Kinetics of Wetting by Drops: Theory and Implications to Inkjet Printing

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Abstract

The kinetics of spreading of inkjet drops on substrates is a key factor in determining the rate of printing and its quality. The mechanisms and fundamental aspects of spreading on non-absorbing substrates and in paper are presented. Semi-empirical correlations are shown to be useful in describing the kinetics. Implications to studying inkjet formulations are demonstrated.

Introduction

Inkjet printing is essentially a wetting process. The print quality is determined by the interaction of the ink drops with the substrate and with each other. Since inkjet printing is a dynamic process, and since the required frequency of jetting is increasing with the advancement of this technology, the kinetics of wetting by the ink droplets is a key factor. Therefore, understanding the kinetics of wetting[1-3] on surfaces is essential for designing inkjet systems.

The fundamental understanding of spreading of a liquid on a solid is far from being complete. Most notable is the seeming contradiction between the theory of hydrodynamics that is based on the assumption of no slip (of a liquid) at a solid wall, and the simple, daily observation of rain drops sliding down a window. Much effort has been invested in understanding this fundamental issue, however much is to be done yet. In addition, the system is complicated by the presence of solutes, surfactants, and suspended particles.

Therefore, much of the progress that has been done so far in understanding wetting kinetics is based on empirical observations. There are many factors to take into account. For example, the solid substrate may be absorbing or no-absorbing, it may also be rough or chemically heterogeneous. The liquid may consist of a single component, a solution of a few components, including surfactants, or a suspension. In addition, wetting kinetics is affected by the contact angle, a combined equilibrium property of the liquid-solid, defined as the angle that the liquid makes with the solid surface.[4] When the angle is zero, wetting is referred to as "complete wetting;" for angles higher than zero, the term "partial wetting" is used.

The present paper reviews the main phenomena observed with various systems, presents empirical equations to be used for the kinetics of wetting, and demonstrates their use for inkjet formulations.

Complete Wetting on "Ideal" Surfaces

An ideal surface is defined as a non-absorbing, non-reacting, rigid, smooth, and chemically homogeneous surface. It is obvious that such a surface hardly exists in practice, but some clean, carefully cleaned or coated solid surfaces approximate an ideal surface. Much research work has been done with such "ideal" surfaces, for purposes of fundamental understanding, as a starting point to studying real surfaces.

The kinetics of complete wetting has been well described by the "power law"[2,3] that gives the dependence of the wetted area (area of the drop base), A_w, on time:

$$A_w/V^{2/3} \equiv A = K\tau^n \qquad (1)$$

V is the volume of the drop, which is used to normalize the wetted area based on the drop size, and make the left-hand side of Eq. (1) the dimensionless wetted area, A. τ is the dimensionless time, defined as

$$\tau \equiv \sigma/(\mu V^{1/3})\, t \qquad (2)$$

where σ is the surface tension of the liquid, μ is its viscosity, and t is the time. K and n are coefficients to be empirically determined. The theoretically predicted values of the power, n, in Eq. (1) are within the range of 0.2-0.28. Experimentally obtained values of n are within the range of 0.2-0.29, with some exceptional values of 0.066 and 0.627.[2]

Complete wetting kinetics is strongly affected by the existence of a primary film that spreads ahead of the visible, macroscopic drop.[5] This film is a means of "communication" between the drop and its surrounding. Early observations[6] demonstrated a very vigorous process of "chasing" of one drop by another, followed by major shape changes of the drops, without any macroscopically visible contact between them. This may be of importance to the interaction between adjacent inkjet drops and their final shape.

Another primary-film phenomenon of great potential importance to inkjet printing is the effect of limited size of the substrate. It was found that wetting kinetics on small surfaces is much faster than on large ones.[7] A visual demonstration of this effect is the migration of a spreading drop towards the corner of the substrate. Substrates for inkjet printing are usually large; however the proximity of other drops makes the "effective" substrate size limited. Hence, this effect may be involved in determining the rate of drop spreading.

It is rare in practice to use single-component liquids. Therefore, it is essential to understand wetting by liquid mixtures. The effect of surfactants will be discussed below. At this point, the wetting by solutions of "simple" liquids is described. Most liquids differ from each other in terms of their surface tension and volatility. A well-known example is water and alcohols. Because of the higher volatility of the alcohol (ethanol, for example) its concentration at the edge of the drop diminishes. As a result, the surface tension of the solution near the edge of the drop increases (the aqueous solution is leaner in ethanol) compared with that of the bulk solution.

A gradient of surface tension induces a flow from a region of low surface tension to a region of high surface tension (this phenomenon was discovered by Marangoni and named after him). Thus, flow in this case is enhanced in the direction of the drop edge. A well-known demonstration of the Marangoni effect is given by the marked rise of a liquid film in a glass of wine (of sufficiently high alcohol concentration), leading to "wine tears." The above description may be generalized to say that wetting kinetics is enhanced by the Marangoni effect, when the component of higher volatility is of the lower surface tension.[8] The opposite effect is also observed: wetting kinetics may be strongly diminished if the more volatile component has the higher surface tension.

