How Narrow Can a Meniscus Be?

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A water meniscus naturally forms in air between an atomic force microscope (AFM) tip and a substrate. This nanoscale meniscus produces a capillary force on the AFM, and also serves as a molecular transport channel in dip-pen nanolithography (DPN). A stable meniscus is a necessary condition for DPN and for the validity of the Kelvin equation commonly applied to AFM experiments. Lattice gas Monte Carlo simulations show that, due to thermal fluctuation, a stable meniscus has a lower limit in width. We find a minimum width of 5 molecular diameters (1.9 nm) when the tip becomes atomically sharp (terminated by a single atom).

When confined between solid surfaces, a vapor will condense into a liquid at a lower vapor pressure than its bulk gas-liquid transition point. This process is known as capillary condensation, and it manifests itself in numerous ways, including adhesion of solids and granular materials [1] and sticking of insects to surfaces [2]. If one of the confining surfaces becomes extremely sharp [as in an atomic force microscope (AFM) tip with a radius typically 10–100 nm], the resulting meniscus is a liquid bridge with submicrometer dimensions. This meniscus gives rise to a capillary force that dominates the pull-off force [3], and it also serves as a channel for molecules to flow from the tip to the substrate in dip-pen nanolithography (DPN) [4]. Despite its general occurrence in AFM experiments and its technological importance in DPN, fundamental understanding of the meniscus properties is poor. Any macroscopic theory, including the venerable Kelvin equation [5], cannot reveal nanometer level details of the liquid meniscus. What are the shape and size of the liquid meniscus? How vulnerable is it to thermal fluctuation [6]? In particular, we are interested in the minimum width of the meniscus as this likely sets the lower size limit for the molecular patterns generated in DPN [4] and for the validity of any macroscopic picture of the meniscus including the Kelvin equation.

Here we present Monte Carlo simulations of meniscus formation for a geometry that realistically mimics an AFM tip close to a flat substrate (Fig. 1). We systematically study the liquid meniscus by varying the tip-substrate distance and vapor pressure (saturation). Considering the large parameter space that needs to be sampled (see below), atomistic simulations [8,9] with a full description of molecular details are beyond our reach. We thus have opted for a lattice gas model that has been widely used in studying hydrophobic effects in confined geometries [7,10]. The model captures the essential features of confined liquids [7], e.g., phase behavior of water confined in a carbon nanotube [9]. In our lattice gas

model, a molecule interacts with its nearest neighbor molecules with attraction ϵ and has its own chemical potential μ. When it is located at one of the nearest neighbor sites on the surfaces, it feels binding energies b_T and b_S from the tip and substrate, respectively. As in our two-dimensional simulations [6], a grand canonical (μVT) Monte Carlo simulation is performed by utilizing the equivalence of the lattice gas model to an Ising model
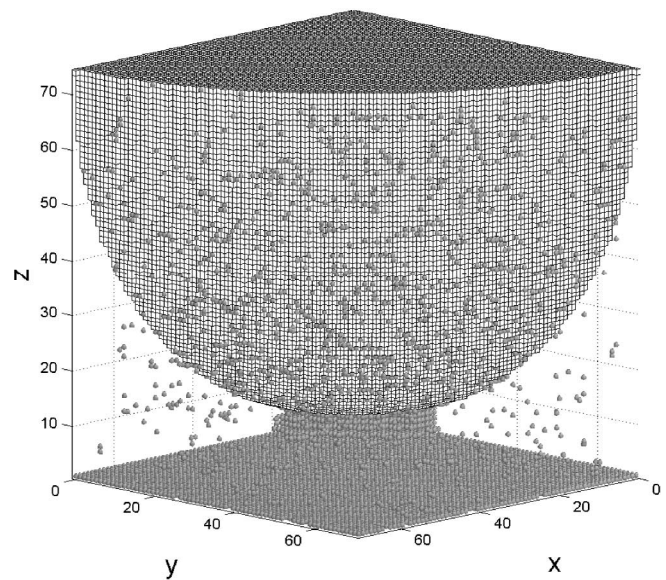

FIG. 1. System geometry and a snapshot of the liquid meniscus. Molecules are drawn as spheres, and the tip sites as cubes on the cubic lattice. At a vapor saturation of 80%, a liquid meniscus connects a partially wetting tip to the completely wetting substrate located at $z = 0$. Only the first quadrant of our system ($0 \leq x, y \leq 70$) is shown. In this and all of the following figures, our length unit is the lattice spacing which can be identified as the molecular diameter (roughly 0.37 nm for water [7]). The spherical tip in the figure has a radius of 70 molecular diameters (26 nm).

