Electronic Supplementary Information

Fast, quantitative and high resolution mapping of viscoelastic properties with bimodal AFM

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Derivation of Equations 12-14

The virial for the *i-th* mode is calculated by

$$V_i = f_i \int_0^{1/f_i} F_{ts}(z_c + z(t)) z_i(t) dt \tag{S1}$$

where the cantilever's deflection is given by

$$z(t) = z_0 + z_1(t) + z_2(t) \tag{S2}$$

For an elastic interaction and in the absence of long-range forces, the above integral is calculated in the time interval [t_a, t_b] for which z_c+$z(t)$ ≤0. By assuming that z_0 and A_2 are negligible with respect to A_1, then the virial of the first mode is given by

$$V_1 = f_1 \int_{t_a}^{t_b} F_{ts}(z_c + z(t)) z_1(t) dt \tag{S3}$$

From t_a to t_b, the force increases from zero to its peak force value at t=t^* and then it decreases to zero at t=t_b. Then, if the contact area is kept constant during approach and retraction

$$V_1 = f_1 \int_{t_a}^{t_b} F_{ts}(z_c + z(t)) z_1(t) dt = 2f_1 \int_{t_a}^{t^*} F_{ts}(z_c + z(t)) z_1(t) dt \tag{S4}$$

The above integral can be performed in the z domain by using the following change of variables

$$u = A_1 \cos(\omega_1 t + \varphi_1) \tag{S5}$$

with

$$du = - A_1 \omega_1 \sin(\omega_1 t + \varphi_1) = - \omega_1 \sqrt{A_1^2 - u^2} dt \tag{S6}$$

then

$$V_1 = \frac{-2}{\omega_1} f_1 \int_{z_c}^{A_1} F_{ts}(z_c + u) \frac{u}{\sqrt{A_1^2 - u^2}} du \tag{S7}$$

The indentation can be expressed in terms of the instantaneous deflection as

$$\delta(z) = \begin{cases} 0, & z_1 < z \\ u - z_c, & z_1 \geq z_c \end{cases} \tag{S8}$$

for u=A_1 we reach the maximum indentation (deformation)

$$\delta_{max} = A_1 - z_c \tag{S9}$$

The above definitions and the fact that the force is only non-zero when $\delta \neq 0$, enable to express V_1 as

$$V_1 = \frac{1}{\pi}\int_0^{\delta_{max}} F_{ts}(\delta)\frac{\delta + z_c}{\sqrt{A_1^2 - (\delta + z_c)^2}}d\delta \tag{S10}$$

Now, we introduce the following definitions

$$F_{ts}(\delta) = v \tag{S11}$$

$$\frac{dF_{ts}}{d\delta}d\delta = k_{ts}(\delta)d\delta = dv \tag{S12}$$

$$dw = \frac{\delta + z_c}{\sqrt{A_1^2 - (\delta + z_c)^2}}d\delta \tag{S13}$$

which implies that

$$w = -\frac{(\delta + z_c + A_1)(-\delta - z_c + A_1)}{\sqrt{A_1^2 - (\delta + z_c)^2}} = \sqrt{A_1^2 - (\delta + z_c)^2} \tag{S14}$$

By applying the integration by parts relationship $\int udv = uv - \int vdu$, V_1 becomes

$$V_1 = \frac{1}{\pi}\left(F(\delta)\sqrt{A_1^2 - (\delta + z_c)^2}\right)_0^{\delta_{max}} - \frac{1}{\pi}\int_0^{\delta_{max}} k_{ts}(\delta)\sqrt{A_1^2 - (\delta + z_c)^2}d\delta \tag{S15}$$

The first term is equal to 0 for both extremes of the integration because $F(\delta)=0$ when $\delta=0$, and $A_1 - z_c, \sqrt{A_1^2 - (\delta + z_c)^2} = 0$ for $\delta=\delta_{max}$

which leads to

$$V_1 = -\frac{1}{\pi}\int_0^{\delta_{max}} k_{ts}(\delta)\sqrt{A_1^2 - (\delta + z_c)^2}d\delta \tag{S16}$$

