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Dynamic AFM on Viscoelastic Polymer Samples with Surface Forces

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ABSTRACT

Dynamic Atomic Force Microscopy (dAFM) is widely used to characterize polymer viscoelastic surfaces in the air/vacuum environments, however, the link between the instrument observables (such as energy dissipation or phase contrast) and the nanoscale physical properties of the polymer surfaces (such as local viscoelasticity, relaxation, and adhesion) remains poorly understood. In order to shed light on this topic, we present a computational method that enables the prediction and interpretation of dAFM observables on samples with arbitrary surface forces and linear viscoelastic constitutive properties with a first-principles approach. The approach both accelerates the computational method introduced by Attard and embeds it within the tapping mode amplitude reduction formula (or equivalently frequency modulation frequency shift/damping formula) to recover the force history and instrument observables as a function of the setpoint amplitude or Z-distance. The method is validated against other reliable computational codes. The role of surface forces and polymer relaxation times on the phase lag, energy dissipation, and

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3 surface deformation history is clarified. Experimental data on energy dissipation in
4 Tapping mode/Amplitude modulation AFM (TM-AFM/AM-AFM) for different free
5 amplitudes and set point ratios are presented on a three-polymer blend consisting of well-
6 dispersed phases of polypropylene, polycarbonate, and elastomer. An approach to
7 experimental validation of the computational results is presented and analyzed.
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18 **Keywords:** Atomic force microscopy, Attard's model, Polymers, Linear viscoelasticity,
19 Relaxation time, energy dissipation.
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1. INTRODUCTION

Dynamic atomic force microscopy (dAFM) offers many advantages and unique capabilities for the nanoscale characterization of advanced polymeric materials¹⁻⁶. dAFM enables the high-resolution imaging of polymer samples in air/vacuum/liquid environments with gentle normal and lateral forces⁷, thus allowing for minimally invasive imaging of these soft samples. Moreover, dAFM mode imaging always provides additional channels of observables (phase contrast, energy dissipation, higher harmonics, bimodal phase, etc.), which can be used to render nanoscale compositional contrast⁸⁻⁹ to complement topography images.

However, the dAFM compositional contrast on polymers can arise from different material properties (elasticity, viscoelasticity, relaxation times, hysteretic, or van der Waals (vdW) adhesion, etc.) and depends on the operating conditions (set point ratio, free amplitude, drive frequency, stiffness, tip radius, and quality factor)¹⁰. Due to the variety of effective parameters that characterize the physical properties of polymers, the interpretation of the instrument's observables on polymer samples is difficult.

In order to understand the link between dAFM compositional contrast on polymers and local material properties, a mathematical model that predicts the interaction between the dAFM oscillating tip and the viscoelastic sample surface is required. For example, in order to interpret contact-mode related AFM methods such as force modulation, or contact resonance, viscoelastic sample models without surface forces are often used¹¹⁻¹⁷. However, such approaches cannot be applied to dAFM, where the tip intermittently interacts with the viscoelastic sample surface and requires an accurate and self-consistent inclusion of both surface forces and surface relaxation dynamics.

Prior efforts linking dAFM compositional contrast on polymers to local properties have key limitations. Early works suggested that dAFM phase contrast under moderate tapping conditions on polyethylene was merely correlated with polymer density and elasticity¹ rather than viscoelastic properties. More commonly, in mathematical simulations of dAFM, viscoelasticity is introduced as an *ad hoc* addition of a Kelvin-Voigt viscoelasticity model within Hertzian or DMT (Derjaguin, Muller, and Toporov) contact mechanics theories¹¹⁻¹⁷.

$$F_{ts}(d, \dot{d}) = \begin{cases} 0, & d > 0 \\ \frac{4}{3} E^* \sqrt{R} (-d)^{3/2} - \eta \dot{d} \sqrt{-Rd}, & d \leq 0 \end{cases} \quad (1)$$

where the tip-sample interaction force F_{ts} depends on the tip-sample gap d and tip velocity \dot{d} through the effective tip-sample elastic modulus E^* , sample viscosity η , and tip radius R . There are two fundamental problems with this *ad hoc* model. First, when the oscillating tip is interacting with the sample ($d < 0$) and it is withdrawing from the sample ($\dot{d} > 0$), it is possible that $F_{ts} < 0$ for sufficiently large \dot{d} and η . However, the Hertz contact model should only include repulsive surface forces ($F_{ts} \geq 0$), so this outcome of the model (Eq. (1)) is non-physical. Put another way, as the tip withdraws, the deformed sample does not return to its original condition instantly, but rather it takes time to relax due to viscoelasticity allowing the tip to detach from the sample before $d = 0$. However, the *ad hoc* model cannot account for this and applies an attractive force forcing the tip to withdraw only as fast as the sample can relax. This is seen clearly in a force-indentation history during a single tap that is simulated using Hertz contact mechanics with an *ad hoc* Kelvin-Voigt viscoelasticity model which is generated by VEDA (Virtual Environment for

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3 Dynamic AFM) ¹⁸ as shown in Figure 1. The presence of attractive forces during the
4 retraction phase arises from the *ad hoc* and incorrect assumption that the contact area
5 history of the tip during the retraction phase of the oscillation for a viscoelastic material is
6 not different from that of a purely elastic material. In contrast, Ting's model ¹⁹ modifies the
7 Hertzian contact model by using the viscoelastic correspondence principle and correctly
8 predicts the contact area evolution for tip interaction with a linear viscoelastic solid.
9
10 However, since surface forces are ignored in Ting's model, it cannot predict surface
11 deformations occurring before tip-sample contact nor spontaneous and non-equilibrium
12 surface instabilities such as sample snap off and jump to contact with the tip. These
13 phenomena are especially relevant for dAFM on soft materials or viscoelastic surfaces
14 with a moderate to large adhesion. In recognition of the likely role of surface relaxation in
15 dAFM, recent works ²⁰⁻²¹ have included surface relaxation within dAFM simulations and
16 modeled the contact as a bed of linear springs and viscous dashpots. However, they do
17 not consider contact mechanics, 3D continuum viscoelasticity, and surface forces in a
18 self-consistent manner.
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38 In summary, understanding dAFM on polymers needs computational approaches in
39 which the relevant physics of the interactions are taken into account in a self-consistent
40 manner. Attard and co-workers ²²⁻²⁶ introduced completely different approach for
41 including the relevant physics of the contact between a tip and an adhesive viscoelastic
42 surface within the Boussinesq solution ²⁷ of a tip-sample contact problem. The approach
43 is akin to a boundary element method in that the sample surface is discretized with a
44 mesh and the surface deformation and pressure are computed at each mesh point in time
45 explicitly. Attard's approach does away with *ad hoc* assumptions of prior models
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discussed before and computes the surface deformation field self-consistently using 3D linear elasticity/viscoelasticity and arbitrary surface forces. However, since the algorithm is based on an iterative loop, it is computationally expensive. Moreover, the approach requires precise knowledge of the tip motion, which is not known *a priori* in dAFM, but rather depends on the material properties and operating conditions.

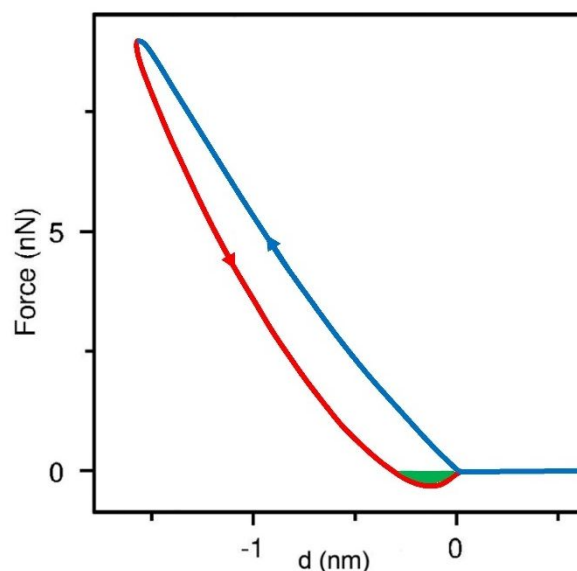


Figure 1. $F - d$ history during a single tapping cycle predicted by the AMAC tool in VEDA²⁸ using the Hertz model including Kelvin-Voigt viscoelasticity in an *ad hoc* manner. The computation uses these parameters: free amplitude: 60 nm, natural and driving frequency: 75 kHz, $Q = 150$, approach velocity: 200 nm/s, tip radius: 10 nm, and the viscoelastic properties used are $E = 1$ GPa, and $\eta = 100$ Pa-s. Note that the retraction phase features a region of attractive forces shaded in green which is an artifact of underlying model assumptions.