[11]. The horizontal range of our system is $-70 \leq x, y \leq 70$. Only the first quadrant of the system ($0 \leq x, y \leq 70$) is varied in the Monte Carlo moves, and then the first quadrant of the system is reflected with respect to the xz and yz planes and the z axis. In calculating molecular interactions at the boundaries of our system, we assume that no molecule exists outside the boundaries. In simulating the ellipsoidal tips discussed later, we used the horizontal range of $-30 \leq x, y \leq 30$ without invoking the reflection symmetries used for the spherical tip. An ellipsoid has a vertical radius (the z direction) of 30 lattice spacings and a horizontal radius (in the x, y directions) of r. We changed the aspect ratio, $30/r$, from 0.7 to 6.0 so that the tip contact diameter (see below) varies from 16 to 1.

A substrate binding energy relative to the molecular attraction $b_S/\epsilon = 1.594$ is chosen to emulate a water-gold binding energy [12] relative to hydrogen bonding strength [13]. With this binding energy, the liquid completely wets the substrate at all temperatures [14]. In terms of the contact angle Θ between the liquid-vapor and liquid-solid interfaces, complete wetting corresponds to $\Theta = 0°$. To study the effect of tip wettability, we have examined three values of the tip-liquid interaction energy: completely wetting ($\Theta = 0°$), partially wetting ($0° < \Theta < 90°$), and partially drying ($90° < \Theta < 180°$) tips. If we identify our liquid as water, these tips can be called strongly hydrophilic, weakly hydrophilic, and hydrophobic, respectively. The binding strength for the completely wetting tip is taken to be the same as the substrate, $b_T/\epsilon = 1.594$. For the partially wetting tip, we take $b_T/\epsilon = 0.75$. The tip binding energy for the partially drying tip is taken to be $b_T/\epsilon = 0.2$ which was suggested for the interaction between water and a hydrophobic surface [10]. Vapor saturation is defined as $\exp[(\mu - \mu_c)/ k_B T]$, where μ is chemical potential and μ_c ($= -3\epsilon$) is the chemical potential at the bulk gas-liquid transition. The bulk critical temperature in our model is known to be $k_B T_c/\epsilon = 1.128$ [14]. To mimic water ($T_c = 647.30$ K) at room temperature (300 K), we set $T/T_c = 0.46$ in our simulation.

The width of a liquid meniscus for a given liquid snapshot is determined by first counting the number of columns that are continuously occupied by molecules from the site just above the substrate to the site right below the tip surface. Such a collection of columns forms an approximate circle when viewed along the z axis, and the number of columns is proportional to the circle area. The liquid meniscus width is then defined as the diameter of the circle. If the meniscus has a concave shape, the width defined this way corresponds to the width at its neck. In order to differentiate it from a molecular monolayer sandwiched between the tip and the substrate, a meniscus is required to have a vertical length of at least 2 molecular diameters.

Figure 1 shows the system geometry along with a snapshot of liquid molecules generated in a typical simulation.

Molecules form a liquid meniscus (with a radius about 19 molecular diameters) between a spherical tip and a plane substrate. First note that, in contrast to the macroscopic (continuum) picture, the snapshot deviates from a meniscus with cylindrical symmetry. Also, the substrate is completely covered (wet) by molecules (contact angle zero), whereas the partially wetting tip is incompletely covered and the liquid meniscus forms nearly a 90° contact angle with the tip surface.

