG; b) 5 passes of ink with 0 vol% EG; c) 1 pass of ink with 25 vol% EG; d) 5 passes of ink with 25 vol% EG.

To quantify the influences of both EG and substrate temperature on droplet size, the average droplet diameter and height were calculated from every 10 droplets printed at different substrate temperatures using the above two inks. The average droplet diameter was calculated from the SEM data. The average droplet height was measured from the PCM data. All the results are shown in Figure 6-5. By comparing the average droplet diameter and height between the 0 vol% EG and 25 vol% EG in
Figure 6-5a and Figure 6-5b, it is obvious that after adding EG the droplets became higher and their diameters smaller. The average diameters of 25 vol% EG droplets were all around 240 μm and the height increases with increasing the substrate temperature. After 5 printing passes, the substrate temperature had a significant effect on all the droplets, in particular on the average droplet height.

Figure 6-5 Quantitative comparisons of droplets printed from inks with 0 vol% EG and 25 vol% EG at different temperatures: a) average droplet diameter of 1 pass; b) average droplet height of 1 pass; c) average droplet diameter of 5 passes; d) average droplet height of 5 passes.

The average ratio between coffee stain height Hc (the largest difference between the edge highest height and centre lowest height) and droplet height H were calculated from every 10 droplets using PCM height information. This ratio was used to quantitative describe the coffee stain effects. When it is a uniformed droplet, Hc = 0, and Hc/H = 0. The ratio Hc/H is a negative number for dome-shaped drops and a positive number for drops showing a coffee stain. The quantified coffee stain data for drops printed with 1 and 5 passes between the inks with and without EG were for
both inks are shown in Figure 6-6. The addition of EG had a significant effect on coffee stain formation and resulted in small domes after drying with average Hc/H around -0.18 at RT (as shown in Figure 6-6a). Thus, the best shape among all the samples involved had been generated by adding 25 vol% EG and printed at room temperature, which is consistent with the drop morphologies shown in Figure 6-3 and Figure 6-4. In Figure 6-6b, the average Hc/H of 5 passes samples also shows a significant difference between the two inks. Increasing temperature shows a gradual increase in dome height with 5 passes of the EG ink but the data for the ink without EG showed no consistent trend. The data shows more scatter with printed single drops results (Figure 6-6a) and although there may be an increase in dome height as substrate temperature increases with the EG containing ink, the data is not conclusive.

The mechanism for controlling coffee stain formation using EG is believed to be the lower surface tension solvent mixture introduced the Marangoni Flow [30]. Temperature has an influence on the ink properties and drying process, which results in a change of coffee stain formation at different temperatures.

6.3.2 The effect of big molecule solvent mixture and substrate temperature on coffee stains

PEG 1500 is a big molecule solid at room temperature and soluble in distilled water with a significantly higher boiling point (> 200 °C) than that of water (100 °C). The big molecule solvent’s influence on the coffee stain within single droplets was investigated by comparing the fully dried morphologies of droplets printed from
ZrO$_2$ ink with the different amount of PEG in solution (5 wt%, 10 wt%, 15 wt% and 25 wt%). A range of substrate temperatures (RT, 45 °C, 60 °C and 90 °C) was applied to study its influence on coffee stain formation. All those printed single droplets were characterised using PCM. All those printed single droplets were characterised using PCM, as shown in Figure 6-7.

Figure 6-7 PCM images of samples with different amount of PEG printed at different substrate temperatures of RT, 45 °C, 60 °C and 90 °C: a1-4) 5 wt%; b1-4) 10 wt%; c1-4) 15 wt%; d1-4) 25 wt%.

