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The influence of capillary effect on atomic force microscopy measurements

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ABSTRACT

The study is focused on capillary phenomena that arise from the indentation of the AFM cantilever probe into a liquid film on the sample surface. We propose a new method to obtain an equation describing the geometry of the interface of three phases (liquid, air and probe) with consideration for capillary actions. It is shown that gravitational forces cannot be neglected at the nanoscale. The opening angles of the probe and the depths of AFM probe indentation into the liquid are analyzed, evidencing that the radius of curvature of the liquid boundary near the probe is much larger than that of the atomic force microscope probe. It has been found that, at the moment of contact with the liquid, the probe immediately dives into the liquid to a depth which is much larger than the nanoscale dimensions. The situation is explored where the surface layer is a thin liquid film of restricted volume, the liquid is gathered near the probe, and the dry surface area appears far away from the probe.

1. Introduction

The application of atomic force microscopy (AFM) makes it possible to study a broad range of nanoscale properties of materials, including topology, friction, adhesion, etc. The AFM uses a cantilever to scan a sample surface. Interesting information about various material parameters at the nanoscale is provided by the AFM operating in the force tapping mode. Scanning is done by approaching and retracting the probe at different points of the material surface. The curves plotted then are analyzed by appropriate mathematical models. To make reliable measurements, it is necessary to properly account for all the forces applied to the AFM probe. When the probe tip is brought very close to the surface of the sample, it feels the attractive force and immediately comes into contact with a sample surface shown in the attractive region of a typical force curve. The cantilever deflection is dependent on its stiffness (Kahrobaiyan, Asghari, Rahaeifard, & Ahmadian, 2010) and can reach several nm. This fact cannot be attributed solely to the van der Waals forces, which act through distances of several angstroms (Garishin, 2012). Probably, such a jump-like attraction of the tip by the sample can be related to capillary phenomena.

It is well known that the sample and the tip are coated with an adsorbed layer when the AFM measurements are made in ambient air. This results in a more complicated interaction between the probe and the sample (Baselt & Baldeschwieler, 1994; Meyer, Rosenberg, & Israelachvili, 2006; Rehviashvilli, Rozenberg, & Dremov, 2008), because the surface tension forces play a key role at such a small scale. There are a number of experimental works and relevant mathematical models used to

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study the formation of adsorbed films, their properties and their effect on the strength of interaction between these films and the probe. It has been established that the degree of interaction between the probe and the sample depends on the ambient relative humidity (He, Blum, Aston, Buenviaje, & Overney, 2001; Molchanov, 2007; Paajanen, Katainen, Pakarinen, Foster, & Lahtinen, 2006). In work (Asay & Kim, 2006), one can find an evidence of the dependence of the adhesive strength and thickness of adsorbed films on relative humidity.

When the AFM probe comes into contact with the liquid film, a liquid meniscus is formed on the surface of the sample and, as a consequence, capillary forces begin to impact the probe. Only few recent works contain analytical and numerical descriptions of the shape of a meniscus and give an estimate of the force in relation to the shape of contact surfaces and the distance between them (Crassous, Ciccotti, & Charlaix, 2011; Komkov, 2007; Scholtès, Chareyre, Nicot, & Darve, 2009). There are also papers in which the equation of motion of a cantilever is considered with account for capillary forces, van der Waals forces, relative humidity and the probe-sample distance (Hashemi, Paul, Dankowicz, Lee, & Jhe, 2008; Zitzler, Herminghaus, & Mugele, 2002). The theoretical description of the experimental data obtained in these studies was done using the Derjaguin–Muller–Toporov model of interaction and the Izrailachvili equation (Derjaguin, Muller, & Toporov, 1975; Israelachvili, 1992).

The curvature of the phase interface is due to the action of surface tension forces, which generate the supplementary capillary pressure, whose magnitude is calculated by the Laplace formula (Roldugin, 2008)

$$p = \alpha\left(\frac{1}{r_1} + \frac{1}{r_2}\right), \tag{1}$$

where r_1 and r_2 are the principal radii of curvature, α is the surface tension coefficient, and p is the pressure difference in the adjacent phases separated by the curved surface. Despite much recent progress in modeling interactions between the AFM probe and the liquid, there are no models accurate enough to describe these interactions. In our opinion, no simplifying assumptions about the surface geometry and its curvature are needed for evaluating the shape of the liquid surface near the AFM probe, and the gravitational force must not be excluded from such considerations. This will provide an objective approach to evaluating the height of the liquid entrained by the probe and the capillary forces appeared under these conditions. Appropriate calculations are discussed below.

2. Equation of the phase interface

Let us assume that the mathematical apparatus of continuum mechanics can be used to model the interaction between the AFM probe and the liquid. We study the behavior of the system at the nanoscale. Most probes used in practice have a radius ranging from 5 to 10 nm. One cubic nanometer contains a large amount of water molecules. That is why, application of continuum mechanics models for the purpose of our investigation seems quite reasonable. Consider the axisymmetric problem of indentation of the conic probe (opening angle 2β and bending radius R) into the liquid of density ρ. The solid body-liquid surface tension coefficient at the prescribed ambient temperature is α, and z is the symmetry axis, cf. Fig. 1. The liquid occupies a semi-infinite plane space at $z = 0$.

Before setting the contact angle value, it is necessary to note the following. According to Young's law, the contact angle ϑ is solely dependent upon the thermodynamic parameters $\alpha_1, \alpha_2, \alpha$:

$$cos(\vartheta) = \frac{\alpha_1 - \alpha_2}{\alpha}, \tag{2}$$

where $\alpha_1, \alpha_2, \alpha$ are the surface tensions at the interfaces: solid body – air, solid body – liquid, and liquid – air, respectively. Therefore, under given conditions (temperature and pressure) the equilibrium angle for each system has a single value. However, it was found experimentally that the measured contact angles are affected by some additional factors, and take thus diverse values (Summ, 1999). In our study, the value of the contact angle, ϑ, between the probe and liquid is assumed to

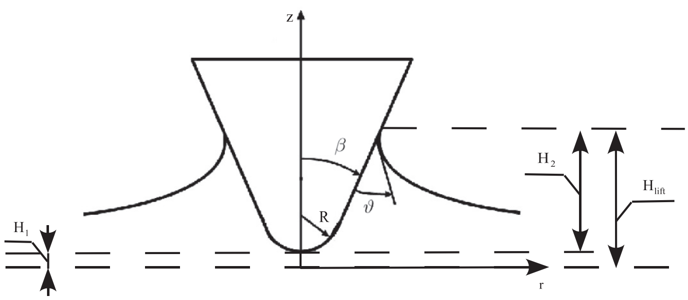

Fig. 1. Schematic illustrating the formation of a capillary meniscus. A – the point of contact between the probe and liquid, H_1 – the distance from the probe tip to the liquid level at a large distance from the probe, H_2 – the maximum height to which the liquid rises along the probe, H_{lift} – the maximum height of the liquid entrained by the probe, R – the bending radius of the probe, and ϑ – the contact angle, z – the coordinate axis.