Dissipation Energy in Tapping-Mode Atomic Force Microscopes Caused by Liquid Bridge *

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The dissipation of energy during the process of contact and separation between a tip and a sample is very important for understanding the phase images in the tapping mode of atomic force microscopes (AFMs). In this study, a method is presented to measure the dissipated energy between a tip and a sample. The experimental results are found to be in good agreement with the theoretical model, which indicates that the method is reliable. Also, this study confirms that liquid bridges are mainly produced by extrusion modes in the tapping mode of AFMs.

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Atomic force microscopes (AFMs) have undergone thirty years of improvements and development, and have become powerful instruments that can be used in a variety of scientific and industrial fields.[1] Among the operation modes of AFMs, the tapping mode (TM) AFM plays a major role, especially for soft materials and biological specimens.[2] Based on a vibration theory, the TM AFM phase image is mainly dependent on the energy dissipation between the AFM tip and the sample.[3] There are basically three types of dissipation mechanisms in the AFM vibration system. The first mechanism is caused by air damping due to cantilever oscillations in the atmosphere.[4,5] The second is caused by the internal friction of the cantilever materials due to the dynamic deformation of the cantilever.[6] The last type is adhesion hysteresis, which is caused by some instabilities during the contact and separation processes of the tip-sample. The instabilities generally refer to mechanical, energetic and thermodynamic ones.[7,8]

Under ambient air conditions, the dissipation energy due to adhesion hysteresis is derived from the capillary forces between the AFM tip and the sample.[9,10] The capillary force between the tip and the samples is provided by the liquid bridge between the two bodies. The formations and ruptures of the liquid bridges in AFMs have been previously completely examined.[9] The previous study proposed the models for the formation of liquid bridges in AFMs, which include an extrusion model, a capillary condensation model, and a motion model of liquid films. The characteristic time of the capillary condensation is ∼ms, while the characteristic time of the liquid film motion is 10^2 μs–10^2 s. The thickness of the water film on the sample is approximately one to several layers (see Eq. (2)). In the oscillation cycle, the contact time of the tip sample is $\cong (h/A)t$, where h represents the thickness of the water film, A is the amplitude of the tip, and t denotes the cycle time of the cantilever. In the majority of the cases, A is determined to be a dozen times or more than h. In most TM AFMs, the frequency of the cantilever is ∼10^2 kHz. Therefore, the contact time is ∼ μs. Therefore, in the TM AFMs the formation of the liquid bridges should occur in the order of ∼ μs.

The dissipation energy in the TM AFM is a very critical key for understanding the image mechanism. Currently, the measuring of the dissipated energy in TM AFM is based on the method proposed by Cleveland *et al.*[3] In our previous study, the rupture energy of the liquid bridge may be obtained by measuring the force curve. However, this method has not been found to be suitable for the rupture of the liquid bridges in the tapping mode, due to the fact that the frequency of force curve measurement is much less than the frequency of the tapping mode. Therefore, due to the limitations of the experimental method, the examinations of the dynamics of the formations and ruptures of the liquid bridges between the tips and samples have not reached a definite conclusion.[9,11–13]

In this Letter, a method is presented to measure the dissipation energy between the tip and sample in a TM AFM. Also, the relationship between the rupture energy of the liquid bridges and the relative humidity is theoretically analyzed for the tapping mode. Comparing the experimental data with the theoretical results, the present results confirm the feasibility of this method. Furthermore, the mechanism of the formation of liquid bridge in this AFM operation mode is successfully verified.

In our experiment, the ensemble of the cantilever, tip, and sample was considered to be a single degree of freedom (SDOF) vibration system. The entire energy of the SDOF system was given by $E_0 = \frac{1}{2}kA^2$,

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where A is the amplitude of the cantilever. It is known that, during a period of SDOF, the dissipation energy of the system resulting from an intrinsic cantilever is $\Delta E_1 = 2\pi E_0/Q_1$, where Q_1 represents the quality factor of the cantilever in air. The quality factor Q_1 depends on the damping mechanisms, which are present in the cantilever. For the cantilevers operated in air, Q_1 is mainly limited by viscous drag, and typically amounts to several hundreds. Meanwhile, for those operated in a vacuum, the internal and surface effects in the cantilever material are responsible for the damping, and Q_1 may reach hundreds to thousands.[2]

