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Ink transport modelling in Dip-Pen Nanolithography and Polymer Pen Lithography

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Abstract: Dip-pen nanolithography (DPN) and Polymer pen lithography (PPL) are powerful lithography techniques being able to pattern a wide range of inks. Transport and surface spreading depend on the ink physicochemical properties, defining its diffusive and fluid character. Structure assembly on surface arises from a balance between the entanglement of the ink itself and the interaction with the substrate. According to the transport characteristics, different models have been proposed. In this article we review the common types of inks employed for patterning, the particular physicochemical characteristics that make them flow following different dynamics as well as the corresponding transport mechanisms and models that describe them.

Keywords: Dip-pen nanolithography, DPN, Polymer Pen Nanolithography, PPL, ink transport

1 Introduction

In 1985 Binnig, Quate, and Gerber introduced the Atomic Force Microscope (AFM) as a new type of microscope capable of imaging and sensing a surface's topography [1]. Ten years later, Jaschke et al. reported that, under certain experimental conditions, the tip was also able to perform additive processes: i.e. the transfer of material onto a substrate [2]. Mirkin and coworkers exploited this phenomenon for a novel AFM based lithographic method

and coined the term Dip-Pen Nanolithography (DPN) in 1999 [3].

The basic principle of DPN entails the transport of material from the tip to the surface either due to differences in concentrations (diffusive inks) or fluid dynamics (liquid inks, polymer inks, thermal dip-pen); sometimes (ink dependent) a combination of both [4,5]. A schematic picture of the transport process is shown in Fig. 1 for the three types of inks.

The tip, similar to those usually employed in contact mode AFM (soft, low k) is coated with the desired ink. Depending on the ink characteristics (solubility, melting temperature, viscosity) different coating techniques are applicable, ranging from simple dip-coating to spotting with inkjet printing [6] or microfluidic networks [7] for addressing specific tips within an tip array with different inks. For diffusive inks the coated tip is sometimes left to dry, to avoid solvent carrier to participate in the ink transport. In the case of liquid inks solvent admixtures are tuned to obtain the liquid characteristics (viscosity, surface tension) that provide the desired ink transport mode. As an example, glycerol is a frequent component employed within these admixtures, since it allows control of the subsequent transport with the Relative Humidity (RH) of the chamber environment.

The tip is then brought close to the substrate. In atmosphere controlled environments, a water (or solvent) meniscus is then condensed from the tip to the substrate. Ink is transported from the tip/meniscus to the meniscus/surface interface. Upon meniscus condensation the ink at the tip becomes suddenly submerged into a water (solvent) environment that may modify the ink state at the tip. Different solvent environments than water vapor can be employed, according to the ink solubility. Liquid inks do not require the formation of a meniscus, since the ink itself is liquid; yet meniscus formation can modify its transport. Typical control parameters for the ink transfer are RH and the time the tip is held stationary over the substrate while ink is delivered (dwell time) [8,9]. Also the tip-surface distance and the wettability of the tip and the substrate play a role in the transport, due to their influence on the

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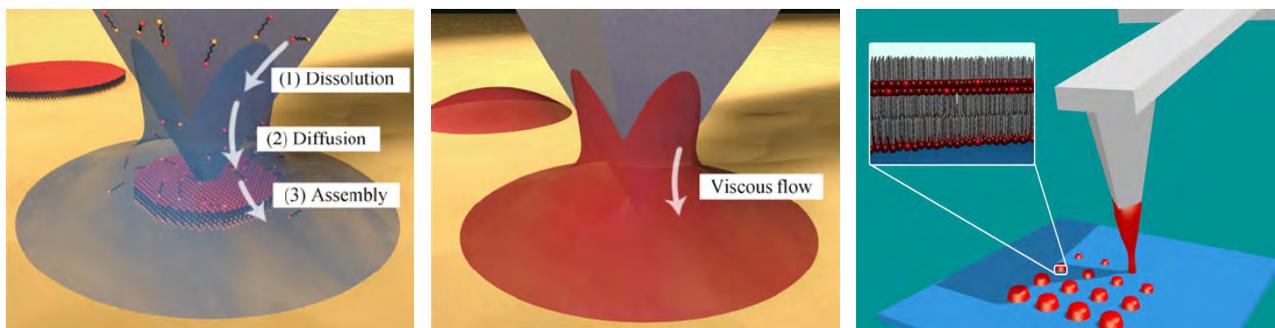


Figure 1. Scheme of DPN transport process. From left to right: diffusive (molecular) inks, liquid inks, lipid inks. Figures taken from [4,5] with permission.

condensed meniscus [10]. Temperature of the tip and of the substrate are also sometimes employed as transport-tuning parameters [11–15].

