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**Inkjet Printing of Functional and Structural Materials -
Fluid Property Requirements, Feature Stability and Resolution.**

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ABSTRACT

Inkjet printing is viewed as a versatile fabrication tool for applications in materials fabrication, as well as its traditional role in graphics output and marking. The unifying feature in all these applications is the dispensing and precise positioning of very small volumes of fluid (1 – 100 pl) on a substrate before transforming to a solid. The application of inkjet printing to the fabrication of structures for structural or functional materials applications requires an understanding as to how the physical processes that operate during inkjet printing interact with the properties of the fluid precursors used. Here we review the current state of understanding of the mechanisms of drop formation and how this defines the fluid properties that are required if a given liquid for it to be printable. The interactions between individual drops and the substrate as well as between adjacent drops are important in defining the resolution and accuracy of printed objects. Pattern resolution is limited by the extent to which a liquid drop spreads on a substrate and how spreading changes with the overlap of adjacent drops to form continuous features. There are clearly defined upper and lower bounds to the width of a printed continuous line, which can be defined in terms of materials and process variables. Finer resolution features can be achieved through appropriate patterning and structuring of the substrate prior to printing, and this is shown to be essential if polymeric semiconducting devices are to be fabricated. Low advancing and receding contact angles promote printed line stability but are also more prone to solute segregation or “coffee staining” on drying.

Keywords

Contact Angle, Drop Formation, Surface Energy, Drying.

INTRODUCTION

Inkjet printing as a distinct concept can be traced back to a patent granted to Lord Kelvin (William Kelvin), the 19th Century physicist and polymath for the direction of droplets through electrostatic forces (1). However, without the means to generate detailed instructions to steer the droplets, inkjet printing remained unused until the 1950s when Siemens used the technique to plot machine output traces. Major advances occurred in the period 1960 – 1980 to develop the technology for computer graphics output; with further advances in manufacturing technology, reducing costs and size of the printers, inkjet printing is now an ubiquitous personal printing tool. The main commercial application for inkjet printing remains in graphics and other conventional printing operations. However, in recent years there has been considerable interest in, and use of, inkjet printing as a fabrication tool in a number of areas of technology including: displays (2), plastic electronics (3), solder dispensing for flip-chip manufacture – either directly or as a solder mask(4), rapid prototyping (5), ceramic component manufacture (6), enzyme based sensors (7) and tissue engineering (8). Inkjet printing is currently at the threshold of becoming a standard fabrication tool with applications in a wide range of materials science (9; 10).

The application of inkjet printing to this disparate group of topics reflects the versatility of the method, which is the accurate positional placement of picolitre

volumes of fluid on an arbitrary substrate. Although couched in rather simple terms, this definition encompasses a number of physical operations that both define and constrain inkjet printing. These are:

- a) Generation of droplets,
- b) Positioning of and interaction of droplets on a substrate,
- c) Drying or other solidification mechanisms to produce a solid deposit.

It is the purpose of this review to explore how these common features of the inkjet process interact with materials during the fabrication of structures by inkjet printing.

DROP GENERATION

Inkjet Printing Technology

There are two different mechanisms by which inkjet printers generate droplets and these are generically known as Continuous Inkjet Printing and Drop-on-Demand Inkjet Printing (DOD) (11). Both methods of drop generation can produce fluid drops in the range 10 – 150 μm : CIJ is mostly used for coding and marking applications with drop diameter around 100 μm ; DOD is dominant in graphics and printing with smaller drop diameter, typically 20 – 50 μm diameter.

In continuous inkjet printing (CIJ) a stream of drops is formed by the Rayleigh instability of a liquid column that is ejected under pressure through a small nozzle. In

order to direct and position these drops, the nozzle is held at a potential relative to ground and this imparts a small charge on each drop as it is formed. Individual drops in the stream are steered by applying a further potential to deflector plates. A schematic diagram of a continuous inkjet printer is shown in figure 1. Drop diameters are typically slightly larger than the nozzle diameter. It is normal practice to impose a small pressure fluctuation on the liquid behind the nozzle through a piezoelectric transducer, this is used to synchronise drop formation if multiple nozzles are operating in parallel.

CIJ, by definition, produces a continuous stream of liquid drops even when no printing is required. Unwanted drops are deflected by the electric field to a gutter and for many applications in product marking and graphics; the unused ink is recycled (figure 1). For most applications in materials science, this recycling after exposure to the environment risks contamination of the ink, hence CIJ is a potentially a wasteful process. Drop positioning is either controlled by steering a drop in flight, or by positioning the substrate where a deposit is required and printing a drop. This second process is termed binary printing as the drop is deposited into one of two locations, either on the substrate or in the recycling gutter. CIJ systems operate with drop generation rates in the region 20 – 60 kHz and drop velocity at the nozzle is typically $> 10 \text{ ms}^{-1}$.

Drop-on-demand inkjet printers generate individual drops when required and are thus more economical with ink delivery than CIJ systems. Drop positioning is achieved by manually locating the printer nozzle above the desired location on the substrate before drop ejection. Drops are formed by propagating a pressure pulse in the fluid in a

chamber behind the printing nozzle. If the pulse exceeds some threshold at the nozzle, a drop is ejected. In the absence of a pressure pulse, liquid is held in place by surface tension at the nozzle. It is normal to also control the static pressure at the nozzle to ensure that the meniscus at the nozzle is stable. In DOD systems, drops are generated at acoustic frequencies (typically 1 – 20 kHz) and resonances within the chamber behind the nozzle strongly influence pressure pulse propagation and drop generation (12; 13). Drop size is typically approximately equal to the nozzle size but it is possible to control both drop size and ejection velocity (within a defined range) by control of the pressure pulse used to form the drops.

Two methods are used to generate the pressure pulse and promote drop formation and ejection. In thermal DOD printing a small thin film heater is located in the fluid chamber, on passing a current through this, the fluid in immediate contact is heated to above its boiling temperature to form a small vapour pocket or bubble (figure 2a); after the current is removed heat transfer leads to rapid bubble collapse. The rapid expansion and collapse of the bubble generates the required pressure pulse. In piezoelectric DOD printing the pressure pulse is generated by direct mechanical actuation using a piezoelectric transducer (figure 2b).

Figure 3 shows the sequence of drop formation observed at a DOD printer. The long extended fluid tail is a characteristic of the DOD process. The drop forms from an initial liquid column that thins to define a leading droplet and the elongated tail or ligament; the final rupture of the ligament can lead to the formation of satellite drops. Often these drops catch up and merge with the leading large drop in flight, prior to impact, in which case their presence is irrelevant. However, if they are still present at

impact, they lead to non-circular impact footprints of the drop, with deleterious influence on deposit precision, resolution and accuracy. In order to facilitate drop merging in flight, it is customary to print at a stand-off distance from the substrate. For DOD printing this stand-off distance is typically 2-3 mm. The appropriate stand-off will also influence drop placement accuracy because drag from air currents in the printing environment can deviate drops from their desired trajectory, to minimise this effect the stand-off distance is normally set at the minimum to ensure stable single drops.

Thermal DOD systems are readily miniaturised and most desk-top or domestic printers use this technology. However, the majority of industrial printers use piezoelectric DOD technology and the majority of reports in the literature concerning inkjet printing of materials use this method. This is for two main reasons. First the need to generate a bubble in thermal DOD limits the fluids to those of a high vapour pressure under ambient conditions. Second with piezoelectric DOD it is relatively easy to change the actuation pulse to control drop size and velocity for any fluid. DOD printing operates at typical acoustic frequencies in the range 1 – 20 kHz, hence, given that the dimensions of the fluid filled chambers used to generate drops have dimensions of the order of 10^{-3} m, significant acoustic resonances can influence drop volume and velocity (12; 13) and thus the shape and amplitude of the actuating pulse can strongly influence printing behaviour (11). Indeed the design of an appropriate pulse to provide stable drop ejection conditions is regarded as critical know-how by manufacturers of inkjet printing equipment.

By far the majority of published work using inkjet technology for materials fabrication has used piezoelectric DOD. However, there has been significant work on thermal DOD as well. CIJ has been little used in materials science applications. This is partly because of the contamination/waste issue but also because a more limited range of fluids can be deposited using CIJ than is possible with DOD and because the spatial resolution of drops on the substrate is lower than that achievable through DOD printing. However, CIJ has been used successfully to print 3-D ceramic objects (14) and silver conducting tracks (15). This review will focus on applications of DOD printing in materials science.

