CHAPTER 1

# *Reactive Inkjet Printing—An Introduction*

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## 1.1 Introduction

'Reactive inkjet (RIJ) printing', or 'reactive inkjet' is a type of inkjet technique whose history in the research literature has been documented for less than ten years. Despite its recent beginnings, it has attracted much attention as a cost-effective and highly controllable method to fabricate patterns, where it elegantly combines the processes of material deposition and chemical reaction. The combination of these two processes creates boundless possibilities for the fabrication of 2-dimensional and indeed 3-dimensional structures whereby it allows functional materials to be synthesized *in situ* at the same time as their final device geometries are patterned.

The concept of micro-dispensation of reactants actually dates back to the 1990s when the first report of a solenoid-based inkjet chemical dispenser, ChemJet, was made for combinatorial library synthesis.[1] Since then, the field has grown from this application to become a combinatorial library synthesis tool for rational coating design, and a tool used for patterning materials directly within devices. Materials that have been reactively printed for direct

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device integration include conjugated polymers, fluorescent quantum dots, metallics and silk. It is the precursors to these materials that are dispensed (*e.g.*, monomer and oxidant) and subsequently react in solution droplets (micro- or pico-litre sized) on a solid support. While performing chemistry in patterned droplets using this printing approach promises high controllability, technical challenges do still remain. Fundamental droplet analysis in terms of size, shape and kinetics must be understood in each application in order to design optimal precursor ink formulations and selection of appropriate print parameters.

A wide spectrum of reactive inks that have been reported allows one to fabricate various patterns that perform different functionalities. In terms of print resolution, RIJ will theoretically have the same resolution as inkjet printing. However, in practice, given the multi-head combinatorial approach often used, maintaining a resolution of single-layer, single-head inkjet printing, is more challenging. Nonetheless, patterning 2D structures at resolutions at the low micron-scale are easily achievable using RIJ.

As this book is concerned with RIJ, it seems prudent that the first chapter introduce to the reader what is meant by this term. By its nature, RIJ requires the use of an inkjet printer, the first chapter will, therefore, survey the various types of inkjet printing (such as piezo and thermal), as well as describing droplet ejection mechanisms and ink considerations. The following chapters will discuss a number of fundamental inkjet areas that will help inform the reader.

The second chapter discusses droplet behaviour from the moment a droplet impacts a surface to where it coalesces with a second or more to form a feature. The various drying phenomena, such as ‘coffee staining’ are discussed, as well as possible phase changes. The third chapter is fascinating; typically, RIJ involves two dissimilar droplets being joined, with their contained reactants meeting to form a product. Chapter 3 discusses how two droplets interact; what is intriguing is the observation that two droplets don’t appear to mix! What this chapter illustrates is the youth of the field of RIJ and that the early focus on applications has now opened up some fascinating physics to explore. The fourth chapter concludes the Fundamentals section with a discussion of the behaviour of high molecular weight polymers in ink. These polymers tend to break apart during jetting which offers the prospect that radical chemistry can be performed.

The third and largest section of the book is given over to a high level overview of many of the application areas that RIJ can be employed in. Alison Lennon illustrates the attraction of using RIJ in metallisation and the production of etchants for use in solar panel manufacture. The use of RIJ to generate HF *in situ* is a particularly compelling example. Ghassan Jabbour and co-authors continue the exploration of RIJ’s use in inorganic chemistry with the synthesis of gold nanoparticles, zinc oxide nanostructures and lead sulphide quantum dots. They begin their chapter by illustrating that RIJ offers organic chemistry applications in their modification of the sheet resistivity of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) by selectively dispensing droplets of aqueous sodium hypochlorite onto the polymer, thereby tailoring the degree of oxidation.

The next two chapters move the focus on to biology with the preparation of silk by RIJ forming the core. The first of this duo looks at the preparation of dental barrier membranes. Here, the degradation rate of silk II can be tuned by RIJ. The second chapter looks at the preparation of Janus-particle like structures, silk micro-rockets, which could be employed in a range of applications such as environmental monitoring, Lab-on-a-Chip diagnostics, and *in vivo* drug delivery.

