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CAPILLARY FORCE AT SINGLE-ASPERITY NANOSCOPIC CONTACTS

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This work presents the principles of atomic force microscopy investigation of capillary force and reports the main results obtained by the author concerning the dependence of capillary force on the contact geometry, hydrophilic property of surfaces, air humidity, and the contact time.
Keywords: capillary force, atomic force microscopy, hydrophilic property, air humidity, asperity

Aceasta lucrare prezintă principiile care stau la baza investigaţiei cu ajutorul microscopiei cu forţă atomică a forţei capilare de la contactele nanoscopice. Lucrarea raporteaza principalele rezultate obţinute de autor în ceea ce priveşte dependenţa forţei capilare de geometria contactului, hidrofilicitatea suprafeţelor, umiditatea aerului si timpul de contact.
Cuvinte-cheie: forţă capilară, microscopia cu forţă atomică, hidrofilicitatea, umiditatea aerului, asperitate

INTRODUCTION

The microscopic liquid-vapor interfaces are usually curved and their curvatures affect the values of equilibrium vapor pressure, p_0. This is happening because molecules escape differently from a curved liquid meniscus (due to more or less interaction with neighbor molecules) than from a flat one. For concave liquid menisci the vapor equilibrium pressure, p_0', is smaller than the vapor equilibrium pressure for the flat liquid-vapor interface, p_0. Lord Kelvin [1] was the first to notice this phenomenon and to explain its consequences for liquid condensation in small gaps, i. e. the capillary condensation. The capillary condensation is the phenomenon of condensation of undersaturated vapor ($p < p_0$) in small gaps (pores, capillary tubes and microscopic contacts between solid bodies). At certain vapor pressure, $p < p_0$, the vapor condenses in a small gap until a liquid meniscus with a certain value of the curvature radius, r_K, is build up. For undersaturated water vapor, the liquid menisci are concave and have negative curvatures, $r_K < 0$. The value r_K is established by the Kelvin equation:

$$\frac{1}{r_K} = \frac{RT}{\sigma V_m} \cdot \ln\left(\frac{p}{p_0}\right), \qquad (1)$$

where R is the constant of ideal gas, σ, the superficial tension of liquid-vapor interface, and V_m the molar volume of liquid. A practical formula for Kelvin radius of water menisci at room temperature ($\sigma = 0.072$ N/m, $V_m = 18$ ml/mol at $T = 293$ K) is:

$$r_k\,[nm] = \frac{0.54}{\ln(p/p_0)}. \qquad (2)$$

For water vapor in air, the relative pressure of water vapor expressed in percents is the relative humidity of air , RH = $100 \cdot p/p_0$, and its value determines the value of curvature radius of water menisci in thermodynamic equilibrium with vapor according to the Kelvin equation. The value of r_k is of the order of few nanometers at moderate values of air RH ($r_k = 5.4$ nm at RH = 90 %). Figure 1 shows a water liquid bridge formed by capillary condensation in the microscopic gap between two hydrophilic bodies. Such water liquid bridges form in very short time after the bodies are brought at a separation distance comparable with r_K (few nanometers). These microscopic water bridges are responsible for the adhesion forces between very small particles as in the case of the sand castles or in sintering process of powders.

Recently, the capillary condensation has received a great deal of attention because of its relevance to the fields of nanotribology [2], micro electro mechanic systems (MEMS) [3], colloidal physics [4], nanolithography [5] and biochemistry [6]. The atomic force microscopy [7] (AFM) is one of the main techniques used for studying the capillary condensation.

Thus, many AFM studies have been dedicated to investigation of the effect of capillary condensation of water on adhesion and friction forces at nanocontacts of solid surfaces [8, 9]. The atomic force microscope allows imaging of surface topography of conducting or insulating samples, in some cases with atomic resolution.

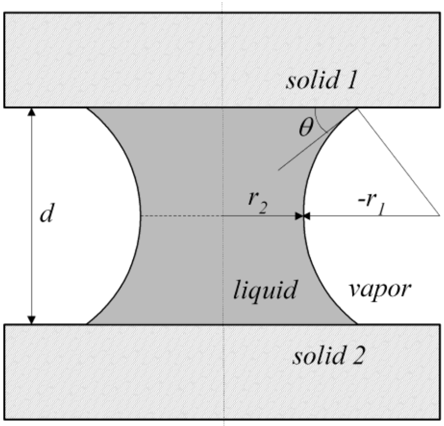

Fig. 1. Formation of water bridges through capillary condensation of water vapor in a small gap (d in the range of few nanometers) between two hydrophilic solid bodies ($\theta < 90°$) bodies. The water meniscus is concave in vertical plane ($r_1 < 0$) and convex in horizontal plane ($r_2 > 0$).