Printable Fluids

The generation of droplets in a DOD printer is a complex process and the precise physics and fluid mechanics of the process are still the subject of much research (11). The behaviour of liquid drops can be characterised by a number of dimensionless groupings of physical constants, the most useful of which are the Reynolds, Weber and Ohnesorge numbers (Re , We , Oh):

$$Re = \frac{v\rho a}{\eta} \quad 1a$$

$$We = \frac{v^2 \rho a}{\gamma} \quad 1b$$

$$Oh = \frac{\sqrt{We}}{Re} = \frac{\eta}{(\gamma\rho a)^{1/2}} \quad 1c,$$

where ρ , η and γ are the density, dynamic viscosity and surface tension of the fluid respectively, v is the velocity and a is a characteristic length.

The earliest significant work attempting to understand the mechanisms of drop generation was by Fromm (16). He identified the Ohnesorge number, Oh , as the appropriate grouping of physical constants to characterise drop formation.

Confusingly, he used the parameter $Z = 1/Oh$ and proposed that $Z > 2$ for stable drop generation. This analysis was further refined by Reis (17) who used numerical simulation of drop formation proposed to propose the following range, $10 > Z > 1$, for stable drop formation. At low values of Z viscous dissipation prevented drop ejection, while at high values the primary drop is accompanied by a large number of satellite droplets.

Another limiting factor for drop generation is the influence of the fluid/air surface tension at the nozzle. A drop must have sufficient energy to overcome this barrier for ejection. Duineveld (18) suggested that this leads to a minimum velocity for drop ejection of

$$v_{\min} = \left(\frac{4\gamma}{\rho d_n} \right)^{1/2} \quad 2,$$

where d_n is the nozzle diameter. Equation 3 can be reformulated in terms of the Weber number to give a minimum value for printing

$$We = v_{\min} \left(\frac{\rho d_n}{\lambda} \right)^{1/2} > 4 \quad 3.$$

Inequality 4 does not include the influence of inertia but is a suitable value for benchmarking fluid properties.

Finally we consider the impact of the ejected drop on a substrate. This process will be considered in more detail later but it is clear that the drop must impact so as to leave a single isolated spread drop. The appropriate threshold to consider here is that of splashing. The mechanisms that lead to the onset of splashing is also a topic of current research but there is a well established experimental threshold for the onset of splashing, first proposed by Stow and Hadfield as a critical dimensionless grouping of variables (19):

$$We^{1/2} Re^{1/4} > f(R) \quad 4$$

where $f(R)$ is a function of surface roughness only. This relationship has been explored by a number of authors and for flat, smooth surfaces $f(R) \approx 50$ (20).

Using equations and inequalities 2 – 4 and the limiting values of $Z = 1/Oh$, it is possible to construct a map in a parameter space, with co-ordinates Re and We , that can be used to define fluid properties that are usable in DOD inkjet systems. This is shown in figure 4. The validity of this predicted regime of printability has been explored for a large range of fluid properties with particle filled systems and it appears to offer a useful guide for fluid properties selection (21). Other aspects of

drop ejection from DOD printers have been found to scale with dimensionless groupings of physical properties. Reis et al found that the volume of an ejected drop scales with the Ohnesorge number and with the displacement of the actuation used to initiate drop ejection (13). Because of the effect of acoustic resonances, the speed of sound in the fluid is also important in controlling printed drop characteristics (22).

Up to this point we have assumed that the fluid behaves in a linear Newtonian manner. However for many applications in materials science it is necessary to print polymer solutions or concentrated dispersions of particles. It is well known that the rheological properties of such fluids can be highly non-linear and thus the printability characteristics of a fluid as displayed in Fig. 4 may need to be further modified.

Haskal *et al* reported that for solutions of poly(*p*- phenylene vinylene) (PPV), the characteristic fluid tail that forms during DOD printing becomes longer and more stable. For 0.5 – 2.0 % solutions in a range of solvents the filament did not detach and no individual drops were formed at molecular weights above 300,000 (23). Similar behaviour has been reported with a number of other polymer solutions, with extended and stable ligaments found with increasing polymer molecular weight and concentration. Xu et al explored the effect of concentration and molecular weight on printed drop behaviour and concluded that the transition from a nearly Newtonian behaviour to one dominated by fluid extensional elasticity can be explained in terms of conventional models of polymer solution behaviour (24). Xu also commented on the beneficial aspects of low polymer concentrations. Newtonian fluids show elongated tails during DOD printing and these can destabilise into a train of satellite droplets that follow the main drop (figure 3). The action of small concentrations of

polymers can stabilise the tail so that it retracts into the main drop during flight through surface tension, to result in a single drop on impact.

DROP/SUBSTRATE INTERACTION

For most applications of interest to materials scientists, the liquid drop will impact on a substrate and a subsequent phase change will transform the liquid into a solid. For some applications this phase change will generate the final desired product, for others a secondary process (e.g. sintering) is required. The liquid/solid phase change can occur by a number of mechanisms including: solvent evaporation, cooling through a transition temperature, gelling of a polymer precursor and chemical reaction. In all these cases solidification occurs post-deposition and the printed pattern must retain some stability in the liquid state prior to solidification. In order to fully understand the processes that occur between the printed drop and the substrate prior to attaining the desired structure, we must identify the interactions that occur between the substrate and the fluid drop prior to solidification.

Drop Impact and Spreading

The behaviour of a liquid drop impacting on a solid surface is controlled by a number of physical processes and can be driven by inertial forces, capillary forces and gravitational forces. The important dimensionless groupings will be the Reynolds, Weber and Ohnesorge numbers as with drop generation but we must also consider the Bond number, $Bo = \rho g a^2 / \gamma$ where g is the acceleration of gravity, when including gravitational forces. Inkjet printed drops have diameters $< 100 \mu\text{m}$. At these small

length scales $Bo \ll 1$, hence gravitational forces can be neglected. Thus the dominant forces will be inertial and capillary. Schiaffino and Sonin considered the impact of relatively low Weber number drops on a solid surface (25). Although their analysis was for solidifying drops, the initial stages after drop impact will be the same for all impacting fluids. They proposed that drop behaviour on impact can be divided into two regimes “impact driven” where the inertial forces dominate and “capillarity driven” where initial drop velocity is unimportant and that the transition in behaviour occurs at a critical value of the Weber number. In addition they characterised the resistance to spreading in terms of the Ohnesorge number, defining regimes as almost inviscous and highly viscous. Figure 5 shows their representation of the regimes of initial impacting drop behaviour, superimposed upon this is the regime of stable DOD drop formation taken from figure 4. We can see that the initial stage of the interaction between an inkjet printed drop and a substrate is “impact driven” in a region of relatively inviscous behaviour.

Yarin reviewed the behaviour of impacting liquid drops in the velocity range $1 - 30 \text{ ms}^{-1}$ and size range $100 - 3000 \text{ }\mu\text{m}$; this is sufficiently close to the regime of inkjet printing to provide a useful reference (26). Drop impact behaviour can be conveniently divided into a number of time scales determined by the dimensionless time after impact, $t^* = t(v/d_0)$, where d_0 is the droplet diameter and v is droplet velocity (27). The initial impact stage is governed by kinematic behaviour and has a duration of around $t^* = 0.1$ (or $< 1 \text{ }\mu\text{s}$ for the dimensions and velocities appropriate for inkjet printing). This is followed by impact driven spreading, recoil and oscillation. At small values of t^* , viscous forces damp the spreading and oscillations and surface tension forces become more important in controlling behaviour. At later

stages the capillary forces begin to dominate until at $t^* \approx 10 - 100$ (0.1 - 1 ms) spreading is fully controlled by capillarity and further extension occurs proportional to $t^{1/10}$ (28). Spreading continues and approaches true equilibrium at $t^* > 1000$. The sequence of these processes is illustrated schematically in figure 6.

