Viscoelastic Response of Soft Surfaces

Dynamic AFM with soft materials is governed by both the elastic and the viscous response of the surface. Dynamic force curves reveal the finite relaxation time of a viscoelastic surface.

Elastic and Viscous Response

The contact of an AFM tip with a surface is usually understood in terms of material compression giving rise to a repulsive contact force. However, attractive or adhesive forces, nearly always present between any two materials, play a dominant role in AFM contact mechanics with very soft materials. Typically the repulsive and attractive forces are taken to be purely elastic, but the dynamic contact of an oscillating AFM cantilever with a soft material is often dominated by viscous forces.

An elastic force depends only on the tip position with respect to the material surface, and it instantly balances the load force applied by the cantilever. A Viscous force depends on velocity, or the rate at which the cantilever loading force is applied to the surface. The viscous damping coefficient of the surface η_s [kg/s], together with the elastic stiffness k_s [N/m], result in a characteristic relaxation time $\tau_s = \eta_s / k_s$ [s]. When the tip is pulled away from an indented surface, the surface does not immediately follow the receding tip, but lags after by the characteristic delay time τ_s. Similarly, a soft surface that is lifted by adhesion, requires a time τ_s to relax after the contact is broken.

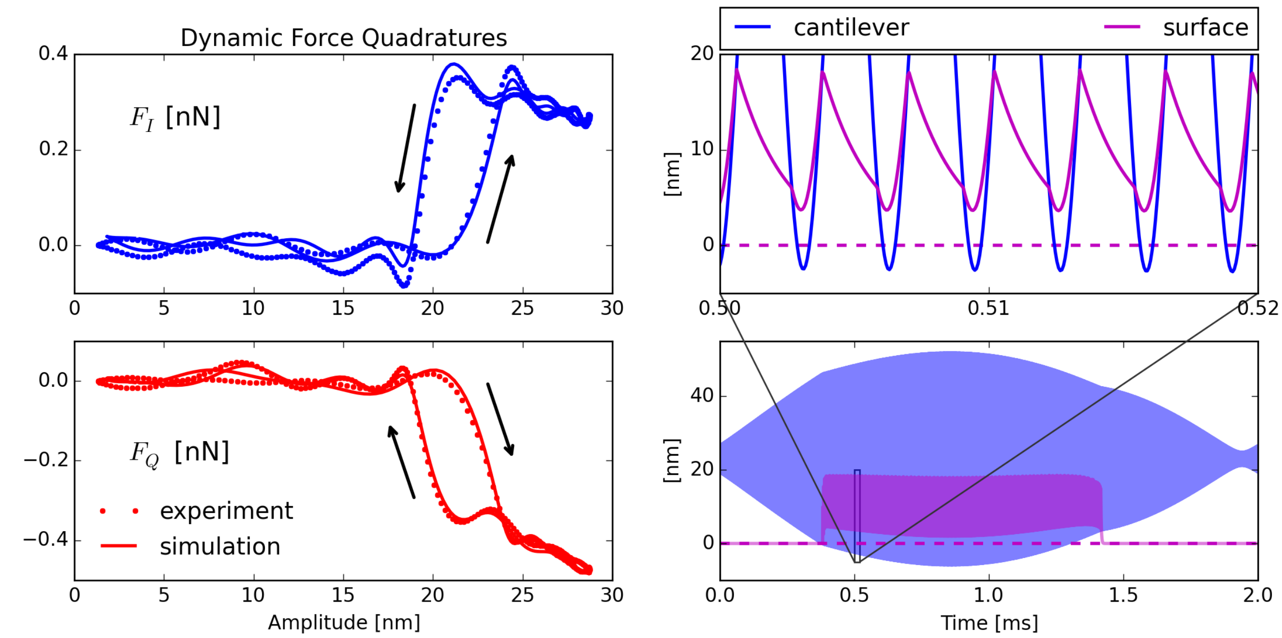

Figure 1: Dynamic force curves for an AFM tip interacting with amorphous Polycaprolactone. The experimental curves are reproduced with amazing accuracy by simulation of the theory, where the latter allows for detailed analysis of the surface motion. The soft, liquid-like surface $k_s = 5.1\text{x}10^{-3}$ [N/m] is lifted by the cantilever far above its equilibrium position before the adhesive contact is broken. Due to the finite relaxation time $\tau_s = 1.8\text{x}10^{-6}$ [s], the viscoelastic surface does not relax before it is pulled up again in next cantilever oscillation cycle. The result is a complex oscillation of the surface, with time-average lifted position.