The final three chapters continue to portray the breadth of application areas where RIJ can make a contribution. Christopher Tuck and colleagues describe the use of RIJ in additive manufacture, whilst Paul Calvert looks at the use of RIJ to form conductive features of either copper or nickel. The use of copper is of particular interest since it is a cheaper alternative to silver. Finally, the focus returns to biology with a discussion of the use of RIJ in the production of alginate- and fibrin-based systems for tissue engineering.

## 1.2 Reactive Inkjet Printing—The Concept

In simple terms, the concept of reactive inkjet printing (RIJ) describes the process where an inkjet printer deposits a droplet of reactant that changes due to a chemical reaction with material on the substrate or with a subsequent printed second reactant (Figure 1.1). Reactive inkjet printing can be used to deposit systems that cannot be deposited in ink form, such as some polyurethanes or to prepare purer forms of systems, such as nanoparticles that no longer require surfactants to stabilise them in suspension.

Inkjet printing is an essential component of RIJ because it produces droplets of uniform, controllable size. The second feature of inkjet is that the produced droplets can be positioned accurately on a substrate in pre-determined locations. The ability to consistently produce droplets whose volume can be predicted allows the droplets to be treated as building blocks, thereby allowing inkjet to be employed as an additive manufacturing technique as well as a synthesis tool. Moreover, this faculty of uniform droplets that are accurately positioned allows inkjet to be widely employed in the field of graphics.

From an RIJ point of view it is the fact that an inkjet printer can be employed as a synthesis tool that is of the greatest interest. In traditional chemical synthesis, the chemist seeks to have a high degree of precision with the aliquots of solution that they mix, as this ensures that the correct stoichiometry is obtained. In RIJ, the inkjet printer is treated as a precise pipette.

**Figure 1.1** Reactive inkjet printing involves adding one reactant to another to form a product.

RIJ can be compared to micro-fluidic chips, ('Lab-on-a-Chip'), in which networks of channels have been etched in to the substrate. Typically, two or more channels each containing a reactive species meet in a chamber where the reactants mix forming a product. In terms of comparison, the channels in micro-fluidic chips are in the region of 300 to 3000 micron wide whereas an inkjet printer typically produces droplets that have contact diameters on the substrate of 100 microns. Due to improved mixing, micro-fluidic chips offer increased reaction yields and decreased consumption of material; these advantages are also enjoyed by RIJ. However, a further advantage of RIJ is that reaction products can also be placed such that the final device geometry is obtained.

Two types of RIJ have been defined.[1] These types are 'Single RIJ' and 'Full RIJ'. Single RIJ involves an inkjet printer dispensing an ink, typically a solution, that reacts with a species that has been deposited on the substrate by another deposition technique, such as spin-coating or spraying. Although an argument could be made for expanding the concept of single RIJ to involve etching of the substrate, this approach isn't covered in this book. Etching, or chemical machining, is typically several orders of magnitude smaller than RIJ such as the etching of silicon to form integrated chips or several of orders of magnitude larger such as in bulk cleaning or smoothing. RIJ, whether Single or Full, requires a substrate that does not take part in the reaction.

The main advantage of Single RIJ is that most research laboratories possess inkjet printers that allow the jetting of one ink only. Although, inkjet printer manufacturers are making machines that dispense more than one ink these tend to be more expensive and complex than single ink systems. Another advantage of Single RIJ is that one reactant can be deposited in bulk which increases the speed of the overall process. The second patterning step forms the desired product and the unreacted material can be removed.

Full RIJ is where an inkjet printer deposits two or more reactants, usually in separate passes from independent printheads. The advantage of Full RIJ is that less waste is generated when compared to Single RIJ and direct patterning is obtained. However, Full RIJ can be more time consuming and in some cases, depending on the solvents used, the drying out of the first reactant may be an issue.