The final spread drop will have a contact diameter or footprint, d_{con} , determined by its volume and the equilibrium contact angle, θ_{eqm} . For drop sizes typical of inkjet printing, the Bond number is sufficiently small that the spread drop shape can be taken as a segment of a sphere, with

$$d_{con} = d_0 \sqrt[3]{\frac{8}{\tan \frac{\theta_{eqm}}{2} \left(3 + \tan^2 \frac{\theta_{eqm}}{2} \right)}} \quad 5.$$

Thus, the resolution, or minimum feature size of an inkjet printed pattern, is controlled by the dimensions of this footprint, which is a linear function of the diameter of the drop in flight. The drop footprint increases with decreasing contact angle and is about $3d_0$ at a contact angle of 10° .

The contact angle is very important in controlling the final shape of a printed drop and patterns built up from the interaction of drops. As a drop spreads after impact it advances over a dry surface, in which case the appropriate contact angle in equation 5 is the static advancing contact angle rather than a true equilibrium value. However, in the production of patterns drops may contact and interact with other drops. This interaction may lead to flow reversals and in such cases the receding contact angle becomes important. Receding contact angles are also important if drop solidification

occurs by solvent evaporation, in which case decreasing drop volume would be expected to lead to the drop footprint decreasing in area. However, drying droplets of solutions (especially polymer solutions) often show contact line pinning from solute deposition; this, combined with increased solvent evaporation rate towards the edge of the droplet can lead to solute deposition in a ring at the contact line; this phenomenon is known as the “coffee stain effect (29), which we will discuss in more detail later. When contact line pinning occurs, the receding contact angle will decrease during evaporation and tend towards zero.

Drop Coalescence and Pattern Stability

Conventional graphics printing requires patterns made up of isolated drops to produce a pixelated image. A key distinguishing feature between materials printing and graphics printing is that for many materials applications we require the drops to overlap to form continuous features. Thus a key behaviour is the interaction of spread or spreading droplets on a substrate to form stable liquid beads or lines or more complex 2-dimensional patterns. 3-dimensional structures are produced by overprinting sequential layers but in this case the interaction of a drop will be with a solidified deposit and would behave in the same manner as deposition on a substrate.

Davis considered the stability of a fluid line or liquid bead on a flat surface subject to the following limiting conditions (30): i) the contact angle at the line is fixed and the contact line is free to move, ii) the contact angle is a function of the moving contact line speed with a limiting value at zero line speed, and iii) the contact angle is free to change but the contact line is fixed. For cases i) and ii) the liquid bead undergoes a Rayleigh instability but for case iii) the liquid bead is stable if the contact angle $< \pi/2$.

Schiaffino and Sonin studied these predictions experimentally and confirmed Davis's work (31).

Inkjet printing forms liquid beads through the overlap of adjacent spread drops. Clearly, if there is no overlap of drops, there is no mechanism for the formation of liquid beads. Two overlapping drops will tend to coalesce and a train of overlapping drops will form a bead if there is significant contact line pinning. The behaviour of overlapping drops and their transformation into liquid beads has been studied by a number of authors. Duineveld investigated the behaviour of inkjet printed liquid drops on a range of substrates with different contact angles and found 3 regimes of behaviour (32). When a liquid shows a constant contact angle (identical or very similar advancing and receding contact angles), the line is unstable as predicted by Davis (30) and observed by Schiaffino and Sonin (31). If there is significant hysteresis in the contact angle, stable tracks could be printed at low values of the receding contact angle. However, even in this case it was not always possible to form a parallel liquid bead and instead bulges were observed, spaced regularly along the printed liquid bead (figure 7). The onset of this bulging instability is a function of both drop spacing and the speed at which the line was printed (i.e. the traversing velocity of the inkjet printer relative to the substrate). Duineveld proposed a mechanism for this instability (32), which was caused by competition between possible flow paths as a newly deposited drop interacts with the leading edge of a liquid bead. If capillary spreading is relatively slow, the new drop at the front of a liquid bead will have a greater curvature at the liquid/air interface than the bead, and thus a difference in Laplace pressure will drive liquid from the front of the deposit along the pre-existing bead. The transition in behaviour occurs if the deposition flow

rate (number of drops arriving per second) exceeds the rate at which capillary spreading reduces drop curvature. Duineveld developed this mechanism into a numerical model and predicted that the instability would occur at small droplet spacing and low traverse velocities (at constant drop generation rate); these predictions showed reasonable agreement with experiment.

Duineveld's observations indicate that there is a maximum stable liquid bead width achievable through inkjet printing. Smith et al considered how a stable liquid bead was formed through droplet overlap (33). At low values of Bond number the liquid bead will have a section equivalent to the segment of a circle defined by the contact angle. The width of the bead, w , can be determined assuming volume conservation, from the drop volume, drop spacing, p , and contact angle, with:

$$w = \sqrt{\frac{2\pi d_0^3}{3p \left(\frac{\theta^*}{\sin^2 \theta^*} - \frac{\cos \theta^*}{\sin \theta^*} \right)}} \quad 6.$$

In equation 6 we define θ^* as the static advancing contact angle rather than an equilibrium value. Minimum line width will occur at the threshold for drop overlap and as the drop spacing decreases, thicker liquid beads will form up to the threshold observed by Duineveld.

Soltman and Subramanian carried out an experimental study of the formation of liquid beads from inkjet printed drops and their observations were consistent with those of both Duineveld (32) and Smith et al (34). At large values of drop spacing, where no overlap of the spread drop footprint occurs, a train of discrete droplets is observed

(figure 7a). At spacing slightly smaller than the diameter of the footprint drop coalescence is observed but the resulting liquid bead is “scalloped” and does not show parallel sides (figure 7b). At smaller deposited drop spacing a stable liquid bead, with smooth parallel sides is found (figure 7c) until finally the drop spacing is too small and the bulging instability occurs (figure 7d). This work demonstrated experimentally that there are two limiting lower and upper bounds to the width of a parallel sided liquid bead produced by inkjet printing, even in the stability regime identified by Davis. They further commented on the fact that the instability proposed by Duineveld was dynamic and thus any consideration of the stability of inkjet printed lines must take into account both printed drop spacing and the rate at which drops are deposited.

Stringer demonstrated that it is possible to use the volume conservation model for liquid bead width (equation 7) to define a lower bound for a stable liquid bead width (35). He was also able to reformulate Duineveld’s model for the bulging instability in an analytical form. Using these two models in combination it is possible to produce a prediction for the limiting conditions (upper and lower bounds) under which inkjet printing produces stable liquid beads on a given substrate (36). These bounds are defined by three printing variable, the dimensionless drop spacing, $p^* = p/d_{con}$, the static advancing contact angle of the liquid on the substrate, and the traverse velocity of the inkjet printer nozzle relative to the substrate, U_T , made dimensionless through the relation $U^*_T = \eta U_T / \gamma$. This produces a simple diagram of the conditions for stable printing as shown in figure 8.

In figure 8 the horizontal line at the top of the diagram represents the fact that for any given printing system, there is a maximum traversing velocity for the printhead and

thus there is a practical upper bound to the stability diagram. The function $g(p^*, \theta)$ increases with decreasing value of the drop spacing, hence the vertical line to the left of the diagram defines the maximum drop spacing to produce a parallel sided liquid bead or the minimum parallel sided line width. The diagonal line defines the onset of the bulging instability at a critical minimum value of p^* , which is a function of the printhead traversing velocity, and defines the maximum attainable line width. The physical value of the line width can be determined from any value of p^* by using equation 6. The function $g(p^*, \theta)$ is such that the diagonal line is invariant with the contact angle but the vertical line is a function of contact angle and moves to the left as θ decreases. Thus Stringer's model predicts that lower contact angle fluid/substrate combinations show a larger range of droplet spacing for stable contact lines (36).

Patterned and Textured Substrates

On a smooth homogenous surface the resolution attainable from an inkjet printer is controlled by the diameter of the spread droplet or its footprint, which is a function of initial drop size and contact angle (equation 5). Given that the smallest drops attainable from the current generation of DOD printers have a volume $\approx 1\text{pl}$, or $d_0 > 10\text{ }\mu\text{m}$, the smallest feature size with a fluid of contact angle $< 10^\circ$ will be $> 30\text{ }\mu\text{m}$. For many applications in printed electronics, higher resolutions are required. To achieve this objective, the fluid flow during the spreading process is directed or restricted through presenting either a physical barrier to spreading by modifying the surface topology, or patterning the substrate to locally control the surface energy and hence contact angle of a spreading drop.