How do the properties of the liquid meniscus depend on the tip-substrate distance? Shown in Figs. 2(A), 2(B), 2(C), and 2(D) are representative snapshots of the system for various tip-substrate distances. As the tip-substrate distance increases from the closest noncontact distance [Fig. 2(A)], the meniscus narrows [Figs. 2(B) and 2(C)],
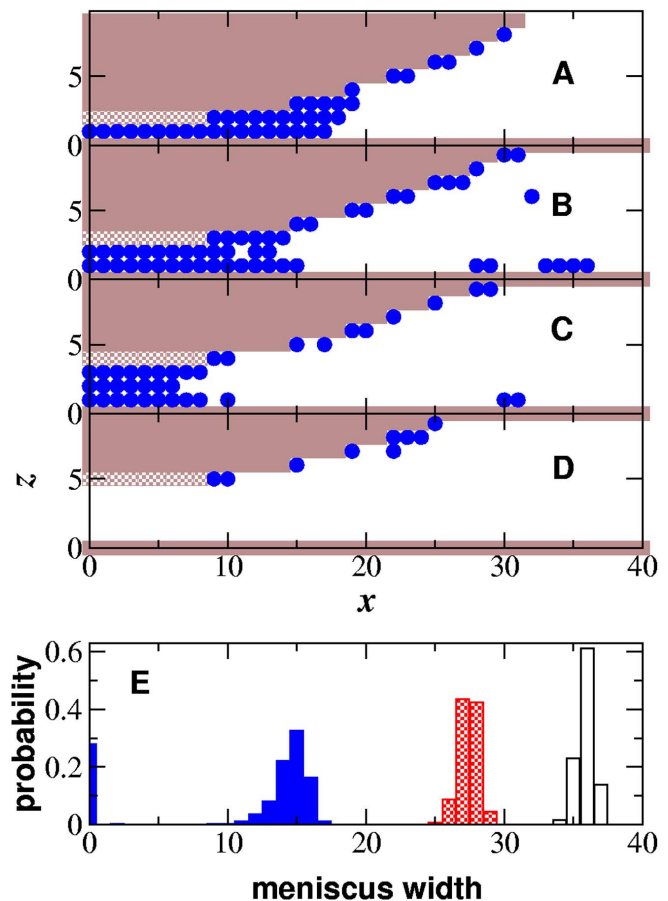

FIG. 2 (color online). Thinning and snap-off of the liquid meniscus and the meniscus width distribution. (A)–(D) Representative liquid snapshots at different tip-substrate distances for the completely wetting tip at a vapor saturation of 30%. Molecules are drawn as circles and the tip and substrate as gray (appearing purple-gray online) areas. The tip contact area is hatched. Only the right half ($x \geq 0$) of the xz cross section of our system is shown. Because of the low humidity, a water monolayer has not formed on the completely wetting substrate. (E) Normalized probability distribution in the liquid meniscus width for (A) (open bars), (B) (hatched bars), and (C) (solid bars).

and eventually snaps off [Fig. 2(D)]. How much does the meniscus fluctuate? For each tip-substrate distance, we generated 40 000 snapshots in our simulation and determined how the meniscus width varies from snapshot to snapshot. The width probability distribution is plotted in Fig. 2(E) for tip-substrate distances corresponding to Figs. 2(A), 2(B), and 2(C). As the tip recedes from the substrate, the meniscus width at the center of the distribution decreases. At a distance just before the snap-off [Fig. 2(C)], the distribution broadens significantly and shows bimodal behavior with peaks at 15 and 0 molecular diameters. This onset of a peak located at zero width indicates that the meniscus is unstable. The instability of a meniscus under a certain size can be interpreted as arising from its large surface/volume ratio. The average width where this first occurs is 15 molecular diameters, which is similar to the width of the tip surface sites closest to the substrate [drawn as hatched areas in Figs. 2(A), 2(B), 2(C), and 2(D)]. We will study this point in more detail below, but first we need to provide a more quantitative measure of stability. To do this, we have calculated the standard deviation in the meniscus width relative to its average, a quantity that we call the fluctuation. After examining a range of vapor saturations (10%–80%) and tip-substrate distances, we find that even the most stable liquid meniscus has a fluctuation of more than 1%. In the following, we will assume that liquid menisci with fluctuations less than 10% are stable menisci (our conclusions do not change if we use 5% or 20% for the cutoff value).