Now we can use the definition of the maximum indentation (equation S9) to replace zc in the above equations,

$$\sqrt{A_1^2 - (\delta + z_c)^2} = \sqrt{A_1^2 - (\delta + A - \delta_{max})^2} = A_1\sqrt{1 - \left(1 - \frac{\delta_{max} - \delta}{A_1}\right)^2} \tag{S17}$$

when the deformation is small respect to the amplitude A_1,

$$x = \frac{\delta_{max} - \delta}{A_1} \ll 1 \tag{S18}$$

we can apply series expansion

$$\sqrt{1-(1-x)^2} \approx \sqrt{2x} - \frac{1}{4}\sqrt{2x^3} - \frac{1}{32}\sqrt{2x^5}\dots \tag{S19}$$

By keeping the first term, an approximation that is valid with the amplitudes and deformations used in bimodal AFM, Eq. S17 becomes

$$A_1\sqrt{1-\left(1-\frac{\delta_{max}-\delta}{A_1}\right)^2} \approx \sqrt{2A_1}\sqrt{\delta_{max}-\delta} \tag{S20}$$

Then equation S16 becomes

$$V_1 \approx -\frac{1}{\pi}\int_0^{\delta_{max}} k_{ts}(\delta)\sqrt{2A_1}\sqrt{\delta_{max}-\delta}\,d\delta \tag{S21}$$

which corresponds to equation 12 (main text).

Now we proceed to calculate virial of the second mode. From equations 4 and 7 (main text) we get,

$$V_2 = -\frac{k_2 A_2^2 \Delta f_2}{f_{02}} = \left(A_2^2/4\pi\right)\int_0^{1/f_1} F_{ts}'(t)dt \tag{S22}$$

$$\frac{\Delta f_2}{f_{02}} \approx -\frac{1}{4\pi k_2}\int_0^{1/f_1} k_{ts}(t)dt \tag{S23}$$

It is more convenient to perform the integral in z domain. To that purpose we use the definitions given in equations S4 and S5,

$$\frac{\Delta f_2}{f_{02}} \approx \frac{1}{4\pi k_2}2\int_{z_c}^{A_1} k_{ts}(u)\frac{du}{\sqrt{A_1^2-u^2}} \tag{S24}$$

which in terms of the indentation ($\delta = u - z_c$)

$$\frac{\Delta f_2}{f_{02}} \approx \frac{1}{2\pi k_2}\int_0^{\delta_{max}} k_{ts}(\delta)\frac{d\delta}{\sqrt{A_1^2-(\delta+z_c)^2}} \tag{S25}$$

Then equation S22 becomes

$$V_2 \approx -\frac{A_2^2}{2\pi}\int_0^{\delta_{max}} k_{ts}(\delta)\frac{d\delta}{\sqrt{A_1^2-(\delta+z_c)^2}} \tag{S26}$$

by using equation S20

$$V_2 \approx -\frac{A_2^2}{2\pi}\int_0^{\delta_{max}} k_{ts}(\delta)\frac{d\delta}{\sqrt{2A_1}\sqrt{\delta_{max}-\delta}} \qquad \text{(S27)}$$

This step finalizes the deduction of equation 13 (main text).

Now we proceed to derive equation 14 (main text). We start from the definition of the energy dissipation (equation 5)

$$E_{disi} = -\int_0^{1/f_i} F_{ts}(t)\dot{z}_i(t)dt \qquad \text{(S28)}$$

we define a dissipative force as

$$F_{dis} = \Lambda(z)\dot{z}(t) \qquad \text{(S29)}$$

where $\Lambda(z)$ is a dissipation function.

by using the definition of u (equations S5 and S6),

$$dt = \frac{du}{-\omega_1\sqrt{A_1^2-u^2}} \qquad \text{(S29)}$$

Then the energy dissipated for the first mode:

$$E_{dis1} = \int_{-A_1}^{A_1} \Lambda(z_c+u)\left(-\omega_1\sqrt{A_1^2-u^2}\right)^2\frac{du}{-\omega_1\sqrt{A_1^2-u^2}} =$$

$$-\int_{-A_1}^{A_1} \Lambda(z_c+u)\omega_1\sqrt{A_1^2-u^2}\,du \qquad \text{(S31)}$$