Sirringhaus et al were the first to use surface patterning to control substrate surface energies, and hence drop contact angles, prior to inkjet printing. They used photolithography and plasma etching, of a polyimide film deposited on a glass substrate, to produce a combined physical and surface energy barrier. This had a step height of about 50 nm and an abrupt change in surface energy, giving a contact angle of about 20-25° on the exposed glass and about 70-80° on the polyimide. Using this pattern they were able to produce linear channels with widths $\approx 5\text{ }\mu\text{m}$ between overlapping printed drops of poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonic acid (PEDOT) (3), illustrated schematically in figure 9. These structures were used to fabricate polymer transistors with channel widths of $5\text{ }\mu\text{m}$, despite the inkjet printer used producing drops that spread to about $80\text{ }\mu\text{m}$ footprint diameter. Wang et al demonstrated that it was possible to achieve similar and smaller width structures through dewetting, by printing a drop onto a fluidphobic stripe patterned on a fluidphilic substrate (figure 10a-c) (37). By optimising the height of the mesa, channel architectures with widths $\approx 500\text{ nm}$ were achieved. Another use of dewetting has allowed channel architectures with dimensions around 100 nm (38). In this method a PEDOT pattern was printed on glass, followed by a plasma surface treatment with CF_4 that decreases the PEDOT surface energy through fluoridation while increasing the surface energy of the glass. On printing a second PEDOT solution pattern, to overlap the original but modified PEDOT, the large contrast in surface energy dewets the overlapping PEDOT, if the receding contact angle is not too small, no pinning occurs and the resulting structure after drying is two adjacent PEDOT deposits separated by a small gap (figure 10d-e). These structures were then used to produce demonstrator transistors, further work has extended this to polymer substrates (39).

Hendriks et al investigated the influence of grooved substrates produced by hot embossing thermoplastic substrates (40). This exploited the principle of “capillary filling”, in which fluids that show low contact angles will preferentially fill channels and textured surfaces (figure 11) (41). Although this work has not explored the ultimate resolution of the method, lines with widths $\approx 5 \mu\text{m}$ were produced with inkjet drops of diameter $> 100 \mu\text{m}$. All these methods that exploit topological or surface energy variation to direct the flow of fluids are not immune to instability, particularly dynamic instabilities as reported by Duineveld on planar surfaces (32). Pfohl discusses this and points out that if two liquid drops are connected by a microchannel, differences in Laplace pressure will drive fluid flow (41), the same driving force as modelled by Duineveld. Thus, although finer lines can be printed than through simple droplet overlap on planar surfaces, other instabilities may remain.

Interactions with Porous Substrates and Drop Infiltration

An important application of inkjet printing in materials fabrication is the printing of a binder phase into a particle bed in order to fabricate 3-dimensional objects (5). For this application there is a competition between spreading and infiltration processes as the drop impacts on the porous surface. These processes were studied by Holman et al (42), who used a simple model for the infiltration of discrete fluid droplets developed by Denesuk et al (43; 44). This model showed that for droplets of the size produced by inkjet printing, infiltration times were in the range 100 – 500 ms, which is significantly greater than the time scales for impact driven and capillary spreading. Wang et al developed this analysis further by measuring the timescale for chemical reactions between an infiltrating fluid and a powder bed (45). They were able to

demonstrate that this occurred at still longer timescales allowing the formation of solid objects by 3-dimensional printing to be considered as three sequential processes of drop spreading, infiltration followed by reaction.

Given the separation of the spreading and infiltration processes in the time domain, the previous discussion on printed line stability and achievable resolution for printing liquid beads on planar substrates should apply to printing on powder beds.

DROP SOLIDIFICATION AND DEPOSIT SHAPE

The transition from a liquid deposit to the final desired solid material is the final step in the printing process. This transformation will almost always be accompanied by a reduction in volume. When solidification occurs by solute evaporation the volume change may be particularly great because, in order to maintain viscosity within a regime suitable for printing, only dilute solutions of long chain polymers and low volumes of particles in suspension are normally printable.

The mechanisms of solid formation through evaporation from a solution is of particular importance in a number of applications of inkjet printing of conducting and semiconducting polymers, and also printing of metal and ceramic nanoparticle suspensions. Solute distribution during drying can strongly influence the shape of a printed drop through the well known “coffee stain” effect when solute strongly segregates to the initial contact line (29; 46; 47). This phenomenon was explained by Deegan, who observed that the rate of solvent evaporation is greatest towards the contact line because of easy vapour transport in the surrounding “dry” substrate. Thus

precipitation occurs first at the contact line and because this deposit will pin the contact line, fluid flow will occur from the centre of the drop to replace the evaporating fluid from close to the contact line. This peripheral flow continuously feeds the solidification at the contact line and the final deposit will show a characteristic ring where the solute has segregated during the drying process. This phenomenon is very important in controlling the shape of inkjet printed drops and also occurs during the drying of liquid beads to result in a characteristic dual ridged line profile after solidification (figure 12).

Deegan solved for the evaporation flux of solvent as a function of radial distance r from the centre of a droplet of contact radius R (29), to find

$$J(r) \propto (R-r)^{-\lambda} \quad 7a.$$

with
$$\lambda = (\pi - 2\theta_{rec}) / (2\pi - 2\theta_{rec}) \quad 7b,$$

where θ_{rec} is the receding contact angle. For fluidphilic surfaces ($\theta_{rec} \ll \pi/2$), λ is positive and thus the flux increases rapidly as we approach the drop edge or contact line. For the case of a pinned contact line, the resulting compensating outward flow of liquid increases as θ_{rec} decreases. Petsi and Burganis (48) solved the equations for the case of a cylindrical section liquid bead and found a similar trend in flow behaviour with contact angle.

Mechanisms to reduce coffee staining chiefly concern methods of modifying the driving force for fluid flow during the drying process. The enhanced evaporation at

the edge of a spread drop occurs because of the large dry substrate surrounding it, this provides rapid vapour transport at the contact line. If the environment around the drying drop has an enhanced vapour pressure, this will reduce the difference in evaporation rates across the drop and will reduce the coffee stain. However, this will reduce the overall drying rate of the deposit and may be difficult to engineer in practice. Soltman and Subramanian observed that PEDOT solutions printed onto a cooled substrate showed reduced coffee staining (34). Heat transfer through the drop is faster towards the edge of the drop where it is thinner and this will generate a radial temperature profile with enhanced evaporation at the drop centre to counter that at the drop edge. An alternative method is to use a more complex solvent composition that contains fluids of different vapour pressure. The higher vapour pressure component will show a greater evaporation flux and this will set up radial concentration gradients in the drying drop. With a suitable choice of fluids this can be used to generate surface tension gradients that induce Marangoni flows to counteract the evaporation driven flow to the drop edge (49; 50). A final mechanism to reduce coffee staining is to impede fluid flow within the drop. This can be easily achieved by inducing a phase change other than through solvent depletion. Wax droplets filled with ceramic powders rapidly solidify on impact with a substrate and no significant segregation of the solid has been seen (6; 51). A similar strategy was used by van den Berg et al, who used a thermoreversible gel that solidified on impacting with a heated substrate (52); this ink displayed coffee staining after printing on a low temperature substrate but with a higher temperature experiment coffee staining was eliminated by the fluid gelling rapidly, even though evaporation of solute occurred at a greater rate.

The majority of work on inkjet printing reported in the literature has concentrated on printing 2-dimensional patterns with limited 3-dimensional capability through overprinting (e.g. for polymer semiconducting device fabrication). However, 3-dimensional objects have been fabricated through inkjet printing for many years, not through the direct printing and solidification of fluids but through the printing of a binder phase onto a powder bed (5). Although commercially successful, printing onto a powder bed is cannot be truly considered 3-dimensional fabrication through inkjet printing, which we define as the fabrication of solid objects through the overprinting of liquid drops. A major limitation in 3-dimensional printing has been the relatively low aspect ratio of a spread drop on a substrate, which after drying and solvent removal may have a height $< 1\text{ }\mu\text{m}$. Realistic 3-dimensional printing of solid objects from ceramics has only been achieved with the development of highly fluid ceramic suspensions with very high solid loading (6; 50; 53-55). With 3-dimensional printing the requirement for accurate placement of drops is paramount to ensure that objects are efficiently built in the z -direction. Evans has demonstrated very high aspect ratio features and thin walled objects but to achieve this, the minimum feature width was defined by two drops and thus a reduced x - y plane resolution penalty is incurred (55).

