

Capillary Condensation in Atomic Scale Friction: How Water Acts like a Glue

K. B. Jinesh and J. W. M. Frenken*

Kamerlingh Onnes Laboratory, Leiden University, P.O. Box 9504, 2300 RA Leiden, The Netherlands
(Received 21 December 2005; published 27 April 2006)

We present atomic-scale friction force measurements that strongly suggest that the capillary condensation of water between a tungsten tip and a graphite surface leads to the formation of ice at room temperature. This phenomenon *increases* the friction force, introduces a short-term memory in the form of an elastic response against shearing, and allows us to “write” a temporary line of ice on a hydrophobic surface. Rearrangements of the condensate are shown to take place on a surprisingly slow time scale of seconds.

DOI: [10.1103/PhysRevLett.96.166103](https://doi.org/10.1103/PhysRevLett.96.166103)

PACS numbers: 68.35.Af, 61.30.Hn, 68.37.Ps

Water is a good lubricant in everyday life, making it “slippery when wet.” It also acts as a lubricant in numerous industrial and biological settings, where it keeps sliding surfaces apart from each other and allows easy shearing. However, if we reduce the dimensions of a sliding contact to the regime of nanometers, the lubricating properties of water in between can change dramatically. Capillary condensation, the phenomenon of water vapor condensing in cavities or between solid surfaces [1–3], takes place in a wide variety of situations, ranging from the geophysics of rocks to nanotechnology. It forms a matter of growing concern in micro- and nanoelectromechanical systems, which often fail due to the large capillary adhesion and stiction forces between the moving parts [4]. A full understanding of these phenomena requires knowledge of the atomic and molecular details of the surfaces and the water in the contact region. Computer simulations suggest that fluids develop order when brought in contact with surfaces [5–8], but water confined between surfaces may present a special case in view of its tendency to expand upon freezing [9]. Although experiments with the surface forces apparatus (SFA) and the atomic force microscope (AFM) indicate layering of confined liquids such as octamethylcyclotetrasiloxane and water [10–17], the influence of this organization on lubrication is a subject of controversy, in particular, for water [18]. While high viscosities have been reported for water films in some SFA and AFM experiments [15–17,19,20], bulklike shear fluidity has been measured in others for confined water films as thin as 1 nm [21]. Capillary condensation of water between tips and surfaces in the friction force microscope (FFM) can make friction decrease [22] or increase, the latter being ascribed to the higher effective normal load and the viscosity of the capillary meniscus [19,23,24]. Recent STM measurements have been interpreted as evidence for electric-field-assisted formation of ice between a tip and a surface at room temperature [25].

In this Letter, we use a high-resolution FFM to show that the small capillary condensate between a hydrophilic tip and a hydrophobic surface behaves like a solid. The slow response of the condensate to changes in tip position

allows us to write a line of ice on the surface with a lifetime of several seconds.

To perform our experiments, we have used a home-built friction force microscope [26]. The specialty of our instrument is the force sensor (Tribolver™), which had a low lateral (X and Y) spring constant of 6.1 N/m, corresponding to a lateral force sensitivity as low as 20 pN in the present measurements, and a comparatively high stiffness along the surface normal (Z) of 30.5 N/m, making it ideal for friction measurements. An etched tungsten tip was scanned back and forth over a freshly cleaved graphite (HOPG) surface. The experiments were carried out at room temperature in a closed chamber, in which the relative humidity (RH) was controlled in the range from 1% to 55% by continually flushing the chamber with mixtures of dry nitrogen and nitrogen passed through distilled water. In all experiments, the normal force was held constant at 3.7 nN.

Figure 1(a) shows a typical “friction loop,” a combination of one forward scan and the subsequent reverse scan. After an initial, elastic buildup of lateral force over the first 0.4 nm, the tip performs well-resolved atomic stick-slip motion over the individual lattice periods. The friction force, defined as the average force opposing the motion, is 1.2 nN. Figure 1(a) was measured under “dry” conditions, $\text{RH} \approx 1\%$. The apparent “noise” in the loop of Fig. 1(b) reflects similar stick-slip force variations when the scan was performed over a larger distance.