Finally, inks deposit onto the surface and form different features. Adsorption and assembly of ink molecules onto the surface generally depend on several parameters, including substrate temperature, relative humidity, the physicochemical properties of the ink and substrate, and the delivery rate of the ink towards the substrate. Molecular diffusive inks lacking inter-molecular interactions, or having intermolecular interactions too weak compared to substrate-ink interaction, will diffuse until they maximize contact with the substrate, creating usually flat features [16]. Liquid inks will form a dome-shaped feature whose wetting angle results from the balance of energies between the substrate-ink and ink intermolecular interactions [17]. Lipid inks will spread and assemble into membranes stacking as multilayers [18]; yet due to their partly fluid character they can form a dome-shaped feature, with multilayered internal structure [5].

Polymer Pen Lithography (PPL) emerged as a combination of DPN and microcontact printing (μ CP). A schematic picture of the patterning technique is shown in Fig. 2. A stamp, similar to that used in μ CP but with an elastomeric array of pyramidal-shaped tips, is set into a DPN system for precise control of movement and position during the printing process [19,20]. The 2D array of elastomeric pens is brought into contact with a substrate in a well-controlled manner with regard to position and applied pressure. Ink coated on the PPL stamp can transfer to the substrate similarly as it does in DPN. However, due to the elastomeric nature of the tips, feature size can be additionally controlled by the applied pressure, since tips deform elastically upon contact yielding a bigger contact area when more pressure is applied [21]. Additionally, due to the ability of direct ink stamping, insoluble inks can also be patterned, being transported by diffusion from the elastomeric pen to the substrate.

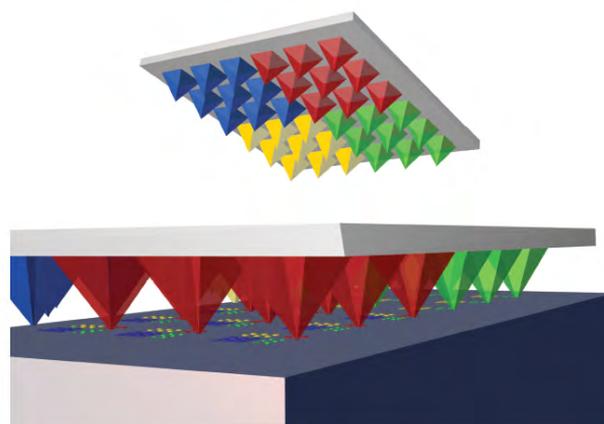


Figure 2. Scheme of Polymer-Pen Lithography patterning. Images taken from Ref. [22] with permission.

2 Ink Transport in Dip-Pen Nanolithography

Inks can be classified within three main categories: diffusive inks, liquid inks, and lipid inks. In this section we will provide a description of the main properties of each category, relate them with their transport characteristics and review the different models associated.

2.1 Diffusive Inks

Here, transport follows three stages [23,24] that are depicted in Fig. 3: (i) ink is chemically dissolved from a solid state into the meniscus at the meniscus/tip interface; (ii) it transports to the substrate through or over the meniscus; (iii) ink spreads over the substrate from a nonzero concentration location at the meniscus/substrate area to a zero concentration at the edge boundary of the feature.

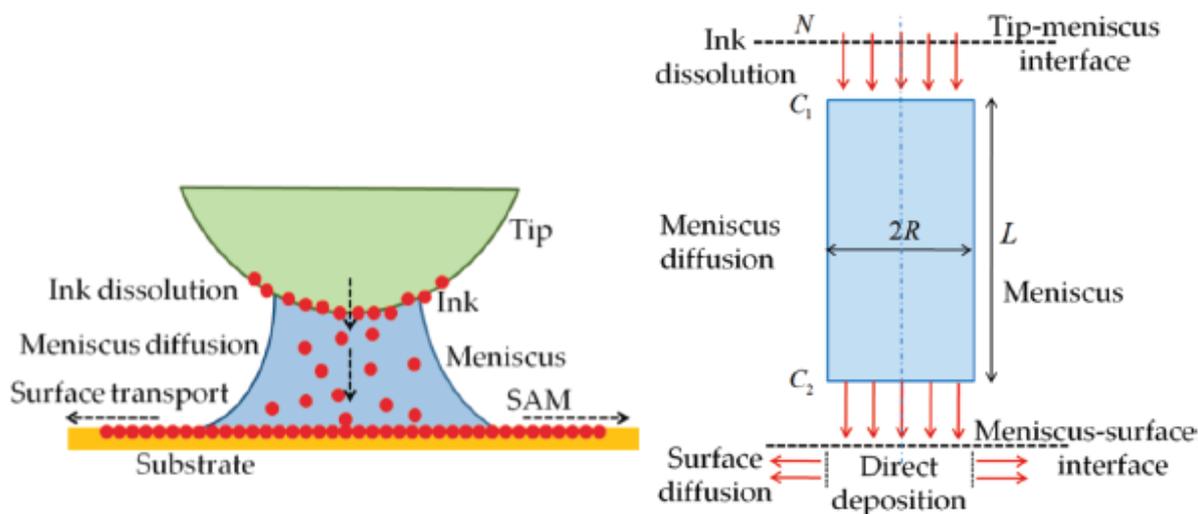


Figure 3: Scheme of the ink transport for a diffusive ink showing three stages: (i) ink-dissolution into the meniscus at the tip/meniscus interface; (ii) flow transport via meniscus; (iii) spreading over the substrate. Figures taken with permission from [23].

