Shape and surface texture of molten droplets deposited on cold surfaces

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1. Introduction

Inkjet printing, a technology for translating signals from a computer into text and images onto recording media such as paper, has gone through extensive development since 1970’s. The inkjet printing process consists of two steps, first generating then depositing small ink droplets. Most inkjet printers using aqueous inks deposited directly on paper. Despite the popularity and widespread use of aqueous inks, their print quality is not very good because of the difficulty in controlling spread of ink droplets on paper. An alternative method, which provides good print quality regardless of the type of print medium, is Solid Ink Jet (SIJ) printing technology [1].

Fig. 1A schematically shows the design of a SIJ printer, which uses solid ink [2] and has a piezoelectric drop-on-demand (DOD) printhead [3] and an intermediate drum [4]. Solid ink (also called hot melt ink or phase change ink) is a mixture of crystalline and amorphous waxes and pigment or dye, which is solid at room temperature. It is melted and maintained at an elevated temperature in printhead so that it can be ejected as a liquid jet during printing, which breaks up into droplets. In SIJ systems, droplets first land and solidify on an intermediate drum to form ink dots. Fig. 1B shows an example of a primary color, formed by drops of cyan ink, and a secondary color, formed by blending drops of magenta and yellow ink. The drum is then rolled over a sheet of paper to which the ink dots are flattened and clung, thus transferring the entire image onto the paper (Fig. 1C). Viewed from afar, these ink dots appear to form solid blocks of color (Fig. 1D). The number density of the dots represents the print resolution, which is usually quantified in dpi (dots per inch). Because the image is first constituted on a drum, rather than directly on paper, SIJ image quality is much less dependent on the nature of the print medium than are water-based inkjet processes.

Many imaging and optical processes use inkjet printing to deposit droplets of material, including fabrication of color filters for flat panel displays [5], multicolor polymer light emitting diodes (PLED) [6] and microlens arrays [7]. These processes use different droplet materials, and the imaging quality and optical properties depend on the characteristics of droplet deposition. One important characteristic is the spread diameter of droplets after impact. Many experimental studies [8–12] have been conducted to study the impact dynamics of droplets, while...
analytical models were developed to predict the spread of droplets \[13–15\]. However, little attention has been paid to the surface characteristics of droplets after impact and solidification.

Solidification in different processes can alter the surface morphology and roughness. For example, the surface of paraffin wax cast against various solid surfaces shows different morphologies \[16\]. In our tests, we observe that different surface textures can be formed on the surface of ink droplets when the droplets impact and solidify on solid surfaces under varied conditions. The surface texture can alter the optical properties of materials, such as light scattering \[17\], optical absorptivity \[18\] and transmittance \[19\]. In addition to optical properties, the surface texture affects the mechanical properties of deposited materials. For example, the surface texture is important in determining interfacial properties between two solid surfaces, such as thermal contact resistance \[20\], sliding friction \[21\] and adhesion \[22\].

This paper presents a study of the deposition of molten ink droplets on solid surfaces. The focus is on the texture formed on the surface of the droplets after they impact and solidify on the solid surfaces. The study aims to correlate the observed surface textures with deposition conditions.

2. Experimental method

Most tests were done using ColorStix 8200 (Xerox Corporation, Rochester, NY), a commonly used commercial solid ink. One set of tests was carried out using Luwax E (BASF, Ludwigshafen, Germany), which is one of the crystalline components in ColorStix 8200. Unless indicated otherwise, the results presented are for ColorStix 8200. Fig. 2 shows the viscosity \((\mu)\) and surface tension \((\sigma)\) of ColorStix 8200 and viscosity of Luwax E as a function of temperature. The solidus and liquidus temperatures of ColorStix 8200 are 60 °C and 115 °C. Other properties of ColorStix 8200 are density \(\rho=820\text{ kg/m}^3\) and thermal diffusivity \(\alpha=9.7561\times10^{-8}\text{ m}^2/\text{s}\). A Phaser 860 printhead (Xerox Corporation, Rochester, NY), maintained at an elevated temperature and driven by a pulsed signal was used as droplet generator to eject ink droplets. By applying an electric pulse, the piezo ceramic element generates a pulsed force on the liquid chamber, which pushes out a liquid jet through small orifices (~20 µm diameter). The pulsed jet quickly forms a spherical drop due to the action of surface tension forces.

