Interplay between an experiment and theory in probing mechanical properties and phase imaging of heterogeneous polymer materials

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Abstract. The analysis of experimental amplitude and phase curves and phase images of polymer blends was performed in combination with KBM (Krylov-Bogoliubov-Mitropolsky) modelling of tapping mode atomic force microscopy (AFM). Different phase and dissipation contrast of images of multilayer polymer blends suggests that phase imaging is better for compositional mapping whereas understanding of the dissipative processes will facilitate a quantitative description of tip-sample force interactions in this mode. The KBM model describes tapping mode amplitude and phase curves in terms of three stationary solutions (two stable nodes, one saddle) verified by the experiment. A simple model of energy dissipation (adhesion avalanche) was also considered.

1. Introduction
Atomic force microscopy (AFM), which was introduced for high-resolution imaging of surfaces, has appeared to be more useful than anticipated by providing an access to different sample properties (mechanical, electric, magnetic, etc) and enabling compositional mapping of heterogeneous materials. Although AFM is broadly applied in academia and industry, its potential has not yet been fully realized. Further progress is needed in high-resolution imaging, fast scanning and quantitative studies of local mechanical properties. These developments are based on a better understanding of physical phenomenon related to AFM and, particularly, tip-sample forces. Such knowledge is invaluable for design of novel instrumentation and for a quantitative analysis of the experimental data.

Recently we performed a study related to molecular-scale imaging with tapping mode, which is most useful AFM method for examination of polymer and biological materials. Interplay between experimental results obtained on an organic crystal and theoretical simulation of AFM images of this sample revealed a dependence of lattice patterns on tip-sample force and dimensions of the tip apex [1]. This suggests a caution in interpretation of molecular- and atomic-scale images of periodical structures, the need of atomically sharp probes, and better force-sensitive instruments for high-resolution imaging. The simulation of tapping-mode images was conducted with KBM (Krylov-Bogoliubov-Mitropolsky) method assuming Hertz contact between the probe and sample atoms [1]. Here we are expanding this approach for simulation of amplitude and phase curves. A comparison of the data obtained on heterogeneous polymer materials with the theoretical simulations shows their similarity. In this paper we describe the use of the KBM approach for quantitative analysis of tapping mode operation.
2. Experimental and theoretical methods

2.1. Samples and procedures

Our experiments were performed on two polymer blends and a Si wafer. The binary blends of polyethylene (PE) with different density (0.86 and 0.92 g/cm³) and polypropylene (PP) with rubber (EPDM) were prepared in a multilayer fashion. Imaging was conducted on fresh cuts across the layers, which were made with a cryoultramicrotome and a diamond knife. Scanning probe microscopes, Dimension 5000 with a NanoScope IIIa controller were used for indentation and MultiMode with a NanoScope V controller - for phase measurements (in the manufacturer convention). For imaging and mechanical studies Si probes with stiffness ~ 40 N/m and different tip diameter: ~10 and ~70 nm were applied [2]. Sharp probes are more suitable for high-resolution imaging and larger ones with spherical tips - for nanomechanical studies, figure 1a, d. A shape of the probes, which is required for quantitative analysis, was determined with TEM. These probes are less subjected to wear than sharp probes. AFM images of triblock copolymer film, which were obtained with probes of both types, show that spherical probes provide reasonable image resolution, figures 1b-c.

Prior to imaging in tapping mode, we measured mechanical properties of the blends’ components using deflection curves and analyzed them with the Oliver-Pharr model. In height images of the blends we distinguished linear borders between individual layers and performed indents on 25 locations in each layer. The data analysis provided elastic moduli (E) of the components: PE (0.92) – E = 0.6 GPa, PE (0.86) – E = 30 MPa; PP – E = 2 GPa and EPDM – E = 10 MPa. This helped correlating the contrast of phase images, which were obtained at different Asp/A0 (A0-amplitude prior to tip engagement, Asp-set-point amplitude), to the blend components. We also recorded amplitude-vs-distance (AvZ) and phase-vs-distance (θvZ) curves on the blends’ components, and Si. Dissipation [(sinθ - Asp/A0)vZ] curves were calculated from θvZ curves.