In this work, we both accelerate the computational method introduced by Attard and embed it within the tapping mode amplitude reduction formula (or equivalently frequency modulation frequency shift/damping formula) to recover the instrument observables (phase contrast/energy dissipation) and force and surface deformation history as a function of the setpoint amplitude or Z distance over adhesive viscoelastic surfaces. The algorithm allows for the self-consistent inclusion of resonant microcantilever dynamics,

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3 surface forces, and linear three-dimensional material viscoelasticity within dAFM
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5 simulations. The approach is validated by comparison with the results of Attard ²², as well
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7 as with VEDA simulations using Ting's model ¹⁹. The approach is then used to study the
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9 effects of polymer relaxation modes and surface forces on interaction force and surface
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11 deformation history, and TM-AFM/AM-AFM observables such as energy dissipation and
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13 phase. Experimental data acquired using TM-AFM/AM-AFM on energy dissipation on a
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15 blend of polypropylene, polycarbonate, and elastomer are described. An approach to for
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17 the experimental validation of computational results is presented and analyzed.
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22 **2. RESULTS AND DISCUSSION**

23 **2.1. Theory of the proposed approach**

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28 In AM-AFM (commonly known as TM-AFM), a microcantilever with a sharp tip is
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30 excited near its fundamental frequency and the microcantilever's vibration while
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32 interacting with the surface of the sample is monitored via a beam bounce technique.
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34 Here we review some key concepts from the analytical theory of AM-AFM upon which the
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36 proposed approach is based, recognizing that the proposed approach can be easily
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38 adapted for frequency modulation AFM (FM-AFM).
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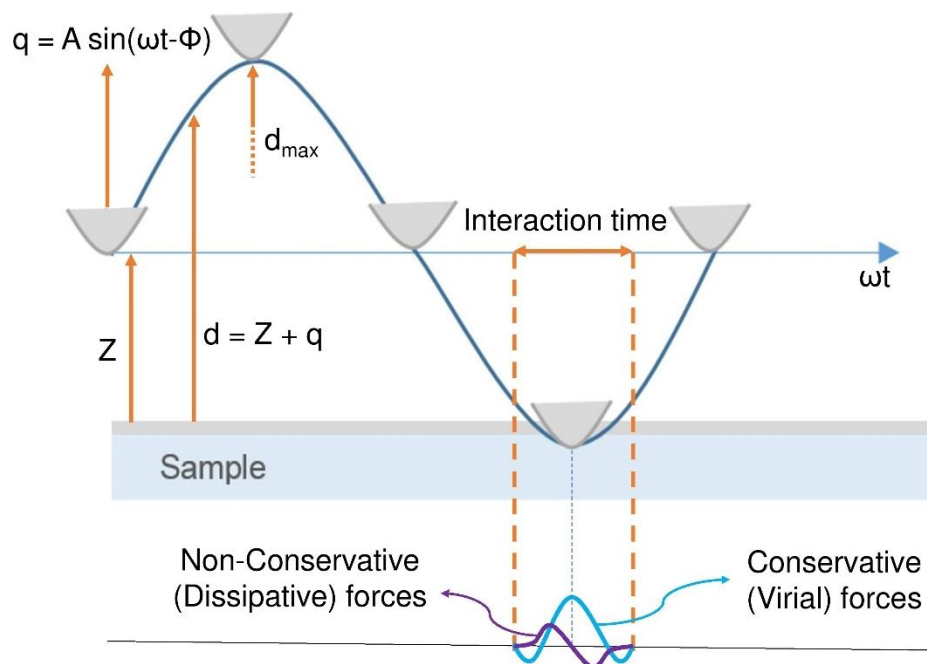


Figure 2. A schematic of an oscillating tip with tip-sample dissipative and conservative forces. d (nm) is the tip-sample gap and Z (nm) is the distance between the unperturbed microcantilever tip and the sample. The average of interaction force history during approach and retraction is the conservative part of interaction since it depends on the instantaneous tip-sample gap d and contributes to the Virial, while the difference of the approach and retraction force history during a cycle is the non-conservative part of the interaction and contributes to the energy dissipation.

For steady-state AM-AFM oscillations in air/vacuum, the tip settles in a well-defined motion²⁹, which is dominated by the fundamental harmonic of tip motion: $q(t) = A \sin(\omega t - \phi)$, where $q(t)$ is the tip deflection, A is the amplitude of the oscillation and ϕ is the phase lag relative to the excitation force. Higher harmonics also occur but they are about two orders of magnitude smaller than the fundamental in air or vacuum applications³⁰⁻³¹. If we assume that the higher harmonics of tip displacement are negligible compared to the primary harmonic, the unperturbed distance of the tip above the sample surface is Z which is adjusted by the Z piezo, the tip-sample gap is: $d(t) = Z + q(t)$ and \dot{d} is the tip velocity. A schematic of an oscillating tip interacting with a

sample is illustrated in Figure 2. During the interaction time, the tip experiences local surface forces, both conservative and non-conservative. The oscillation amplitude A of the resonant probe decreases once the Z piezo approaches and the microcantilever begins to interact with the sample surface. Under these conditions, the virial $V_{ts}(A, Z)$ and energy dissipation $E_{ts}(A, Z)$ can be calculated as follows:

$$V_{ts} = \frac{1}{T} \int_0^T F_{ts}(Z + A \sin(\omega t - \phi), \dot{Z} + A\omega \cos(\omega t - \phi)) \times A \sin(\omega t - \phi) dt = V_{ts}(A, Z), \quad (2)$$

$$E_{ts} = \int_0^T F_{ts}(Z + A \sin(\omega t - \phi), \dot{Z} + A\omega \cos(\omega t - \phi)) \times A\omega \cos(\omega t - \phi) dt = E_{ts}(A, Z), \quad (3)$$

where, F_{ts} is the tip-sample interaction force and T is the time-period of the oscillation.

Furthermore, $A^{\text{ratio}} = A / A^{\text{free}}$, known as the amplitude set point ratio (dimensionless), is the ratio of the resonant amplitude A during interaction and the free amplitude (A^{free}) far from the sample. A^{ratio} is related to $E_{ts}(A, Z)$ and $V_{ts}(A, Z)$ using the amplitude reduction formula, which is derived by rearranging the virial and energy dissipation equations³²⁻³⁴ of AM-AFM. Specifically,

$$A^{\text{ratio}} = \frac{1/Q}{\sqrt{\left(\frac{-2V_{ts}(A, Z)}{kA^2}\right)^2 + \left(\frac{1}{Q} + \frac{E_{ts}(A, Z)}{\pi kA^2}\right)^2}}, \quad (4)$$

where, V_{ts} (eV/cycle) is the virial, E_{ts} (eV/cycle) is the energy dissipation, k (N/m) is the equivalent microcantilever stiffness of the driven eigenmode³⁵ and Q is the quality factor of the microcantilever. Eq. (4) highlights the implicit relationship between amplitude reduction and tip-sample interactions. In particular, the amplitude A appears both on the left-hand side and on the right-hand side (through the E_{ts} and V_{ts} terms) of Eq. (4).

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 3 We propose an algorithm for using Eq. (4) to find the Z-distance for each
 4 desired/observed A^{ratio} and thus predict the AM-AFM observables and surface
 5 deformation and force history as a function of A^{ratio} . As illustrated in Figure 3, $A_{\text{current}}^{\text{ratio}}$ is
 6 the desired/observed amplitude ratio, $A_{\text{new}}^{\text{ratio}}$ is the computed amplitude ratio, tol is the
 7 tolerance band, dZ (nm) is a small decrement in Z, and ΔZ is the initial guess for the Z
 8 piezo increment. The value for dZ is updated at each iteration to facilitate a faster
 9 convergence. In the proposed approach, the procedure starts with an initially guessed Z-
 10 distance value, which is adjusted (increased /decreased) such that the A^{ratio} obtained by
 11 computing E_{ts} and V_{ts} using Attard's method and inserting into the right-hand side of Eq.
 12 (3) matches the desired A^{ratio} on the left-hand side of Eq. (3), within tol, the defined
 13 tolerance. When the difference between the computed and desired A^{ratio} falls within tol,
 14 all observables like Z, energy dissipation, virial, indentation, amplitude, tip-sample force
 15 history, sample deformation history are recorded for the specific A^{ratio} . Additionally, the
 16 phase lag ϕ can be calculated for each desired A^{ratio} as follows:

$$\tan \phi = \frac{\frac{1}{Q} + \frac{E_{\text{ts}}(A, Z)}{\pi k A^2}}{\frac{-2V_{\text{ts}}(A, Z)}{k A^2}} \quad (5)$$

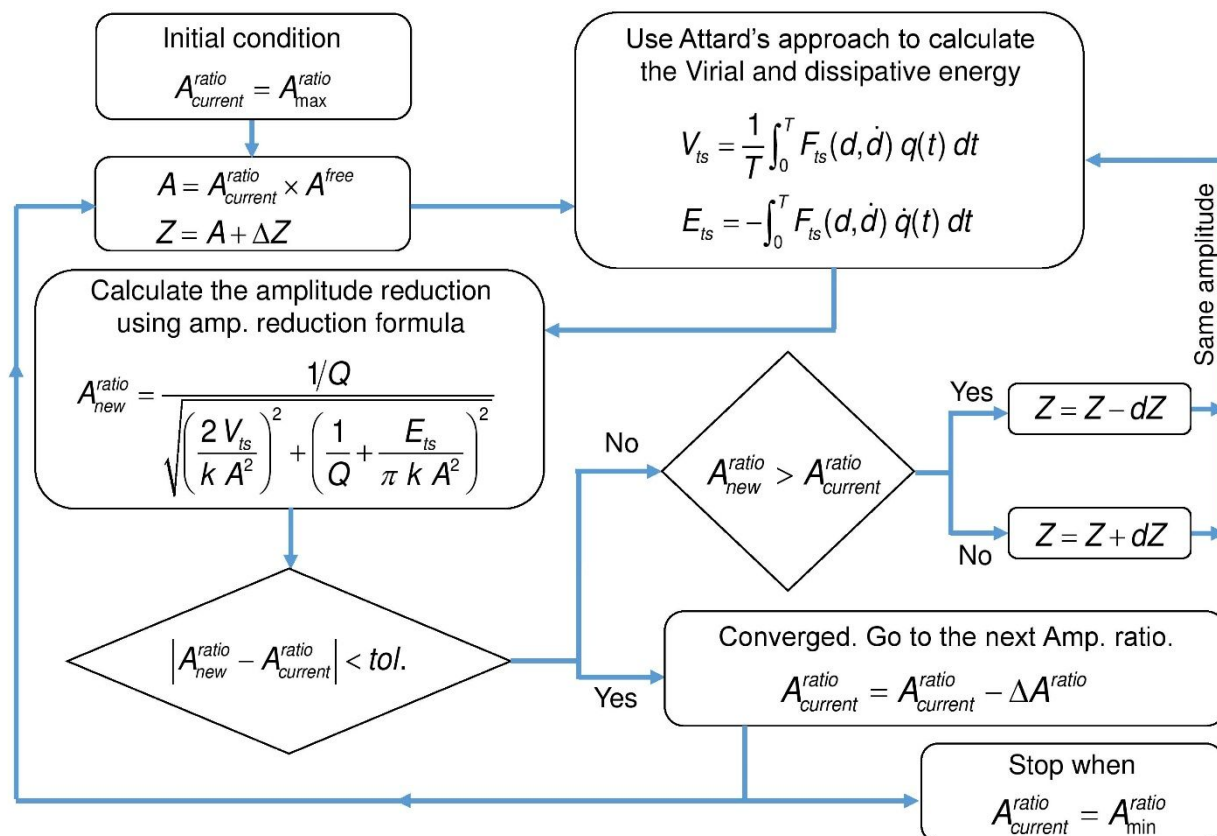


Figure 3. The proposed algorithm for predicting instrument observables by embedding Attard's model into the AM-AFM amplitude reduction formula.