FUTURE CHALLENGES

It would be fair to state that the challenge that is facing the use of inkjet printing for applications in advanced materials applications is resolution. The resolution of any printed object is clearly limited by the volume of the ejected drop. At present the limiting droplet size is approximately 1 picolitre, or a diameter of around $12\text{ }\mu\text{m}$. Although smaller liquid droplets can be generated by other technologies (e.g.

electrostatic droplet ejection from a Taylor cone), it is unlikely that much smaller droplets will be available from inkjet printheads in the near future because of the limiting physics of the droplet generation process (11).

It is possible to achieve feature resolution better than the drop size limit through patterning or structuring the substrate before printing (3; 37-40). However the use of patterning effectively changes the advancing contact angle of the liquid and as was demonstrated by the initial work of Davis (30) and its development by Duineveld (32) and Stringer (36), the stability of liquid lines is critically dependent on the behaviour of the advancing and receding contact line. These analyses of liquid line stability have been determined for planar homogenous surfaces and it is not clear that they are applicable to the stability of liquid beads confined by topographical or surface energy barriers. These prior studies have been simplified in order to make the problems tractable to analysis. New models need to be developed to identify the minimum feature size achievable through structuring. They should also consider the earlier impact driven stages of drop/substrate interaction rather than just the capillary spreading stage. This is particular important as it is known that the splashing transition is a function of surface roughness (equation 4) (19; 20) and thus the interaction of impact driven flow with structured surfaces must be studied.

The physics of drop drying is also of great importance in the manufacture of structures, with fluid flow and solute distribution strongly influenced by capillary and Marangoni flows (29; 49). In reality drying phenomena are considerably more complex than the limiting condition modelled by Deegan with drying drops breaking free from pinning sites before repining at a smaller contact line radius. Models of fluid

flow during drying have to date chiefly considered simple symmetric structures (29; 46-48). Studies of drying droplets on structured surfaces where contact angles are controlled and/or fixed during evaporation would be a useful addition considering the use of structured surfaces in determining pattern resolution. There are as yet no good models of the drying process that attempt to predict and include Marangoni flows that are formed through the evaporation of solvent mixtures. Such models would be very useful in predicting and controlling “coffee staining” and drying defects. Capillary forces can be considerable during the drying of nanoparticle suspensions and these can be exploited to structure deposits. For example carbon nanotubes show strong orientation dependence on location within drying drops (56). Strong fluid flows are also expected when surface energy or surface topography patterning is used to define fluid location on a surface. The influence of these flows in concert with drying induced flows needs further investigation, particularly if they are used to structure and organize particle suspensions.

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Figure Captions

Figure 1 Schematic diagram showing the principles of operation of a continuous inkjet printer (CIJ).

Figure 2 Schematic diagram showing the principles of operation of drop-on-demand inkjet printing systems. Drops are ejected by a pressure pulse generated in a fluid filled cavity behind the printing orifice. This pressure pulse can be generated by: a) a vapour pocket or bubble generated by a thin film heater (thermal inkjet), b) a mechanical actuation from a piezoelectric transducer (piezoelectric inkjet).

Figure 3 High speed photographic image showing three drops ejected from a DOD inkjet printer at different stages of drop formation. The drop forms from a single ejected liquid column which rapidly forms a leading drop followed by an elongated thin liquid tail. The tail is seen to break up into a trail of satellite droplets behind the primary drop. Reproduced with permission from reference [11].

Figure 4 Equations 2 – 4 and the range of $Z = l/Oh$ that allows stable printing can be plotted in a co-ordinate system defined by the Reynold's and Weber number to illustrate the regime of fluid properties where DOD inkjet printing is possible.

Figure 5 Parameter space defined by axes of Ohnesorge and Weber numbers showing the driving force for initial drop spreading after impact. The conditions for DOD inkjet printing are shaded indicating that initial drop behaviour is described by inertial or impact forces. Drawn following the schematic diagram of Schiaffin and Sonin (25).

Figure 6 Schematic illustration of the sequence of events that occur after droplet impact on a substrate. Initial impact is followed by a series of damped oscillations before capillary driven flow occurs. Illustration provided by Dr. H.K. Hsiao, Institute of Manufacturing, University of Cambridge, UK.

Figure 7 A liquid bead can form when a line of spread drops coalesce: a) drop spacing is too large for drop coalescence, b) initial coalescence leads to irregular sided liquid bead, c) after sufficient overlap a parallel sided bead occurs, d) if the drop spacing is too small a bulging instability forms, the critical spacing is a function of the printhead traverse speed relative to the substrate.

Figure 8. Stable, parallel side liquid beads are bound by two stability criteria, which can be represented in a parameter space bound by a function of the drop spacing and contact angle, $g(p^*, \theta)$ and a dimensionless printhead traverse velocity U_T^* . For a given contact angle there is a maximum droplet spacing above which the bead shows regular undulations (note that $g(p^*, \theta)$ is inversely related to the drop spacing). There is also a minimum droplet spacing, which is a function of inkjet traverse speed, below which a dynamic instability leads to regular bulges on a continuous constant width bead (36).

Figure 9 Fabrication of architectures by inkjet printing with dimensions smaller than a spread drop: a) droplet spread to its equilibrium configuration on a substrate, b) the presence of a fluidophobic stripe will arrest spreading, c) combination of two arrested drops defines the channel width for an all polymer printed transistor (3).

Figure 10 Fluid flow from dewetting can also be exploited to fabricate channels much smaller than drop dimensions: a) fluid drop is printed onto a fluidphilic substrate above a fluidphobic stripe; b) fluid flow within the drop is driven by dewetting energetics; c) final structure results in the fluid drop dividing into two drops separated by the narrow fluidphobic stripe; d) PEDOT solution drop is printed onto a solidified PEDOT structure that has been plasma treated to generate a fluidphobic surface; e) the second drop is driven from the surface of the initial drop by dewetting; two drops are separated by a narrow region after solidification.

Figure 11 If a channel is cut or moulded into a fluidphilic surface the energetics of wetting will drive the fluid along the channel if a drop is deposited on it.

Figure 12 Observations of coffee staining from printed nanoparticle silver ink (image reproduced from ref. 33): a) Interferometric image of a track formed from the drying of a liquid bead showing distinct ridges at the edges that have formed by fluid flow during drying; b) Two line profiles across the track showing the variation in height across the track.