Figure 6-7a1 shows that the coffee stain was suppressed at room temperature by adding 5 wt% PEG. The suppression is believed to be caused by a combination of Marangoni convection from surface tension gradients [30] and an increase in ink viscosity. However, from Figure 6-7 b1-d1 the coffee stain is reduced by adding more PEG. This phenomenon can be explained because the ink viscosity increases with increasing concentration of PEG. This reduces the outward flow velocity and prevents particle accumulation at the contact line during drying.
Comparing the coffee ring in Figure 6-7 a4-d4 with that of Figure 6-7 a1-d1, it is clear that in all cases the coffee stain becomes more evident with increasing substrate temperature. This suggests that the time constants for evaporation and Marangoni flow change with temperature in a different manner and that the Marangoni flow is relatively less important at higher temperatures. However, some smaller rings were observed at high temperature especially in the inks with more PEG, which were quite likely to be the result of PEG made the solvent vapor harder than water. In addition, PEG remained as the polymer after drying. Thus, the PEG amount should be limited when printing 3D ceramic objects. At higher PEG contents the drops show higher solid volumes because the PEG solidifies.

To quantify the influence of PEG and substrate temperature on droplet size, the average droplet diameter and height were calculated from every 10 droplets printed at different substrate temperatures using 5 vol% ZrO$_2$ with different amount of PEG mixtures. All the quantitative results were compared as shown in Figure 6-8. As shown in Figure 6-8, the substrate temperature had an effect on all PEG ink droplet diameters and heights. Almost all the droplet heights were increased with the amount of PEG in the inks.

![Figure 6-8](image)

Figure 6-8 Quantitative comparisons of droplets printed from inks with different amount of PEG at different temperatures: a) average droplet diameter; b) average droplet height.

Hc/H was calculated from every 10 droplets printed at different substrate temperatures from 5 vol% ZrO$_2$ with PEG mixtures (shown in Figure 6-9). As can be seen, 5 wt% PEG droplets dried at room temperature conditions were dome-shaped droplets with the ratio between the coffee stain height (Hc) and the droplet height,
namely Hc/H, around -0.2. 25 wt% PEG droplets printed at 45 °C and 60 °C also had good structures. However, this concentration of PEG was so large (significantly greater than the amount of ceramic present) for future practical 3D printing. Although large molecule PEG is effective in controlling the coffee stain formation, it introduced in defects to the 3D printed structures after sintering as a polymer. Thus, the PEG amount was limited to 10 wt% in the following research on 3D printed structures.

Figure 6-9 Quantitative comparisons of average Hc/H from droplets printed at different temperatures.

6.3.3 Surface defects of inkjet printed 3D structures

To study the influence of a coffee stain on the surface after printing, one-layer, two-layer and multilayer structures were printed using inks with 5 wt% polyethylene glycol (PEG) and characterized by SEM. Figure 6-10 shows SEM images of a single printed layer of the 5 wt% PEG ZrO₂ ink on a glass substrate and an overprinted sample with two layers. These were printed with a drop spacing of 100 μm in both x- and y-directions. This spacing was smaller than the equilibrium diameter of a single drop on glass, which was 120 μm. Figure 6-10a shows a single printed layer of a vertical printing direction. There is a clear striped contrast visible that correlates with the width of an individual printed track. The insert shows a higher magnification.
image of the selected area by the blue square. A missing drop defect is indicated by the arrow on the image. Figure 6-10c shows a higher magnification image of the edge of the printed layer shown in Figure 6-10a. There is a clear difference between the edge of a printed track and the centre. The edge appears to be denser and free from any micro-void defects that were clearly visible in the central region. This is believed to be a result of a coffee stain outward flow during drying and has been reported previously when rows of drops coalesce to form a continuous track [145]. The edge of the specimen shows the presence of satellite drops and also a waviness which was analogous to defects seen during the printing of individual lines [31], [103]. In the case of ceramic printing, the ink contains a substantial volume fraction of nanoparticles in suspension. These are believed to influence the process of drop shape evolution during the flight, and their presence may destabilize the drop from the point of formation and lead to the premature formation of satellites during flight.

Figure 6-10 SEM images of 5 wt% PEG samples: a) 1 layer; b) 2 layers; c) a higher magnification image of the edge of the printed layer shown in Figure 6-10a; d) a higher magnification image of the edge of the printed layer shown in Figure 6-10b.