At higher humidities, $\text{RH} \geq 10\%$, the friction loops are surprisingly different from the “classical” shape of Figs. 1(a) and 1(b). As is illustrated in Figs. 1(c) and 1(d) for $\text{RH} = 50\%$, the atomic-scale details disappear completely. The loops develop an overall tilt at short scan ranges [Fig. 1(c)]. At longer scan ranges of 5 nm and more, the lateral force in each loop first levels off [at 2.2 nN in Fig. 1(d)] to increase again just before the end of the scan line (both on the forward and on the reverse path). To our knowledge, nanoscale force loops with such unusual shapes have not been reported before. We have measured increased tip-surface attraction during approach-retraction cycles, which indicates capillary condensation at

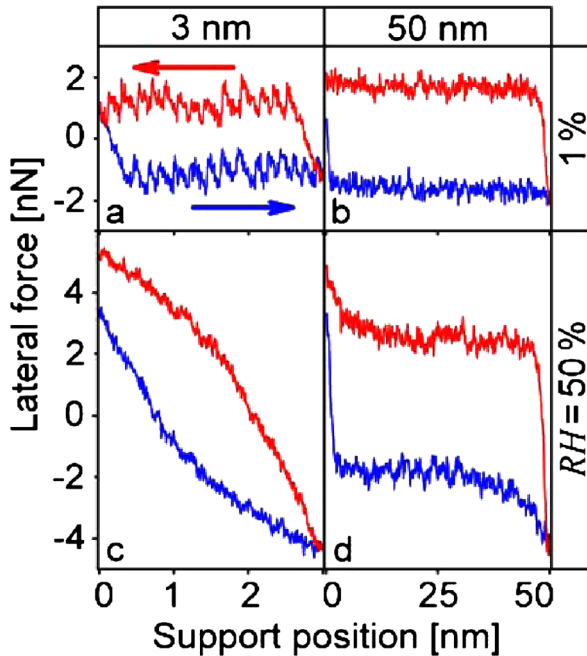


FIG. 1 (color online). Lateral force loops (blue = forward, red = reverse motion) obtained with a tungsten tip on HOPG at two values of the RH and for two scan ranges, at a normal force of 3.7 nN. At low humidity (a),(b) the tip moves in traditional “stick-slip” fashion over the surface. At high humidity the entire loop is tilted for short scan ranges (c), while for larger ranges (d) peaks develop in the lateral force, just before the end of the forward and reverse parts of the loop.

these RH values of water between the hydrophilic tip [27] and the hydrophobic surface [20,28].

The size of the lateral force peak (width and height) scales linearly with the scan range (Fig. 2) [29]. Figure 3 shows that an abrupt increase in scan range from 25 to 50 nm resulted in a dramatic widening of the peak, which slowly relaxed to its new width and height on a time scale in the order of 2 s. When the scan size is reduced stepwise the first force loops exhibit the “traditional” shape, i.e., without friction peaks near the ends and the friction peaks reappear only after a delay in the order of 1 s. In spite of the slow response, all changes are completely reversible without a trace of hysteresis. There is also a long time scale involved in the tilting of the short-range loops, which gradually disappears when the scanning is slowed down to speeds below 0.1 nm/s [30].

We propose a simple scenario that provides a consistent explanation for the remarkable results of Figs. 1–3. Figure 4(a) illustrates the situation at low humidity, where the tip only senses the potential corrugation of the substrate lattice and performs stick-slip motion through this potential energy landscape. At higher humidity capillary condensation takes place between the tip and the surface [Fig. 4(b)]. Since we no longer observe atomic stick-slip motion, we conclude that the water actually intervenes between the tip and the surface. The tilting of the lateral

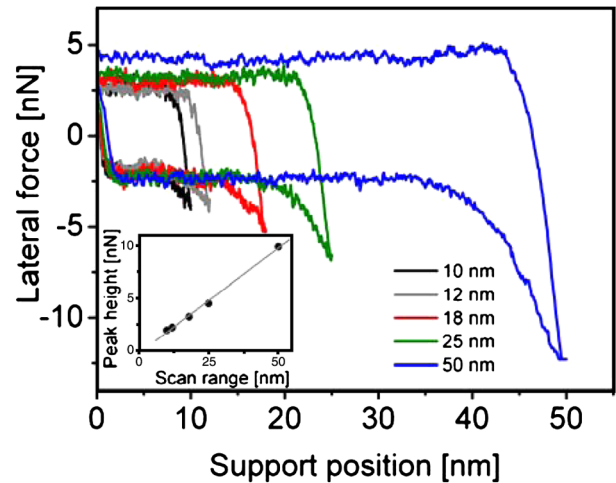


FIG. 2 (color online). Variation of the lateral force peak with the scan range (RH = 23%). Width and height of the (negative) peak in the forward (i.e., lower) part of the force loop are both proportional to the scan range (see inset). Each loop was measured sufficiently long after setting a new scan range to avoid transient effects (Fig. 3).