The instrument is based on the detection of the interaction force between a microscopic sharpened tip and a sample surface. The attribute "atomic" comes from the fact that the interaction region between the tiny tip (radius of 10 nm) and sample includes a limited number of atoms. In the case of AFM measurements in air, capillary condensation of water vapor leads to formation of a water bridge that surrounds the nanoscopic contacts between the very sharp AFM tips and sample surfaces. Basically, the interaction between the AFM tip and sample surfaces is the result of the superposition of van der Waals, electrostatic, capillary and interfacial tension forces [10]. The latter two forces arise due to the capillary water bridge, which usually occurs at the tip-sample contact region in the ambient air, and their contribution to the tip-sample adhesive force is dominant [11]. Therefore, in the following the adhesion force measured by AFM pull-off experiments in air is interpreted as the capillary force, i. e. the force generated by the capillary water bridge formed at the AFM tip-sample surface.

Fig. 2 shows the typical variation of tip-sample interaction force in a pull-off experiment along with a sketch of the AFM probe position at three moments of time during the experiment.

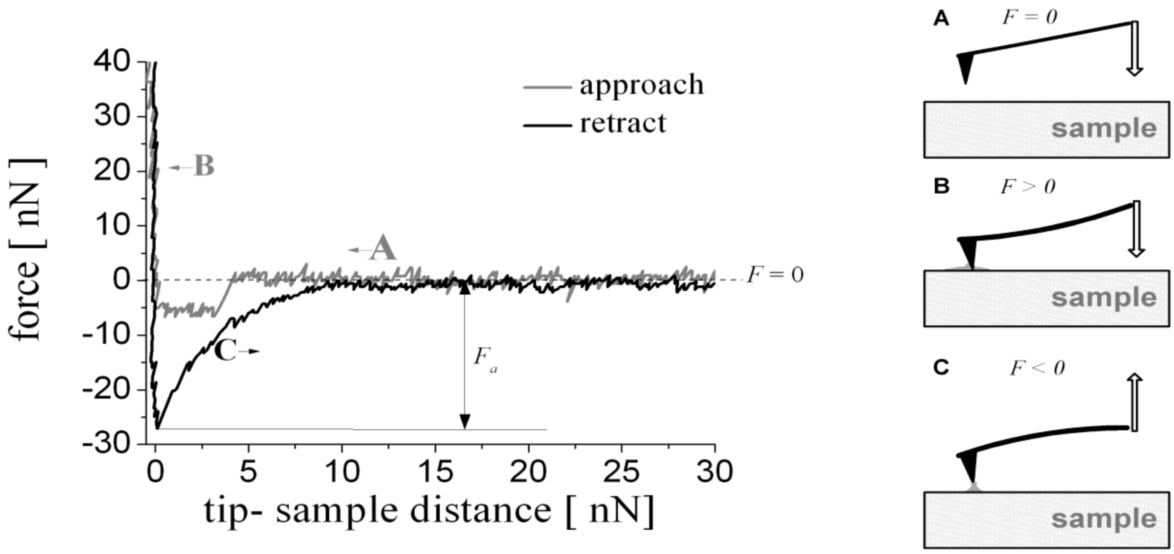

Fig. 2. Typical force displacement curve recorded in an AFM pull-off experiment. (**A**) The AFM tip is approaching the sample surface while the interaction force is negligible (F = 0). (**B**) The AFM tip is pushing on the sample surface. During the contact, the water vapor from the ambient air forms through capillary condensation a water neck that surrounds the tip-sample contact. (**C**) The AFM tip is retracting while the water bridge is elongated. The attraction force caused by the water bridge is the capillary force measured as the tip-sample adhesion force, F_a.

In such experiments the AFM tip is approached to the sample surface until contact. While the distance between the tip and sample surfaces is larger than 10 nm the tip-sample interaction force is zero (in absence of long range electric and magnetic forces). After contact, the movement of the

probe continues until certain value of the repulsive interaction force (positive) is reached. Then, the movement of the AFM probe is reversed and it is retracted until the initial position. The maximum attractive force (negative) measured during tip retraction is considered as the tip-sample adhesive force.