Figure 6-10b and Figure 6-10d show SEM images from a two-layer printed specimen. On comparison with Figure 6-10a and Figure 6-10c, it is apparent that the overprinting has reduced the number of microvoid defects and possibly also reduced the extent of coffee staining. As shown in Figure 6-10d, the two-layer structure had a rougher edge than the single printed layer, because of the partial incorporation of the
satellite drops. As shown in Figure 6-10a and Figure 6-10c, coffee stains (microvoids and height variation) and satellites were observed in the one-layer sample. Comparing this with two-layers sample (Figure 6-10b and Figure 6-10d), the overprinting has reduced the number of microvoids caused by coffee stains, but the satellites deposited outside the printed pattern range remain as shown in Figure 6-10b and Figure 6-10d.

Figure 6-11 shows SEM images of the top surface of printed multilayer (200 to 500 layers) samples. These objects were fabricated using the 5 wt% PEG ZrO$_2$ ink with a droplet spacing of 100 µm in both the x- and y-directions. In all cases, the multilayer 1 mm × 1 mm printed objects retain the surface contrast identifying the printing direction. However, the contrast was less distinct than seen with two-layer printed structures (as shown in Figure 6-10b). Thus, coffee stain induced surface relief was retained, but its amplitude was reduced with increasing numbers of layers printed. For all multilayer printed objects, satellites deposited outside the print pattern range and surface microvoids were still visible (arrowed in Figure 6-11, a-d). Coffee stains and satellites mainly caused the surface defects in 3D printed objects.

Figure 6-11 SEM images of multilayers 5 wt% PEG samples: a) 200 Layers; b) 300 Layers; c) 400 Layers; d) 500 Layers.
6.3.4 3D internal structures characterized using X-ray tomography

To investigate the influence of ink composition on the final printed 3D structures, multilayer structures were printed using inks containing 5 wt% and 10 wt% PEG. Two different drop spacings (100 μm and 125 μm in both the x- and y-directions) were also studied to find whether there is a critical range of drop spacing for defect-free structures in accordance with 1D models developed in Manchester [103]. SEM images give valuable information about the surface of a printed ceramic structure. In order to probe the structure and behaviour of multilayer structures, it is necessary to image the interior specimen morphology. The internal structures of the objects were characterized using X-ray tomography. The dimensions of the objects were limited to 1 mm × 1 mm to allow for signal attenuation and retain < 1 μm spatial resolution during X-ray tomographic imaging. The scans were performed using the 20 × objective lens giving a reconstructed voxel size of 0.51 μm, with 2001 projections taken over 360° with an exposure time of 30 s.

Figure 6-12 shows a slice of a reconstructed X-ray CT image and 3D segmentation with volume rendering from the 100-layer sample. The images showed two types of defect. The first type is characterized as microvoids with size much smaller than the 100 μm drop spacing of the printed structure (arrows in Figure 6-12a and yellow segmentation in Figure 6-12b). The second defect type is described as larger crack like defects towards the bottom of the multilayer structure (arrow in Figure 6-12b). These cracks had linear dimensions comparable with the drop spacing.

Figure 6-12 100-layers 5 wt% PEG sample with 100 μm droplet spacing: a) X-ray tomography slice; b) 3D segmentation with volume rendering.
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To investigate the effect of printing parameters, multilayer structures printed using an ink containing the same loading of ZrO$_2$ particles and PEG with a larger drop spacing. Figure 6-13 shows a reconstruction slice and 3D segmentation with volume rendering from an 180 layer structure printed using the 5 wt% PEG ink with a 125 μm × 125 μm drop spacing. This selected spacing is the largest drop spacing, at which a structure forms by drop coalescence. This sample retained its shape and a square cross-section after drying. In this printed object the voids appear to be segregated to two distinct regions at different layer heights within the structure. Very few cracks were found after segmentation, but microvoids of 1~10 μm were evident throughout the bulk of the material.