When the tip touches the sample, a liquid bridge would be formed between the AFM tip and the sample. As the tip is drawn from the sample, the liquid bridge becomes ruptured. When ignoring the mass of the liquid bridge, the elastic and damping effects of the liquid must be introduced into the SDOF system. The dissipation energy of the drawn liquid bridge to rupture is taken into account as a damper. Therefore, the effective quality factor of the SDOF system can be written as $Q_{\text{eff}} = 2\pi E_0/(\Delta E_1 + \Delta E_2)$, where ΔE_2 represents the dissipation energy caused by the liquid bridge. Then,

$$\frac{\Delta E_2}{E_0} = \frac{Q_1 - Q_{\text{eff}}}{Q_1 Q_{\text{eff}}}. \tag{1}$$

Therefore, in different relative humidities, by measuring the quality factor Q_1 of the cantilever where the tip is far away from the sample, along with the quality factor Q_{eff}, where the tip hits the sample once, as a vibration cycle, the relationship between the rupture energy and the relative humidity can be indirectly known.

In the experiment, silicon wafers were treated using a hydrophilic process. The cleaned silicon wafers were placed into the chamber of a plasma machine (Diener Electronic Co., Germany) for hydrophilic coating, using oxygen ions for approximately 3 min. The water contact angle on the hydrophilic silicon was measured to be approximately 8°. The non-conductive silicon AFM probe was used in our test. The cantilever stiffness is about 43 N/m as determined by the thermal method, which is a basic function described by the AFM manual. The MFP-3D AFM had a humidity chamber for the control of the relative humidity during the AFM operation. Wet nitrogen gas and dry nitrogen gas were mixed in a long tube, and the mixed gas was introduced into the humidity chamber. To achieve the desired humidity, two mass controllers were used to control the flow of the wet and dry gasses. A humidity sensor (EK-H5, Sensor Co.) was put in the outlet tube.

To obtain the quality factor Q_1 of the system, the cantilever was tuned when the AFM tip was 1–2 mm above the sample's surface. The target amplitude voltage (cantilever response amplitude) was then set to 1 V, to determine the given drive amplitude (excitation voltage). This means that, in the given excitation voltage, the amplitude of the cantilever at a resonant frequency of free vibration was 1 V. The tip was then slowly lowered, keeping the given excitation voltage unchanged. The response of the cantilever was observed to be increasingly smaller as the interaction between the tip and sample became stronger. Figure 1 shows the amplitude-frequency response curves (AFRCs) of the cantilever at different relative distances between the tip and the sample. The percentage of the curve represents the ratio of the response amplitude to the free response amplitude at different positions. Therefore, the Q values of the system could be obtained from the AFRCs.

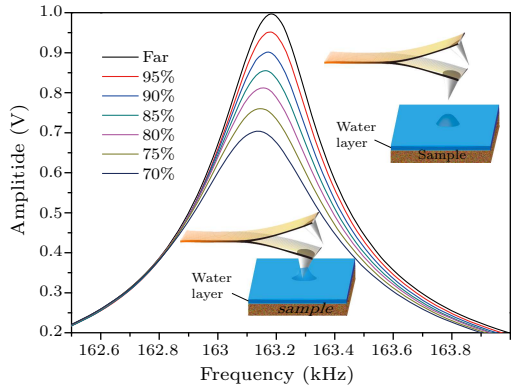

Fig. 1. Amplitude-frequency response curves at different locations of the AFM tip from the sample. The relative humidity in the chamber is 45%. The cantilever stiffness is approximately 43 N/m, which is determined by a thermal method. As the tip approaches the sample, the amplitude of the cantilever at the resonance frequency starts to decrease.