force loops implies that, even when the tip is moving with respect to the substrate, an elastic force is building up. This must be a force exerted by the condensate and it suggests that the tip is elastically deforming the capillary neck, as sketched in Fig. 4(b). At larger scan ranges, beyond ~ 5 nm, the scans contain a constant-friction plateau, still without a trace of stick-slip motion, and a distinct peak

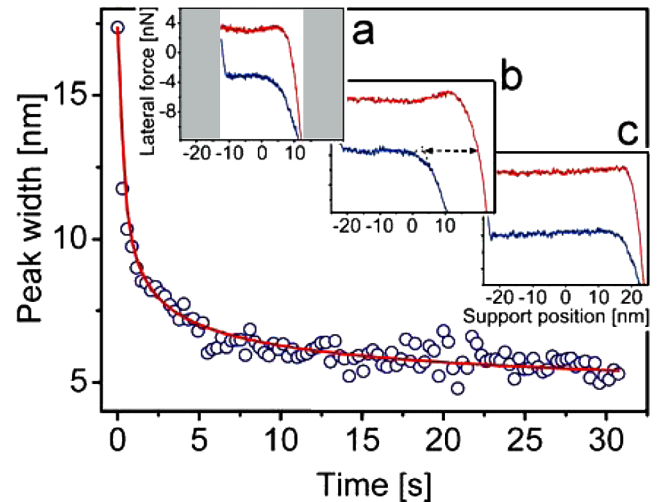


FIG. 3 (color online). Response of the lateral force peak to a stepwise increase in scan range (RH = 23%). The insets show (a) the last force loop at a scan range of 25 nm, (b) the first and (c) the 102nd loop at 50 nm range ($t = 0$ and 29.6 s, respectively, after the change in scan range). The force peaks shown here all exceeded the 12 nN maximum detectable force of our sensor. The main panel shows the slow relaxation of the width of the lateral force peak.

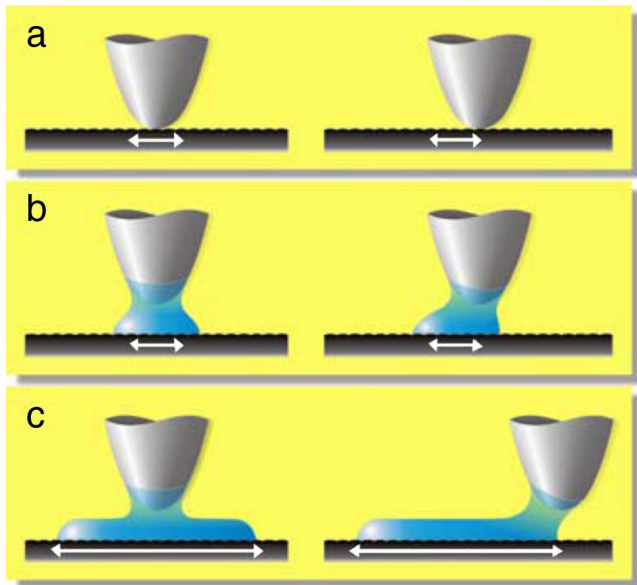


FIG. 4 (color online). Scenario proposed to explain our observations. (a) Under dry conditions the tip is in direct contact with the carbon atoms of the graphite substrate and it performs stick-slip motion. (b) When the humidity is noticeable capillary condensation of water takes place between the tip and the substrate. The condensate is solid and exerts elastic forces on the tip during small scans with a range up to the diameter of the condensate, which makes the entire lateral force loop tilt. (c) When the scan range is increased beyond the original size of the capillary neck, the condensate is forced to grow to a more elongated shape; at the end of the scan range, the condensate is again exerting an elastic force on the tip, which is reflected in the lateral force peaks.

near the end of the scan. This suggests that the tip remains in contact with the condensate over its entire trajectory and that it reaches the end of the condensate just before the end of each scan line. This means that under these circumstances the condensate is elongated to a length that spans a large fraction of the scan range [Fig. 4(c)]. In other words, the tip “writes” a stripe of water on the hydrophobic substrate [28]. Up to the maximum scan range of 250 nm in our experiment, we have not observed any indication of the tip detaching from the condensate. Also the maximum abrupt change in scan size of 100 nm was not accompanied by any sign of detachment. At the end of the large scan range, the situation is similar to that at the end of the smaller scan ranges, with an additional elastic force building up as the tip is deforming the end of the condensate. The scan range of approximately 5 nm, at which the shape of the scans crosses over from a tilted loop to the plateau-and-peak structure, can be used as a crude estimate of the diameter of the equilibrium shape of the capillary neck.