2.2. Krylov Bogoliubov Mitropolsky (KBM) method for modelling tapping mode AFM

Using Euler-Bernoulli equation with adequate boundary conditions, the following system of differential equations was derived for AFM tip oscillation near the first resonance mode:

\[
\begin{align*}
\dot{x} &= -\xi \left( \frac{1}{\omega_1^2} \Phi(x \cos(\zeta - \theta), -\omega_1 x \sin(\zeta - \theta)) + d \sqrt{\omega_2^2 + 4g^2} \cos^2 \zeta \right) \sin(\zeta - \theta) \\
\dot{\theta} &= \xi \left( \frac{1}{\omega_1 x} \Phi(x \cos(\zeta - \theta), -\omega_1 x \sin(\zeta - \theta)) \cos(\zeta - \theta) - \frac{d \sqrt{\omega_2^2 + 4g^2}}{x} \cos \zeta \right) \cos(\zeta - \theta) + g \\
\dot{\zeta} &= \omega \nabla
\end{align*}
\] (1)

Figure 1. (a), (d) - TEM & SEM images of a sharp and spherical probes; (b), (c) - height images of triblock copolymer obtained with sharp and spherical probes, respectively.
This equation is written in Van der Pole’s [3] coordinates: amplitude \( x(t) \), phase difference \( \theta(t) \) and full phase \( \zeta(t) \) of piezo drive. Parameters in (1) are as follows: \( \omega_0 [\text{Hz}] \) is the (piezo) driving frequency; \( \omega_0/2 [\text{Hz}] \) is the 1st eigenfrequency of the cantilever (calculated using Euler-Bernoulli equation); \( \varepsilon = Q^{-1} \) (where \( Q \) is quality factor of the cantilever) assumed to be a small parameter; \( g = Q(\omega - \omega_0) [\text{Hz} \cdot \text{Q}] \) characterizes scaled (small) difference between driving frequency \( \omega \) and the eigenfrequency \( \omega_0 \); \( d [\text{m}] \) is a free-oscillation amplitude (without tip-sample interaction) that depends on parameters of the cantilever and piezodrive (e.g. \( \omega \) and \( \omega_0 \)); function \( \Phi \) is defined as

\[
\Phi(\xi, \dot{\xi}) = \frac{F(Z_c + \xi, \text{sgn} \dot{\xi})}{m} - \omega_0 \dot{\xi}
\]

where \( Z_c [\text{m}] \) is the central position of the cantilever during tapping oscillation; and \( m [\text{kg}] \) is an “effective mass” parameter calculated using Euler-Bernoulli equation and cantilever parameters. \( F(z, \text{sgn} \dot{z}) \) is a tip-sample force that consists of approach \( F_a(z) \) and retract \( F_r(z) \) parts

\[
F_a(z) = F(z-1) \quad F_r(z) = F(z+1)
\]

Note that \( F \) may also depend on \( \dot{z} \) (nonlinear viscoelasticity), but this is out of the paper content.

Equation (1) has two slow variables, \( x \) and \( \theta \) (their derivatives are proportional to small parameter \( \varepsilon \)), and one fast variable \( \xi \). The first two equations of (1) are periodic with respect to the fast variable. According to KBM method, the first order approximation of equation (1) is obtained by averaging the first two equations of (1) over the fast variable. After some algebra and integration, the averaged system comes out to be

\[
\begin{align*}
\dot{x} &= -\frac{\varepsilon}{2 \pi \omega_0} \left\{ \frac{1}{m} \int_0^\pi [F_a - F_r] (Z_c + x \cos y) \sin y dy + \pi \omega_0^2 x - \pi \omega_0 \sqrt{\omega_0^2 + 4 g^2} \sin \theta \right\} \\
\dot{\theta} &= -\frac{\varepsilon}{2 \pi \omega_0} \left\{ \frac{1}{m} \int_0^\pi [F_a + F_r] (Z_c + x \cos y) \cos y dy + \pi \omega_0 \sqrt{\omega_0^2 + 4 g^2} \cos \theta + \varepsilon \right\} + \varepsilon g
\end{align*}
\]

In this paper we consider only the case when driving frequency \( \omega \) is equal to the cantilever eigenfrequency \( \omega_0 \), i.e. \( \varepsilon = 0 \). In this case the equations for the stationary points \( \dot{x} = \dot{\theta} = 0 \) are

\[
\begin{align*}
\sin \theta &= \frac{1}{N} \int_0^\pi [F_a - F_r] (Z_c + x \cos y) \sin y dy + \frac{x}{d} \\
\cos \theta &= -\frac{1}{N} \int_0^\pi [F_a + F_r] (Z_c + x \cos y) \cos y dy
\end{align*}
\]

where \( N = \pi m d \omega_0^2 \) and has the unit of force.

Equations (4) can be used for simulation of images (\( x = A_{ip} \) and the equations are used to resolve unknown height \( Z_c \) and phase \( \theta \)) and amplitude \( x/\text{phase} (\theta) \) curves vs \( Z_c \) (for each \( Z_c \), amplitude \( x \) and phase \( \theta \) are to be found from equations (4)). These stationary points must be analyzed on stability using equations in variation of (3) [3]. If tip-sample forces \( F_a \) and \( F_r \) are modeled with unknown properties of samples (e.g. modulus \( E \) and adhesive energy \( \gamma \)) these parameters can be found from (4) based on the amplitude and phase curves. The approach works the best when integrals in (4) are presented in closed analytical form (e.g. Lennard-Jones).