To simulate the deposition of ink droplets on the intermediate drum, we have conducted a series of experiments on the deposition of ink droplets on solid surfaces under varied conditions. The parameters varied include printhead temperature \((T_j): 140 \text{ °C and 145 °C})\), substrate temperature \((T_s): \text{from 60 °C to 80 °C in increments of 5 °C})\), gap distance between printhead and substrate surface \((L): 0.5 \text{ mm and 1 mm})\), and type of substrate surface (uncoated aluminum surface, viton-coated surface or oil-coated surface). The initial diameter of the droplet \((D)\) is measured to be 39 µm, and droplet velocity is 2.81 m/s at \(L=0.5 \text{ mm}\) and 2.56 m/s at \(L=1 \text{ mm}\). The temperature of the droplet at the instant of impact is calculated by considering its in-flight cooling, and is found to decrease by ~4 °C after traveling 0.5 mm and by ~8 °C after traveling 1 mm.
Three types of substrate surfaces are used. The first is a bare aluminum plate with average roughness 0.05 μm, which is referred to as the uncoated substrate surface. The second is an aluminum plate coated with 1.8 μm thick layer of viton (DuPont Corporation, Wilmington, DE), the proprietary name of a fluoroelastomer that is heat resistant to 200 °C and can be applied to drums in printers to reduce adhesion of wax droplets. The viton coating does not measurably change surface roughness. The third is an oil-coated substrate surface, which is prepared by wiping a bare aluminum surface with a cloth soaked in silicone oil, leaving an oil layer approximately 1 μm thick on the surface. Applying coating to substrate surface would change wettability and thermal resistance of the surface. The wettability is evaluated by measuring the equilibrium contact angles of small molten ink droplets sitting on the three types of substrate surfaces held at 120 °C. Measurements showed that the equilibrium contact angle is 1° for the uncoated substrate surface, 12° for the viton-coated substrate surface and 28° for the oil-coated substrate surface. Heat transfer analysis shows that the thermal resistances of the viton and oil layers are two orders of magnitude lower than that of ink droplets, implying that they would have negligible thermal effect.

After impact, droplets are allowed to anneal for 5 min at the substrate temperature before naturally cooling down to room temperature. No visible change of shape is observed during this cooling process. Scanning electron microscope (SEM) is used to take pictures of solidified ink droplets. Care is taken to avoid any phase change of ink droplets during the sample preparation stages for SEM visualization.

3. Experimental results

When a droplet of molten ink impacts on the substrate surface, which is at a lower temperature than the molten ink, it spreads out and may retract, producing a wax bump (or ink dot) sticking to the substrate surface. The process of impact can be divided into two stages: spreading driven by inertial forces and subsequent oscillation driven by surface tension forces. Both stages involve viscous dissipation and solidification.

For a liquid droplet impacting on a solid surface without phase change, the final shape of the droplet is determined by its equilibrium state depending on the properties of liquid and substrate materials and temperature [13, 23]. Deposition of small molten droplets on cold solid surfaces, which includes solidification, is a complex fluid/thermal problem. The final shape of droplets is not determined by fluid flow alone, but depends on the thermal histories of droplets during impact since they may freeze before reaching their equilibrium shape. The coupling between solidification and fluid dynamics can lead to a variety of solidified shapes and surface textures of deposited droplets, and there are no simple models to predict what these will be. The final shape can be characterized by droplet base diameter, apparent contact angle and height.