Mechanically, the condensate behaves much more like ice than like water. Whereas regular water cannot sustain any static stress at all, Figs. 1(c) and 1(d) show that before the tip starts to slide there is an initial, fully elastic re-

sponse, with a lateral spring coefficient of 12 N/m, fully independent of scan speed and scan range. For a cylinder with the above diameter of 5 nm and a height of 1.2 nm [estimated Kelvin radius (of ice) at room temperature [1]] this corresponds to an elastic modulus of 0.23 GPa, which is a substantial fraction of the value for bulk ice (9.9 GPa). Sliding sets in at a well-defined force of 1.7 nN, again independent of scan speed and scan range. This force corresponds to a maximum shear stress of 90 MPa, which is in the order of the yield stress of ice (~ 100 MPa). An important observation is the kink at 1.2 nN present in all force loops, separating the static response from the sliding. This value did not change over the three decades in velocity that we could probe in the experiment. We have performed additional frequency dependence experiments [30], from which we derive a lower estimate of the condensate’s effective viscosity of 10^8 Pa s, which is 10 orders of magnitude above that of bulk liquid water.

Additional evidence for the presence of ice comes from the observation of regular structure, different from that of graphite. Measurements of friction as a function of normal load indicate layering of the condensate. At very low scan velocities (< 2.5 nm/s) and intermediate relative humidities ($5\% < RH < 30\%$) we have observed pronounced stick-slip motion in the force loops with an average period of 0.41 ± 0.1 nm, very different from the 0.25 nm distance typical for graphite and close to the 0.45 nm lattice constant of hexagonal ice. These results will be discussed in a separate publication [30].

Also, the extremely long relaxation time scale of 2 s seen in Fig. 3 indicates that the condensate is very different from liquid water [28]. At the bulk viscosity of water ($\eta = 0.9 \times 10^{-3}$ Pa s) we would expect characteristic times of picoseconds for rearrangements of films of a few nm thickness, comparable to the time scale for molecular rearrangements in water [31]. At first sight a response time of 2 s seems surprising in view of the short time of microseconds to milliseconds estimated for the formation of a capillary neck via adsorption of water molecules from the water vapor at room temperature and $RH = 50\%$ [24,32]. However, if we accept that the condensed water is immediately converted into ice, the subsequent time scale will be that of rearrangements of the ice, by plastic deformation, by (surface dominated) diffusion, or by sublimation-condensation dynamics. Each of these processes should be orders of magnitude slower than liquid water. Nevertheless, we cannot explain time scales in the order of seconds. For example, using the sublimation rate [33] and surface free energy of ice, we estimate that the elongated condensates should ball up under the influence of sublimation-recondensation dynamics within $20 \mu\text{s}$.

From our measurements we draw the additional conclusion that during the long scans, the *entire* elongated condensate is solid rather than liquid, i.e., not just the water immediately below the tip. If the water would be solid only

locally, the remainder of the condensate would have the opportunity to ball up at a speed characteristic for water. This implies that the condensate does not require confinement between *two* solids, the tip and the substrate, to be solid, but that the mere presence of a *single* interface with the graphite substrate is sufficient [28].

In summary, our FFM results provide strong evidence that a nanoscale capillary water condensate can solidify at room temperature and behave like glue rather than like a lubricant. This conclusion stands in sharp contrast with the interpretation of earlier experiments with the surface forces apparatus that suggest lubrication by water down to the nanoscale [21] and absence of noticeable “ice structure” [19]. We find that the FFM tip can write a temporary stripe of ice on the substrate. Further work will be necessary to obtain detailed information on the structure of the solid condensate and to identify the mechanism of its slow rearrangements. It will be important to determine whether other tip-surface combinations and other contact geometries can make the condensate stay liquid. Finally, it remains to be investigated to what extent the icelike behavior contributes to friction under practical circumstances.