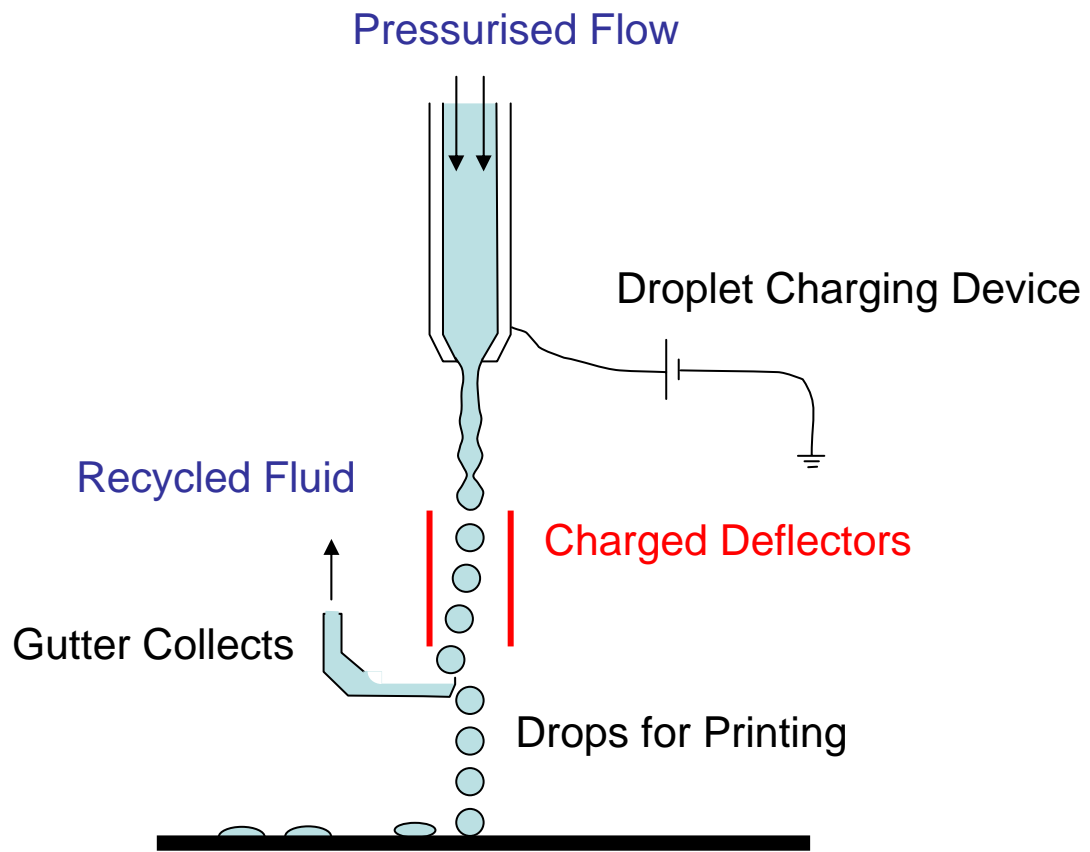


Figure 1

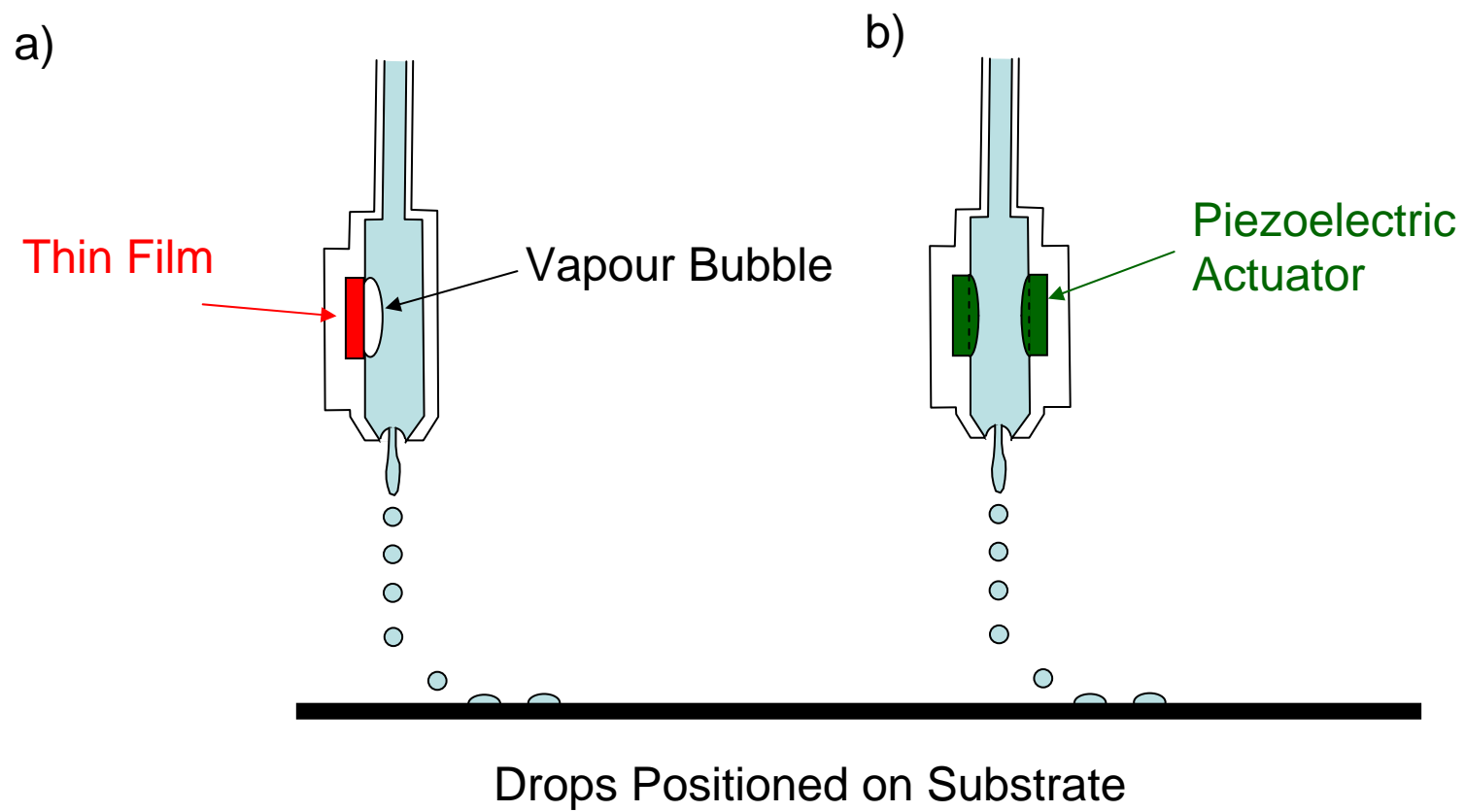


Figure 2

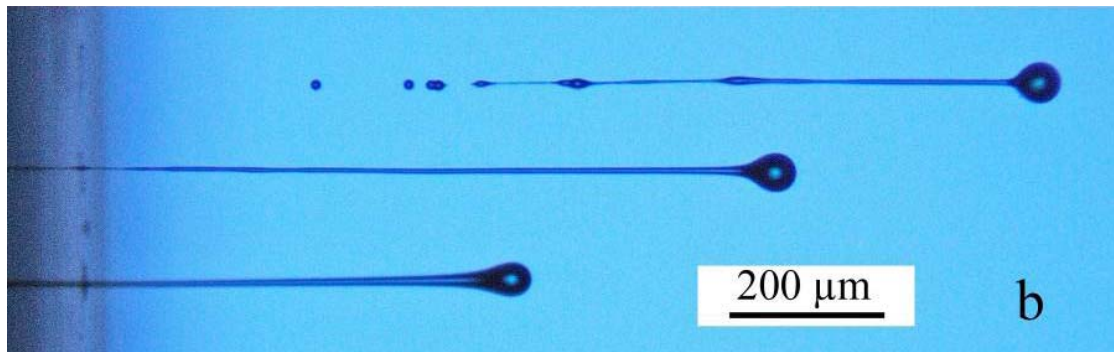


Figure 3

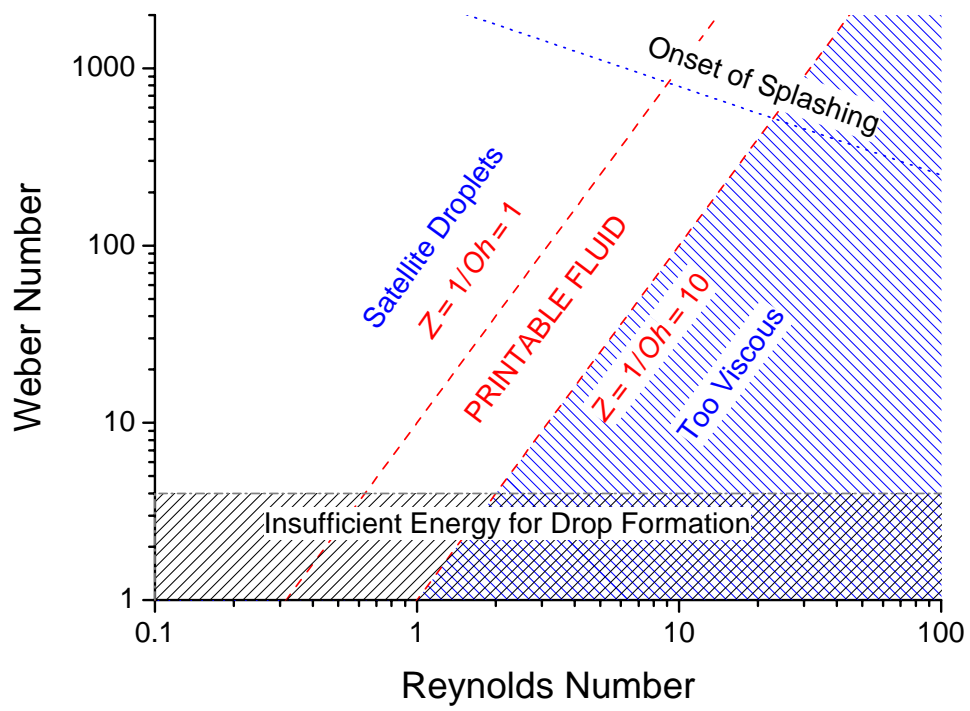


Figure 4

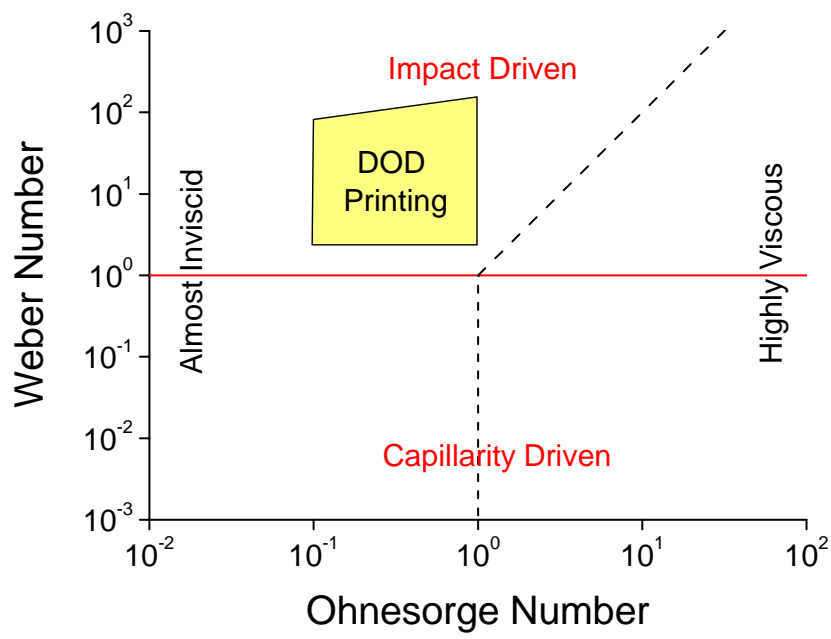