3.1. Final shape

Fig. 3 shows the effect of varying the substrate surface, printhead to substrate distance L, and substrate temperatures T_s on final droplet shape. The final shape of solidified droplets is sensitive to substrate temperature. Fig. 3A shows droplets ejected with T_s = 140 °C and L = 1 mm on the uncoated substrate surface. As the substrate temperature increases, they spread out to larger extents, so that the height and contact angle decrease and base diameter increases. In Fig. 3B the substrate surface is held closer to the printhead (L = 0.5 mm) and larger base diameters and smaller contact angles are formed. The final shape is mainly determined by the arrest of contact line during the impact process. Droplets impacting at L = 1 mm have a lower initial temperature (implying more solidification and viscous effects) and a lower velocity (lower inertial forces) than those at L = 0.5 mm. The contact line of droplets impacting at low substrate temperatures (T_s < 70 °C) with L = 1 mm seems to have been arrested during the spreading process. This is deduced from the regular peripheries observed on the SEM.

![Fig. 3. Scanning electron microscopic (SEM) images of ink droplets deposited on substrate surfaces at varied substrate temperatures (T_s: from 60 °C to 80 °C). (A) Droplets deposited on the uncoated substrate surface with T_s = 140 °C and L = 1 mm. (B) Droplets deposited on the uncoated substrate surface with T_s = 140 °C and L = 0.5 mm. (C) Droplets deposited on the uncoated substrate surface with T_s = 145 °C and L = 0.5 mm. (D) Droplets deposited on the viton-coated substrate surface with T_s = 140 °C and L = 0.5 mm. Note: comparing (A) and (B) shows the effect of L; comparing (B) and (C) shows the effect of T_s; comparing (B) and (D) shows the effect of substrate surface.](image-url)
images and from the increasing base diameter with substrate temperature (Fig. 3A). Due to a higher temperature and higher velocity for droplets with $L=0.5 \text{ mm}$, the arrest of contact line at low substrate temperatures ($T_s<70^\circ \text{C}$) occurs after droplets reach maximum spread, thereby forming larger spread diameters and smaller contact angles (Fig. 3B). At high substrate temperature ($T_s=80^\circ \text{C}$), the contact lines are arrested at a later stage of impact, and the droplets, therefore, have enough time to approach equilibrium before solidifying. This results in similar final shapes at $T_s=80^\circ \text{C}$ for $L=0.5 \text{ mm}$ and $1 \text{ mm}$.

Increasing printhead temperature ($T_j$; from 140 °C to 145 °C) also changes the final shape (Fig. 3, C in comparison to B). The final shapes formed with $T_j=145^\circ \text{C}$ appear to be two-tiered, with a rounder central section surrounded by a wider “skirt” (Fig. 3C). The skirt becomes smaller as $T_s$ increases. Droplets ejected at 145 °C initially have higher temperature than those at 140 °C. Therefore, they have more time to spread to larger diameters and retract due to surface tension forces. The skirt represents the region that is brought to rest by cooling, while the cap on top remains fluid enough to reach an equilibrium shape before solidifying.

Fig. 3D shows the final shapes of droplets ejected at 140 °C and landing on the viton-coated substrate surface held at $L=0.5 \text{ mm}$. The effect of substrate surface can be seen through comparing the images in columns D and B. Smaller spread diameters and larger contact angles are formed on the viton-coated substrate surface. Earlier studies showed that the dynamic contact angle increases with equilibrium contact angle [24] and that the maximum spread of droplet decreases as the dynamic contact angle increases [12,14,25]. The droplets impacting on the viton-coated substrate surface (which has poor wettability, with an equilibrium contact angle of 12°) experience less deformation than those impacting on the uncoated substrate surface (with good wettability and an equilibrium contact angle of 1°), thus causing smaller spread diameters and larger contact angles.