In the first stage (i), the rate of forward ink transport can be envisaged as the kinetics of a chemical reaction. It should be noted that ink molecules are not detaching from the surface of the AFM tip, but rather they are detaching from the surface of a bulk solid phase of the ink that has precipitated onto the tip during the inking process. The rate then depends on the concentration of ink at the tip/meniscus interface (i.e. in contact with the water (solvent) meniscus) [25,26], on the dissolution and diffusion kinetics of the ink molecules [8], and on the reaction kinetics parameters, as the temperature at the tip and the activation energy of the ‘reaction’ [13]. Due to the diffusive character of the ink, the rate of backward reaction (ink molecules coming back to the tip) depends on the ink concentration at the tip/meniscus interface. The net ink flow of the first stage is the balance between forward and backward reaction rates [8,26].

The first analytical description of this stage was provided by Weeks et al. [8], who proposed that it is stage (i) that governs the complete transport dynamics. This idea was later supported by Giam et al. [26] who reported that deposition rates are governed by the ink coverage at the tip. Later on, Chung et al. showed flow is controlled by the thermal activation of the dissolution kinetics [13].

In the second stage (ii) the ink travels from the tip/meniscus to the meniscus/surface interface due to a difference in concentration (Fickian diffusion). Within this stage, the role of the meniscus has been quite controversial. Piner and Mirkin were the first to show that water adlayers were transported onto the substrate surface, mediated by the meniscus that condenses as the

tip is held stationary over a substrate [27]. Subsequently they proposed that molecular inks actually flow from the tip to the substrate by capillary action [3]. Some reports then showed meniscus existence [28,29], and demonstrated a dependence of meniscus width on the tip-substrate distance and ambient humidity [30–32]; it has also been reported that a minimum distance is required to grow a stable meniscus [10,33], and the role of surfaces wettability [34,35] and roughness [36] on the meniscus. Certainly, these parameters influence the meniscus size, but it does not inevitable prove that ink transport is really taking place through the meniscus. Yet it has been shown that transport of water compatible inks (i.e. soluble or hydratable) depends on the relative humidity [12,37], contrary to observations with water insoluble inks [38]. Subsequent studies reported that a ‘water compatible’ ink as mercaptohexadecanoic acid (MHA) was able to transport even at very low humidity conditions, though transport was enhanced at higher RH [37]. Remarkably, the ink flow rate for water compatible inks is in agreement with the water meniscus growth rate [39]. Nafday et al. reported ring features corresponding to a transport of the ink over the meniscus surface, due to a water meniscus condensed internally [40]. In conclusion, it can be said that water compatible inks follow a meniscus-based model in the regime with higher RH, when a water-meniscus enhances the transport, and under these conditions show a dominantly meniscus dependent rate.

The transport of ink, either enhanced by the meniscus or not, is due to differences in concentration at the tip/meniscus and the meniscus/surface interface

(Fickian transport). As a first approximation the flow can be considered proportional to the differences in concentration [23]. It also depends on the diffusive character of the ink, represented by its diffusion coefficient. When the meniscus participates in the transport, its influence can be described, in analogy with the current density through an electrical resistance, as proportional to the area of the meniscus and inversely proportional to the length of it [23].

In the third stage (iii), molecular inks diffuse until they bind to the substrate. Usually, surface diffusion is pictured as originating at a central source of molecules positioned at the meniscus/substrate interface from where the ink travels to the periphery of the feature, until surface binding takes place. Here two approximations are frequently employed: (a) a constant flow approach [16] or (b) a constant concentration approach [9,41]. At short dwell times, as a first approximation, constant flow can be assumed [16,42]. This approach is usually followed by inks with a substrate spreading rate fast compared to the tip-surface ink flow rate [11] in which the driving energy is the ink-substrate interaction. In these systems, at short dwell times, feature area is proportional to dwell time, with a slope that depends on the balance between ink delivery flow and surface diffusion [8,16]. On a larger time scale, ink transport is better described by the approximation of constant concentration. Now the balance between the ink delivery and surface diffusion rates over time [8,11] leads to an area increasing as t^α , where $\alpha < 1$ [41].

The previous description is adequate for dot features, in which the tip is held still over the substrate for a defined dwell time, and the flow achieves an equilibrium within time. However, in line writing, the tip is constantly exposed to clean surface areas as it travels so ink flow rate does not reach an equilibrium flow regime [23,24]. This difference is due to the Fickian transport character of molecular inks, i.e. transport is due to differences in ink concentration. In line writing surface spreading follows better the approximation of a constant concentration source, with the size of the tip footprint, that diffuses towards the edge [23,24].