![Micro-void](image_url)

Figure 6-13 180-layers 5 wt% PEG sample with 125 μm droplet spacing: a) X-ray tomography slice; b) 3D segmentation with volume rendering.

All previous structures were printed using a 5 wt% PEG ZrO$_2$ ink with different drop spacings. Here, for comparison, a multilayer structure was printed using an ink containing the same loading of ZrO$_2$ particles but now with 10 wt% PEG with a drop spacing of 100 μm × 100 μm. Figure 6-14 shows an X-ray tomography slice and 3D segmentation with volume rendering from this object. Increasing the PEG concentration in the ink reduces the number or microvoids within the bulk of the material (or reduced their size to below the detection threshold). However, there were very clear large voids located near the base of the structure, and there was also significant slumping of the printed object with the cross-section at the base much wider than at the top. There were also significant cracks visible in the structure (Figure 6-14a).
Figure 6-14 200-layers 10 wt% PEG sample with 100 μm droplet spacing: a) X-ray tomography slice; b) 3D segmentation with volume rendering.

Figure 6-15 20 printed layers 10 wt% PEG sample with 125 μm droplet spacing: a) X-ray tomography slice; b) 3D segmentation with volume rendering.

The influence of missing drops on the final printed multiple layer structures was also investigated. In the centre of the sample shown in Figure 6-15, a deliberately introduced or designed defect of a single missing drop in the printing pattern was observed. In addition to this large defect, many cracks (purple) and microvoids (yellow) were found. From the size of the introduced large defect, it is clear that the missing droplet has resulted in a defect larger than the scale of a single droplet. This suggests that the printed structure was controlled by the mutual interaction of many drops and that the presence of defect the size of a single drop influences the structure beyond the nearest neighbour drops in the structure. The image of the designed defect was not circular but has an irregular shape, this may indicate that interrupting the regular ink delivery for a single drop ejection may have disturbed subsequent drops, or possibly that the smaller number of layers printed in this object may lead to an influence of the free surface on the shape of the defect.
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The two inks will have different microstructures after printing and drying. If assuming all the water is lost during the drying process, the 5 wt% PEG ink will result in a printed structure containing approximately 50 vol% ZrO₂, while the 10 wt% PEG ink will contain approximately 33% by volume ZrO₂. It is believed that the slumping seen in Figure 6-14 was a result of the low ZrO₂ content after drying. Low ZrO₂ content allows the microscale slumping through creep and also allows small microvoids to heal. In all cases studied, there were a significantly larger proportion of defects visible closer to the original substrate on which the structures were built.

6.3.5 Quantitative analysis of 3D internal structures using Avizo software

Defect volume and volume fraction (V₅) in 3D inkjet printed ZrO₂ structures can be calculated after X-ray tomography by using image segmentation. Quantified data for these four structures is presented in Table 6-1. The complete tomographic dataset was analyzed, with the total volume of microvoid defects and crack-like defects measured and presented in Table 6-1, both in absolute terms and as a fraction of total specimen volume. The defects that are approximately equiaxed in shape are designated as microvoid defects. Those defects that are primarily planar or are deformed planar in nature were designated as crack-like defects.

From the data in Table 6-1, it is clear that the total defect volume fraction was small for objects produced with the 5 wt% PEG ink using both drop spacings. However, the total void or defect volume was larger in the object produced with the 125 μm drop spacing. In both structures, the majority of the microvoid defects were substantially smaller than the expected drop volume after drying, and these were believed to be associated with poor drop coalescence or within drop defects such as coffee stains. The largest void imaged in the 100 μm × 100 μm drop spacing structure was substantially smaller than a single drop. However, in the 125 μm × 125 μm drop spacing specimen the largest microvoid was similar to the volume of a printed drop and thus may be a missing drop defect. The biggest crack present has a volume comparable to that of a single drop. Indeed it is clear that a single crack accounts for over half the total crack volume in the 100 μm × 100 μm drop spacing specimen. This crack has a volume of $2.58 \times 10^4 \, \mu m^3$, which has an area of $5 \times 10^4 \, \mu m^2$ which was approximately 4 × the footprint of a single drop spread on the glass substrate. Note that the mean drop size used during printing was 110 pl or $1.1 \times 10^5$
μm$^3$ and after the removal of water, each drop is expected to occupy approximately $10^4$ μm$^3$. Thus, the microvoids appear to be associated with defects in a single drop, and the crack-like defects were probably related to imperfect bonding between adjacent drops and can extend across more than one drop.