After meeting the tolerance criteria for a given A^{ratio} , the algorithm goes to the next A^{ratio} in the range. The A^{ratio} range considered in the flowchart (Figure 3) is between and A_{min}^{ratio} with ΔA^{ratio} steps. The advantage of the above algorithm is that it allows for the computation of the amplitude/phase/energy dissipation as a function of A^{ratio} without time-domain simulations of nonlinear governing equations of AFM microcantilever dynamics as in VEDA²⁸.

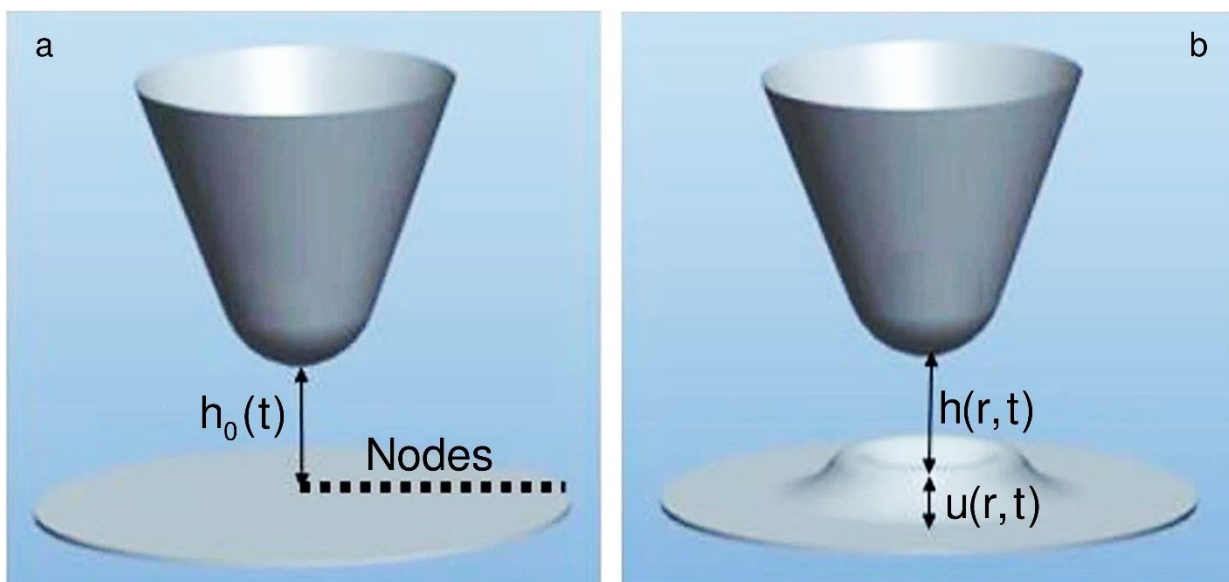


Figure 4. Attard's viscoelastic model assumes an axisymmetric rigid tip interacting with a flat polymer surface. In order to model the viscoelasticity of the sample, creep compliance of a standard three element viscoelastic model is utilized (Eq. (8))³⁶ in conjunction with arbitrary surface force models. (a) and (b) show the un-deformed and deformed sample, respectively.

The described algorithm (Figure 3) thus only needs the fast computation of E_{ts} and V_{ts} using Attard's model²²⁻²⁶ for tip oscillation amplitudes A and Z distances for which it is called to execute. The underlying principle of Attard's model is highlighted in Figure 4, where an axisymmetric rigid tip is shown in close proximity to the sample surface. The radial coordinate r measures the radial distance along the undeformed surface from the projected location of the center of the tip. $h_0(r,t)$ is the gap between the tip and the undeformed surface. Specifically, when called by the proposed algorithm (Figure 3), with a specific A , Z , and ω value, $h_0(r,t)$ takes the following explicit time-dependent form:

$$h_0(r,t) = \left(1 + \frac{r^2}{2R}\right) (Z + A \sin(\omega t)), \quad (6)$$

Furthermore, $u(r,t)$ is the vertical displacement (deformation) of the sample, $h(r,t) = h_0(r,t) - u(r,t)$ is the gap profile between the tip and the deformed surface, and the illustrated nodes (Figure 4) show the spatial discretization on the surface of the sample. The spatial discretization is referred to by i/j indices. The Lennard-Jones pressure accounts for the surface force between the tip and the sample:

$$p(h(r,t)) = \frac{H}{6\pi h(r,t)^3} \left(\frac{z_0^6}{h(r,t)^6} - 1 \right) = \frac{H}{6\pi (h_0(r,t) - u(r,t))^3} \left(\frac{z_0^6}{(h_0(r,t) - u(r,t))^6} - 1 \right), \quad (7)$$

where H is the Hamaker constant and z_0 is the equilibrium distance. Alternative surface force models can also be included in the approach. The viscoelasticity of the sample is incorporated by the creep compliance of a standard linear solid (three element) viscoelastic model³⁶, however, the approach can in principle include any linear viscoelastic constitutive relation:

$$\frac{1}{E(t)} = \frac{1}{E_\infty} + \frac{E_\infty - E_0}{E_\infty E_0} e^{-t/\tau}, \quad (8)$$

$$\frac{1}{E(t)} = \frac{1 - \nu^2}{E_s(t)}, \quad (9)$$

where, $E_s(t)$ and $E(t)$ are the time-dependent Young modulus and reduced elastic modulus of the sample as defined in Eq. (9), respectively, E_0 and E_∞ are short and long-time reduced Young's modulus of the sample ($E_0 > E_\infty$), and τ is the relaxation time for the creep compliance function. The rate of the change of the sample surface deformation and its deformation is correlated by²³:

$$\dot{u}(r, t) = -\frac{1}{\tau}(u(r, t) - u_{\infty}(r, t)) - \frac{1}{E_0} \int_0^{\infty} k(r, s) \dot{p}(h(s, t)) s ds, \quad (10)$$

where, \dot{u} and \dot{p} are time derivatives of sample deformation and the pressure, respectively. The long time static deformation (u_{∞}) and $k(r, s)$ are given by

$$u_{\infty}(r, t) = -\frac{1}{E_{\infty}} \int_0^{\infty} k(r, s) p(h(s, t)) s ds, \quad (11)$$

$$k(r, s) = \begin{cases} \frac{4}{\pi r} K(s^2/r^2) & s < r \\ \frac{4}{\pi s} K(r^2/s^2) & s > r \end{cases} \quad (12)$$

where, K is the complete elliptical integral of the first kind. Equations (10) and (11) can be spatially discretized by trapezoidal integration as follows:

$$\dot{u}(r_i, t) = -\frac{1}{E_0} \sum_{j=1}^N \dot{p}(h(r_j, t)) \Delta r_j k(r_i, r_j) r_j - \frac{1}{\tau}(u(r_i, t) - u_{\infty}(r_i, t)), \quad (13)$$

$$u_{\infty}(r_i, t) = -\frac{1}{E_{\infty}} \sum_{j=1}^N p(h(r_j, t)) \Delta r_j k(r_i, r_j) r_j \quad (14)$$

where, $\Delta r_j = r_j - r_{j-1}$ and N is the number of radial nodes. As can be seen, \dot{u} appears explicitly and implicitly (through $\dot{p}(h)$) on both sides of Eq. (13). In order to solve this equation, Attard²³⁻²⁴ used a slow iterative approach in which a value of \dot{u} is guessed at each time step and refined iteratively until the left and right-hand sides of Eq. (13) are within a defined tolerance.

It is important to emphasize that Attard's model represents the exact solution to the field equations of 3D elasticity and through the correspondence principle allows for any

linear viscoelastic constitutive relationship to be included. Interested readers are referred to Attard's papers for a complete theory of the employed model²²⁻²⁵.

In contrast to Attard's algorithm for solving these equations, we propose to take all the explicit \mathbf{b}_i terms in Eq. (13) to the left side as follows:

$$\mathbf{b}_i(r_i, t) = \mathbf{J}_{ij}^{-1} b_i \quad (15)$$

$$\mathbf{J}_{ij} = \frac{1}{E_0} (p'(h(r_j, t)) \Delta r_j k(r_i, r_j)) - \delta_{ij} \quad (16)$$

$$b_i = \frac{1}{E_0} \sum_{j=1}^N p'(h(r_j, t)) h_0(r_j, t) \Delta r_j k(r_i, r_j) r_j + \frac{1}{\tau} (u(r_i, t) - u_\infty(r_i, t)) \quad (17)$$

$$p'(h(r_j, t)) = \frac{dp}{dh} = \frac{H}{2\pi(h_0(r_j, t) - u(r_j, t))^4} \left(1 - \frac{3z_0^6}{(h_0(r_j, t) - u(r_j, t))^6} \right) \quad (18)$$

where, δ_{ij} is the Kronecker delta. Eq. (15) is thus a large set of nonlinear coupled ordinary differential equations with explicit time-dependent forcing through the $h_0(r_j, t)$ term. This is solved by discretizing time and evaluating the left-hand side of Eq. (14) at each time step, and using the deformation velocities at the nodes to step forward to the new position of the deformed surface. The code is implemented in both FORTRAN for future deployment in VEDA and in MATLAB. In both codes, the time is discretized per uniform increments/decrements of the tip-sample gap (d) and the surface is spatially discretized into nodes with equal radial increments. The selection of the appropriate number of temporal/radial discretization points is made through numerical studies to ensure that the solution is converged, and the predictions are independent of the number of discretization points. This allows for the explicit computation of $u(r_i, t)$ and consequently $h(r_i, t)$ and thus

$p(h(r_i, t))$. With this computation in place, it is easy to determine the tip-sample interaction force history as follows:

$$F_{ts}(t_k) = 2\pi \Delta r \sum_{j=1}^N p(h(r_j, t_k)) r_j. \quad (19)$$

Once the tip-sample force history is calculated during an oscillation cycle for a specific Z and A value, the result can be plugged into the Eq. (3) and Eq. (4) to compute $E_{ts}(Z, A)$ and $V_{ts}(Z, A)$, which is needed to determine the Z value required to achieve a certain A and ϕ . Once this is computed as described in Figure 3, all the relevant dAFM observables such as sample deformation/relaxation history per cycle, energy dissipation, force history, virial, phase lag etc., can be determined at the desired A^{ratio} .