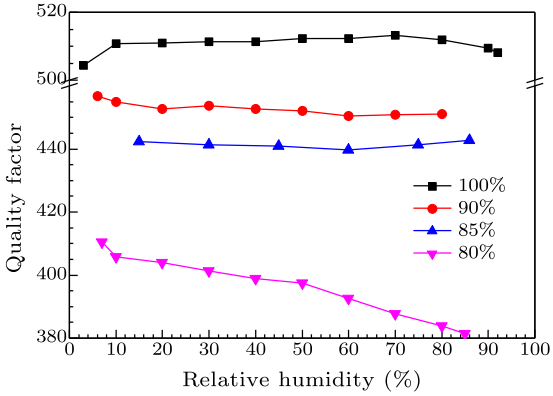

Fig. 2. Quality factor variations of the cantilever at different positions and different relative humidities. The black curve represents the quality factor Q_1 of the cantilever, where the tip is far away from the sample. It can be seen that the quality factor experiences a sudden drop at the 80% curve, when compared with the other three curves. Meanwhile, it has changed with the relative humidity. Therefore, it is considered that the liquid bridge has been formed at this position.

Through a method of frequency response curves, a series of the quality factors Q under different positions and relative humidities were obtained (Fig. 2). Then, to reduce statistical errors, the quality factors were measured to be more than 15 times with the same

position and relative humidity, and the averages were taken as the final quality factor. It can be inferred from Fig. 2 that the liquid bridge was not formed between the tip and the samples at the spacial positions of 100%, 90% and 85%. Therefore, the energy dissipation between the tip and the sample is determined to be less affected by the humidity. However, a liquid bridge has been formed between the tip and the samples at certain humidity at the spacial position of 80%. As described above, it is known that the liquid bridge is formed by the extrusion of a water film on the tip and samples.

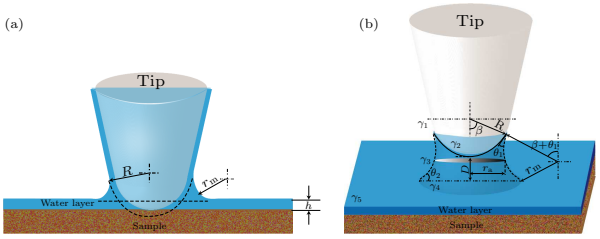

Fig. 3. (a) Squeeze model, due to the existing thin water film on the surfaces of the tip and samples, when the AFM tip approaches the sample, some of the water is squeezed out from the contact zone, and subsequently a liquid bridge is formed. The volume of the squeezed water is the overlapping region shown in the figure. The thickness of the thin water film is represented by h. (b) System of the liquid bridge, two phases of vapor and liquid, and five interfaces: 1 tip-vapor interface; 2 tip-liquid interface; 3 vapor-liquid interface; 4 liquid-sample interface; 5 vapor-sample interface.

When the tip is in contact with the sample, a water bridge will be formed around the contact zone, due to the squeezed water existing in the overlap zone of the adsorbed water film (Fig. 3(a)). In this study, using a simple analysis, it is determined that the volume of water squeezed out to the slit zone between the tip and the sample is $V = \frac{4\pi}{3}h^2(3R + h) \approx 4\pi Rh^2$. This volume is of a sphere cap immersed in the water film. Here the tip radius is $R \gg h$, with h representing the thickness of the water film. In equilibrium, the Young–Laplace pressure in the liquid bridge is equal to the disjoining pressure in the liquid film. Therefore, the thickness of a thin water film over the surface could be obtained as follows:

$$h = \sqrt[3]{\frac{Av_{\rm m}}{6\pi k_{\rm B}T \ln H_{\rm r}}}, \qquad (2)$$

where A is the Hamaker constant, $v_{\rm m}$ is the molar volume of the vapor, $k_{\rm B}$ is the Boltzmann constant, T is the absolute temperature, and $H_{\rm r}$ represents the relative humidity at an ambient pressure.

When the tip is withdrawn from the sample, the water bridge is extended to a limited length until it ruptures. In the scanning mode of the TM AFM, the time of this process is so short that the water liquid has no time to evaporate or flow into the outer zone. Therefore, it is likely to be a constant volume of the water bridge in the extended process, and the volume of the water bridge is the squeezed volume of the contact.