Table 6-1: Quantified X-ray microtomography data were showing the volume and volume fraction of microvoid and crack-like defects in inkjet printed multilayer ZrO$_2$ ceramic structures before sintering.

<table>
<thead>
<tr>
<th>Calculated data</th>
<th>5wt% PEG: 100μm drop spacing</th>
<th>5wt% PEG: 125μm drop spacing</th>
<th>10wt% PEG: 100μm drop spacing</th>
<th>10wt% PEG: 125μm drop spacing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total printed volume /μm$^3$</td>
<td>$1.30 \times 10^8$</td>
<td>$1.92 \times 10^8$</td>
<td>$1.80 \times 10^8$</td>
<td>$1.97 \times 10^7$</td>
</tr>
<tr>
<td>Micro-void volume /μm$^3$</td>
<td>$4.13 \times 10^4$</td>
<td>$2.71 \times 10^5$</td>
<td>$1.05 \times 10^7$</td>
<td>$2.04 \times 10^4$</td>
</tr>
<tr>
<td>Crack volume /μm$^3$</td>
<td>$4.83 \times 10^4$</td>
<td>$3.41 \times 10^3$</td>
<td>$1.25 \times 10^6$</td>
<td>$9.94 \times 10^3$</td>
</tr>
<tr>
<td>Designed void volume /μm$^3$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$4.39 \times 10^3$</td>
</tr>
<tr>
<td>Largest microvoid /μm$^3$</td>
<td>$2.70 \times 10^3$</td>
<td>$1.74 \times 10^4$</td>
<td>$4.51 \times 10^6$</td>
<td>$7.59 \times 10^4$</td>
</tr>
<tr>
<td>Largest crack /μm$^3$</td>
<td>$2.58 \times 10^4$</td>
<td>$2.24 \times 10^3$</td>
<td>$3.54 \times 10^5$</td>
<td>$8.83 \times 10^3$</td>
</tr>
<tr>
<td>Microvoid volume fraction ($V_f$)</td>
<td>$3.18 \times 10^{-4}$</td>
<td>$1.41 \times 10^{-3}$</td>
<td>$5.87 \times 10^{-3}$</td>
<td>$1.03 \times 10^{-3}$</td>
</tr>
<tr>
<td>Crack $V_f$</td>
<td>$3.72 \times 10^{-4}$</td>
<td>$1.78 \times 10^{-5}$</td>
<td>$6.99 \times 10^{-4}$</td>
<td>$5.05 \times 10^{-4}$</td>
</tr>
<tr>
<td>Designed void $V_f$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>$2.23 \times 10^{-2}$</td>
</tr>
<tr>
<td>Total natural defect $V_f$</td>
<td>$6.90 \times 10^{-4}$</td>
<td>$1.43 \times 10^{-3}$</td>
<td>$6.56 \times 10^{-3}$</td>
<td>$1.54 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

The data from the 10 wt% PEG ink printed at a 100 μm spacing (Figure 6-14) appears to be anomalous with the microvoid data distorted by the very large defects present at the base of the printed object. These defects had a volume of 100 or more printed drops and coupled with the slumped shape of the object and the observation that the total volume of internal cracks was an order of magnitude greater than found in other specimens. There were two possible explanations for this behaviour. It is possible that the larger quantity of PEG in the ink will reduce the water evaporation rate from the ink, which leads to the structure creeping and surface tension resulting
in the rounding seen in Figure 6-14a and Figure 6-14b. The increased cracking could be caused by drying stresses. However, no similar behaviour was observed with the structure printed from the same ink with 125 μm drop spacing (Figure 6-15a and Figure 6-15b). Thus, a more likely reason for the large defects at the bottom of the object and the crack-like defects is that external mechanical damage might have occurred during handling before insertion into the X-ray tomography system.