2.2. Verification

By directly solving the set of ODE's in the time domain rather than an iterative solver as in Attard's original work, the present approach is nearly an order of magnitude faster than the original computational approach presented by Attard²². We present here the computational verification and validation of the proposed approach.

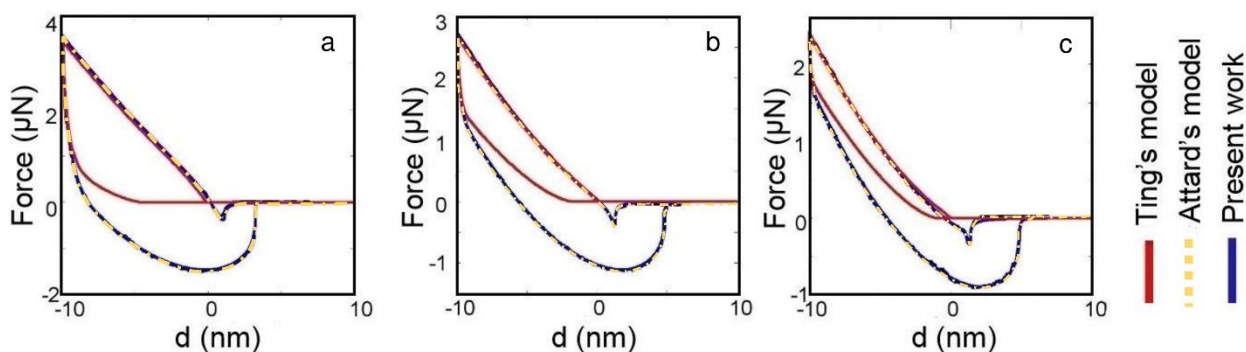


Figure 5. Attard's viscoelastic model results²², Ting's analytical viscoelastic model²⁸, and the code developed in the present work are compared with a prescribed triangular motion

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3 time profile of a rigid spherical tip. The triangular drive velocities are (a): $\pm 5 \mu\text{m/s}$, (b):
4 $\pm 2 \mu\text{m/s}$, and (c): $\pm 1 \mu\text{m/s}$. Tip radius is $10 \mu\text{m}$ and the other material parameters
5 used are identical to the ones used by Attard to facilitate comparison ²².
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8 In order to verify the accelerated computational approach presented, we compare the
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10 predicted $F-d$ histories for a prescribed triangular tip motion with the ones in Attard's
11 original work (Figure 5) ²². These results are also compared with simulations performed
12 using identical parameters but using Ting's viscoelastic model of contact mechanics
13 without surface forces, which is calculated by using the VEDA set of tools ²⁸. The number
14 of temporal discretization points is 10^4 , the simulations are performed for an effective tip
15 radius of $10 \mu\text{m}$, and 600 radial nodes are used within a radius of 500 nm of the surface
16 to ensure convergence of the solution. The characteristic relaxation time for the creep
17 function is 1 ms, the short-time Young's modulus of the sample (E_0) is 10 GPa, and the
18 long-time Young's modulus of the sample (E_∞) is 1 GPa. For Attard's viscoelastic model,
19 the Hamaker constant H is 10^{-19} J, equilibrium position z_0 is 0.5 nm. A triangular
20 oscillation with amplitude 20 nm with three different tip velocities are prescribed into the
21 model and h_0 oscillates between 10 nm and -10 nm. The predictions of the developed
22 code predict excellently the ones presented by Attard ²² and are in close agreement with
23 Ting's model prediction during the approach phase but not during the retraction phase.
24 This result is consistent with the lack of surface forces in Ting's model.
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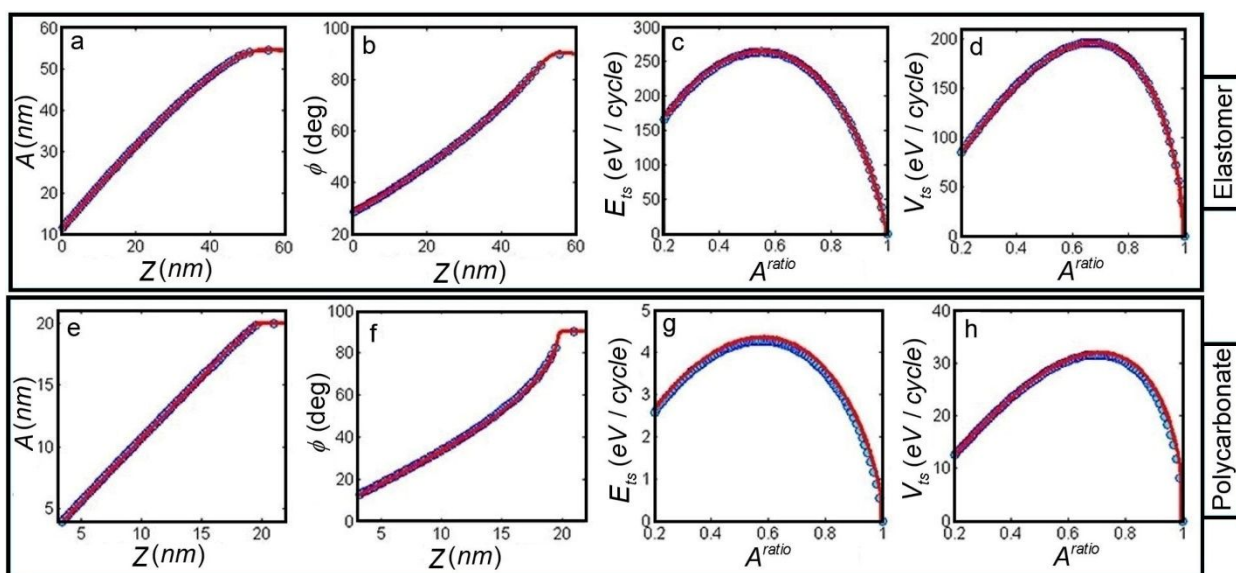


Figure 6. A comparison between the dynamic approach curves results predicted by using the present algorithm (Figure 3) and the ones from the AMAC tool which includes explicit microcantilever dynamics for elastomer (upper row), and polycarbonate (lower row). The blue circles are from the proposed algorithm and the red solid lines are the VEDA-AMAC tool's outputs. The used material property data for these simulations are listed in Table 1. The equivalent microcantilever properties are: $K = 28 \text{ N/m}$ and $Q = 542$, and the oscillation period is $3 \times 10^{-6} \text{ s}$.

Next, we validated the proposed algorithm (Figure 6) for computing the dynamic approach curves when using Attard's model for tip-sample interactions. AMAC (Amplitude Modulated Approach Curves) is an already validated tool on VEDA, which includes full microcantilever dynamics and makes reliable predictions for tapping mode AFM²⁸. This tool can accurately use Ting's model (but not Attard's) as the tip-sample interaction model, which we choose for the validation of this algorithm. Therefore, the comparison between the instrument observables predicted by computing force-distance histories and embedding them within the AM-AFM amplitude reduction formula (Figure 3) and the ones computed directly from the AMAC tool help us to ensure the validity of the proposed algorithm. As illustrated in Figure 6, the A , ϕ , V_{ts} , E_{ts} graphs show an excellent match for both elastomer and polycarbonate material properties. Since polycarbonate is stiffer

than the elastomer, the energy dissipation and virial values for the elastomer are greater than the ones of polycarbonate. The parameter values used for the polymers in these simulations are listed in Table 1.

Table 1. The parameter values used for the simulations in verification and computational results sections.

	τ	E_0	E_∞	H	z_0	A_0
	sec	GPa	GPa	J	nm	nm
Elastomer	5.47×10^{-8}	0.143	0.029	7.99×10^{-20}	0.6	60
Polycarbonate	6.56×10^{-8}	2.960	2.08	8.82×10^{-20}	0.3	20

2.3. Computational results

In order to visualize the physics of the tip-sample interaction during a single cycle, a simulation is carried out for a prescribed sinusoidal tip motion interacting with an elastomer sample (Figure 7). The elastomer sample is represented by a standard linear viscoelastic solid (three element) model with the data provided in Table 1. The complete set of parameters used for this simulation is provided in the caption of the figure. The number of temporal discretization points is 10^5 , the simulations are performed for an effective tip radius of 100 nm, and 100 radial nodes are used inside a radius of 50 nm on the surface to ensure convergence of the solution. Figure 7 shows the force history during one cycle as a function of d and ϕ (inset). These force histories clearly show the dependence of hysteresis and adhesion on both d and ϕ . The series of tip-sample geometries corresponding to 12 instants during the force history (Figure 7b) are captured from the output video of the code, which is provided as the supplementary material.

During the tip approach, the material's surface slightly deforms upwards from its initial flat state, and then snaps on to the tip and then deforms downwards with the tip movement. However, it gradually peels away from the tip during the retraction process, until a final detachment occurs. After the detachment, the surface continues to relax until it returns to the initial state. These surface instabilities are in line with predictions by Attard's model³⁷⁻³⁸. The cycle then repeats at every tap, unless the sample has not fully relaxed prior to a subsequent tap. This latter condition has not been explored in the present work where we assume the sample eventually fully relaxes prior to a subsequent tap. It is worth mentioning that the phenomena that are captured by the model and demonstrated in this figure are not fully accounted for by any of the classical models such as Hertz, JKR (Johnson, Kendall, and Roberts), DMT, or Ting's model.