Since the slowest transport stage dominates the process, in some systems one or two of these stages can be neglected thereby transport being controlled by dissolution at the tip [8], surface diffusion [9,16], or transport and subsequent diffusion [11]. Saha et al. developed a complete analytical model that includes the three steps in the ink transport of molecular inks [23,24]. Additionally, surface spreading can be intentionally suppressed, e.g. by exchanging molecules from a pre-assembled monolayer with ink molecules, termed molecular editing when done

in liquid phase as source for the exchange molecules [43,44] or as dip-pen nanodisplacement lithography (DNL) [45] under ambient conditions with the exchanged molecules stemming from the tip as in conventional DPN. As spreading is eliminated, very high resolutions can be achieved in this alternative ink delivery approaches in DPN.

Though this is the common picture, some reports show that depending on the ink/substrate combination, molecular diffusive inks do not always rearrange in an independent fashion [46], neither spread independently [47] up to the point of showing anisotropic patterns instead of the conventionally expected round features [48]. Within this anisotropic spreading intermolecular interactions of the ink dictate the spreading dynamics and then are molecule dependent. Description of transport in these systems requires numerical simulations.

Let us finally mention that some reports also show molecular diffusive inks can grow in 3-D, i.e. they can form domed features as liquid inks do, when the ink delivery rate is faster than the surface spreading rate [11]. In this particular experimental conditions, description of the transport follow more closely that of the lipid-like inks (Section 2.3).

2.2 Liquid Inks

In DPN of liquid inks, transfer occurs by a growth of an ink droplet that gets snapped off upon tip retraction leaving behind a droplet on the substrate, as depicted in Fig. 4 [17,49]. Transport to the surface is now governed by fluid dynamics. A pressure gradient drives fluid flow, which is slowed down by viscous forces. The pressure gradient can have different origins, depending on the ink, the transfer process itself, and the writing procedure. While in classical DPN the pressure gradient is built up by capillary pressures, thermal DPN exhibits more diverse sources of pressure gradients, as it includes also changes in surface tension of ink by temperature [50]. The complex determination of these pressure gradients and their dependence on the ink parameters make the modelling of liquid inks transport especially challenging.

The simplest situation includes: (i) temperature equilibrium, implying no gradient of temperature all along the liquid and steady ink fluidity; (ii) liquid ink with no assembly of constituents, stating viscosity does not change with time; (iii) stationary tip, allowing to neglect shear force. In this situation, transfer process becomes easier to model. In this case, a Laplace gradient of pressures between tip and substrate drives the liquid flow [49,50].

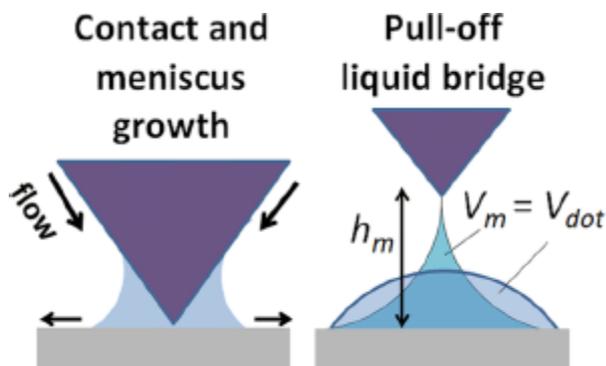


Figure 4: Scheme of the ink transport for a liquid ink showing first ink transport by liquid dynamics, and then droplet snap-off and rearrangement upon tip retraction. Figures taken with permission from [49].

At the tip/meniscus interface, Laplace pressure is larger than at the meniscus/substrate one, where the liquid ink becomes deposited. The difference between Laplace pressures arises from different curvatures of the liquid-air interface at the tip/meniscus interface as compared with the meniscus/substrate one [49]. Curvatures in both locations depend on different factors. At the meniscus/substrate interface, liquid-air interface curvature changes with time due to the growth of the building droplet feature. The shape of the droplet depends on the balance between the air-liquid-substrate interface energies, that decides the wetting angle over the substrate. At the tip/meniscus interface, Laplace pressure depends on the amount of ink at the tip [49]. Resting time between patterning sequences allows ink rearrangement at the tip, changing pressure at the tip, and promoting larger transport [51]. Therefore, the gradient of pressure changes with time and, accordingly, resulting transport. If at some time pressures become equilibrated, the transport stops. Usually, interface energies air-liquid-substrate allow a wetting angle giving a pressure at the meniscus/substrate interface that is always lower than at the tip/meniscus interface, so that growth of the droplet continues indefinitely. Additionally, within the balance of transport kinetics, the viscosity of the liquid ink should be considered as it partly depletes the energy provided by the pressure gradient, slowing down feature growth rate [50,52].

Liquid inks display different feature growth with time, e.g. showing a volume increasing exponentially with time [49] or saturating with it [50], even for the ‘simplest’ case. Since liquid-air curvature at the tip/meniscus interface depends on the amount of ink at the tip, deposition rate decreases dramatically over the course of an experiment [51].