Figure 5

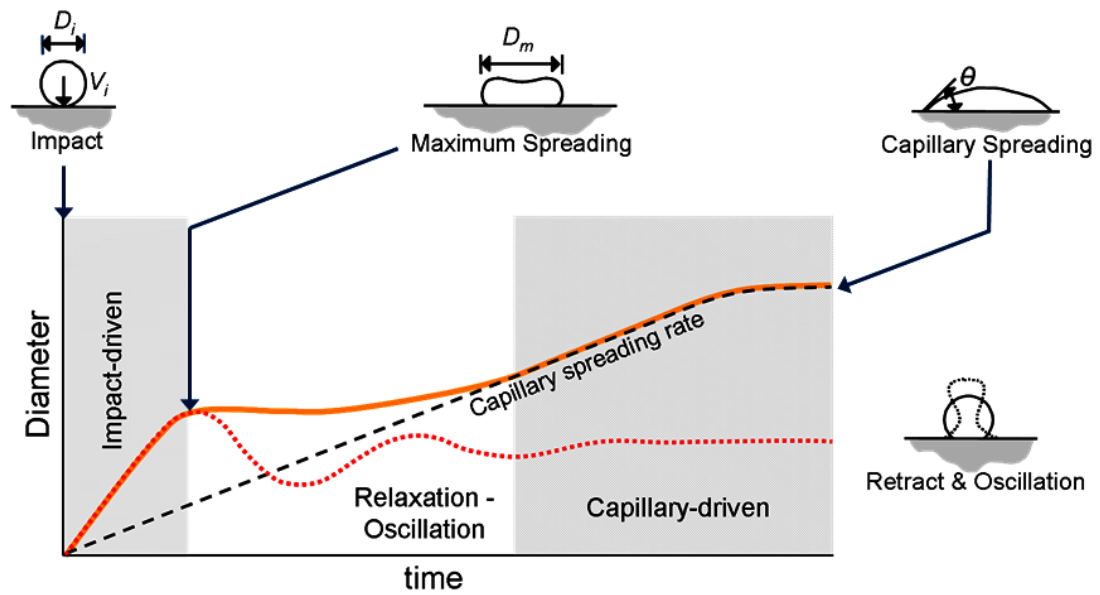


Figure 6

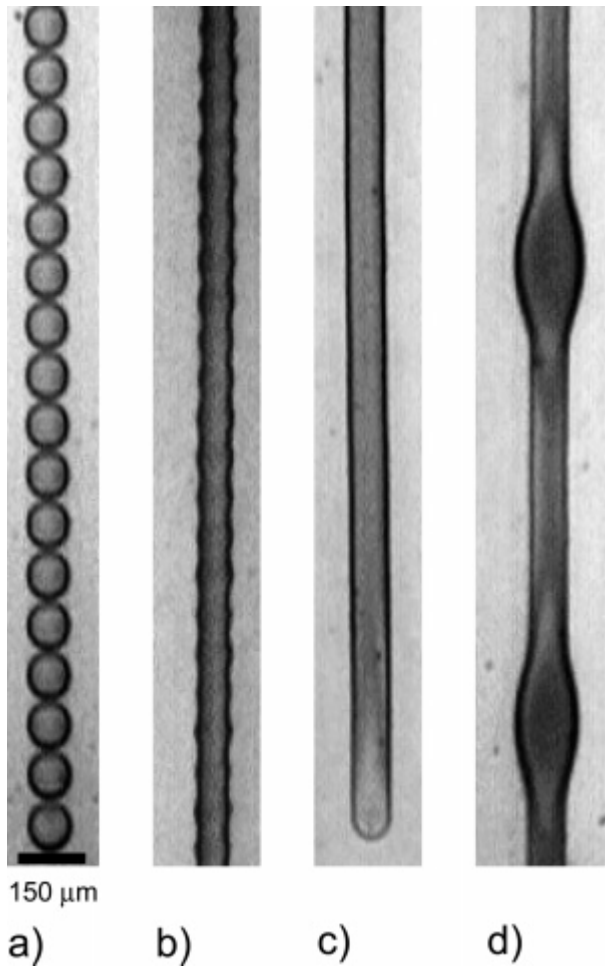


Figure 7

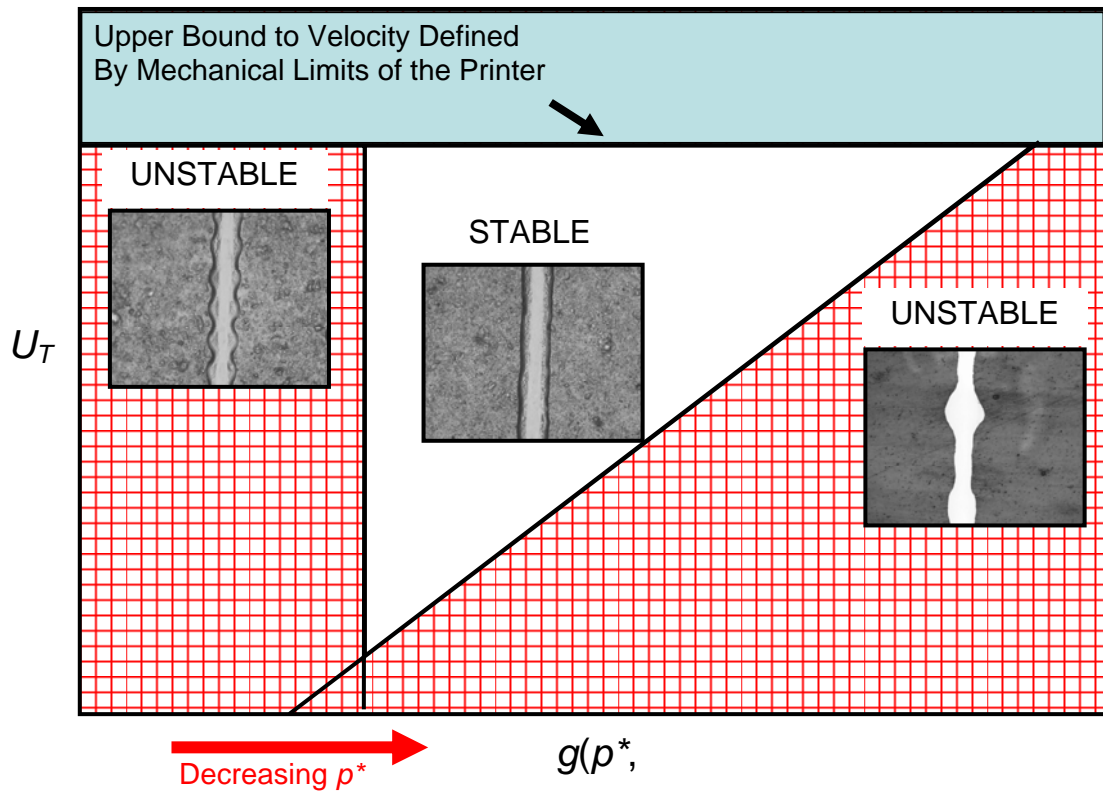
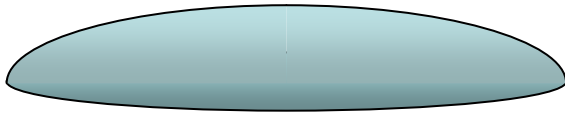
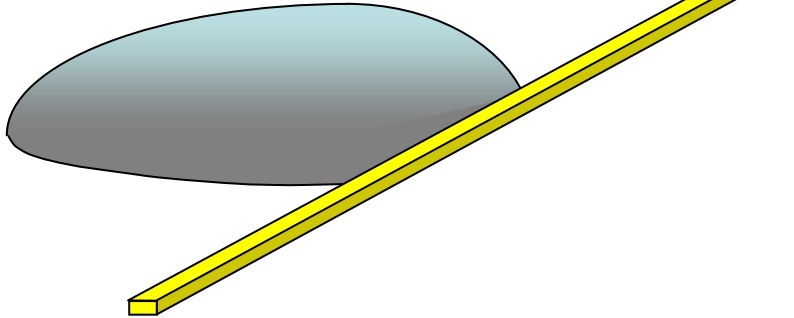


