ENERGY DISSIPATION DUE TO CAPILLARY INTERACTIONS: HYDROPHOBICITY MAPS IN FORCE MICROSCOPY

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In this paper, the energy dissipation process involved in the formation and rupture of a nanometer-sized capillary-condensed water bridge is theoretically analyzed [1]. With the help of numerical simulations, the dissipation contrast in amplitude-modulated (AM) atomic force microscopy is shown to be a result of a non-trivial interplay between the energy dissipated [2] in each rupture process and the bi-stable motion of the cantilever [3,4]. In the repulsive high amplitude regime, the dissipated power is a function of the tip and sample contact angles being independent of the elastic properties of the system. Working in this regime, energy dissipation images in air can be regarded as surface hydrophobicity maps.

Atomic Force Microscopy (AFM) has become a standard tool to image and manipulate surfaces with nanometer resolution. In order to minimize sample deformations due to the tip interaction, AFM images are usually taken by using different dynamic operation modes [5]. Phase contrast images, obtained by recording the phase lag of the cantilever oscillation relative to the driving signal, often provides significantly more contrast than the topographic image. At fixed feedback amplitude, phase shift variations are directly linked to energy dissipation processes [6,7]. However, most of the phase and energy dissipation images are purely qualitative, mainly due to the absence of simple relationships relating phase changes and energy dissipation with specific surface properties.

In air ambient condition, the phase contrast is strongly influenced by capillary forces [8]. When the tip approaches the sample, water condensation can induce the formation of a nanometer-sized water bridge. The relevance of liquid bridges for both imaging and nanofabrication have driven numerous experimental and theoretical [8-15] efforts to understand nanometer-sized systems involving capillaries. Understanding capillary contrast in AFM maps would be particularly interesting for biological applications, where the recognition of different species is frequently based on their hydrophilic or hydrophobic nature.

In this paper we present a theoretical analysis of the energy dissipation involved in the formation and rupture of capillary-condensed water bridges. Based on a simple model sketched in figure 1, we predict a quantitative relation between the energy dissipated and tip and sample contact angles and relative humidity (RH).
Our theoretical approach can be divided in two parts. First, the calculation of the water neck geometry for each experimental configuration through the minimization of condensation energy. The second is the simulation of an AFM device in AM mode together with a substrate plus the capillary interaction calculated in previous part.

Main findings are depicted in figure 2. We show that capillary dissipation contrast in AM-AFM strongly depends on the operation regime. In the attractive regime (phase shift $\phi>90$) the dissipated power changes as a consequence of the beating phenomena [9]. Only in the repulsive regime ($\phi<90$) the energy dissipated per oscillation is independent on the amplitude and elastic properties of the system. For a given tip and RH, the dissipated power is just a function of the sample contact angle. As a consequence, only when working in the repulsive

regime, energy dissipation images of biological samples in air can be regarded as surface hydrophobicity maps.

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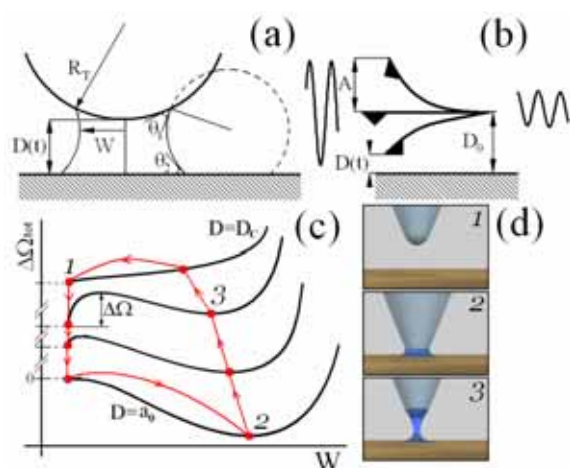
Fig 1. (1a) Sketch of the water bridge geometry. (1b) Tip-cantilever-driver system. (1c) Schematic represent-tation of the formation/rupture process in tapping mode. (1d) Graphic representation of water neck formation/rupture.
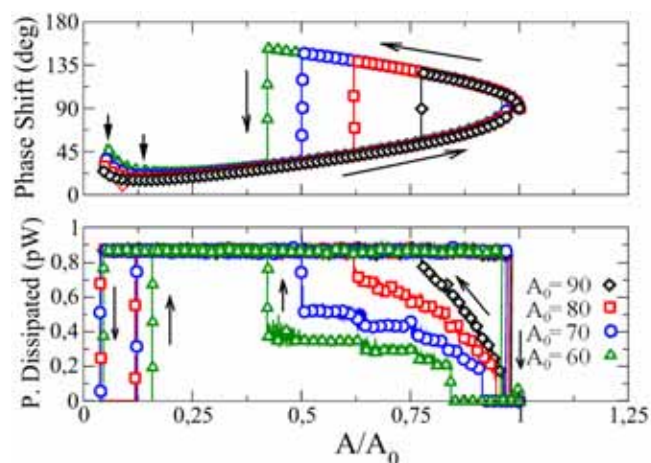

Fig 2. Phase (a) and power dissipated (b) vs normalized amplitude from simulated tapping mode operated AFM including capillary interactions.