When considering the designed missing drop defect in the 10 wt% PEG 125 μm drop spacing sample, it has already been noted that this was a highly irregular defect with a volume of $4.39 \times 10^5$, which was approximately 4 times larger than a single drop before drying. Such a significant defect suggests that rather than a single drop not being printed, several drops were omitted from the printing sequence. Note, that once the volume of the “designed defect” was removed from consideration, the total defect density in both the 5 wt% and 10 wt% PEG specimens printed at a drop spacing of 125 μm were similar. In both objects printed with 5 wt% PEG ink at a 100 μm drop spacing, the largest “natural microvoid” was significantly smaller than the volume of a printed drop (approximately $10^4 \, \mu m^3$) caused by within drop segregation processes during drying, while the largest crack-like defect had an estimated surface area 2-4 times the size of an individual printed spreading drop (approximately $10^4 \, \mu m^2$) and hence was likely to be formed by poor drop-drop coalescence.

6.3.6 Defect analysis in sintered 3D printed structures

This above study has been confined to characterizing the internal structure of printed ceramic objects before sintering. The next step is to characterize printed structures after sintering to determine whether defects below some critical size are removed during sintering. To investigate the defects change after sintering, three green bodies showed in Figure 6-12b, Figure 6-13b and Figure 6-14b were sintered at 1210 °C and characterized using X-ray tomography. 3D images after segmentation of the sintered structure were presented in Figure 6-16. Microvoids and crack-like defects were also visible in all the 3D printed structures after sintering. All the 3D structures shrunk by 75-80% after sintering. The morphology of the 10 wt% PEG sample shown in Figure 6-16b has a bigger change than that of the other two shown in Figure 6-16a and Figure 6-16b, which was mainly a result of the larger quantity of PEG making it easier to deform during sintering.
Figure 6-16 X-ray tomography 3D images of inkjet printed structures after sintering: a) 5 wt% PEG sample with 100 μm drop spacing; b) 10 wt% PEG sample with 100 μm drop spacing; c) 5 wt% PEG sample with 125 μm drop spacing.

6.4 Conclusions

The substrate temperature has a significant influence on the drop dimensions and coffee staining. It is found that coffee stain effect was more obvious at high substrate temperature. Adding EG and PEG as solvent mixtures strongly influenced on the droplet shape. The mechanism for the behaviour of the solvent mixtures is most likely to be the lower surface tension introducing the Marangoni Flow after concentration changes induced by a differential evaporation rate for the components of the ink. When adding 25 vol% EG or 5 wt% PEG, the coffee stain is reduced or non-existent at room temperature among all the samples involved.

X-ray tomography has been demonstrated as a valuable tool for the characterization of 3D printed objects. Microvoids and cracks have been found within the printed ceramic volumes using X-ray tomography but with a resolution limit of approximately 0.7 μm. Maximum defect volume and defect rate can be calculated after X-ray tomography image segmentation. The majority of the microvoid defects were significantly smaller than the volume of the printed drops, while the largest of the crack-like defects have an area greater than the area of single printed drops. From
this, it is believed that the majority of the microvoid defects are associated with mechanisms and processes within a single drop, e.g. segregation during dryings such as the formation of coffee stains or coffee rings. Conversely, the results indicate that the crack-like planar defects are formed by an inter-droplet defect, mechanism, which is possibly related to imperfect drop coalescence. Also, it is found that drop spacing has a strong influence on the presence of microvoids with a larger drop spacing producing apparently solid structures but containing a large number of small microvoids. The size or distribution of microvoids can be controlled by changing the ink formulation, with higher PEG content inks showing lower concentrations of microvoids.