Figure 8

a)



b)



c)

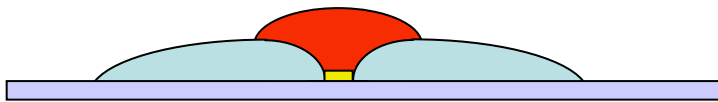


Figure 9

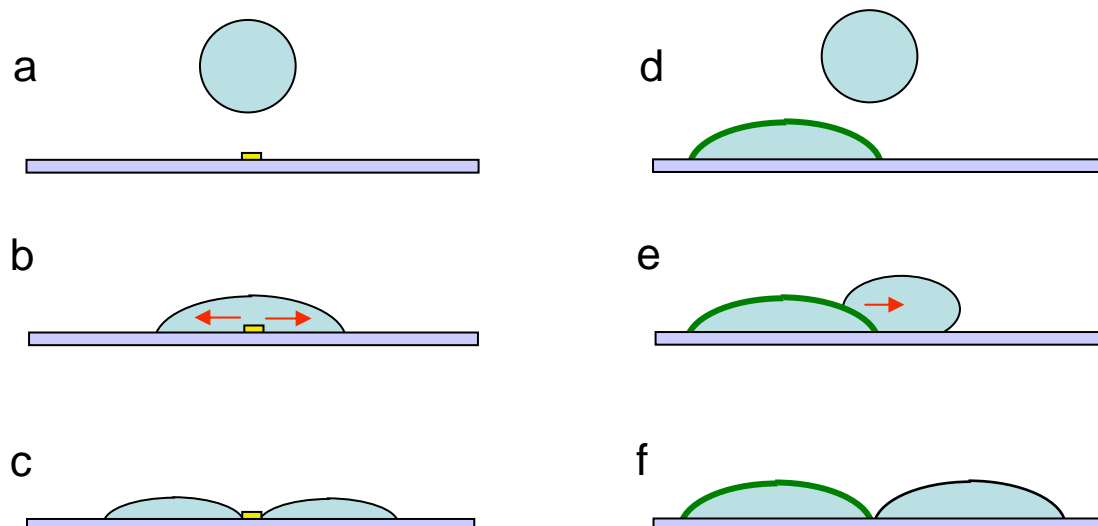


Figure 10

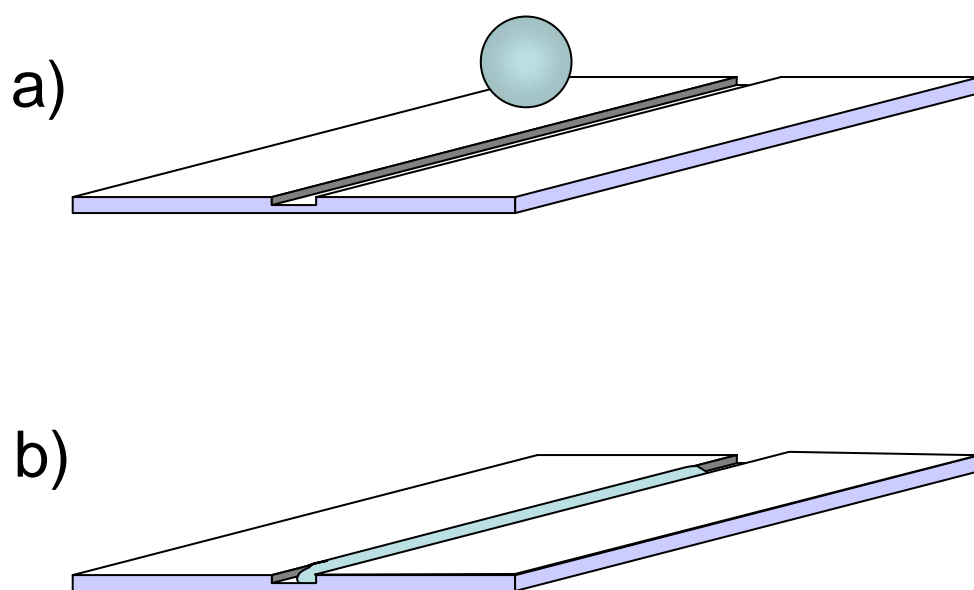


Figure 11

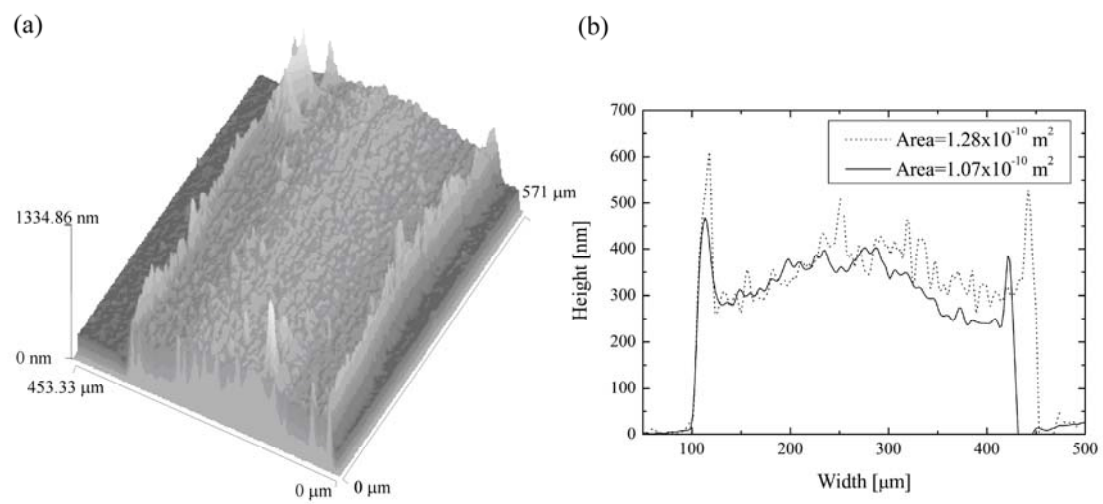


Figure 12