*Electronic address: frenken@physics.leidenuniv.nl

- [1] J.N. Israelachvili, *Intermolecular And Surface Forces* (Academic, London, 2002), 2nd ed.
- [2] M. Urbakh, J. Klafter, D. Gourdon, and J.N. Israelachvili, *Nature* (London) **430**, 525 (2004).
- [3] J. Jang, G.C. Schatz, and M.A. Ratner, *Phys. Rev. Lett.* **92**, 085504 (2004).
- [4] B. Bhushan, *Wear* **259**, 1507 (2005).
- [5] P.A. Thompson and M.O. Robbins, *Science* **250**, 792 (1990).
- [6] M. Odelius, M. Bernasconi, and M. Parrinello, *Phys. Rev. Lett.* **78**, 2855 (1997).
- [7] O.M. Braun and M. Peyrard, *Phys. Rev. E* **68**, 011506 (2003).
- [8] J. Gao, W.D. Luedtke, and U. Landman, *Phys. Rev. Lett.* **79**, 705 (1997).
- [9] E.A. Jagla, *Phys. Rev. Lett.* **88**, 245504 (2002).
- [10] M.L. Gee, P.M. McGuiggan, and J.N. Israelachvili, *J. Chem. Phys.* **93**, 1895 (1990).
- [11] B. Bhushan, J.N. Israelachvili, and U. Landman, *Nature* (London) **374**, 607 (1995).
- [12] S.J. O’Shea, M.E. Welland, and J.B. Pethica, *Chem. Phys. Lett.* **223**, 336 (1994).
- [13] J. Klein and E. Kumacheva, *J. Chem. Phys.* **108**, 6996 (1998).
- [14] Y. Zhu and S. Granick, *Phys. Rev. Lett.* **93**, 096101 (2004).
- [15] M. Antognozzi, A. D.L. Humphris, and M.J. Miles, *Appl. Phys. Lett.* **78**, 300 (2001).
- [16] R.M. Pashley and J.N. Israelachvili, *J. Colloid Interface Sci.* **101**, 511 (1984).
- [17] S.P. Jarvis, T. Uchihashi, T. Ishida, H. Tokumoto, and Y. Nakayama, *J. Phys. Chem. B* **104**, 6091 (2000).
- [18] S. Ohnishi and A.M. Stewart, *Langmuir* **18**, 6140 (2002).
- [19] Y. Zhu and S. Granick, *Phys. Rev. Lett.* **87**, 096104 (2001).
- [20] X. Zhang, Y. Zhu, and S. Granick, *Science* **295**, 663 (2002).
- [21] U. Raviv and J. Klein, *Science* **297**, 1540 (2002).
- [22] M. Binggeli and C.M. Mate, *Appl. Phys. Lett.* **65**, 415 (1994).
- [23] L. Sirghi, *Appl. Phys. Lett.* **82**, 3755 (2003).
- [24] E. Riedo, F. Levy, and H. Brune, *Phys. Rev. Lett.* **88**, 185505 (2002).
- [25] E.M. Choi, Y.H. Yoon, S. Lee, and H. Kang, *Phys. Rev. Lett.* **95**, 085701 (2005).
- [26] M. Dienwiebel *et al.*, *Rev. Sci. Instrum.* **76**, 043704 (2005).
- [27] M. Schenk, M. Fütting, and R. Reichelt, *J. Appl. Phys.* **84**, 4880 (1998).
- [28] A. Gil, J. Colchero, M. Luna, J. Gómez-Herrero, and A.M. Baró, *Langmuir* **16**, 5086 (2000).
- [29] At high humidities and large scan ranges we have observed both symmetric friction loops, with friction peaks on both sides [Fig. 1(d)], and asymmetric loops, with peaks that were not equally large or with only a single peak (Figs. 2 and 3). The observations that the asymmetry was independent of scan location and scan size and that it changed primarily between subsequent tip-surface approaches suggest that it is related to the detailed shape of the tip.
- [30] K.B. Jinesh and J.W.M. Frenken (unpublished).
- [31] A.W. Omta, M.F. Kropman, S. Woutersen, and H.J. Bakker, *Science* **301**, 347 (2003).
- [32] R. Szoszkiewicz and E. Riedo, *Phys. Rev. Lett.* **95**, 135502 (2005).
- [33] J.G. Davy and G.A. Somorjai, *J. Chem. Phys.* **55**, 3624 (1971).