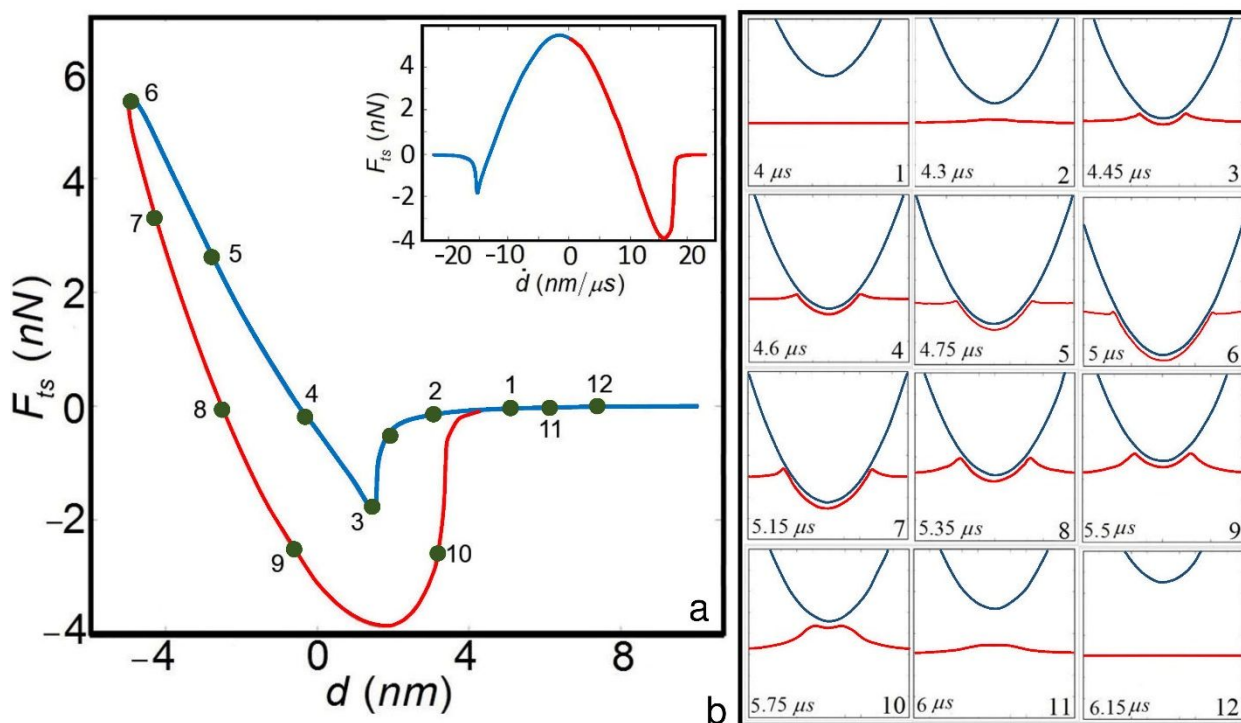
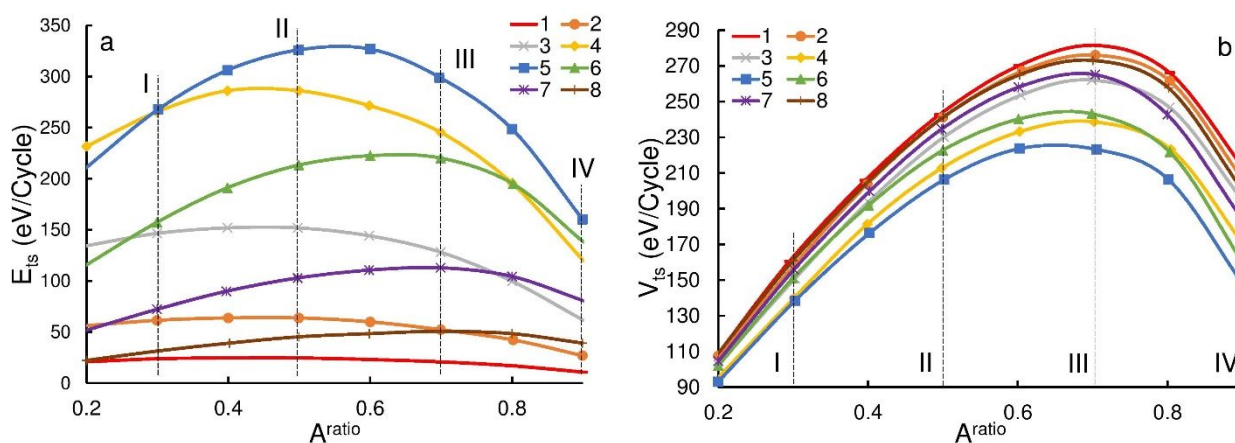


Figure 7. The interaction between a rigid axisymmetric tip and the elastomer sample surface is computed using the approach of the present work. The viscoelasticity of the

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3 elastomer is modeled by using a standard linear solid (SLS) model with the data provided
4 in Table 1. The tip travels through a sinusoidal wave with 100 kHz frequency and
5 $Z = 45$ nm. The oscillation amplitude is 50 nm and tip radius = 100 nm. In (a) the $F-d$
6 and the $F-\dot{d}$ history (inset) are graphed. In (b), the deformation history during a
7 sequence of time instants labeled 1-12 is graphed. The full video is provided as the
8 supplementary materials.
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11 In order to study the effect of diverse relaxation modes of polymers³⁶ on AM-AFM
12 observables, a set of the relaxation times τ ranging between 2.9×10^{-6} and 2.8×10^{-9} (s)
13 is used in the developed code as prescribed in Figure 3, and their effect on the outputs
14 of the model such as V_{ts} , E_{ts} , F_{ts} , and indentation depth vs. A^{ratio} is investigated. The
15 relaxation time τ determines how fast the instantaneous Young's modulus of the sample
16 changes from E_0 to E_∞ . All the other parameters except τ are identical for all the
17 simulations.
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45 Figure 8. (a) Energy dissipation (E_{ts}) and (b) Virial (V_{ts}) vs. set point ratio (A^{ratio}) for a
46 set of relaxation time (τ) values: 1: $2.9 \mu\text{s}$, 2: $1.1 \mu\text{s}$, 3: $0.40 \mu\text{s}$, 4: $0.15 \mu\text{s}$, 5: 54.7 ns ,
47 6: 20.3 ns , 7: 7.6 ns , and 8: 2.8 ns . The Lennard-Jones parameters for all simulations
48 are: $H = 8 \times 10^{-20} \text{ J}$, and $Z_0 = 0.6 \text{ nm}$, and additional material properties are provided in
49 Table 1 for the elastomer. The oscillation period is $3 \times 10^{-6} \text{ s}$, the equivalent
50 microcantilever properties are: $K = 28 \text{ N/m}$ and $Q = 542$, and the tip radius is 15 nm . The
51 vertical lines marked by roman numerals are discussed in Figure 10.
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As illustrated in Figure 8, energy dissipation values are significantly affected by τ . E_{ts} reaches its maximal values at specific relaxation times. Figure 8a also demonstrates an additional key result. The A^{ratio} at which maximum energy dissipation occurs³⁹ is highly dependent on τ . However, as depicted in Figure 8b, contrarily, the V_{ts} does not vary substantially when τ is changed.

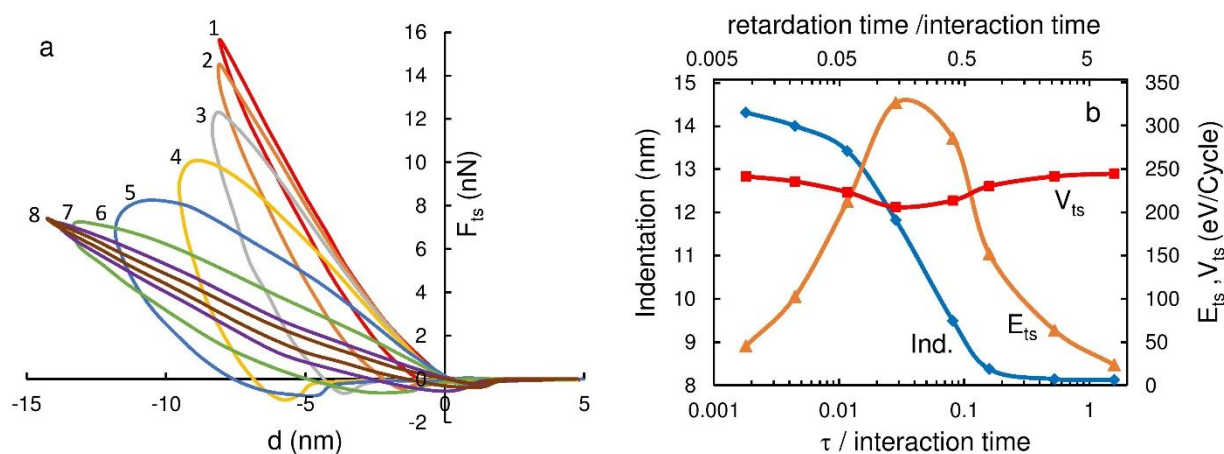


Figure 9. F – d histories and indentation depth predictions at $A^{ratio} = 0.5$ for a range of relaxation times (τ) are demonstrated. The τ values and other simulation parameters are identical to the ones in Figure 8 (b). The indentation depth, E_{ts} , and V_{ts} corresponding to the F-d histories in (a) are graphed as a function of τ non-dimensionalized by the tip-sample interaction time. Note that each of the cycles 1-8 in (a) has a different interaction time.