6.5 Acknowledgement

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CHAPTER 7 CONCLUSIONS AND FUTURE WORKS

CHAPTER 7 Conclusions and Future Works

7.1 Conclusions

This thesis aims to enhance the understanding of DOD inkjet printing processes. It has been divided into three major research topics. First, drop ejection and flight were investigated for fluids of different physical and rheological properties to compare the ink printability between different modes of printheads using solvent mixtures. The relationship among the print pulse voltage, the ink physical properties and the inkjet printability for two different modes of printheads was investigated and characterised using two dimensionless numbers, $Z$ (the inverse of the Ohnesorge number), which is independent of drop velocity, and the Weber number. The printable range is wider with $1.17 \leq Z \leq 36.76$ for the 10 pl shear-mode Dimatix printhead. However, the printable range using an 80 μm squeeze-mode MicroFab printhead is narrower with $4.02 \leq Z \leq 16.2$. However, both printheads have a printable $We$ range of $0.4 < We < 20$. When designing inks for future printing work, not only must the fluid properties be considered, but also the drop velocity and hence the actuating pulse voltages need to be adjusted as well.

Second, the drop impact, spreading and solidification processes of drops containing nano ZrO$_2$ particles were investigated to enhance understanding of coffee stain formation using time-resolved in-situ synchrotron X-ray radiography. The drop stacking process was also studied to check whether defects form between or within the dried drops during the stacking process. In-situ synchrotron X-ray radiography provides a promising tool to study time-evolved solid segregation within printed drops during drying on three different substrates at three different substrate temperatures. Both the initial contact angle and substrate temperature during printing strongly influence the drying process and the final dried deposit shape. 2D X-ray radiography images show that the drops were first pinned and then there was a slight sliding of the three-phase contact line. Bubbles and microvoids form at the interface between two drops during stacking. Drops were deformed by the stacking drops when printed on the Kapton tapes and the silicon wafers, but not on the glass slides, presumably due to the small contact angle on glass slides. Crack-like defects were found at the edges of the final dried drops.
CHAPTER 7

CONCLUSIONS AND FUTURE WORKS

Third, the coffee stain within single inkjet printed droplets and the 3D structures before and after sintering were investigated to find out whether the ink properties, printing parameters and substrate temperature influence the inkjet printed structures. The substrate temperature has a significant influence on the drop dimensions and coffee staining. It is found that coffee stains were more obvious at high substrate temperature. Adding EG and PEG as solvent mixtures were found to strongly influence the droplet shape. The mechanism for the behaviour of the solvent mixtures is most likely to be surface tension gradients introducing Marangoni Flow after concentration changes induced by a differential evaporation rate for the components of the ink. When adding 25 vol% EG or 5 wt% PEG, the coffee stain is reduced or non-existent at room temperature among all the samples studied.

X-ray tomography has been demonstrated as a valuable tool for the characterization of 3D printed objects. Microvoids and cracks have been found within the printed ceramic volumes using X-ray tomography but with a resolution limit of approximately 0.7 μm. Maximum defect volume and defect rate can be calculated after X-ray tomography image segmentation. The majority of the microvoid defects were significantly smaller than the volume of the printed drops, while the largest of the crack-like defects have an area greater than the area of single printed drops. From this, the majority of the microvoid defects are associated with mechanisms and processes within a single drop, e.g. segregation during drying such as the formation of coffee stains or coffee rings. Conversely, the results indicate that the crack-like planar defects are formed by an inter-droplet defect, mechanism, which is possibly related to imperfect drop coalescence. Also, it is found that drop spacing has a strong influence on the presence of microvoids with a larger drop spacing producing apparently solid structures but containing a large number of small microvoids. The size or distribution of microvoids can be controlled by changing the ink formulation, with higher PEG content inks showing lower concentrations of microvoids.

