

3D AFM in dense fluids: What can we infer of their results?

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Atomic Force Microscopy (AFM) has been a powerful tool to measure the structure of non-metallic surfaces. Normally, it operates in ultra high vacuum and low temperatures. In order to achieve high resolution, this is performed due to the direct interaction cantilever substrate. However, the use of AFM within a dense liquid has to take into account also the interaction between the structure of the liquid profile generated by cantilever and substrate. This kind of interaction is typically of long range, hence may mask direct cantilever substrate interaction and loose high resolution. On the other hand, we can measure directly the structure of the fluid performing 3D maps of phase shift and amplitude [1]. In Ref. [1] was found a spatial dependence in phase shift similar to the profile derivative of the liquid in contact with the surface. But, is this general? How we should interpret the results? Which framework will reproduce the results?

To answer this open question we develop a close framework. As usually done, we will model the dynamics of the AFM cantilever as a mass-point like forced and damped oscillator, given its classical dynamics by

$$m_{\text{eff}} \frac{\partial^2 x_p}{\partial t^2} + b \frac{\partial x_p}{\partial t} + k_0 x_p^2 = F_0 \cos(\omega t) - \left\langle \vec{\nabla} \Omega[\rho(\vec{x})] |_{\rho_{\text{eq}}} \right\rangle (x_p), \quad (1)$$

where the effective mass takes into account the drag force relative to the acceleration of the cantilever, while b is related to the part proportional to the velocity. In other words, contrast and also quality factor are mainly given by the hydrodynamics of the system. On the other hand, the force which gives the spatial structure of the phase shift and amplitude corresponds to the differences in the grand potential of the fluid. This could be computed as the minimum of the grand potential Ω at an instantaneous position of the cantilever x_p , due to the several orders of differences between the characteristic times of the cantilever and relaxation of the fluids. The grand potential used here includes DIFMT to reproduce entropy contribution, and mean field theory of different interactions (Yukawa and Lennard-Jones).

Hence, our description assumes that contrast is given by the hydrodynamic contribution, while the spatial variations are mainly due to different profile structure of the fluids, which correspond a grand potential minimum of each cantilever spatial configuration.

A remarkable result obtained from these assumptions is that $\Omega[\vec{x}_p]$ presents the same decays that equilibrium profile of the substrate, i.e., the characteristics complex poles given by the bulk correlation. Which gives, as can be seen in Fig. 1, the oscillatory-exponential decay of the phase shift of the cantilever. This is also in amplitude results, but in a

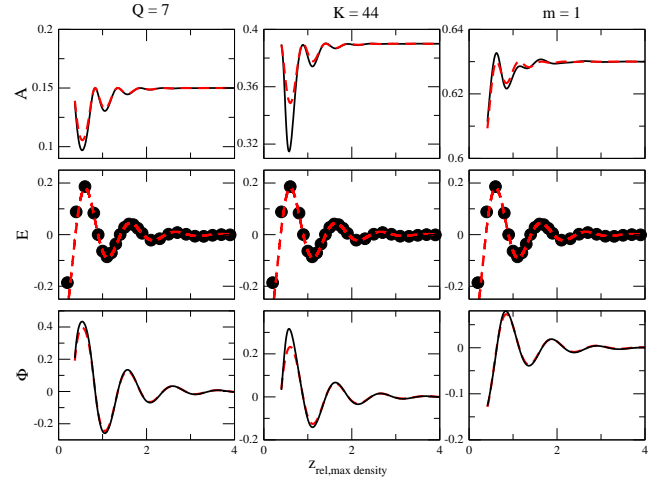


Fig. 1. The first row corresponds to the amplitude obtained, while the third row represents the phase shift. In both the straight line corresponds to the numerical results, while the dashed line (red) corresponds to a theoretical approach. The second row shows the values of $\Omega[\vec{x}]$ obtained by minimization (black points), while the dashed lines represents the fit using the decays of the bulk correlation.

complex way that depends strongly of the regime used in measurements of the AFM.

The results can be understood by the interference between the structure generated by the cantilever with that corresponding to the substrate. This interference is induced by the boundary layers of cantilever and substrates, which generate a strong first density peak in the cantilever which its relative position to it is nearly fixed. Then, as long as you move the cantilever, this first peak performs a kind of topography of the density profile generated by the substrate. Which is traduced in the oscillatory-exponential decay observed in the energy excess of this system, and explain why the decays are given by the characteristic poles of the bulk correlation. Hence, only two parameters, phase shift and interaction strength of the energy, depend given a bulk density of the external interaction and geometry of the cantilever, which are related with how strong is the structure generated over the profile. In order to characterize both parameters, we refer the energy to the distance of the first peaks of cantilever and substrate.

[1] D. Martin-Jimenez, E. Chacon, P. Tarazona, and R. Garcia, Atomically resolved three-dimensional structures of electrolyte aqueous solutions near a solid surface, *Nat. Commun.* **7**, 12164 (2016).