## 1.3 Types of Inkjet Printer

Inkjet printing can be divided into two types: continuous inkjet and drop-on-demand ink. A further division can be made with drop-on-demand (DoD) into piezo DoD and thermal DoD, with the divisor being the actual method of actuation employed. Regardless of the type of inkjet method used, the in-flight diameters of the produced droplets range from 150 micron down to 10 micron.[2]

### 1.3.1 Continuous Inkjet Printing

There are a number of ways droplets are produced in continuous inkjet (CIJ), however all methods involve the droplets passing between a set of electrodes. Domino's A-Series SureStart print head contains a vibrating drive rod, which creates ultrasonic pressure waves in the ink, breaking it up into individual droplets.[3] Linx CIJ technology involves the ink being pulsed inside the ink chamber by a piezoelectric crystal, which causes the ejected ink column to break up into droplets.[4] Other CIJ versions involve the droplets forming by the Rayleigh instability of the ejected ink column that has been forced out of the nozzle under pressure.[2]

In CIJ (Figure 1.2), the charged droplets pass through a set of deflector plates that direct the droplets either towards the substrate or towards a gutter, where they are collected and recycled. As its name implies droplet production in CIJ is continuous, droplets are either used or recycled. The predominant use of CIJ is in product marking, with bar-codes being an oft-cited example. Typically, a CIJ ink contains a pigment, a carrier and additives (*e.g.* humectant) to ensure ink lifetime and performance.

CIJ is fast, and droplet generation can reach up to 60 kHz; however, the main drawbacks from an RIJ point of view are a limit on the range of inks that can be printed due to the droplets having to be able to carry a charge, and more significantly the risk of contamination due to recycling. However, CIJ should not be discounted from RIJ, as Wheeler and Yeates discuss in Chapter 4.

### 1.3.2 Drop-on-demand Inkjet Printing

Unlike CIJ, in which a continuous stream of droplets is generated and either placed on the substrate or recycled, drop-on-demand (DoD) printers are so-called because droplets are only generated when required. As such, all droplets generated by DoD are positioned on the substrate.

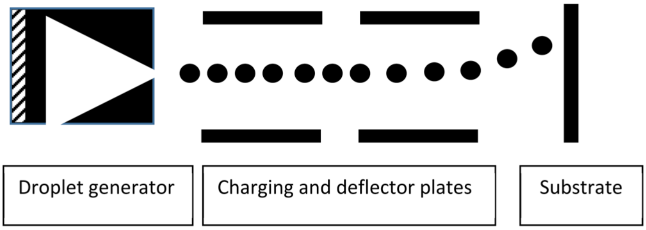

**Figure 1.2** A simple schematic of a CIJ printhead, showing droplets generated due to the action of a transducer (diagonal hatching), passing through a set of charging plates before being directed by deflector plates onto a substrate. Droplets that are not deflected are collected by a gutter (not shown) and recycled.

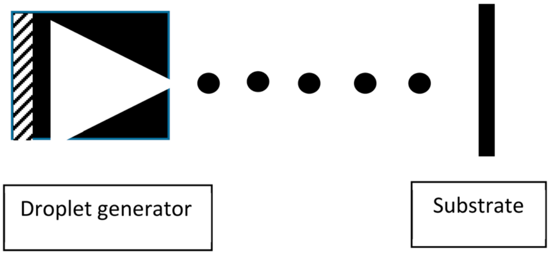

**Figure 1.3** A simple schematic of a DoD printhead, showing droplets generated due to the action of a transducer (diagonal hatching), which can either be a heater or a piezoelectric material.

As mentioned earlier, DoD (Figure 1.3) can be divided into thermal DoD (often called TIJ – thermal inkjet) and piezo DoD. In TIJ, a thin film resistor is placed inside the ink chamber, a current is passed through the thin film causing it to rapidly heat up and inducing localised vaporisation of the ink in the chamber nearest to the heater. The vaporisation results in a bubble (which is why TIJ is also called bubble jet). The current passing through the resistor is then stopped, causing the thin film to cool down and triggering the collapse of the bubble. The rapid switching on and off of the current through the resistor and the subsequent rapid formation and collapse of the bubble causes pressure pulses throughout the ink in the chamber, which results in a droplet being generated.

