Nucleation Time of Nanoscale Water Bridges

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Water capillaries bind together grains of sand. They also can bind an atomic force microscope tip to a substrate. The kinetics of capillary condensation at the nanoscale is studied here using friction force microscopy. At 40% relative humidity we find that the meniscus nucleation times increase from 0.7 to 4.2 ms when the temperature decreases from 332 to 299 K. The nucleation times grow exponentially with the inverse temperature $1/T$ obeying an Arrhenius law. We obtain a nucleation energy barrier of 7.8×10^{-20} J and an attempt frequency ranging between 4 and 250 GHz, in excellent agreement with theoretical predictions. These results provide direct experimental evidence that capillary condensation is a thermally activated phenomenon.

Recent developments in science and technology emphasize the key role of water in controlling solid-solid interfacial adhesion, friction, and wear [1]. Depending on material hydrophilicity and experimental conditions, e.g., pressure, temperature, and humidity, water molecules can form different kinds of structures on a solid surface. One can observe ordered water layers, small droplets, thin films, or capillary bridges [2–6]. Of these examples, capillary bridges are probably the most ubiquitous. The water bridges provide stability to sand castles, act as transport channels for dip-pen nanolitography [7], and increase adhesion and friction in microdevices and nanodevices such as microelectromechanical systems [1,8–10]. Despite the crucial role of water bridges in widespread fields, fundamental knowledge about capillary condensation is still very incomplete.

We know from classical thermodynamics that the balance between pressure and surface energy gives rise to the meniscus curvature as described by the Young-Laplace equation [11] $\Delta P = \gamma_{LV}(r_1^{-1} + r_2^{-1})$, where ΔP is the difference between the pressure inside and outside the meniscus, γ_{LV} is the liquid-vapor surface tension of water, and r_1, r_2 are the principal radii of the meniscus curvature. The values of r_1 and r_2 at thermodynamic equilibrium are determined by the Kelvin radius r_K through the Kelvin equation [11]:

$$\frac{1}{r_1^{eq}} + \frac{1}{r_2^{eq}} = 1/r_K = [k_B T/(\gamma_{LV} \upsilon_M)]\ln(p/p_s). \quad (1)$$

Here, k_B is Boltzmann's constant, T is the temperature, υ_M is the molecular density of water, and p/p_s is the relative humidity defined as the ratio of the water pressure p to the saturated water pressure p_s. Since Eq. (1) is based on classical thermodynamics, it is a matter of debate whether it is valid at the nanoscopic scale [12,13]. Previous experiments with surface force apparatus (SFA) have shown that the Kelvin equation is valid for cyclohexane and water menisci with radii as small as 4–5 nm [13,14].

The dynamics of capillary condensation is very poorly understood. SFA investigations in almost saturated water pressure find menisci growth rates between 0.5 and 2 nm/s for menisci growing from 20 to 60 nm [15]. The authors used a model based on Langmuir's theory of droplet growth to explain their results. However, the model gave consistently larger condensation times. Some recent studies of the time dependence of frictional forces suggest that capillary nucleation is thermally activated [16,17]. Numerical simulations [18,19] using a time-dependent Landau-Ginzburg model confirm this idea, but direct experimental evidence is still missing.

In this Letter, we determine the nucleation times for nanoscopic water capillaries from measurements of temperature and time-dependent nanoscopic frictional forces. We find that the nucleation times grow exponentially with $1/T$ obeying an Arrhenius law. The resulting nucleation energy barrier is in excellent agreement with theoretical predictions. The attempt frequency is of the same order of magnitude as the mean vibrational frequency of nanoscopic water droplets.

To investigate capillary condensation at the nanoscale, we study frictional forces, F_F, between the spherical tip of an atomic force microscope (AFM) and a slightly rough surface in humid air. The pressure difference, described by the Laplace equation, produces an attractive capillary force between the tip and the surface. The relationship between nanoscopic dynamic friction and capillary forces, F_{cap}, is well approximated [6] by

$$F_F \simeq \mu(F_N + F_{cap}), \quad (2)$$

where μ is the coefficient of friction and F_N is the normal load. Information on the kinetics of capillary condensation is obtained from friction measurements at varying scanning velocities, υ [20], for different temperatures at fixed relative humidity.