Wetting by surfactant solutions is a complex process. Surfactants are usually added in order to improve wetting by aqueous inks, because they reduce the surface tension of such inks. However, surfactants may adsorb not only at the ink-air interface, but also at the solid surface. If surfactant molecules are carried by a primary film, the may change the nature of the solid surface ahead of the macroscopic drop.[9] This may lead to a retraction of the drop. In addition, the presence of surfactant may lead to instabilities of the drop edge[9] affecting print quality.

Partial Wetting on "Ideal" Surfaces

The process of partial wetting, until the drop gets to its equilibrium state, usually takes a fraction of a second (strongly depending, among other parameters, on the liquid viscosity). This is in contrast to the process of complete wetting that may last a few seconds and longer. This is probably the reason why the kinetics of partial wetting has been only recently studied.[10]

Based on the shape of the experimental curves for the kinetics of partial wetting, the following empirical equation has been proposed:

$$A/A_f = 1 - \exp\left(-K\tau^n/A_f\right) \qquad (3)$$

Here, A_f is the final dimensionless wetted area (base area of the drop). This equation is referred to as the "exponential power law" (EPL). It is important to notice that Eq. (3) transforms into Eq. (1) for complete wetting. This is so, since for complete wetting $A_f \rightarrow \infty$; therefore, $\exp(-K\tau^n/A_f) \approx 1 - K\tau^n/A_f$. Consequently, $A = K\tau^n$, as in Eq. (1).

The EPL has been used for studying wetting of various inkjet formulations. Significant differences have been found in some cases between the K and n values of various formulations. Of special interest are differences between different colors made with the same basic formulation.

Wetting on Rough Surfaces

Wetting of rough surfaces by drops is characterized by a competition between two processes: wetting in-between the capillary grooves of the roughness, and wetting on top of the surface.[11,12] If the former is the faster process, a visible halo (rim) is formed around the drop. This, obviously, may have implications on print quality and interaction between adjacent drops.

Using drops of PDMS (a polymeric liquid that exists with viscosities varying over orders of magnitude, but with the same surface tension) it was shown that the key factor in this competition is the viscosity. High-viscosity liquids penetrate very slowly in-between the roughness grooves, therefore a halo does not form for such liquids. However, halo formation may be prevalent in cases of wetting of rough surfaces by low-viscosity liquids.

Wetting of Absorbing Surfaces

Wetting of paper surfaces is of major interest for inkjet printing. This process takes place in two stages: (a) penetration of the drop into the paper (actually, into its outer layer), and (b) radial spreading of the wet spot inside the paper. It is mostly the second stage that determines the shape of the drop, hence the print quality.

The rate of spreading of the wet spot was also quantified using a power law,[13]

$$A_s = k\,t^n \qquad (4)$$

where A_s is the area of the wet spot, and k is an empirical coefficient. The power n was found to be about 0.3, which is a surprisingly low value compared with the value of about 0.9 that is expected from theory.[14] At first, it is also surprising that the spot spreads at all, since the liquid may be expected to reach some equilibrium state, once the drop penetration stage is completed.

The mechanism underlying spot spreading was elucidated using a very simple experiment.[15] Liquid was fed into a filter paper from a Petri dish through a very short capillary. As long as the capillary fed the liquid into the paper, the spot expanded according to Eq. (4), with $n \approx 0.9$, as predicted by theory.[14] However, when the capillary was disconnected, the spot continued to grow, but with $n \approx 0.3$, as in the case of a single drop. These observations led to the conclusion that the slow ($n \approx 0.3$) spreading of the spot stems from the finite amount of liquid in it, in contrast to the case an infinite liquid supply that leads to spreading with

$n \approx 0.9$. When the liquid amount is finite, the mechanism of spreading is different: the small pores in the paper draw the liquid from the larger pores, because of the higher capillary pressure difference in them. Thus, the process is not penetration into pores from a liquid reservoir at atmospheric pressure, but transfer of liquid between large pores and small pores, for which the driving pressure difference is much smaller.

Conclusion

The kinetics of wetting is an essential factor in inkjet printing. Its understanding and control may very much affect print quality, especially as the printing speed is required to increase. Much work has been done so far to understand the kinetics of the fundamental wetting processes, however much is yet to be done in order to fully understand wetting phenomena in real inkjet systems.

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Biography

Prof. Marmur has been working on interfacial phenomena for almost thirty years, has published many papers on wetting processes, and has been consulting for major companies. He was also an editor of Reviews in Chemical Engineering, on the advisory committee of J. of Colloid and Interface Science, and is on the advisory committee of J. of Adhesion Science and Technology. Prof. Marmur received at the Technion awards for excellence in teaching and in research.