Supporting Information

Liquid ink deposition from an atomic force microscope tip: deposition monitoring and control of feature size

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SUPPORTING INFORMATION

1. Relationship between adhesion force and feature size

The maximum adhesion force exhibits a direct relationship with dot radius. Figure 1 (A) shows a plot of maximum adhesion force (black filled circles) versus deposited dot radius. The R^2 value of the fitted linear trendline is 0.951. An illustration of the meniscus geometry and the resulting forces of adhesion is given in Figure 1 (B). We now discuss the origin of the relationship between adhesion force and dot radius.

The force acting upon the cantilever during retract derives from the summation of two main components, the capillary force (F_{Cap}) and the Laplace force (F_{Lap}):[27,32]

$$F = F_{Cap} + F_{Lap} \quad (3)$$

The capillary force component arises from the surface tension of the liquid (γ) acting on the ink-tip contact line (given by 2π times the radius of contact, $R_{m,tip}$), and normalized to the vertical using the angle φ_{tip}:

$$F_{Cap} = -2\pi\gamma R_{m,tip} Cos\varphi_{tip} \quad (4)$$

The Laplace force component arises from the Laplace pressure (ΔP_m, negative for negative meniscus curvature) acting on the area of contact with the tip:

$$F_{Lap} = \pi {R_{m,tip}}^2 \Delta P_m Cos\varphi_{tip} \quad (5)$$

The capillary force pulls the tip down to the substrate, and is therefore negative. The Laplace force also pulls to the substrate if the Laplace pressure is negative (true within a meniscus of negative curvature).

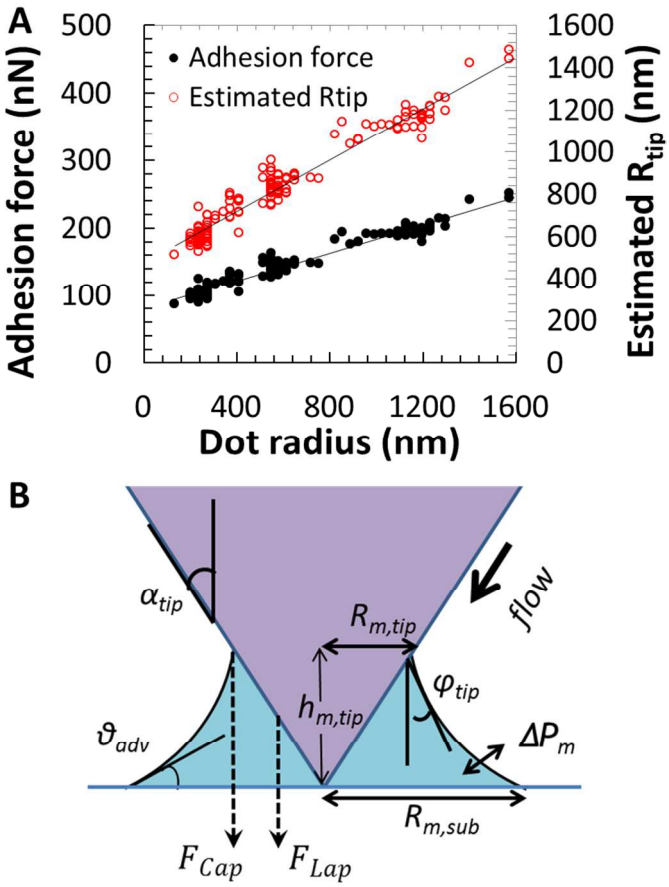

Figure 1. Relating maximum adhesion (or 'pull-off') force to resulting dot radius. (A) A plot of maximum adhesion force (black filled circles) versus deposited dot radius for 180 dots exhibits a linear relationship (equation of trendline: y = 0.1034x + 80.806, R^2 = 0.951). This adhesion force can be used to calculated the radius of meniscus contact on the tip, $R_{m,tip}$, (red open circles). The $R_{m,tip}$ value is typically about 60% of the resulting dot radius (equation of trendline: y = 0.6093x + 476.32). (B) The adhesion force originates from the capillary and Laplace forces defined by the geometry of the meniscus between tip and substrate.

Despite the direct correlation between maximum adhesion force and dot radius, we find that the adhesion force is not ideal for monitoring the deposited feature size as the calculation

invokes several unknown variables. Both contributing forces, F_{Cap} and F_{Lap}, depend critically on the radius of ink contact around the tip, $R_{m,tip}$, and not directly on the radius of the deposited feature. This crucial $R_{m,tip}$ value is difficult to independently measure, and has only previously been inferable as an adjustable parameter in simulations.[27] We can estimate $R_{m,tip}$ at the instant of pull-off, by assuming the maximum adhesion force is due entirely to the dominant capillary force acting at the angle $\varphi_{tip} = 0$ (i.e. $Cos(0)=1$). Our estimated $R_{m,tip}$ values are plotted as the open red circles in Figure 1 (A); thus, $R_{m,tip}$ is estimated to be about ~60% of the resulting dot radius. The adhesion force can, in principle, be used to reconstruct the meniscus geometry at pull-off, although several more parameters must be accounted for. As we show in Figure 1 (B), the geometry of the ink meniscus is defined by many parameters including; the meniscus radius at the substrate ($R_{m,sub}$), the meniscus height on the tip ($h_{m,tip}$), the ink-substrate (advancing) contact angle (θ_{adv}), the ink-tip contact angle (θ_{tip}), and the pyramidal shape of the tip itself (α_{tip}). All of these parameters are difficult to independently verify. Furthermore, if the ink-tip contact line is not pinned, the $R_{m,tip}$ value may change during retraction. The decreasing forces during retraction are due mainly to modification of the F_{Cap} and F_{Lap} forces by changing $R_{m,tip}$ and φ_{tip} values. The meniscus is 'pulled' down to the apex of the tip as it is distended. Detailed discussions of the changing adhesion force profile during retraction have been provided by both Chaudhury and Ondarçuhu.[27,32] As the resulting dot dimensions cannot be directly computed from $R_{m,tip}$, we conclude that the maximum adhesion force is not an ideal parameter for monitoring the deposited feature size.

The adhesion contribution due to ambient water may also distort the correlation when applied at different relative humidity.