It is instructive to examine in Figure 9a, the F-d histories acquired as a part of the simulations presented in Figure 8 for a fixed A^{ratio} as the τ is changed in the stated range above. In Figure 9a, the force loops show minimal hysteresis when τ is small compared with the contact time, reach a maximum hysteresis when for an intermediate value of τ , and the hysteresis vanishes when τ is very large. To be more quantitative, we estimate the contact (interaction) time in each F-d history in Figure 9a from the time $A^{ratio} = 0.5$ spent in the repulsive interaction regime. Then we plot the corresponding indentation, E_{ts} ,

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3 and V_{ts} as a function of τ non-dimensionalized by the contact time in Figure 9b, all at
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6 $A^{ratio} = 0.5$. Figure 9b illustrates that the indentation depth increases with decreasing τ .
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8 For $\tau \ll$ contact time, the material has enough time to completely relax during the
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10 interaction time and therefore the modulus behaves more like E_{∞} during both approach
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12 and retraction leading to a larger indentation, and small hysteresis leading to low energy
13
14 dissipation E_{ts} . Likewise, when $\tau \gg$ contact time the material responds with a stiff E_0
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16 leading to a less indentation and small hysteresis leading to low energy dissipation E_{ts} .
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18 Figure 9b shows that E_{ts} is maximized when τ /contact time $\sim 0.01-0.1$. Put another way,
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21 E_{ts} is maximized when the ratio of creep (retardation) time ($= \frac{E_0}{E_{\infty}} \tau$) to contact time \sim
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24 $0.05 - 0.5$. Thus, if a polymer surface were to have many relaxation modes, those whose
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26 relaxation and creep times are $\approx 0.01-0.1$ and $\approx 0.05-0.5$ of the contact time,
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28 respectively, are likely to contribute most to the energy dissipation. In this sense, the
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30 energy dissipated in AM-AFM on a viscoelastic sample may be considered as a “narrow
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32 band filter” for capturing the effect of a narrow range of polymer relaxation times.
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40 Figure 10 illustrates V_{ts} and E_{ts} vs. τ for four selected set point ratios: 0.3, 0.5, 0.7,
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42 and 0.9. These are extracted from the same set of simulations as in Figure 8 and are
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44 shown by vertical dashed lines marked by roman numerals. The results show that while
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46 E_{ts} varies more significantly than V_{ts} with τ , E_{ts} is maximized and V_{ts} is minimized when
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48 the creep time is $\approx 0.05 - 0.5$ of the contact time.
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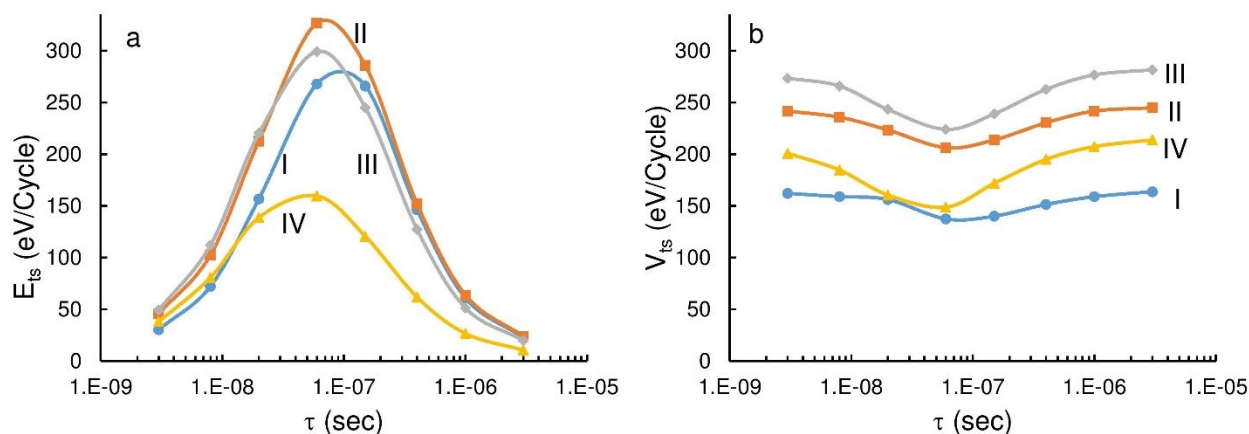


Figure 10. (a) Energy dissipation (E_{ts}) vs. relaxation time (τ) and (b) Virial (V_{ts}) vs. τ for a series of $A^{\text{ratio}} = 0.3, 0.5, 0.7$, and 0.9 that are specified in Figure 8 by vertical dashed lines labeled I, II, III, IV, respectively. All of the simulation parameters are identical to the ones in Figure 8.

The surface pressure parameters (H, z_0) that define the resultant surface adhesion, are also expected to play a role in the observed energy dissipation and hysteresis. In order to assess the sensitivity of E_{ts} vs A^{ratio} to these parameters, a range of H values between $2 \times 10^{-19} - 10 \times 10^{-19}$ J and a range of z_0 values between $0.5 - 0.8$ nm are used in the model. For smaller values of z_0 chosen in this range, surface instabilities are observed with increased hysteresis. However, those simulations are also associated with computational instabilities. The range of z_0 chosen in these simulations is both comparable to prior computational results and appropriate for small roughness polymer surfaces⁴⁰. As shown in Figure 11, within the range of chosen surface pressure parameters, E_{ts} increases as H is increased or as z_0 is decreased. This result is in line with the expectation that energy dissipation should increase with an increase in surface forces.

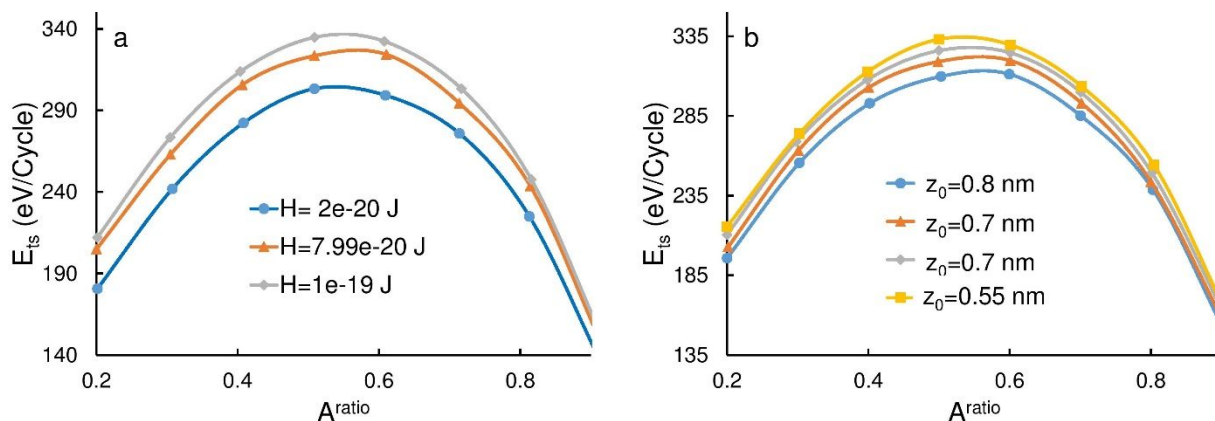


Figure 11. The Energy dissipation (E_{ts}) vs setpoint ratio (A^{ratio}) for (a) different Hamaker (H) constant values, (b) different values of equilibrium position (z_0). For (a), $z_0 = 0.6$ nm and for (b), $H = 8 \times 10^{-20}$ J. The material properties are the ones recorded in Table 1 for the elastomer.

2.4. Experiments

In order to demonstrate how the proposed computational approach relates to experimental data acquired on polymers, a set of experiments using tapping mode (TM) or AM-AFM at 326.1 kHz, and quasi-static (QS) at 1 Hz are conducted on the surface of a three-component polymer blend sample. The sample consists of a glassy polymer, polycarbonate; a semicrystalline polymer, polypropylene; and a polyolefin-based elastomer. The full description of the employed instruments and sample preparation is provided in the methods section. A typical sample data is shown in Figure 12 that are acquired over a rectangular region with the TM microcantilever with $A^{free} = 35.9$ nm and $A^{ratio} = 0.7$. The resulting topography image (Figure 12a) shows areas of smooth PC are interspersed with areas of PP with more surface roughness. Smaller areas of elastomer are found embedded in and surrounded by PC and PP domains. The acquired phase data are converted to phase lag ϕ and adjusted so that when drive frequency equals the

microcantilever's natural frequency far from the sample then $\phi = 90^\circ$. For these operating conditions, the AFM mostly operates in the net repulsive regime ($\phi < 90^\circ$, throughout the scan region) as seen in Figure 12b. The E_{ts} values (eV per tap) are extracted from the phase lag images by using the following relation³²⁻³³:

$$E_{ts}(Z, A) = \frac{\pi k A A_0}{Q} (\sin(\phi) - A^{\text{ratio}}) \quad (20)$$

and mapped to the scan region as shown in Figure 12c. Histograms of E_{ts} and ϕ acquired over rectangular regions of the PP, PC, and elastomer phases are shown respectively in Figures 12 d and e.