Noticeably, for inks with low viscosity, the influence of changes in the curvature at the tip dominates the influence arising from other factors. Here, differences arising from different ink viscosities or substrate wettabilities become negligible as compared to the influence of liquid-ink tip loading [51]. Since deposition rate changes significantly during an experiment, dwell time may not be the most useful method to control feature size, but the control over the tip loading itself.

Other sources of pressure gradients include thermal Marangoni Forces arising from the temperature dependence of the surface tension. Their magnitude becomes comparable to Laplace pressure in thermal DPN [50].

Finally, when the tip is drawn away from the surface, the ink meniscus connecting tip and surface snaps [17]. Upon retraction, the tip removes part of the ink droplet. This amount depends on tip and substrate wettabilities (i.e. the energy of binding between the ink and the surface of either the tip or the substrate) as well as on tip retraction speed [17]. At low retraction speeds, ink has time to rearrange towards the most energetically favourable configuration [51].

In order to model the transfer process, forces that drive the ink flow (mainly Laplace, Marangoni or shear stress) are equated to viscous forces [50]. As discussed, their magnitude and contribution depend on the type of liquid ink, substrate, and writing procedure. Ultimately tip retraction determines the amount of ink left on the substrate [17]. Thereby for each combination of experimental parameters a different equation describes the process. Up to now there is no complete ink transfer model that includes all these factors, making the analytic description of liquid inks an open question.

2.3 Lipid inks

Lipids are amphiphilic molecules composed of a polar headgroup and hydrophobic carbon chains [53]. Lipid inks exhibit quite a variety of structures depending on the nature of the molecules, their hydration, and the external conditions (temperature and pressure). The chemical composition of the carbon chains governs the temperature below which the lipid ink undergoes phase transition into chain-ordered phase. Above, they keep a fluidity that allows them to be patterned. They can be hydrated upon exposure to a water vapor atmosphere, in which water diffuses towards the polar groups, inducing structural rearrangements on the molecular length scale. Yet, groups in the carbon chains induce stable packing, promoting ordered structures. Lipids structural order and

fluidity can be tuned upon careful selection of the carbon chain saturation and the degree of hydration. In the liquid phase, amphiphilic molecules spontaneously assemble on solid surfaces forming macroscopically oriented molecular structures. Hydrated lipids usually assemble into multi-bilayer-water stacks, with their planes oriented parallel to the substrate [53].

Di-oleoylphosphatidylcholine (DOPC), with a transition temperature of $T_m = -17^\circ\text{C}$, is the main carrier usually employed in Dip-Pen Nanolithography of lipids (L-DPN). Water molecules insert intra and inter membranes, mainly around the lipid phosphocholine headgroups, providing a high fluidity of the assembled membranes [54,55]. Its diffusion coefficient depends on the degree of hydration [56]. Ink transfer in L-DPN is strongly influenced by the relative humidity [57].

Within this fluid character it is not surprising that patterned features form 3D-domed features, as do liquid inks, with a wetting angle depending on the substrate [5] and the ink [58]. On the other hand, lipids diffusion and spreading follows Fickian transport, i.e. arises due to differences in the concentration of lipids [5]. Remarkably, not only their fluidity but their assembly characteristics ultimately determine the geometry of the final structure [59]. These characteristics are typical for a diffusive-like ink, while fluid attributes discussed in the previous paragraphs are usually assigned to liquid inks.

The combination of liquid attributes and diffusive attributes makes the transport of lipid inks to exhibit an interesting phenomenology [5]. They diffuse like a molecular ink, moving from high concentration regions to lower concentration ones; yet their flow can be modified by tuning their fluidity, via RH, changing meniscus size, or by mixing with other lipids. As lipids interact with each other, in addition to interacting with the substrate, controlling the strength of the interaction between lipid molecules as compared with that of lipid-substrate, the ink flow and shape of the final feature can be tuned. From the experimental point of view, the physicochemical characteristics of the lipid ink need to be precisely known in order to be able to control its transport and pattern reproducible features. From the theoretical point of view, these systems offer a unique opportunity to study fluid dynamics in a system combining diffusive and liquid transport.

Many empirical studies have identified the experimental variables that influence feature size in L-DPN. Some initial quantitative studies addressed the writing process [60,61], the thickness dependence with tip speed and humidity [57], and membrane stack organization [18]. All reports agree that humidity controls the phase of the ink at the tip and their diffusive properties [57,58], in

agreement with the discussed amphiphilic nature of the phospholipids. Yet the balance between the energy of interaction between lipids and with the substrate controls the final feature shape [59]. Though these experimental parameters have been experimentally known to influence L-DPN transport, yet there is only one work that reports a systematic and complete study of the ink transport of lipids [5]. This study was fully conducted in a particular system of DOPC over glass, for full ability to reproducibly control the transport with the experimental parameters. In the following, the lipid transport and the analytical model developed in that work is described.

For L-DPN, transport follows the stages of diffusive inks, as depicted in Fig. 5: (i) ink dissolution at the tip; (ii) ink transport through the meniscus; (iii) spreading and assembly.