In our experiments we used a Molecular Imaging AFM system (PicoPlus II) with a silicon rectangular cantilever

(Pointprobes from Nanosensors). The normal and lateral spring constants ($k_N = 0.1$ N/m and $k_L = 24.5$ N/m, respectively) were calculated from the geometrical dimensions of the cantilever obtained by scanning electron microscope (SEM) images. The friction measurements employed loads of 15 ± 1 nN. Subsequently, the tip radius R was determined as 25 ± 5 nm by SEM imaging. We maintained the relative humidity at $37\% \pm 2\%$ [21] during all the measurements by flushing the experimental chamber with streams of dry and humid argon [22]. The temperature of the experimental chamber was varied from 332 to 299 K [23]. We estimated the temperature rise at the top of the tip due to laser heating by solving heat transfer equations similar to those presented in [24], but including the effect of heat conduction through the air. We found a maximum temperature rise of 10 K. Since we also calculated that the tip thermal resistance was 3 orders of magnitude larger than the resistance of the cantilever, we concluded that the temperature rise at the tip-surface contact was not larger than 1–2 K. Our sample was a sterilized 1.5 mm thick slide of soda lime glass (Erie Scientific, USA) used without any surface treatment. The static contact angle of a water droplet on our sample was $10° \pm 2°$. The root mean square roughness was about 1 nm over an area of 1 μm^2. These sample properties were optimal for the study of the formation of water capillaries at room temperature in time scales accessible to our measurements [25].

Figure 1 shows friction vs velocity curves at different temperatures and 37% relative humidity. For each temperature, we identify two different regimes. At low velocities, F_F decreases linearly with log$v$. At high velocities, F_F is almost constant. A critical velocity v_c, which varies with T, marks the abrupt transition between the two regimes. The influence of capillary condensation on the time dependence of frictional forces has been extensively studied [6,26,27]. It is now accepted that capillary forces are

time dependent since the capillary bridges need time to form and grow until thermodynamic equilibrium is established. This phenomenon is clearly seen in friction vs velocity curves such as those shown in Fig. 1. Low velocities correspond to longer contact times and hence to larger and/or more numerous water bridges. The frictional force decreases with increasing velocity up to the moment when the contact time is so short that the water capillaries do not have enough time to form and produce a detectable capillary force. For larger velocities, no velocity dependence due to capillaries is expected. Thus, v_c at the intersection of these two regimes defines the onset of capillary bridge formation. We note that nanoscopic friction in a dry environment slightly increases with velocity due to thermally activated stick and slip [28,29]. In Fig. 1, the stick and slip action is noticeable in the high velocity measurements at 299 and 306 K, but is masked elsewhere.

In order to determine the mean capillary nucleation time τ, we need to know how far the AFM tip can travel with respect to one asperity before capillary nucleation stops. This transversal (with respect to the bridge main axis) distance, d_t, can be estimated as the ''apparent'' tip-sample contact diameter, $2a$, i.e., the contact diameter that would occur if the glass surface was atomically smooth. We can thus write

$$\tau = 2a/v_c. \tag{3}$$

The value of a is obtained from a widely used formula [30] valid in the case of a stiff contact: $a = [(R/Y) * (F_N + F_{adh})]^{1/3}$. Here, Y is the reduced tip-sample Young modulus [31] and F_{adh} is the tip-sample adhesion force obtained from the pull-off force measurements done before and after each series of measurements. The nucleation times determined from our F_F vs log$v$ curves (some are not shown here) are reported in Table I. The values of τ range from 4.2 to 0.7 ms for experimental temperatures varying from 299 to 332 K and relative humidity of $37\% \pm 2\%$. From the data in Table I it is clear that τ decreases with increasing temperature; i.e., capillaries form more easily at higher T. This is consistent with the increase of the slopes in Fig. 1
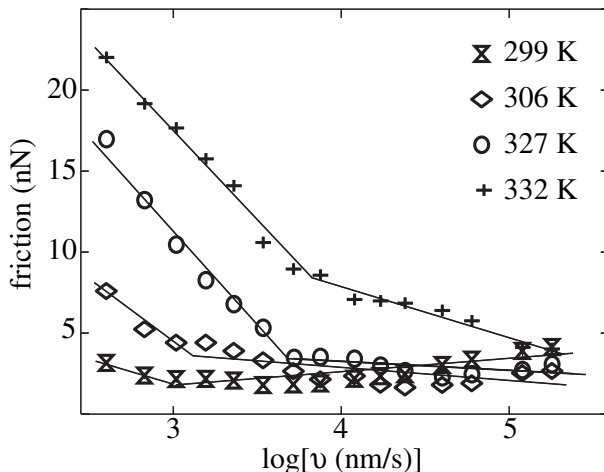

FIG. 1. Friction force as a function of log$v$ for four different temperatures.