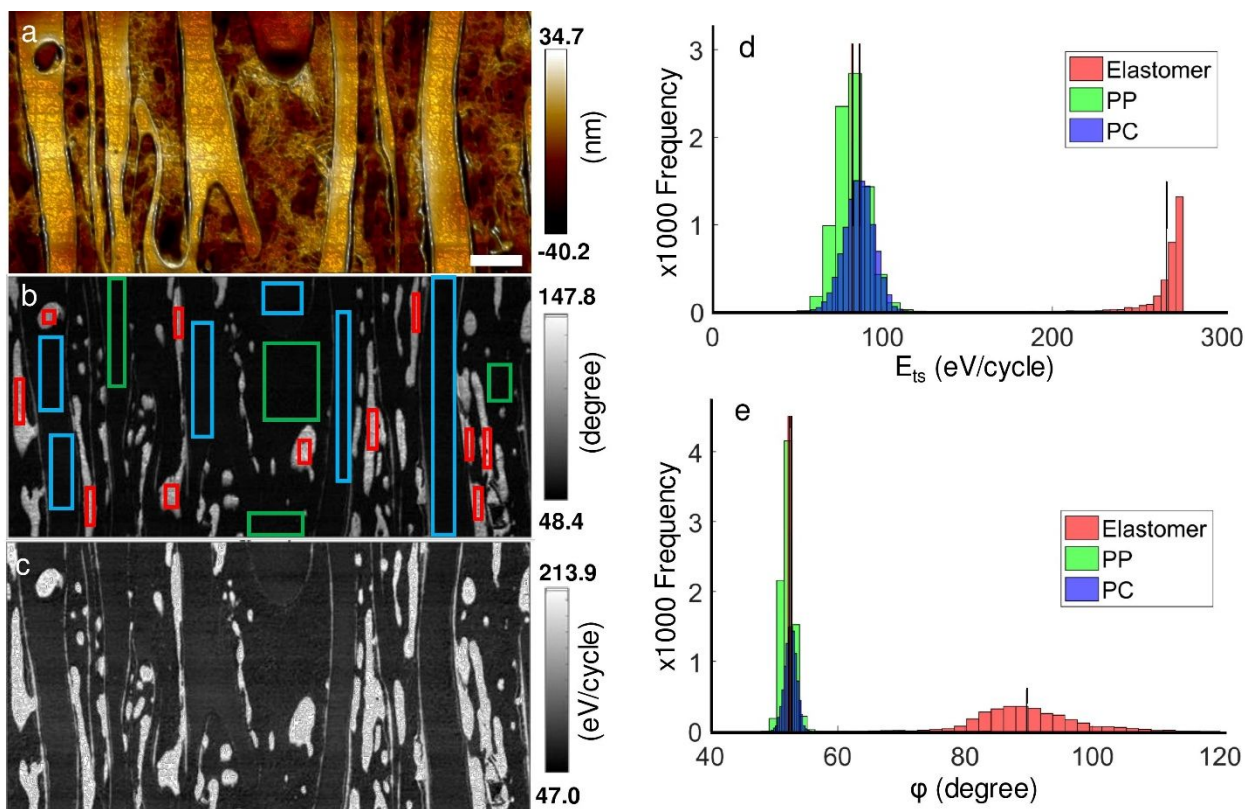


Figure 12. (a) Topography image, (b) Phase lag image, (c) Extracted energy dissipation on a three-phase blend polymer sample with $A^{\text{ratio}} = 0.7$ and $A^{\text{free}} = 35.9$ nm. (d) and (e) show histograms of the extracted energy dissipation and phase lag values acquired over

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3 the selected rectangular areas of the PC, PP, and elastomer marked in (b) with
4 corresponding colors. The vertical bold lines shown for each histogram in (d) and (e)
5 represent the mean value for each polymer. The scale bar is shown in (a) represents 1 μm
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9 The experimental validation of our computational approach is challenging due to
10 uncertainties associated with the model parameters. For example, viscoelastic bulk
11 properties can be measured using Dynamic Mechanical Analysis (DMA). However, their
12 correlation with viscoelastic surface properties measured using AFM methods remains
13 an active topic of research. Specifically, with moderate to large net indentation, contact
14 resonance (CR) method based AFM studies have reported local elasticity values
15 consistent with bulk DMA⁴¹⁻⁴². However, in AM-AFM in which gentler forces are used,
16 indentations are much smaller and the local properties may be more influenced by surface
17 effects⁴³⁻⁴⁹. Moreover, the sample under consideration features significant interphase
18 effects due to the mixture of small volumes of the three phases. Even if the AFM
19 measures properties far from interphase regions on the sample surface, there can be
20 sub-surface interphases that influence surface AFM measurements. Last, but not the
21 least, the surface force parameters z_0 and H are very hard to estimate experimentally.
22 While H can be approximated using theory, there is no clearly accepted method to
23 approximate z_0 for the specific sample.
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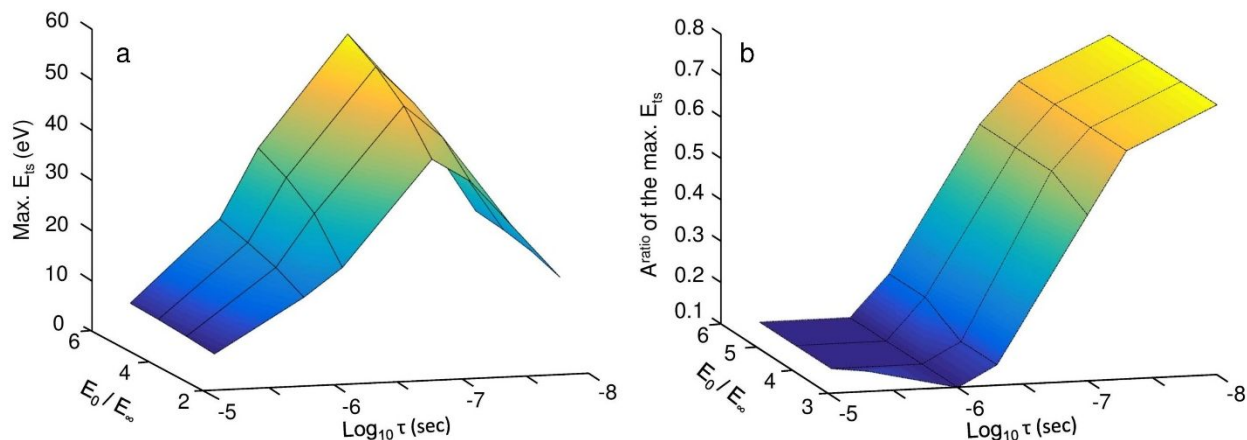


Figure 13. Maximum E_{ts} and A^{ratio} at which the maximum E_{ts} occurs plotted as a function of the relaxation time (τ) and E_0/E_∞ ratio for PP. The employed material properties are listed in Table 2, $A^{free} = 18 \text{ nm}$, $K = 28 \text{ N/m}$, and other parameters are identical to the ones described in the experiments section.

We chose to adopt the following strategy for estimating parameters for subsequent experimental validation:

1. We estimate the Hamaker constants between native Si oxide on the tip surface and the specific polymer using Lifshitz theory⁴⁰. z_0 is chosen within the range of prior works⁴⁰ and is made as small as possible to enable stable computation.
2. We use the QS force curves acquired on each of the three phases to estimate the long-time scale elastic modulus E_∞ using Hertz contact mechanics. This is a reasonable approach since the QS curves are performed at extremely slow rates (1Hz) and the quantification of uncertainties in measuring surface elastic modulus using standard force-distance curves is well understood⁵⁰.
3. We then estimate E_0 and τ by fitting these numbers to match various features of the E_{ts} vs A^{ratio} curve acquired on the three polymer phases with $A^{free} = 35.9 \text{ nm}$.

Specifically, for each of the polymer domains:

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3 a. τ is adjusted until the A^{ratio} at which maximum energy dissipation occurs in
4 simulations results matches within 10% the one found in experiment. This is
5 based on a key theoretical prediction that the A^{ratio} at which the maximum E_{ts}
6 energy dissipation occurs is mostly affected by τ (Figure 13b) and to a much
7 lesser extent by E_0 / E_∞ . As an initial starting guess τ is chosen to be 1% of the
8 cantilever oscillation period.
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18 b. E_0 value is increased from E_∞ so that the maximum energy dissipation (E_{ts})
19 of the model matches within 10% of the peak value of the fitted curve.
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23 c. τ is again tuned to ensure that the A^{ratio} at which maximum energy
24 dissipation occurs in simulations remains within 10% the one in experiment.
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29 The estimated values for the material properties using this approach are provided in
30 Table 2. The resulting computational and experimental E_{ts} vs A^{ratio} are compared in
31 Figure 14. As can be seen, the computational results using material properties estimated
32 with the experimental data set at $A^{\text{free}} = 35.9 \text{ nm}$ matches the experimental results within
33 5% across a wide range of A^{ratio} . These estimated material properties are inline with the
34 results provided by others⁵¹⁻⁵².
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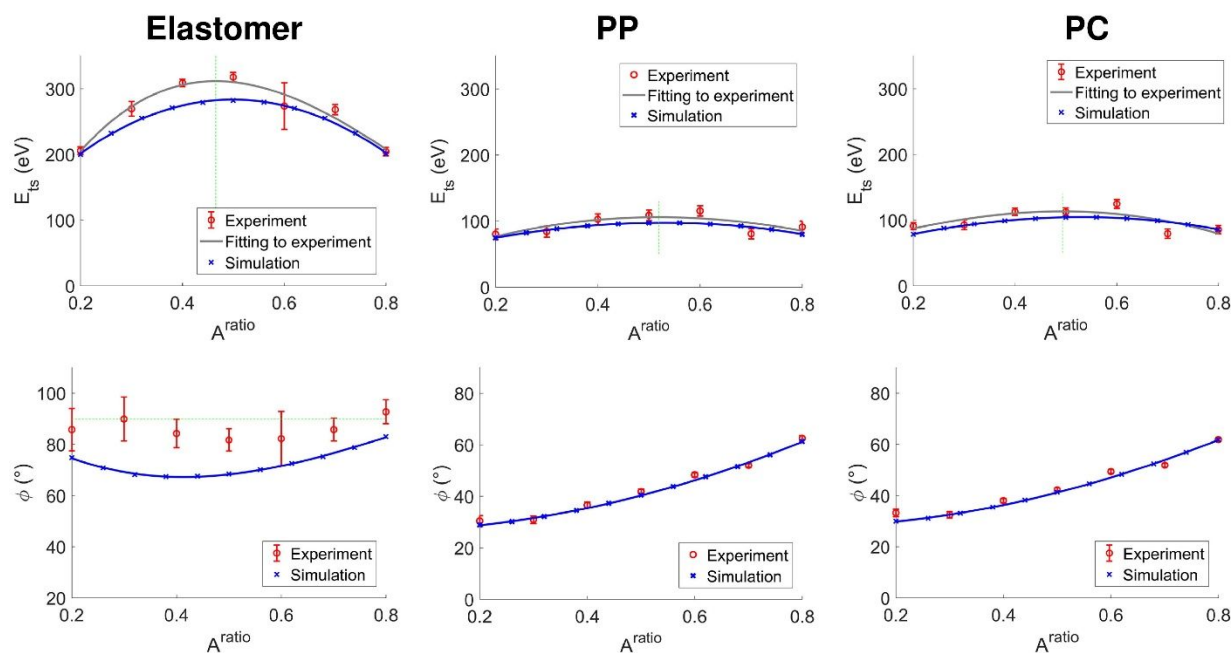


Figure 14. Comparison between theory and experiment for the three phases following calibration of τ and E_0 to best match the amount E_{ts} and the A^{ratio} at which it occurs in the experimental data acquired with $A^{free} = 35.9$ nm. A cubic polynomial is fitted to theory and experimental data to facilitate identification of the maximum E_{ts} location and magnitude. In order to help to clarify the regime of the oscillation, the 90-degree phase lag is marked by a green horizontal dashed line.