Fig. 4. Top view SEM images showing surface textures of ink droplets deposited at $L=0.5 \text{ mm}$. Three types of substrate surfaces are used: uncoated substrate surface (A, D), viton-coated substrate surface (B), oil-coated substrate surface (C). Two printhead temperatures $T_j$ are used: 140 °C (A to C), 145 °C (D). The effect of $L$ can be found by comparing this figure with Fig. 5.
3.2. Surface texture

Droplets impacting under varied deposition conditions can also generate dramatically different surface textures. This can be observed from SEM images taken from the top, as shown in Figs. 4 and 5. Droplets deposited at $L = 0.5$ mm (Fig. 4) have irregular peripheries and rough surface textures, while those at $L = 1$ mm (Fig. 5) form round and smooth surfaces. The effect of the distance $L$ diminishes at high substrate temperature (compare the images for $T_s = 80$ °C in Figs. 4 and 5).

Fig. 4 shows SEM images of droplets deposited on different substrate surfaces held at $L = 0.5$ mm from the printhead. Fig. 4A–C shows droplets ejected at 140 °C and impacting on the uncoated substrate surface (Fig. 4A), viton-coated substrate surface (Fig. 4B) and oil-coated substrate surface (Fig. 4C). Comparison between columns A, B and C shows clear variations of surface texture with the type of substrate surface. The surface texture also varies with the substrate temperature.

For any specific substrate surface, similar textures are formed for low substrate temperatures ($T_s$: 60 °C to 70 °C). The texture becomes uniform across the droplet surface at $T_s = 75$ °C, and smooth at $T_s = 80$ °C. At $T_s = 80$ °C, the effect of substrate surface appears to be small. Column D in Fig. 4 shows the droplets ejected at a higher temperature ($T_j = 145$ °C) and landing on the uncoated substrate surface. Comparison between columns A and D shows the significant effect that increasing the initial temperature of droplets has.

For droplets traveling a longer distance ($L = 1$ mm) before impacting on the substrate surfaces, smooth surface textures are formed (Fig. 5). Columns A, B, C in Fig. 5 show the droplets deposited with $T_j = 140$ °C on the uncoated, viton-coated and oil-coated substrate surfaces, respectively, while column D shows the droplets deposited with $T_j = 145$ °C on the uncoated substrate surface. Very smooth droplet surfaces are formed for low substrate temperatures ($T_s < 70$ °C), but become relatively rougher for high substrate temperatures ($T_s$: 75 °C and 80 °C).

Fig. 5. Top view SEM images showing surface textures of ink droplets deposited at $L = 1$ mm. Three types of substrate surfaces are used: uncoated substrate surface (A, D), viton-coated substrate surface (B), oil-coated substrate surface (C). Two printhead temperatures $T_j$ are used: 140 °C (A to C), 145 °C (D). The effect of $L$ can be shown by comparing this figure with Fig. 4.
Although the effect of substrate surface is still visible (compare column A–C in Fig. 5), it becomes less appreciable than it is at \( L = 0.5 \text{ mm} \), as shown in Fig. 4. Increasing the initial temperature of droplets from 140 °C to 145 °C creates relatively rough textures (compare columns A and D in Fig. 5).

For molten droplets deposited on cold substrate surfaces, three transient physical processes precede the formation of final shapes and surface textures: viscous damping, oscillation and solidification. To compare the effects of the processes, we consider two non-dimensional numbers. Prandtl number, defined as

\[
Pr = \frac{\mu}{\rho x} \quad (1)
\]

that compares the time scales for viscous damping and thermal diffusion. Using the properties of ColorStix 8200 at 140 °C, \( Pr \approx 130 \) in our tests, showing that viscous effects are much more important than solidification. The other important non-dimensional number is the Ohnesorge number, defined as

\[
Oh = \frac{\mu}{\sqrt{\rho Da}} \quad (2)
\]

The Ohnesorge number compares time scales for oscillation and viscous damping, and \( Oh \approx 0.4 \) in our tests.