Piezoelectric DoD works in a similar way to TIJ in that droplets are ejected due to an induced pressure pulse. However, in piezo DoD the actuator is based on a piezoelectric crystal, which changes shape as a consequence of a current being passed through it. In some printhead designs, the piezo component pushes into the ink chamber to create pressure pulses, in others it surrounds the chamber or forms a wall of the chamber.

## 1.4 Droplet Formation

An example of a piezo DoD printhead is shown in Figure 1.4(a). The operating principle is described as follows: pressure waves form as a result of a sudden volume change, which is caused by a voltage being applied to the piezoelectric actuator, and begin propagating throughout the capillary. When a positive pressure wave approaches the nozzle, a column of fluid is pushed outwards. The ink column, or droplet, is ejected when the transferred kinetic energy exceeds the surface tension required to form a droplet. The droplet's velocity is linked to the amount of kinetic energy transferred, with large actuating voltages producing droplets with higher velocities. The initial velocity of a droplet needs to be several metres per second to overcome the decelerating action of ambient air.[6,7]

The next few paragraphs describe the process of ejecting a droplet more fully. Figure 1.4(b) illustrates the pressure waves as boxes, below the line the boxes represent negative pressure waves, above positive. The arrows inside

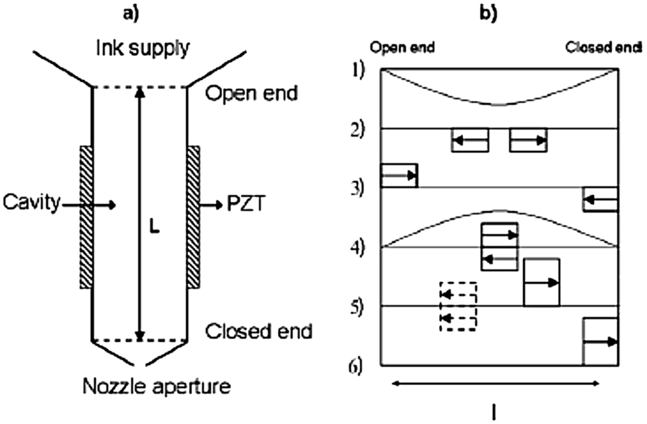

**Figure 1.4** (a) Schematic diagram of a piezoelectric inkjet printhead. (b) Schematic representation of wave propagation and reflection in a piezoelectric tubular actuator. Reproduced from ref. 5 with permission from the Royal Society of Chemistry.

the boxes represent the direction of travel. At the start of the process, the piezoelectric actuator expands as a consequence of the applied voltage generating two negative waves (stage 2 in Figure 1.4(b)). These negative pressure waves mean that the ink is withdrawn to the centre; the ink at the nozzle retreats upwards, away from the nozzle aperture. The ink at the reservoir also retreats but as it does so it draws in more ink.

The nozzle is considered as closed, according to acoustic wave theory, as the size of the nozzle orifice is small compared to the overall cross-sectional area of the ink chamber. The end of the ink chamber that connects to the reservoir (ink supply in Figure 1.4(a)) is considered as open since the inside diameter of the ink supply is usually larger than the ink chamber. The pressure wave reflected from the nozzle keeps its phase, whereas the wave reflected from the reservoir—the open end—has its phase reversed. Another way of explaining this reversal is that the negative wave at the reservoir causes additional ink to be drawn in.