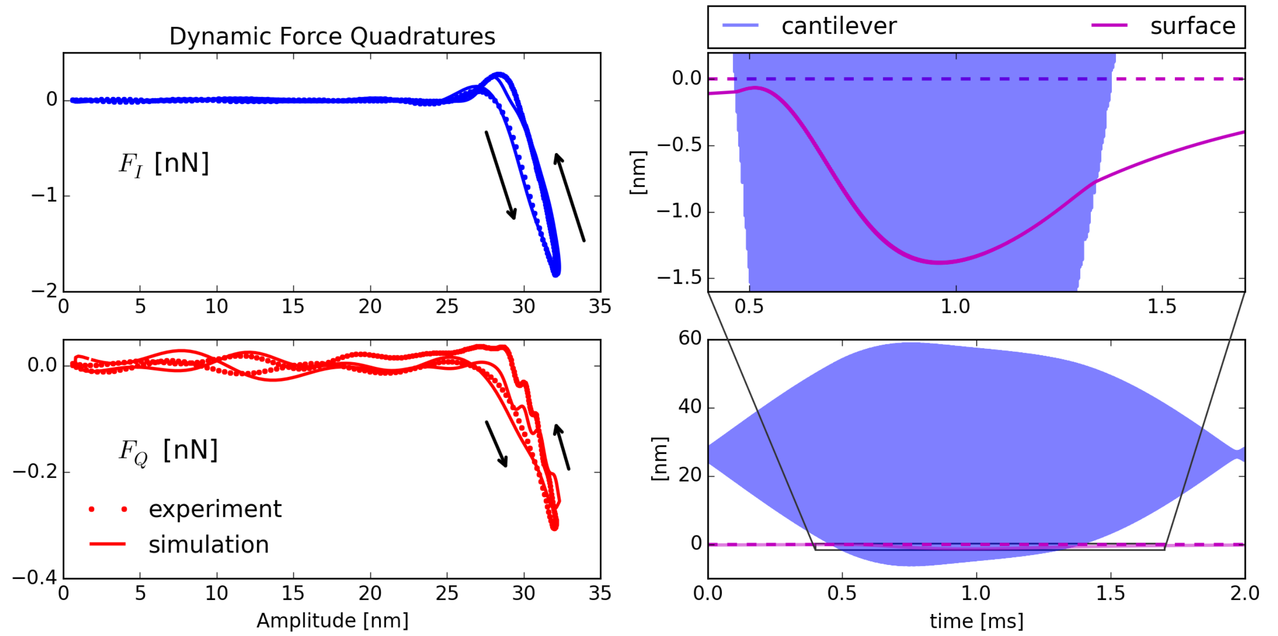

Figure 2: Dynamic force curves on Polystyrene also show remarkable correspondence between experiment and simulation of the theory. The stiffer material $k_s = 5.3\text{x}10^{-1}$ [N/m] is much more viscous than Polycaprolactone, giving it a much longer time constant $\tau_s = 5.4\text{x}10^{-4}$ [s]. The slow relaxation suppresses fast oscillatory surface motion, but repeated taps by the tip slowly drive a deeper indentation of the surface as the oscillation amplitude increases. This slow relaxation causes in a different dynamic force curve on increasing and decreasing amplitude.

Dynamic Force Quadratures

Intermodulation AFM enables the measurement of two dynamic force curves at each pixel of the scan: $F_I(A)$ is the integrated force in-phase with the cantilever oscillation, and $F_Q(A)$ the integrated force quadrature to the harmonic motion, or in phase with the velocity. Together these curves tell about both the elastic and viscous nature of the contact, and how they change with the oscillation amplitude A. The Dynamic Force Quadratures are an AFM form of Dynamic Mechanical Analysis (DMA), a method use for bulk material characterization in polymer science.

Hysteresis

The nonlinear contact forces in AFM give rise to rich structure in the dynamic force curves, which can be understood with theroetical modeling. The curves can be multi-valued, depending on the history of the amplitude modulation (see fig. 1). This hysteresis is a direct consequence of the finite relaxation time of the viscoelastic contact. Using a simple model of a linear, viscoelastic surface interacting with a cantilever resonance through nonlinear contact forces, we can simulate the cantilever and surface dynamics, and extract the mechanical properties of the surface[2].

Figure 1 shows interaction with a very soft material. Adhesion between the tip and surface cause the cantilever to pull the soft material nearly 20 nm above it's relaxed position before contact breaks. The interaction is almost purely attractive $F_I > 0$, and the surface motion gives rise to a large dissipative force F_Q.

Figure 2 shows the interaction with a stiffer surface that is much more viscous. The increased stiffness gives small surface motion with lower dissipation and the elastic force becomes dominantly repulsive $F_I < 0$. In spite of the larger elastic forces, hysteresis can be seen due to the slow relaxation (large viscousity) of the surface.

References

1) Interacting imaging with amplitude-dependence force spectroscopy. D. Platz, D. Forchheimer, E. A. Tholén and D. B. Haviland. Nature Comm. 4, 1360 (2013).

2) Probing viscoelastic response of sot material surfaces at the nanoscale. D. B. Haviland, C. A. Van Eysden, D. Forchheimer, D. Platz, H. G. Kassa and Philippe Leclere. Soft Mater, (2015) DOI: 10.1039/c5sm02154e