Before approaching the tip to the substrate, the lipids at the tip become hydrated as water molecules from the environmental water vapor insert within the lipid structures. As the tip approaches towards the substrate, a water meniscus condenses between the tip and the substrate. In the first stage (i), the hydrated lipid ink contacts the water meniscus at the tip/meniscus interface. Lipids in touch with the meniscus become fully hydrated and start spreading towards the substrate, letting water propagate inwards to the tip, thereby increasing the concentration of lipids that become fully hydrated. At this stage, lipids form a particular hydrated lipid ink phase in the water meniscus. This is supported by the experiments of Lenhart *et al.* [62] in which L-DPN under water requires the meniscus to be formed in air, prior to immersion into water for subsequent writing. Depending on the geometry of the meniscus, this phase will have different fluidity and, subsequently, different ink delivery rates from the tip, as suggested in Ref. [62]. Therefore, the amount of ink delivered by the tip will depend on the humidity, in agreement with Ref. [5] (inset Fig. 14).

It should be underlined that this hydrated ink phase is different from that described for diffusive molecular inks [11]. In the latter, the ink is chemically dissolved from a solid state into the meniscus at the tip/meniscus interface. Lipid molecules do not need to chemically dissolve, but rather undergo a diffusive hydration process. Therefore, in lipid inks the key parameter affecting the ink supply kinetics will be hydration diffusion, not chemical dissolution kinetics. The hydration will rely on the water provided for lipid diffusion, i.e. the meniscus size. The modelling of this stage follows then closely that of molecular inks but with a forward rate following a hydration diffusing process instead of a thermal activated detachment (first-order chemical reaction).

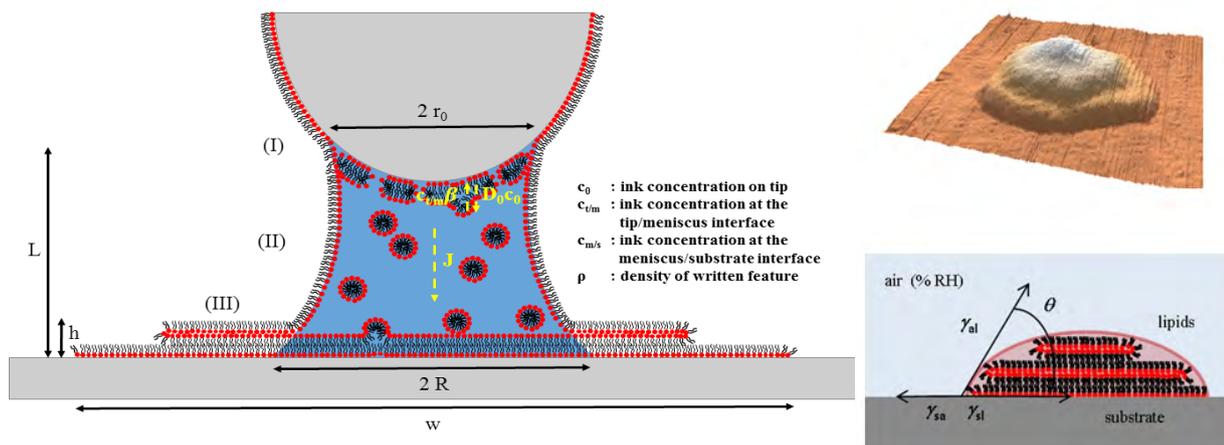


Figure 5: Left. Scheme of the lipid ink transport showing three stages: (i) ink-dissolution into the meniscus at the tip/meniscus interface; (ii) flow (J) transport via meniscus as a 1-D Fickian diffusion due to differences between the concentration $C_{\text{tip/meniscus}}$ and $C_{\text{meniscus/substrate}}$; (iii) spreading and assembly over the surface. Right. AFM image of a feature on a hydrophilic surface with the corresponding scheme below displaying the droplet with internal membrane structure. Figures taken with permission from [5].

In the second stage (ii), the lipids will transport towards the substrate. Due to the amphiphilic character of lipid molecules it is expected that the meniscus plays an important role. It has actually been reported [5], that the flow rate, i.e. the amount of delivered material by the tip through the meniscus towards the surface per unit of time, depends on the relative humidity in agreement with the water meniscus size dependence on relative humidity [29]. Furthermore, as relative humidity dictates meniscus size, at larger RH the lipid ink will hydrate faster and the meniscus flow rate will become stable earlier at high humidities, with an initial faster flow rate, as reported in Ref. [5]. Considering this dynamic picture of the second stage (ii), a transient regime is expected until the lipid concentration at the meniscus/substrate interface achieves equilibrium. Lipid ink will therefore diffuse, due to differences in concentration between the tip/meniscus and the meniscus/substrate interface, from the tip towards the substrate, mediated by the meniscus.

As in molecular inks, modelling of this second stage can be represented in analogy with the current flow through an electrical resistance, in which the flow is proportional to the difference of concentrations between the tip/meniscus and the meniscus/substrate interface, the ink diffusion coefficient, and a factor that depends on the geometry of the meniscus [5].