The two reflected waves travel back to the centre of the ink chamber (Stage 3). At this point, the voltage applied across the piezo is reset (or lowered below the starting value) causing the actuator to contract (Stage 4). The contraction of the actuator generates a positive pressure wave that travels towards the reservoir and the nozzle meeting the incoming initial waves. The negative wave that is returning from the nozzle is cancelled whilst the positive wave travelling from the reservoir is magnified (Stage 5). The magnified positive pressure wave travels to the nozzle, ejecting a column of ink.[8]

Bogy and Talke reported on a series of experimental observations using piezo DoD printheads. Their study examined the dependence of four operating characteristics on the length of the ink chamber. They concluded that DoD inkjet phenomena are related to the propagation and reflection of acoustic waves within the ink chamber.[9] The four measurable quantities that were found to be linearly dependent on length ($l$) and the speed of sound ($c$) in the ink were the optimum pulse width, which is equal to $l/c$; the delay time before the meniscus starts to protrude, which is equal to $3l/2c$; the period of meniscus oscillation, which is equal to $4l/c$; and the period of low frequency resonant and anti-resonant synchronous operation, which is equal to $4l/c$.

As mentioned earlier, the velocity of a droplet is influenced by the actuating voltage, with larger voltages generating droplets with higher velocities. The volume of a droplet is also influenced by the actuating voltage – larger droplets are caused by larger voltages. Figure 1.5 shows how a droplet's volume and velocity are linearly determined by voltage. In terms of reactive inkjet printing (RIJ) the data shown in Figure 1.5 is of significant interest, as it demonstrates that the dispensed droplet volume can be adjusted.

Typically, in a laboratory when one generates a droplet three values can be set, which are actuating voltage, pulse width (when the two pressure waves recombine and the voltage across the piezo actuator is reset) and frequency. Although all three terms have some effect on droplet volume, that of voltage is most straightforward. A sine-wave type effect on droplet volume can be observed when pulse width is varied. From an RIJ point of view, the experimentalist is advised to optimise pulse width and then keep the value constant.

Piezo DoD printheads can operate at frequencies as high as 20 kHz.[2] However, operating piezo printheads at such high frequencies can result in chaotic droplet ejection events, which is because earlier pressure waves have not been damped out, but have instead interacted with subsequent pressure waves. From an RIJ point of view, high frequency droplet ejection is not recommended since a degree of control over, and confidence in, droplet volume is desired. In the early stages, the RIJ experimentalist is interested in

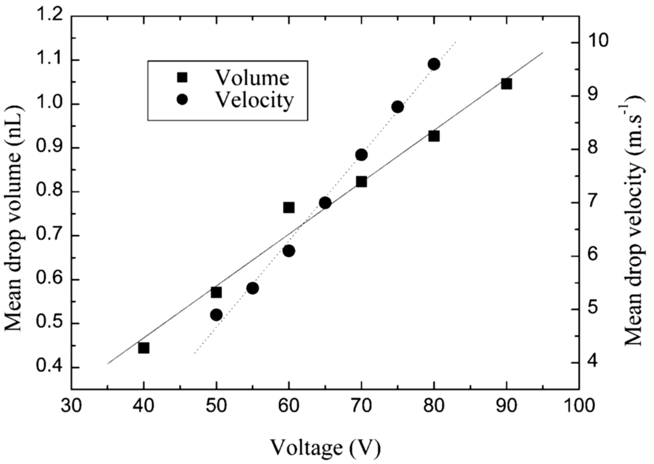

**Figure 1.5** The influence of driving voltage on ejected droplet volume. Reprinted from N. Reis, C. Ainsley and B. Derby, *Journal of Applied Physics*, 2005, **97**, 094903, with the permission of AIP Publishing.[8]

determining if their target system can be synthesised by inkjet, in later stages high frequencies may be employed if speedier fabrication is a particular goal.

The viscosity of an ink, or solution (as is usual for RIJ), affects the residence time of the residual waves. A more viscous ink/solution eliminates pressure waves quicker. Wallace and Antohe compared ethylene glycol, which is more viscous, to water and found the decay time of residual waves was shorter than in water.[10]

## 1.5 Printability and *Z* Number

Fluid properties such as viscosity and surface tension have an influence on the formation of droplets from an inkjet printer. The Reynolds number, which is the ratio of inertia and viscosity, and Weber number (inertia and surface) are combined to form the Ohnesorge number.