What will be the minimum width of the stable menisci defined above? At various vapor saturations, we determined the minimum width for a given saturation by varying the tip-substrate distance. The results are plotted in Fig. 3 for the partially and completely wetting tips. For the drying tip, we found only a monolayer of liquid that is sandwiched between the tip and the substrate. This monolayer is entirely due to the completely wetting substrate, and is not considered as part of the meniscus. Figure 3 shows that no stable meniscus exists at low saturations (<20% for the completely wetting tip, <40% for the partially wetting tip). Overall, the minimum width increases as vapor saturation goes up. For the completely wetting tip, however, the smallest width jumps up at 30% saturation, down at 40%, then back up at 50%. To understand this, note that enhancing the saturation not only results in a broader meniscus for a given tip-substrate distance but causes a meniscus to form at a longer tip-substrate distance. As the saturation rises from 30% to 40%, the tip-substrate distance corresponding to the minimum width increases from 2 to 3 molecular diameters. In this case, thinning of the meniscus due to an increased tip-substrate distance [as illustrated in Figs. 2(A), 2(B), and 2(C)] wins over meniscus broadening due to the saturation rise from 30% to 40%. Upon raising the saturation from 40% to 50%, however, the tip-substrate distance remains the same,
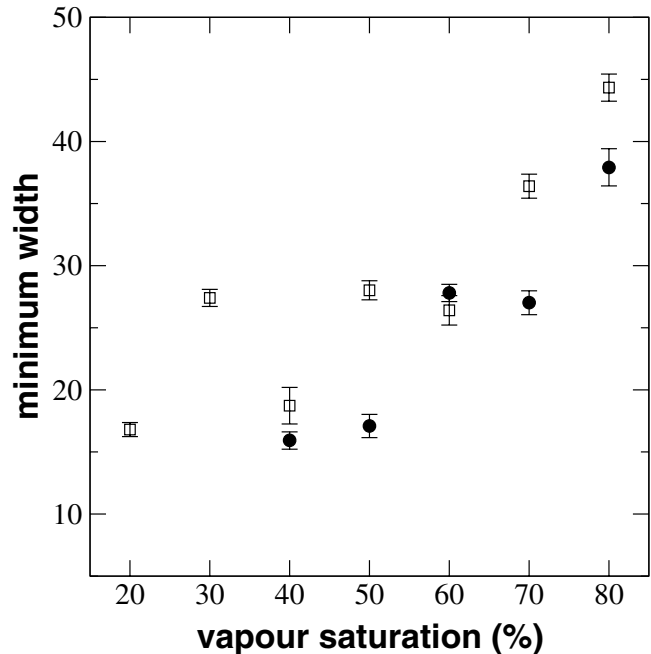
FIG. 3. Minimum width of stable liquid meniscus vs vapor saturation for the tip in Fig. 2. Liquid menisci with width fluctuations less than 10% are considered. At vapor saturations ranging from 10% to 80%, we determined the minimum width for a given saturation by varying the tip-substrate distance. The minimum width is then plotted as a function of saturation for the partially wetting (circles) and completely wetting (squares) tips. The standard deviation in the width is drawn as an error bar in the figure.

and thus the meniscus widens because of the higher saturation.

How small can we make the meniscus by adjusting vapor saturation, tip-substrate distance, and tip wettability? The minimum menisci (regardless of saturation) in Fig. 3 are approximately 16 and 17 molecules wide for the partially wetting, and completely wetting tips, respectively. These diameters (in physical dimensions relevant to water, 6 nm) are close to the diameter of the *tip contact area* [area of the tip sites closest to the substrate, hatched in Figs. 2(A), 2(B), 2(C), and 2(D)]. Therefore, the smallest possible meniscus width is primarily governed by a geometric constraint (the contact area), and is rather insensitive to whether the tip is partially or completely wetting. It is to be noted that the tip wetting property dramatically changes the liquid meniscus structure for a fixed vapor saturation and tip-substrate distance: For example, at a saturation of 50% and tip-substrate distance of 2 molecular diameters, the meniscus shows a substantial increase in width (from 30 to 43) as we vary the tip wettability from partially wetting to completely wetting. It does not, however, play a role in determining the smallest possible width of liquid meniscus.