In the third stage (iii), upon transition to the substrate lipids rearrange and self-assemble into multilayer

membranes. Some of the meniscus water can be kept, mainly intra layers, providing the membrane stacks fluidity [57]. In this stage the freshly formed membrane is rather fluid, enabling the incorporation of new amphiphiles at the meniscus/substrate interface while the membrane front spreads out over the substrate. Layer feeding from the upper bilayers has been reported by Mohamed et al. [63], showing that lipids are transported to the bottom layer through dislocation places when humidity is increased up to the point in which the membrane transits into fluid phase; the fluid location in L-DPN would be just below the tip, at the meniscus/substrate interface. This fluid behavior is in agreement with the lipid membrane fluidity reported by Lenhert et al. above a threshold RH [58]. As more lipids arrive through the meniscus the concentration at the meniscus/substrate interface increases while the surface spreads outwards (thereby reducing the concentration at the meniscus/substrate again). Eventually, the net flow at meniscus/substrate interface gets into a dynamic equilibrium, and surface spreading follows a steady-state like kinetics. Finally, when the tip is removed the concentration is no longer increased at the tip/surface. Membrane growth and spreading then stops.

We shall emphasize some distinct features emerging in L-DPN substrate assembly and spreading, as compared with similar systems. First, at the meniscus/substrate interface, due to the balance between the delivered ink flow rate and the surface spreading rate, the

concentration of lipids changes with time. Depending on this balance, either a meniscus kinetics controlled or a surface spreading controlled growth regime emerges [5]. This makes a difference compared to the usual membrane spreading studies, in which a dry lipid membrane is wetted to allow its spreading [64,65]. In dry-wetted membranes, driving energy is the formation of a bilayer-substrate contact that at stationary equilibrium equals the energy dissipated by friction, leading to the well-known dependence of the spreading speed on time as $t^{1/2}$, even in monolayer spreading [64,66]. In L-DPN the driving force is the balance between the flow rate of lipids arriving from the tip vs. the surface spreading rate and so this balance governs the kinetics, showing a surface spreading following t^α , where α depends on the particulars of this balance. Second, though these systems may resemble molecular diffusive ones due to their Fickian transport, lipids interact with each other more strongly, in addition to interactions with the substrate. Also, lipid concentration is dynamically increased at the meniscus/substrate interface by the tip delivery, while lipids self-assemble and spread over the surface keeping a fluid state. All in all, this allows for the creation of 3D features whose wetting angle depends on the surface tension between the lipids and the substrate, i.e. on the lipid-lipid and lipid-substrate interaction energies. Due to the dynamics of transport and spreading, the modelling of this last stage follows the constant concentration approach [5], in which the flow that provides the surface spreading is that provided by the meniscus in the second stage (ii). Flow mass conservation links the three stages (i), (ii), and (iii) providing an analytical expression that describes L-DPN transport [5].

3 Ink Transfer in Polymer Pen Lithography

Since PPL combines aspects of DPN and μ CP, ink-substrate physico-chemical properties do not entirely define the ink transfer process here, but instead an additional degree of control is available: the tip contact area increases due to the elastic deformation of the pyramidal tip [19]. Now the lithography technique itself conditions the nature of the ink transport. When the polymer pens are brought only into near vicinity of the substrate, a meniscus condensation is required for ink transfer; in this case, writing mode approaches then DPN. When stamped forcefully into the substrate, the transfer mode approaches more μ CP. In between these extremes, ink transfer may follow closer the characteristics of one or the other [22]. Under some

experimental conditions, these modes may also both act in combination.

Due to the permeable nature of the stamps material (PDMS and admixtures) an unexpected degree of control should also be considered in this technique, meaning the solvent permeation into the stamp, and posterior release while stamping, that play a role in the transport process dynamics [67].

Unfortunately, for PPL ink transport there is currently no broad systematic study in the literature as reported for DPN, likely due to the relative novelty of the technique. As in DPN, molecular diffusive inks have been the first ones to be patterned. Yet the studies are limited to the influence of the stamp [19,21,68–70]. Surface spreading follow the usual $S \propto t$ reported in DPN [21,68] but with a slope that depends on the elastic properties of the stamp [68,71]. This is in agreement with the diffusive character of these inks [26] as elastic deformation of the pen apex modifies the ink source area available [21]. Though not analyzed, apex deformation is expected to additionally modify the size and shape of the condensed meniscus, influencing subsequently the transport through the meniscus.