The Ohnesorge number is given as $\sqrt{}$We/Re or $\frac{\eta}{(\gamma\rho a)^{1/2}}$ where $\eta$ equals dynamic viscosity, $\gamma$ is surface tension, $\rho$ is density and $a$ is a characteristic length (usually the diameter of the printhead's nozzle). The issue is then complicated somewhat since the inverse of the Ohnesorge number is used to determine printability. The inverse is known as the *Z* number.

Fromm predicted that if *Z* was greater than 2, drop formation in DoD systems was possible.[7] Derby *et al.* refined this prediction saying that if *Z* lay between 1 and 10 an ink was printable.[8] If Z was less than 1 then viscosity would damp out the pressure pulse, whereas if *Z* was above 10 satellite droplets would form. Satellites are smaller droplets that form in a droplet ejection event. Typically, a column of liquid is ejected, which then, ideally, contracts into a sphere. However, in a number of cases the front of the column forms a spherical bulb and the rest of the column forms a long tail, as can be seen in Figure 1.6.[11] It can also be seen in Figure 1.6 that in some cases the droplet's tail has broken up into more than one droplet. From an RIJ point of view satellites are problematic if they do not re-combine with the main droplet either during flight or during impact.

Derby *et al.* also observed that *Z* has an influence on droplet volume too. As *Z* increases there is an increase in volume. However, the volume increase reaches a plateau once *Z* equals 10. Recently, Moon and co-workers have provided an additional refinement of what *Z* number means in terms of ink printability[12] by saying that if *Z* is between 4 and 14 then an ink is printable.

The picture is further complicated when one considers the work of Schubert *et al.* who found that a number of common solvents with low viscosities, ranging from 0.4 to 2 mPa.s, and surfaces tensions ranging from 23 to 73 mN/m were printable. The calculated *Z* numbers for these solvents varied from 21 to 91![13] In fact, they judged that the main factor affecting printability was vapour pressure. If values of vapour pressure were above 100 mm Hg then droplet formation was either unstable or non-existent.

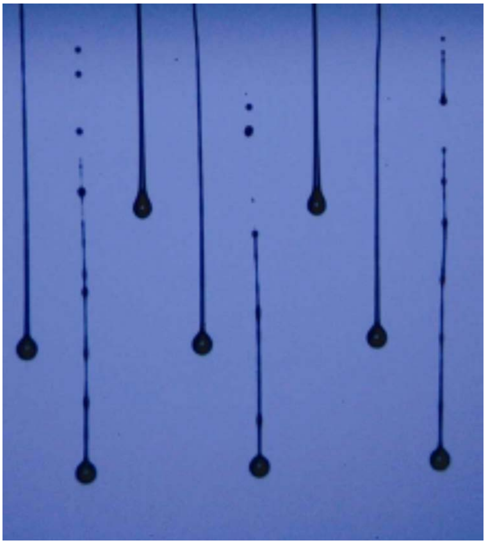

**Figure 1.6** Jets formed from solutions of polymer in diethyl phthalate (0.4% monodisperse polystyrene with MW = 110 000) before and after detachment from the nozzle plane. Reprinted from ref. 11 with permission of IS&T: The Society for Imaging Science and Technology, sole copyright owners of *NIP23: Twenty-third International Conference on Digital Printing Technologies and Digital Fabrication 2007*.

In his recent review of inkjet printing where he discussed fluid property requirements, Derby identified where the region of printable fluid lies. Although the preceding discussion has illustrated that there is a variety of opinion as to what exact values of $Z$ predict printability what can be said is as follows. At low values of $Z$, viscosity dominates. If an ink or solution is too viscous droplets cannot be ejected. At high values of $Z$ satellites are, or may be observed.

To summarise this section, the science behind inkjet printing regarding droplet size and velocity is well understood. Key papers that have contributed to this understanding are influenced, in piezo DoD printheads, by the voltage applied to the piezoelectric actuator. Viscosity is the principal limiting factor in terms of droplet ejection. If an ink is too viscous then the pressure waves are nullified and the kinetic energy dissipated.

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