CAPILLARY FORCE

Very often capillary condensation of water at single-asperity contacts of two solid bodies is modeled for a small spherical particle in mechanical contact with a flat surface of a second body. This is happening to be the case of microscopic dust particles that adhere to the flat surface of a macroscopic body, but the model describes correctly also the water capillary condensation at the contact of the AFM tip (modeled by the spherical particle) and the sample (modeled by the flat surface). In short time after contact, the water vapor from the humid air condenses and builds up a water neck that surrounds the contact of the two bodies. The system has a cylindrical symmetry and the water meniscus has a concave curvature in vertical plane ($r_1 < 0$) and convex curvature in horizontal plane ($r_2 > 0$). Formation of the capillary water bridge at the single-asperity nanocontact of two solid bodies generates an attractive (adhesion) force called the capillary force. To understand the origin of this force and to find its mathematical expression let us consider the model of the capillary water bridge that surrounds the contact between a spherical microscopic particle and a flat surface (Fig. 3) and recall the fact that according to the Young-Laplace equation the pressure inside the concave water meniscus is smaller than the vapor pressure with $\Delta p = \sigma/r$, where r is total curvature of the water meniscus, which at thermodynamic equilibrium is equal to the Kelvin radius.

It is this pressure difference that generates the capillary force. If r_2 ($r_2 << R$) is the radius of the meniscus contact line with the spherical particle and we consider that Δp acts uniformly on a surface πr_2^2, than the capillary force is:

$$F_c \cong \frac{\sigma}{r_1} \cdot \pi r_2^2 \cong 4\pi \sigma R_t \cdot \cos\theta, \qquad (3)$$

where the so called geometrical approximation of the meniscus shape for water menisci much smaller than the solid bodies in contact ($R >> |r_2| >> |r_1|$) has been used. In this approximation the meniscus shape in vertical plane is considered as a portion of a circle with radius $-r_1$ with $r_1 \cong r_K$.

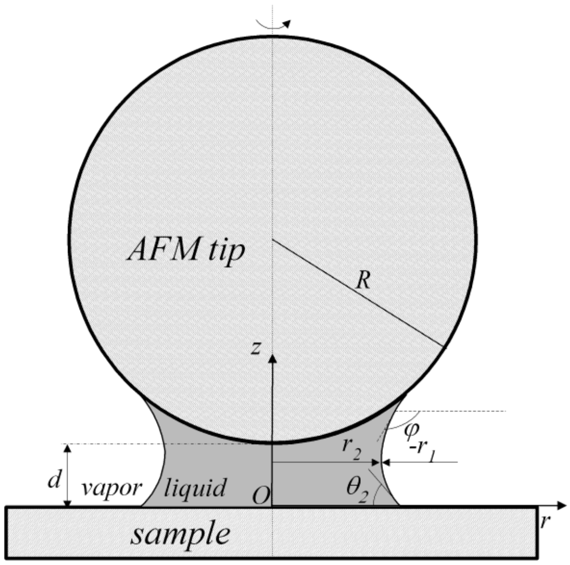

Fig. 3. Geometry of a water bridge formed by capillary condensation in the nanoscopic gap between a spherical particle (solid 1) of radius R and a flat solid surface ($R = \infty$, solid 2). The radii r_1 and r_2 are meniscus curvature radii in vertical and horizontal planes, respectively, φ the meniscus surface tilting angle with respect to the horizontal plane, and z and r are cylindrical coordinates used for computing of meniscus shape.

Moreover, since $|r_2| >> |r_1|$, it is easy to show that:

$$r_2^2 \cong 2R \cdot |r_1| \cdot (\cos\theta_1 + \cos\theta_2) \quad (4)$$

where θ_1 and θ_2 are the water contact angles of the tip and sample surfaces, respectively. With these approximations for r_1 and r_2, the equation (3) derives the formula of O'Brien and Hermann [12] of capillary force:

$$F_c \cong 2\pi \sigma R \cdot (\cos\theta_1 + \cos\theta_2), \quad (5)$$

which for $\theta_1 = \theta_2 = \theta$ becomes:

$$F_c \cong 4\pi\,\sigma\,R\cdot\cos\theta \qquad (6)$$

The equation shows that the capillary force is proportional to the size of particles in contact (R can be considered the equivalent radius of two spherical particles in contact or, in case of AFM measurements, the equivalent radius of the AFM tip and sample: $1/R = 1/R_t + 1/R_s$, where R_t is the AFM tip radius and R_s is the local curvature of the AFM sample). The equation shows also that F_c is proportional with the superficial tension of water and depends on hydrophilicity of the solid surfaces in contact. No capillary meniscus and no capillary force exist between particles with non-wetting surfaces ($\theta \geq 90°$). However, the formula is not accurate and a more careful analysis is based on an exact solution of the Young-Laplace differential equation of the water meniscus [13].