In the case of liquid inks (i.e. inks that still remain in a fluid state on the PPL stamp), as formulations mixed with glycerol or low chain length PEG to prevent ink drying, PPL leads to ink micro-droplets on the sample surface [70,72]. It is expected that in these systems, ink will flow from the polymer pens and spread on the sample also by fluid dynamics as in DPN patterning. Since the polymer pen apex stamps onto the substrate, capillary pressure gradient is expected to be different depending on the piezo extension. Higher pressures of the stamps involve wider meniscus, and thereby, feature sizes increase with z-piezo extension [70]. A capillary rupture process is expected to play an important role since the tip in this case fully stamps into the substrate. Interestingly, the ink transport can also be tuned on tip via UV light [73]. Here, polymerization and remixing tunes the ink viscosity in-situ on the PPL tips, hence changing the ink transfer. This technique could be very helpful for more detailed studies of the ink transfer processes in PPL.

Lipid inks displaying a combination of diffusive and liquid features comprise the most complex ink transport mechanism in PPL [22]. They transport from the tip to the surface over the stamp, due to their diffusive character, but also through the water-meniscus built up upon contact with the surface, with a fluidity dependent on the meniscus-volume (i.e. on the piezo extension). The DPN-meniscus mediated transfer mode can be selected to dominate the process, by patterning at low stamping pressure [22]. At higher pressures, lipids pattern as the stamp shape; in

addition lipids flow from the tip/substrate contact location as a membrane over the substrate, forming multilayered structures [22]. As they diffuse by Fickian transport, flow is due to differences in concentration between the tip and the substrate. Therefore, there is not a big ink depletion at the tip when patterning for long times, which happens in diffusive inks: lipids will just spread from a bigger ink source area [22].

No model has been proposed up to now to describe the ink transport by PPL. Yet, some detailed quantitative studies are required to fully comprehend the parameters that control the ink transfer process.

4 Conclusions and perspectives

Transport in DPN of diffusive molecular inks follows three stages: ink dissolution, meniscus transport, and surface spreading. The first stage has been shown to play an important role in the transport of molecular inks. In some situations, it even dominates over the other two. In these systems, surface diffusion is fast as compared to the ink flow delivery, providing a feature spreading area proportional to the dwell time. When inks are water compatible RH additionally enhances the transport rate. Due to the fact that their delivery is mainly governed by tip kinetics, not only RH but temperature also controls the transport. These systems have been widely analyzed and models that account for their ink transport have been proposed. The model developed by Saha et al. [23] includes a complete description of the ink transfer process.

Liquid inks transfer from tip to substrate by means of fluid dynamics. Driving forces comprise a gradient of Laplace pressures between tip and substrate, Marangoni forces and shear stress. These forces are dampened by the viscosity upon fluid flow. The balance between the involved forces provides the feature growth kinetics. However, many parameters influence the magnitude of the Laplace pressures, making the modelling of these systems particularly complex. Up to now there isn't a complete analytical model fully describing the ink transport in these systems.

DPN with lipids can be analyzed and characterized in terms of liquid ink transport and molecular diffusion transport, as the ink behaves like a combination of both. The area spread increases with the dwell time with a time exponent governed by the parameter that mostly controls the transport in these inks: the relative humidity. As lipids behave like diffusive inks whose transport is due to differences in concentration, the balance between surface spreading rate and ink supply rate modifies the concentration at the meniscus/substrate location. As a

consequence, two regimes emerge: a meniscus dominated regime at low dwell time and a surface dominated regime at higher dwell times. An analytical model has been proposed to fully describe the ink transport [5].

PPL exhibits a combination of aspects from DPN and μ CP ink transport. At high writing forces, the system approaches μ CP. As the tip gets further away from the substrate DPN like transport emerges. Despite great effort has gone into understanding DPN, there is a complete lack of studies concerning the theoretical understanding and modelling in PPL ink transport. It could actually represent an opportunity for furthering the understanding of ink transport mechanisms also in DPN, particularly for those inks whose transport is not fully understood (as e.g. ODT).

Though an extensive analysis of transport has been performed, there are still open questions remaining. DPN of molecular diffusive inks have been widely analyzed and a complete model was developed. Yet, there is no experimental verification of the application of this model in the study of the influence of temperature. Considering the relevance of the dissolution kinetics on the transport of these inks, it would be interesting to study the existence of the phase transition reported by Cho et al. in other inks. Also the possibility of growing 3D structures by cooling down the surface diffusive transport will provide interesting information about the assembly of molecular systems.

DPN of liquid inks has yet to be explored with the extensive detailed analysis performed for molecular inks. Though some tentative models have been proposed, a full transport description has not been yet accomplished.

DPN of lipid inks should extend the preliminary work to other systems, including different inks mixtures and substrates. In particular, studies involving different substrates with higher binding energies (wettability) will provide information about the interactions involved in surface spreading (long range / short range forces). A model describing surface spreading including the corresponding underlying physics, as for example the interactions involved, is yet pending.

PPL is a young technique that has to be fully experimentally explored and analyzed yet. Here a limitation arises from the different results obtained by using different stamps, comprising different elasticities and different solvent absorption.

All in all, diffusion physics behind the experimental results in the transport and spreading in DPN and PPL may be compared and correlated with Molecular Dynamics simulations. The physics behind these transport phenomena opens an interesting research line for analyzing general diffusive mechanisms.

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