The analysis above supports our earlier interpretation of the images in Fig. 3. The time scales for viscous damping and oscillation are of the same order of magnitude, so both processes contribute to the formation of the observed surface textures. It should be noted that since the viscosity of ColorStix 8200 changes by orders of magnitude as its temperature drops below \( \approx 90 \text{ °C} \) (Fig. 2), viscous damping is very sensitive to the transient temperature of the droplet during the impact process. It should also be noted that the impact velocity determines the oscillation amplitude, which is not considered in the non-dimensional analysis in Eq. (2). Due to the lower impact temperature and lower velocity of droplets with \( L = 1 \text{ mm} \), droplet oscillations are damped out quickly, and smooth surface textures, therefore, are formed (Fig. 5). The droplets impacting at \( L = 0.5 \text{ mm} \) have higher temperature and higher velocity at the instant of impact, implying less viscous damping and stronger oscillation during the impact process. The strong interaction between viscous damping and oscillation causes rough surface textures (Fig. 4). This also explains the more appreciable effect of substrate surface on surface texture for \( L = 0.5 \text{ mm} \) (compare Figs. 4 and 5).

Figures 4 and 5 also show that the surface textures of the droplets deposited on the uncoated substrate surface for \( L = 0.5 \text{ mm} \) (column A) and \( L = 1 \text{ mm} \) (column B) are different. Hemi-spherical shapes are formed at low substrate temperatures (\( T_s \); from 60 °C to 70 °C), and much larger splats are formed (<5 µm thick) at high substrate temperatures (\( T_s \); 75 °C, 80 °C). As shown in Fig. 6, the surface texture of the Luwax droplets tends to be sensitive to substrate temperature but does not change much with distance \( L \). The surface textures formed at

\[ 80^\circ C \]

are rough, while the surface textures formed at

\[ 60^\circ C \]

are smooth.

The long radial fingers around droplet peripheries shown in Fig. 5D are caused by the coupling of flow dynamics and solidification. There are no fingers at \( T_s = 60 \text{ °C} \) and very few at \( T_s = 80 \text{ °C} \). When a molten droplet lands on a cold surface, it first begins to freeze around its periphery. If the outward flowing liquid has sufficient momentum, it jets over this solid rim, becomes unstable, and forms fingers [26,27]. At the lowest substrate temperature (\( T_s = 80 \text{ °C} \)), the ink viscosity increases and prevents the formation of fingers; at the highest substrate temperature (\( T_s = 80 \text{ °C} \)), solidification around the rim is delayed, minimizing the number of fingers.

The surface textures observed from Figs. 4 and 5 also depend on the properties of the droplet material, since crystallization of wax is also an important factor. Complex materials such as ColorStix 8200 contain both crystalline and amorphous components, which make the crystallization process very complicated. To reveal the effect of crystallization, we chose one of the crystalline components in ColorStix 8200, Luwax E (BASF, Ludwigshafen, Germany) and used it to repeat the tests shown in Figs. 4A and 5A. Fig. 6 shows SEM images of Luwax droplets deposited on the uncoated substrate surface for \( L = 0.5 \text{ mm} \) (column A) and \( L = 1 \text{ mm} \) (column B). Hemispherical shapes are formed at low substrate temperatures (\( T_s \); from 60 °C to 70 °C), and much larger splats are formed (<5 µm thick) at high substrate temperatures (\( T_s \); 75 °C, 80 °C).

The surface texture of the Luwax droplets tends to be sensitive to substrate temperature but does not change much with distance \( L \). The surface textures formed at
high substrate temperatures ($T_s$: 70 °C to 80 °C) appear in the temperature range where viscosity changes rapidly (Fig. 2), due to high nucleation and crystallization rates at these temperatures [28]. The results for Luwax droplets show a strong dependence of surface texture on substrate temperature.

4. Conclusions

Experiments have been carried out to investigate the deposition of small molten ink droplets on cold solid surfaces. We observe that the final shape and surface texture of the droplets are strongly dependent on the deposition conditions including substrate temperature, printhead temperature, gap distance between printhead and substrate, and type of substrate surface. The observed changes in texture are explained considering the physical processes involved in droplet deposition, which include solidification, viscous damping and oscillation. Our results for crystalline wax show that droplet material is also a major factor affecting the surface texture, in that the nucleation and crystallization rates are strongly affected by substrate temperature. The observed textural phenomena that occur in solid inkjet printing can also be of importance to many other applications of inkjet printing technology.

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