About the Quantitative Mapping of the Mechanical Properties of Polymeric Materials at the Nanoscale

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Dynamic Atomic Force Microscopes (AFM) are often used to probe nanomechanical properties of soft materials, in particular for polymers. The last two decades have seen numerous efforts to interpret height and phase images in terms of mechanical properties and dissipating processes. Beyond the technical difficulties, mostly related to a proper knowledge of the size and shape of the tip, extracting quantitative information requires a model (ideally providing analytical expressions), in turn allowing the recorded data to be analyzed. Any attempt to model oscillation behavior when the tip touches the sample faces several difficulties, making models of the interaction truly cumbersome.

On one hand, when the tip is in contact with the sample, it is possible to get quantitative mapping of the mechanical parameters by a technique named *Contact Resonance AFM*. On the other hand, with the recent development of *multifrequency AFM* based techniques, analysis of the cantilever motion in dynamic AFM can describe the force acting on the tip, from which we can hopefully intuit the viscoelastic properties the studied surface. Progress in the field of instrument/cantilever calibration, and methods of force measurements set the stage for a critical examination of the different physical models commonly used in this growing field of research. These models are of paramount importance for our understanding and interpretation of the data to provide the (ideally quantitative) mapping of the material mechanical properties. In this work, we will review most of them by illustrating their capabilities but also their limitations on a series of samples based on polymer blends and block copolymers.

Material property mapping based on this approach faces many problems, mainly since the measurements are performed too rapidly, provoking the appearance of viscous forces. More importantly, when the sample is very soft, the tip penetrates the surface and its interaction with the surface may include entropic forces, capillary forces arising from surface curvature that is not usually considered. Actually, many of the methods developed so far employ a linear approximation, treating the mechanical response as changing the parameters of an effective cantilever resonance assumed in rigid contact with the surface.

By using *Intermodulation AFM* data [1-2], we clearly show that we can go beyond the linear response and the rigid interaction models to explain the AFM data. Our analysis based on the dynamic force quadratures, very like the macroscopic *Dynamic Mechanical Analysis*, clearly show that significant viscous response may be explained by a soft material flow, giving the surface its own dynamics. From the comparison with simulations of the dynamics of the system including the surface deformation in a simple model describing the cantilever eigenmode coupled to a linear viscoelastic surface, we can find remarkably good agreement between experiment and simulation, providing quantitative mapping of the mechanical properties of (very soft) polymeric-based materials essentially at any point of the (viscous) surface.

References

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