TABLE I. Experimental data. T, p/p_s, r_K are calculated from Eq. (1), v_c is obtained from F_F vs log$v$ curves, and F_{adh} is measured from pull-off force curves. The error estimated for v_c and F_{adh} is 10%. The error calculated for a and τ is 20% and 30%, respectively.

T (K)	p/p_s	r_K (nm)	v_c (μm/s)	F_{adh} (nN)	a (nm)	τ (ms)
299	0.39	−0.55	1.0(1)	12(1)	2.1(4)	4.2
306	0.39	−0.53	1.3(1)	13(1)	2.1(4)	3.4
312	0.37	−0.48	1.7(2)	14(1)	2.1(4)	2.6
314	0.37	−0.48	2.9(3)	36(4)	2.6(5)	1.8
318	0.36	−0.45	3.3(3)	27(3)	2.4(5)	1.5
327	0.35	−0.42	4.9(5)	15(2)	2.2(4)	0.9
332	0.35	−0.41	6.3(6)	21(2)	2.3(5)	0.7

with increasing T at low v. In fact, it was shown in Ref. [6] that the slope of F_F vs $\ln v$ is proportional to the capillary force.

Homogeneous liquid water nucleation under supersaturated pressures is a first order phase transition with a corresponding free energy barrier. It has been suggested that capillary condensation is also a thermally activated first order gas-liquid phase transition [19,32]. Therefore, we should be able to access the nucleation energy barrier and the attempt frequency from the Arrhenius law,

$$\tau = \tau_0 \exp[\Delta\Omega^\dagger/(k_B T)], \qquad (4)$$

where $1/\tau_0$ is the attempt frequency and $\Delta\Omega^\dagger$ is the nucleation energy barrier. We plot the logarithm of the experimental nucleation times versus the inverse temperature in Fig. 2. The observed linear behavior confirms the thermally activated nature of capillary condensation. By fitting the data in Fig. 2 with Eq. (4) we find that the nucleation energy is $\Delta\Omega^\dagger = (7.8 \pm 0.9) \times 10^{-20}$ J and the attempt frequency, $1/\tau_0$, ranges between 4 and 250 GHz. We discuss these results in the next paragraph. First, however, we note that the upper limit for d_t is given by the diameter of the area where a capillary bridge can form, $2a_{max}$. This value was estimated in Ref. [26] to be $4(Rr_K)^{1/2}$, which in our experiments is about 14 nm. Using $2a_{max} = 14$ nm to calculate τ in Eq. (3), we obtain $\Delta\Omega^\dagger = 8.48 \times 10^{-20}$ J and $1/\tau_0 = 45$ GHz. We conclude that the values of $\Delta\Omega^\dagger$ and $1/\tau_0$ do not depend critically on d_t.

In Ref. [19] a statistical description based on the grand canonical ensemble is applied to describe capillary condensation in a gap. The authors obtained an explicit formula for the nucleation energy barrier,

$$\Delta\Omega^\dagger = \pi\gamma_{LV}H_0^2\left(\frac{\pi^2}{8}\frac{[1-(H_0/2H_c)]^2}{1-(H_0/H_c)}+\frac{H_0}{3H_c}-1\right), \quad (5)$$

where H_0 is the initial meniscus height just after nucleation and H_c is the meniscus height at thermodynamic equilib-
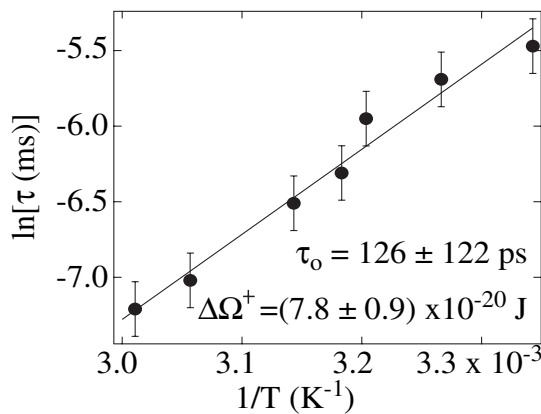

