Time-resolved study of phase transition in the nanoscale water bridge: Formation and rupture processes

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The formation and rupture processes of nanoscale water bridges are studied by time-resolved dynamic force microscopy. The temporal behaviors of the water bridges, formed in the nanometric gap between the probe tip and the substrate, are measured. From the results, one can determine whether the formation and rupture processes occurring in the nano-gap are thermally activated or spontaneously occurring. We expect that this technique allows one to study the phase transitions of nanoscale liquid bridges.

Capillary condensation, a gas-liquid phase transition between two solid surfaces, has been widely studied especially for water.[1–4] The thermodynamic processes associated with the water bridges, such as the formation, rupture and hysteresis, have been studied in the viewpoint of their energy barriers by Zhang and his co-workers.[3] In addition, Sahagún *et al*[5] proposed a representation of the energy barrier versus the neck width of water bridges for different tip-sample distances. Although several theoretical studies of vapor-liquid transition have been presented, the experimental investigations of such processes at finite distances still have remained a challenge. In this Letter we present an understanding of vapor-liquid transition and the stability of nanoscale water bridges by means of time-resolved dynamic force microscopy. The results may provide not only a deeper understanding of the phase transitions in the nanoscale region as well as an experimental tool for time-resolved study of the associated dynamic processes.

Figures 1(a) and 1(b) show the formation process of the nanoscale water bridge formed in each approach. In the gray-painted part of Fig. 1(a), the normalized amplitude experienced an abrupt change after a time delay while the separation was kept fixed. On the other hand, the amplitude decreased as soon as the distance changed in Fig. 1(b). It can be understood that the water bridge forms after a finite time even at the fixed separation because the time is required to overcome an energy barrier associated with thermal activation (see A in Fig. 1). On the contrary, the formation occurs as soon as the separation changes when there is no energy barrier to be the liquid state (see B in Fig. 1). In addition, spontaneous condensation occurs more frequently than thermal-activated one at closer tip-substrate separations. Notice that the time constant of the part B in Fig. 1(b) is 119 ms which is longer than twice of the time constant of force sensor while that of the part A is 40 ms. It may be that time is needed for the water bridge to grow. Likewise, this analogy can be also applied to the rupture process of the water bridge in Fig. 1(c) and (d). Figure 1(c) corresponds to thermally activated rupture (C in Fig. 1) and 1(d) shows spontaneous rupture (D in Fig. 1). It should be emphasized that this observation and resulting interpretation can be only achieved by our TRDFM technique, but not by traditional AFM.

In summary, we have developed the TRDFM technique and applied it to the study of mechanical stability of the nanoscale water bridge by observing the temporal hysteresis of the stiffness and damping measurement. It provides the unique capability to determine whether the vapor-liquid transition of the water bridge is thermally-activated or spontaneously occurring.

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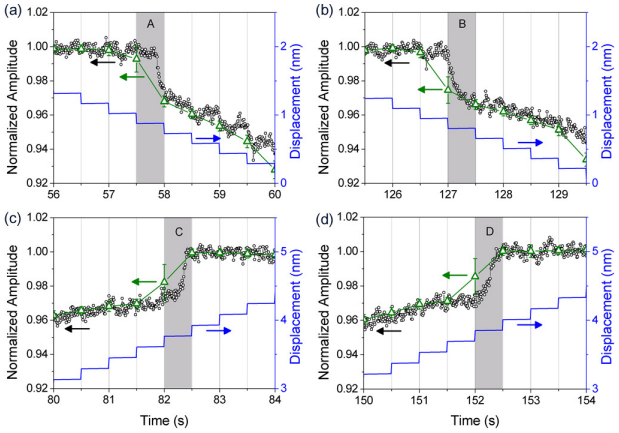

FIG. 1. The normalized amplitude measured during formation (a,b) and rupture (c,d) of the nanoscale water bridge. The gray-painted parts of (a) and (c) show a time lag of the change in amplitude, whereas there is no time lag in (b) and (d).