We now study the correspondence between the smallest width and the tip contact diameter for variable tip geometry. Specifically, we consider ellipsoidal tips with
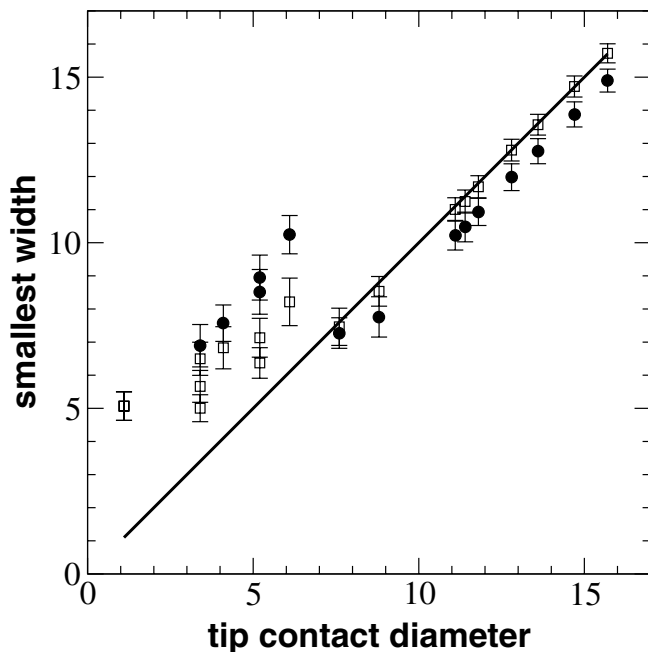
FIG. 4. Smallest meniscus widths for various tip contact diameters. The smallest possible width for a fixed tip geometry is determined by examining stable liquid menisci that form at saturations ranging from 10% to 80%. The smallest width is then plotted as a function of the tip contact diameter for the partially (circles) and completely (squares) wetting tips (the standard deviation in the width drawn as an error bar). The line refers to the case where the smallest width is given by the tip contact diameter. Multiple points for a given contact diameter correspond to tips with different sharpness (aspect ratio). For the completely (partially) wetting tip, humidities at the smallest width are 20%, 20%, 20%, 20%, 20%, 20%, 20%, 20%, 40%, 50%, 30%, 30%, 60%, 40%, 40%, 40%, 80%, and 80% (40%, 40%, 40%, 40%, 40%, 40%, 40%, 40%, 50%, 70%, 70%, 80%, 80%, and 80%) in increasing order of tip contact diameter.

various aspect ratios so that the tip contact diameter ranges from 1 to 16 molecular diameters. We determine the smallest width by using the same range of vapor saturations and tip-substrate distances used for the spherical tip. In Fig. 4, we plot the smallest width vs the tip contact diameter for the partially and completely wetting tips. The equivalence of width and diameter, especially for the completely wetting tip, is excellent for tips with contact diameters as small as 8 molecular diameters. Upon further decreasing the contact area down to just one molecule wide, the smallest width deviates from the corresponding contact diameter and converges to 5 molecular diameters.

In summary, the minimum width of the meniscus formed between an AFM tip and a substrate is determined by a subtle interplay of vapor saturation and tip-substrate distance. As a result, increased saturation does not always result in a broader meniscus, and indeed in some cases one can get a thinner meniscus at a higher saturation by increasing the tip-substrate distance. The liquid meniscus is unstable when it is narrower than the diameter of the tip-substrate contact area. This means that the smallest width of a stable meniscus is determined by the tip contact diameter. In the limit of the sharpest possible tip, i.e., where the contact diameter is just one molecule wide, the width converges to 5 molecular diameters (1.9 nm). Since this result does not depend on fine details of our model, this suggests that 5 molecular diameters is the ultimate size limit for a meniscus. This should also determine the resolution of DPN and a lower limit to use of the Kelvin equation.

Our results can be used to assess a key issue for any macroscopic theory of meniscus formation (including the Kelvin equation), the stability of meniscus. A stable meniscus, however, does not necessarily mean that the Kelvin equation works quantitatively. Can a meniscus be described by two principal radii? Is it possible to use a bulk surface tension to describe a nanoscale meniscus which is sometimes only 5 molecules wide? It requires a separate and thorough investigation to answer those questions. What will be the effects of tip roughness and shape on the meniscus size? Our observation in Fig. 4 suggests that, regardless of tip roughness and shape, it is the contact diameter of the tip that determines the minimum meniscus size.

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