Using the material properties estimated using the calibration data (Table 2) we validate the computational approach by comparing predictions with experimental data for $A^{free} = 18.0$ nm. As illustrated in Figure 15, the predicted and measured E_{ts} are within 10% over a wide range of A^{ratio} for both PP and Elastomer. The good match obtained on the elastomer is particularly interesting since for $A^{free} = 18.0$ nm most of the approach curve is in the attractive regime of oscillation.

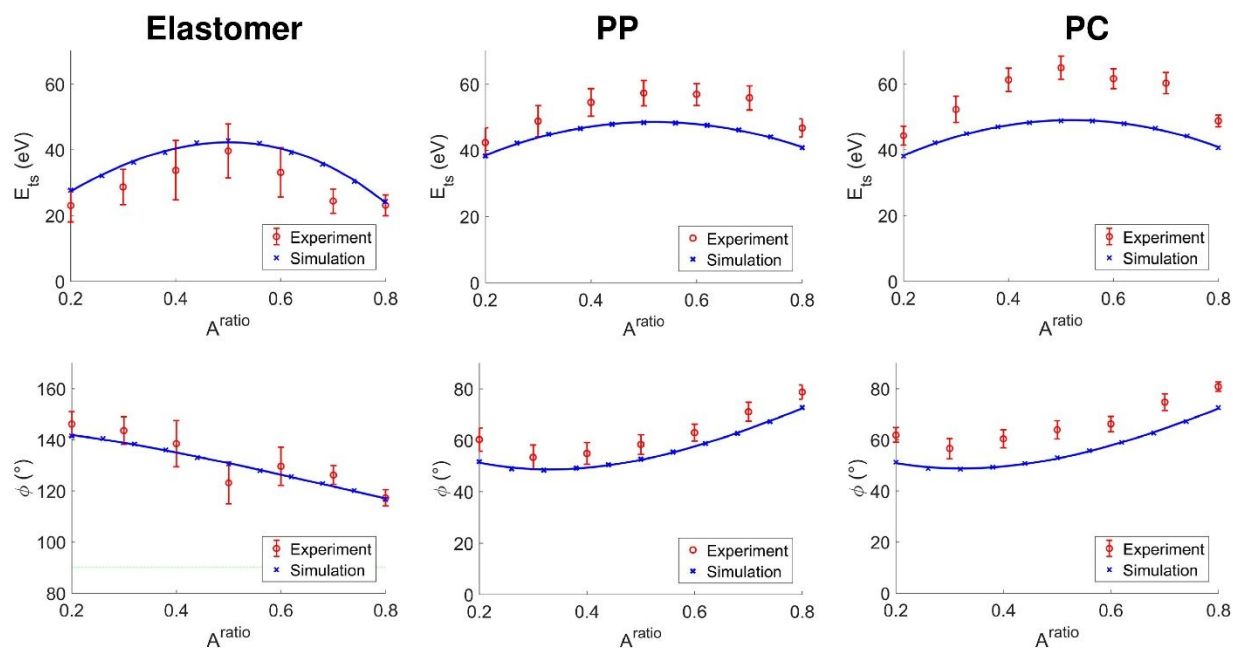


Figure 15. Comparison of computational predictions and experimental results for $A^{free} = 18$ nm on the three polymer phases. The material property data used for the computation (Table 2) are based on quasi-static force curves, theoretical estimates, and with τ and E_0 calibrated from similar data acquired for $A^{free} = 35.9$ nm (Figure 14). The observed discrepancy between simulation and experimental results are less than 11%, 11%, and 22% for Elastomer, PP, and PC, respectively.

However, the computational approach underpredicts actual energy dissipation by over 20% for PC. In contrast with the other polymer phases in the blend, PC is hydrophilic, so that under the ambient conditions of the experiment, water bridges may form leading to capillary forces and significant additional energy dissipation that are unaccounted for in the present approach⁵³⁻⁵⁵. In order to estimate the influence of capillary forces on the total observed energy dissipation, a set of Peak Force Tapping experiments were conducted under ambient and dry nitrogen flushed conditions. Based on the observed results, the hysteresis of a single force cycle at ambient condition is about 8%, 7%, and 50% higher for PP, elastomer, and PC respectively under ambient conditions compared

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3 to under dry nitrogen. Thus, capillary forces are likely to contribute more to AM-AFM under
4 ambient conditions on PC than on PP or elastomer and might have resulted into
5 unrealistic predictions for PC.
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10 Finally, it is worth mentioning that there is a potential bi-stability between attractive and
11 repulsive regimes of oscillation in AM-AFM^{10, 56-57}. Under the free oscillation amplitudes
12 considered in these simulations, the tip either remained exclusively in the attractive (for
13 example, on the elastomer in Figure 15) or repulsive regime of oscillation in the range of
14 set point amplitudes considered. If there is an initial attractive regime, the algorithm tracks
15 that solution until that solution bifurcates and the algorithm jumps to the repulsive regime
16 as the set point is decreased.
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27 Table 2. The material property estimations/extracted from the set of experiments with
28 $A^{\text{free}} = 35.9 \text{ nm}$ and used for subsequent validation with a another set of experiments with
29 $A^{\text{free}} = 18 \text{ nm}$ on the three blend polymer sample.
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	τ	E_0	E_∞	H	z_0
	sec	GPa	GPa	J	nm
Elastomer	1.05×10^{-8}	2.5	0.115	8×10^{-20}	0.26
Polypropylene	2.18×10^{-8}	9.01	1.64	7.6×10^{-20}	0.19
Polycarbonate	4.5×10^{-9}	110	3.7	8.8×10^{-20}	0.19

3. CONCLUSIONS

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3 Understanding dAFM on polymers needs computational approaches in which the
4 relevant physics of the interactions are taken into account in a self-consistent manner. By
5 accelerating Attard's model computations and embedding it within dAFM amplitude
6 reduction formulas it is possible to efficiently compute key dAFM observables such as
7 surface deformation history, indentations, energy dissipation, phase, etc. as a function of
8 the amplitude ratio. This allows the inclusion of arbitrary surface forces and linear 3D
9 viscoelasticity in a self-consistent manner in such simulations, representing a significant
10 advance in computational AFM on polymers. This method alleviates the issues with the
11 artifacts arising from the use of *ad hoc* viscoelastic contact mechanics models. The code
12 and algorithm have been validated against prior results and other reliable codes.
13
14 Experimental data on energy dissipation in TM-AFM/AM-AFM for different free amplitudes
15 and amplitude ratios are presented on a three-polymer blend consisting of well-dispersed
16 phases of polypropylene, polycarbonate, and elastomer. An approach to experimental
17 validation of computational results is presented using TM-AFM data on a blend of PP-
18 elastomer-PC. The computational and experimental approaches presented in this work
19 clarify the role of surface forces and polymer relaxation times on the phase lag, energy
20 dissipation, and surface deformation history. Such approaches are expected to aid
21 ongoing efforts to interpret dAFM observables on polymers in terms of quantitative
22 physical properties.
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46 47 **4. Experimental methods** 48 49

50 **Instrument.** All TM/AMAFM and QS measurements were made on a Bruker
51 MultiMode 8 AFM with a Nanoscope V controller running v8.15 Nanoscope software. For
52 the TM measurements, a Bruker TESP silicon microcantilever was used with a quality
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3 factor, spring constant, and fundamental frequency of 542, 28.0 N/m, and 326.1 kHz,
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5 respectively. These values were measured using thermal tuning of the undriven
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7 microcantilever. TM-AFM/AM-AFM experiments are performed on a 10×5 μm rectangular
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9 region with 512 points/line resolution level and a scan rate of 0.5 Hz using two different
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11 free amplitudes (18.0 and 35.9 nm) and 9 different amplitude ratios (0.9, 0.8 ... 0.1). For
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13 the TM imaging, the phase was zeroed when the microcantilever was within 100 nm of
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15 the surface for each amplitude ratio measurement. QS force curves are acquired over
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17 the same sample at 200 points (5 rows x 40 columns evenly spaced) on the same region
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19 using a Bruker TESP silicon type microcantilever whose spring constant was 21.2 N/m.
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21 Using a blind reconstruction method, the tip radius of the QS microcantilever was
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23 estimated to be 14.2 and tip radius of TM microcantilever was determined to be 14.0 nm.
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29 **Sample Preparation.** The sample consists of a glassy polymer, polycarbonate
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31 (Calibre™ 302-6, Trademark of Trinseo); a semicrystalline polymer, polypropylene
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33 (Inspire™ 404, Trademark of Braskem); and a polyolefin-based elastomer (Engage®
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35 8003, Registered Trademark of The Dow Chemical Company). The sample was
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37 fabricated using injection-compression molding providing 2 inch x 2 inch x 1/8 inch
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39 plaques. Pieces of the plaque were removed via a punch and mounted into vice holders.
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41 Trapezoid faces were cryo milled in the plaques pieces at -120°C and then polished in a
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43 cryo-microtome at -120°C to produce block faces for AFM investigation.
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48 **Conflicts of interest**

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51 There are no conflicts to declare.
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ACKNOWLEDGEMENTS

The authors would like to thank Mary Ann Jones for the molding of the three-component polymer blend and Carl Reinhardt for the cryomicrotomy of the blend. Both are from The Dow Chemical Company. Financial support for this research provided by the Dow Chemical Company and the National Science foundation through grant CMMI - 1726274 GOALI is gratefully acknowledged.

SUPPORTING INFORMATION

The interaction between a rigid axisymmetric tip and the elastomer sample surface is illustrated in a supplementary video which is complementary to the information provided in Figure 7.

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