The schematic diagram of the liquid bridge between the AFM tip and the sample is shown in Fig. 3(b). Both the tip and the sample are assumed to be rigid. The curvature of the liquid bridge is characterized by two radii: azimuthal $r_{\rm a}$ and the meridional radius $r_{\rm m}$. The former $r_{\rm a}$ is counted to be positive due to the fact that it is located inside the liquid. The latter $r_{\rm m}$ is counted to be negative. The drop in pressure across the liquid bridge interface is controlled by the Young–Laplace equation. It is a rather tedious process to calculate the exact shape of the liquid bridge. Fortunately, an approximation could be derived for an AFM tip which is in contact with a sample. Generally speaking, $r_{\rm a} \ll r_{\rm m}$. Therefore, a highly accurate approximation can be produced by describing the cross section of the vapor-liquid interface as a circle.[9]

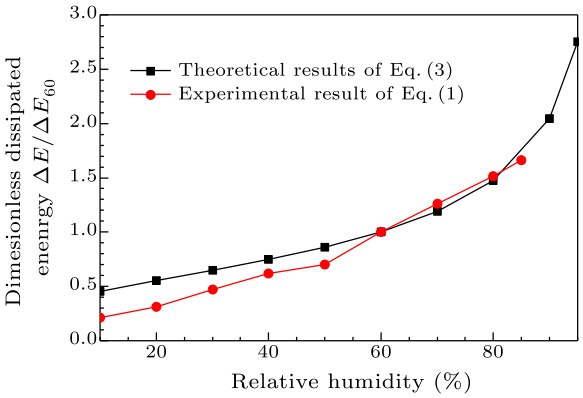

Fig. 4. Energy dissipated due to the rupture of the liquid bridge versus the relative humidity. Here ΔE_{60} is the dissipation energy at the relative humidity of 60%. The tip contact angle is assumed to be 30°, and the sample contact angle is 8°.

In this study we consider a simplified model of an AFM tip in contact with a sample, as shown in Fig. 3(b). It is assumed that the liquid bridge is composed of liquid phase, and vapor phase, and the surface and interface phases γ_i ($i = 1, 2, 3, 4$ and 5). Here $\gamma_3 = \gamma$, the surface tension of water. Also, the tip and sample are assumed to be unchanged. Then, based on a thermodynamic theory, the energy required to draw the tip from the sample surface is $\delta W = \sum_{i=1}^{5} \gamma_i dA_i$. Due to the fact that $dA_1 + dA_2 = 0$, $dA_4 + dA_5 = 0$, $\gamma_1 = \gamma_2 + \gamma\cos\theta_1$, and $\gamma_5 = \gamma_4 + \gamma\cos\theta_2$, the rupture energy of the liquid bridge will subsequently be reduced to

$$\Delta E = \int \delta W = \gamma \int dA_3 - \cos\theta_1 dA_2 - \cos\theta_2 dA_4, \qquad (3)$$

where θ_1 and θ_2 are the contact angles on the tip and the sample, respectively. The experimental results show that the critical rupture length of the liquid bridge is proportional to the cube root of the volume

of the liquid bridge,[14,15]

$$D_{\rm cr} = \frac{1}{2}\Big(1 + \frac{\theta_1 + \theta_2}{4}\Big)V^{1/3}. \quad (4)$$

Following the nondimensionalization, the dissipation energy due to the liquid bridge, along with the relationship between the energy dissipation and the relative humidity, can be seen in Fig. 4. Due to the fact that the prediction thickness of Eq. (2) displays a large deviation from the experiments in the lower relative humidity, this study chooses the relative humidity to be 60% as the standard for the nondimensionalization. Figure 4 shows that the experimental data agree well with the theoretical results. Therefore, it is confirmed that the method of tune cantilever is feasible for the investigations of energy dissipation between tips and samples. Furthermore, this method is also feasible for the investigations of the dynamic growth and rupture processes of liquid bridges.

In conclusion, we have presented a method for measuring the relative dissipated energy in TM AFMs. Of course, in the cases of knowing the stiffness and amplitude of the cantilever, this method also has the ability to measure the absolute value of the dissipated energy. It is thereby confirmed by this method that liquid bridges are mainly formed by extrusion effects in the tapping mode of AFMs.

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