According to the first equation of (4), \( (\sin \theta - x/d) \) characterizes the energy dissipation in agreement with [4,5]. In addition, equations (3)-(4), which were rigorously derived with KBM asymptotic theory [3], describe dynamics of amplitude \( x \) and phase difference \( \theta \) with accuracy of the order \( 1/Q^2 \). They portray dependences of stationary stable and unstable points on parameters (e.g. \( Z_c \)) that follows bifurcations known from general non-linear dynamic systems theory [3] (see examples below). Equations (3) can be applied to tapping and frequency modulation modes.
3. Results and discussion

Compositional mapping of polymer blends, which is the valuable feature of AFM, is best achieved in phase images when imaging is performed at elevated tip-forces (hard tapping) [6]. Phase changes are related to dissipation in a way (\(\sin \theta - \frac{A_{sp}}{A_0}\)) that not necessarily provides the same contrast in the images. This is evident from a set of height, phase and dissipation images of multilayer PE, which were obtained in light and hard tapping. A pronounced contrast between PE(0.86) and PE(0.92) layers in the phase image is consistent with 0vZ curves in figure 3.

Figure 2. Height, phase & dissipation (\(\sin \theta\)) images of the blend PE(0.86) and PE(0.92) obtained at light tapping (\(\frac{A_{sp}}{A_0}=0.95\)) - top and at hard tapping (\(A_{sp}/A_0=0.5\)) - bottom. Scans - 3.5 \(\mu\)m \(\times\) 7 \(\mu\)m.

In the 0vZ curves recorded on different PE, a gradual phase transition from negative to positive, which is consistent with a tip-force change from attractive to repulsive, took place at small Z-travel in PE(0.92) and at large Z-travel in PE(0.86). This transition was abrupt in AvZ and 0vZ curves obtained with the sharp probe on PE(0.92) - dotted circles.

Figure 3. Amplitude, phase & dissipation curves obtained on PE (0.92) – top and on PE (0.86) – bottom. Spherical & sharp probes were used for recording the 6 left and 6 right curves, respectively. Phase data are shown in the manufacturer’s convention.

The situation is different for PP/EPDM blend where in hard tapping the phase and dissipation images are similar, figure 4. In general, for compositional mapping, phase images at elevated forces might be more sensitive than dissipation images. Yet understanding of dissipative processes in tip-sample interactions is crucial for analysis of the images and force curves.

Figure 4. Height, phase and dissipation (\(\sin \theta\)) images of PP/EPDM blend recorded at light tapping (\(\frac{A_{sp}}{A_0}=0.95\)) – top and hard tapping (\(A_{sp}/A_0 = 0.5\)) – bottom. Scans - 3 \(\mu\)m \(\times\) 8 \(\mu\)m.

Our simulation of tapping mode showed that in amplitude/phase coordinates the differential equations (3) have either one (stable) or three stationary points: two stable (nodes) and one unstable (saddle). Depending on Z, the points’ positions are prone to change. Approach of the saddle to one of the nodes may cause their annihilation. The birth of node and saddle solutions
can happen when Z changes to the opposite direction. This phenomenon - saddle-node bifurcation has been observed in simulated and experimental AvZ and 0vZ curves. In the simulated curves obtained in a non-dissipative case (figure 5a), at small Z-travels the amplitude and phase have only single stationary solution (solid curve). At some point, two additional solutions (node – solid line and saddle – dotted line) appeared and on further Z change the saddle approaches initial node and causes the transitions of amplitude/phase from this initial node to another one. The related abrupt changes of the AvZ and 0vZ curves are marked with dotted circles, right part of figures 5b,c.

Annihilation of the saddle and initial node was sustained until their birth at larger Z. This revamps instability of the system and spontaneous jumps between nodes best seen in the 0vZ curves (dotted circles at the lower left part of figures 5b,c). The experimental curves obtained on Si with the sharp probe (small dissipation) are more similar to the simulated ones.

Furthermore, we have considered a simple dissipative model – adhesion avalanche [7], which happens when the cantilever is not stiff enough. The related AvZ and 0vZ curves show that the transitions between nodes take place at larger Z-travels than in the non-dissipative case, figure 6. The overall shape of the simulated 0vZ curve is similar to those observed on the blends’ components. The use of the spherical probe (increased adhesion) shifted the transition from attractive to repulsive force transition to larger Z and made it smoother in the 0vZ curves. This behavior correlates with a gradual approach of the saddle to the node in the attractive force part.

A more detailed analysis of tapping mode with the KBM method will be presented later.

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