7.2 Future works

This thesis presented the study of ink printability for two modes of inkjet printheads, and provides a useful guide for ink design. This work also demonstrated the use of in-situ synchrotron X-ray radiography to investigate the drop drying and interaction
process. In addition, the effects of small molecule EG, big molecular PEG and substrate temperatures on the coffee stain phenomenon were investigated and demonstrated the use of micro-XCT to characterise the internal structures of inkjet printed 3D structures. According to the study results and conclusion, the following recommendations are worthwhile to explore for the future work.

In chapter 4, it is found the printable range is similar for shear-mode Dimatix printhead and squeeze-mode MicroFab printhead. It is worthwhile to check this range with smaller or bigger sized DOD printheads e.g. 1 pl Dimatix printhead, 30 μm and 120 μm MicroFab printhead, Xaar printhead, and other modes of piezoelectric printhead e.g. push-mode Trident printhead and bend-mode Xerox printhead. To find out whether this is a universal range or not. Also, both ranges found the similar peak of printability around $Z = 8$, it is worthwhile to investigate this further to find out the mechanisms leading to this behaviour.

In chapter 5, radiography indicates a film-like structure forms on the drop surface for the non-stained drop. Such an increase in surface density is not predicted by current models for coffee stain formation and needs further investigation. The drop stacking experiments found that there was significant bubble formation, which was unexpected. This needs further investigated and more experiments to determine the origin of the bubbles. It might be the PEG, or the beamline heating, or the high-frequency printing, or the ink is viscous and the bubbles are introduced by milling and shaking, not enough time for them to escape out. After this, models could be built for how nanoparticle suspensions dry.

It is also a good idea to print drops on pre-printed layers rather than on single drops to study the drop interaction and stacking process in a geometry more appropriate for 3D printing. This is important for the fabrication of ceramics, because inkjet printing is always on a porous layer of ceramic powder printed layer by layer.

As there is a large working space for the beamline, it would be possible to build a system to print a line instead of a single droplet and thus study the real time drop/drop interaction process, which will give more useful information and help with 3D printed structure design. In addition, the in-situ synchrotron X-ray radiography was found to be useful for studying the dynamic drying process of nanoparticle
suspensions. However, it is found that the Diamond Light Source pink light beamline’s resolution of 1.1 μm. It is not sufficient to provide good information for the single droplet drying process. A higher resolution beamline is needed to study single droplet drying processes. This could be further investigated to show a real-time model for single printed nanoparticle suspension droplet drying and provide value information for printing design of 3D printing.

In chapter 6, the 25 vol% EG and 5 wt% PEG were found to reduce the coffee stain at room temperature. Thus, it is worthwhile to combine these two to check whether more uniform structures could be obtained. In addition, this work found that X-ray tomography is useful in characterising internal structures. However, there is still further work needed to investigate the structures changing during sintering with more samples. In this study, there are satellites present in the 3D printed structures, in the future it is worthwhile to adjust the printing waveform especially the pulse voltage as guided by the chapter 4’s result to obtain stable and single droplets without satellites. Also, other nanoparticle materials could be applied to build up models for inkjet printing structures, e.g. 3 mol% yttria stabilized zirconia (3YSZ) and 8 mol% yttria stabilized zirconia (8YSZ) are useful to printed for future usage of dental and other piezoelectric materials for a bright future. It is worthwhile to investigate more inks and different printing parameters to suppress the coffee staining and other defects. It is also a good idea to compare the structures of 3D inkjet printed objects with that made of other traditional methods.
References


REFERENCES


[34] W. Thomson, “Improvements in telegraphic receiving and recording instruments,” 2147, 1867.


REFERENCES


REFERENCES


185
REFERENCES


REFERENCES


REFERENCES

REFERENCES


REFERENCES


Y. Rho, K. T. Kang, and D. Lee, “Highly crystalline Ni/NiO hybrid electrodes
processed by inkjet printing and laser-induced reductive sintering under ambient conditions,” *Nanoscale*, vol. 8, no. 16, pp. 8976–8985, Apr. 2016.