FIG. 2. $\ln\tau$ as a function of $1/T$. The experimental data (scattered circles) are fitted (solid line) with the Arrhenius law [Eq. (4)]. A correlation coefficient of 0.997 is obtained.

rium for given relative humidity. Equation (5) should be applied with caution at microscopic scales, because it relies on macroscopic concepts like surface tension, pressure, and thermodynamic equilibrium. However, the same concepts worked well in explaining AFM measurements on CrN surfaces [17] and in predicting the radii of nanoscopic menisci [13].

In order to calculate $\Delta\Omega^\dagger$ from Eq. (5) we need to estimate H_0 and H_c. We begin with H_0. Our AFM tip is covered by silica, and since our glass substrate displays similar hydrophilicity we therefore expect that it exhibits a similar thickness, d_0, of initially adsorbed water. Theoretical [11] as well as experimental [33–36] results agree that at low and medium relative humidity (roughly up to 40%) d_0 is less than 1 monolayer (ML) on various hydrophilic materials, e.g., SiO_2, and does not depend critically on the surface composition. The value of d_0 can be estimated by taking into account the van der Waals disjoining pressure and neglecting the effects of the double layers and hydration forces [11]. Therefore, we can write $d_0 = [(-Ar_K)/(6\pi\gamma_{LV})]^{1/3}$, where A is Hamaker's constant for quartz surfaces interacting through water [11]. For our experimental conditions: $p/p_s = 0.37$, $r_K \simeq -0.5$ nm (see Table I), and $A = 10^{-20}$ J. The resulting value of d_0 is about 0.16 nm, and it corresponds to a mean coverage of 2/3 ML of water (0.25 nm). Since it is shown in Refs. [37,38] that due to van der Waals forces a water meniscus spontaneously coalesces at distances equal to $3d_0$, we estimate that $H_0 = 3d_0 = 0.48$ nm.

To estimate H_c, we first notice that the equilibrium cross sectional diameter of the meniscus is about 4 nm for $R = 25$ nm and $r_K = 0.5$ nm. Since this value is much larger than d_0, it is reasonable to approximate the final meniscus height using the case of an infinitely wide meniscus [11] where $H_c \simeq -2r_K$. From the above estimates of H_0 and H_c the energy barrier calculated from Eq. (5) is $\Delta\Omega^\dagger = 2.7 \times 10^{-20}$ J. This agrees very well with our experimentally measured activation energy $\Delta\Omega^\dagger = 7.8 \times 10^{-20}$ J.

To discuss the value of τ_0 obtained from the fit presented in Fig. 2, we identify $1/\tau_0$ with the frequency of an eigenmode that carries the system over the energy barrier for capillary condensation. This, in turn, should be related to the vibrational eigenmodes of a water film (and/or droplets) initially adsorbed onto the glass surface or onto the tip. Since the initial surface coverage is very small (less than 1 ML), we neglect the bulk modes and consider only the surface modes.

Tamura and Ichinokawa [39] have extensively studied the mechanical vibrations of small water droplets accounting for their atomicity. They found that surface modes are characterized by high spectral density, and thus their mean frequency is a meaningful quantity. Such mean frequency was experimentally determined to decrease monotonically from 300 GHz for a water droplet of 1 nm radius to 100 GHz for water droplets of 10 nm radii [40]. These

results are in good agreement with our fitted attempt frequency. We acknowledge that surface phonons could also have an impact on τ_0. However, to estimate the frequencies of surface phonons, it is necessary to know the size of the "membrane" that is the water film. Therefore, τ_0 may also be used to determine the mean size of the islands of adsorbed water molecules.

In conclusion, this Letter provides the first direct experimental evidence that capillary condensation of water is a thermally activated phenomenon. The capillary nucleation times are found to grow exponentially with $1/T$ obeying an Arrhenius law. The times increase from 0.7 up to 4.2 ms for T decreasing from 332 to 299 K. We find a nucleation energy barrier of 7.8×10^{-20} J in excellent agreement with classical thermodynamic models. The attempt frequency ranges between 4–250 GHz. We suggest that this frequency is related to the surface vibrations of nanoscopic water droplets adsorbed on the contacting surfaces.

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