DEPENDENCE OF THE CAPILLARY FORCE ON HUMIDITY

According to the approximate equation (6), the capillary force does not depend on air humidity. This result is somehow counterintuitive, because computation of r_K shows that the size of the water meniscus increases steeply by the increase of RH. However the increase of the meniscus size with the increase of RH is compensated by the corresponding decrease of the Laplace pressure (which decreases with the increase of RH). The results of numerical computation of the capillary force based on the solutions of Young-Laplace equation for rotationally symmetric menisci with values of the total curvature radius r_K corresponding to different values of RH shows a slight decrease of the capillary force by the increase of RH (Fig. 4). The dependence of capillary force on RH was experimentally checked by AFM measurement of pull-off force between an AFM probe (NSC 36 from Mikromash, Inc.) and a flat sample [silicon wafer Si(1,0,0)]. The measurements were performed by a commercial AFM apparatus with an environmental chamber. Relative humidity (RH) of the measurement medium was controlled by flowing high purity nitrogen and water vapor through the environmental chamber.

The obtained experimental results show a weak dependence of capillary force on humidity in agreement with the approximate equation (6). In this case the approximation worked well due to the large value of the tip radius, R_t = 50 nm, tip spherical shape at the tip apex. However, a strong dependence of capillary force can be obtained in the case of a blunt AFM tip (Fig. 5).

In this case, the meniscus size at small values of RH is larger than in the case of the ideal spherical tip and this causes a strong increase of capillary force at low humidity. An strong increase of capillary force can be obtained in the case of AFM tips with a very sharp singularity at the tip apex.

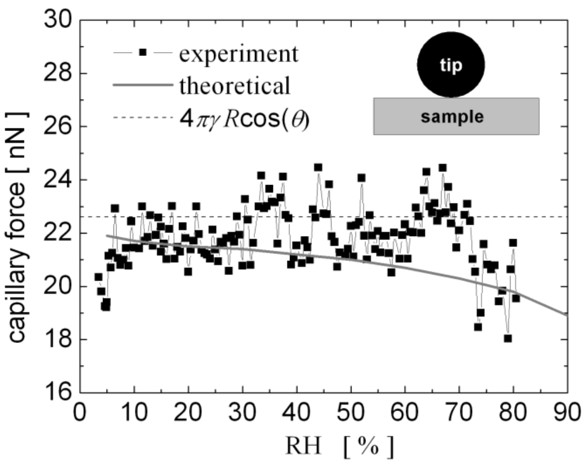

Fig. 4. Comparison of theoretical and experimental values of capillary force between an AFM tip (spherical silicon tip with curvature radius of 50 nm and water contact angle of 60°) and a sample (polished silicon wafer).

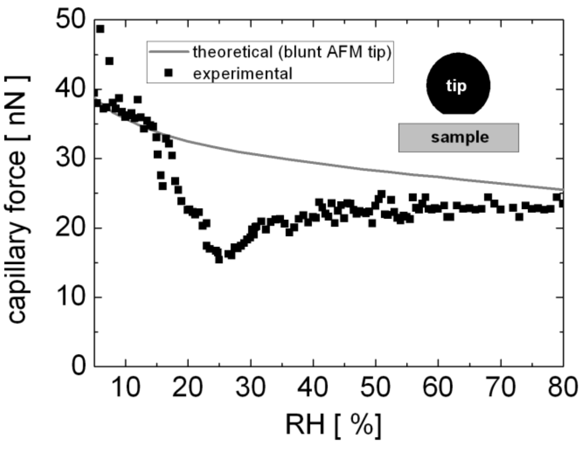

Fig. 5. Comparison of theoretical and experimental values of capillary force between a blunt AFM tip (curvature radius of 50 nm and water contact angle of 60°) and a flat sample (polished silicon wafer).

CONCLUSION

Atomic force microscopy is one of the main techniques used in study of the capillary condensation of water at nanoscopic contacts. The phenomenon occurs in short time after the very sharp tip of the AFM is brought in contact with the sample surface and results in formation of a water meniscus that surrounds the contact. The size of the water meniscus depends on air humidity. Increase of the air humidity results in increase of the water meniscus size. The capillary force is generated by the water meniscus that surrounds the tip-sample contact mainly as an effect of the Laplace pressure. The capillary force is directly measured by AFM pull-off experiments as the maximum attractive force experienced during tip retraction. Pull-off experiments performed with a spherical tip proved that capillary force has a weak dependence on air relative humidity, while similar experiments performed with a blunt AFM tip showed a strong decrease of the capillary force with the increase of humidity.

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