by using

$$\sqrt{A_1^2-u^2} = \int\frac{-u}{\sqrt{A_1^2-u^2}}du \qquad \text{(S32)}$$

and the definitions

$$v = \sqrt{A_1^2-u^2}\,;\quad dv = \frac{-u}{\sqrt{A_1^2-u^2}}du \qquad \text{(S33)}$$

$$dw = \Lambda(z_c+u)du;\quad w = M(u) = \int du\,\Lambda(z_c+u) \qquad \text{(S34)}$$

we apply the integration by parts formula

$$\int_{-A}^{A} \Lambda(z_c + u)\sqrt{A_1^2 - u^2}\, du_1 = \sqrt{A_1^2 - u^2} M(u) - \int_{-A_1}^{A_1} M(u)\frac{-u}{\sqrt{A_1^2 - u^2}} du \tag{S35}$$

The first term is zero, then the energy dissipated by mode 1 is

$$E_{dis1} = -\omega_1 \int_{-A_1}^{A_1} \Lambda(z_c + u)\sqrt{A_1^2 - u_1^2}\, du_1 = \omega_1 \int_{-A_1}^{A_1} M(u)\frac{u}{\sqrt{A_1^2 - u^2}} du \tag{S36}$$

, which resembles equation S10, then by analogy we deduce

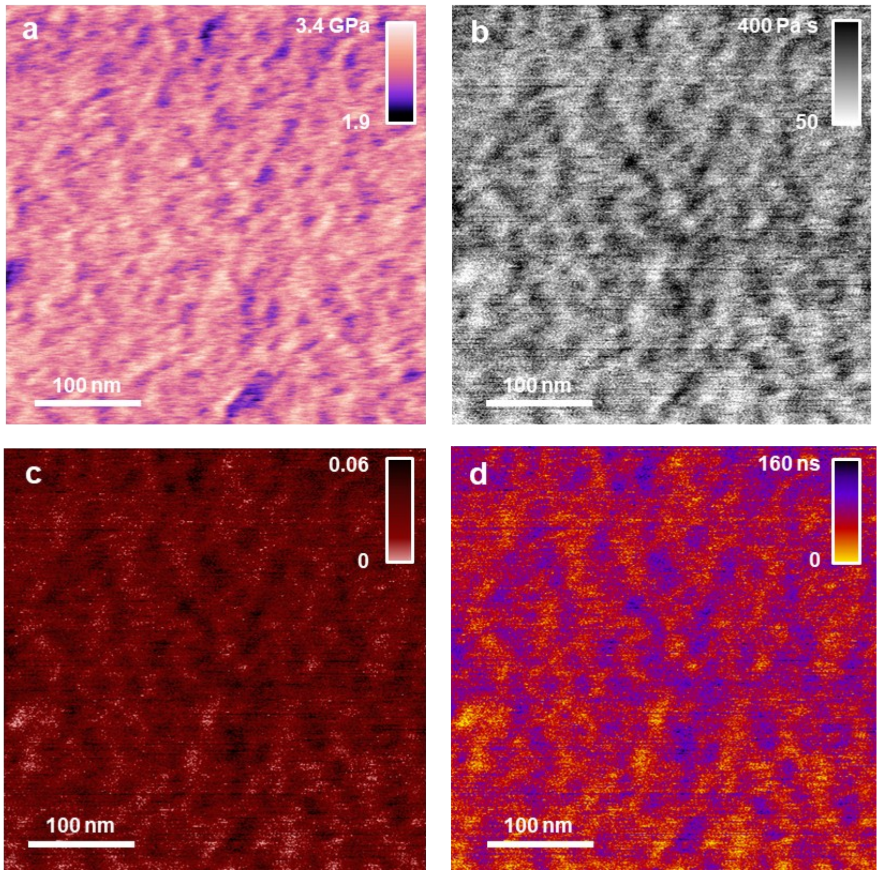
$$E_{dis1} = 2\int_{0}^{\delta_{max}} g_{int}(\delta)\sqrt{2A_1}\sqrt{\delta_{max} - \delta}\, d\delta \tag{S37}$$

where g_{int} is the dissipative equivalent of k_{int} in a conservative interaction force.

Calibration of bimodal AM-FM

The value of the Young's modulus given by bimodal AM-FM has been determined with a calibrated polystyrene sample of Young's modulus = 2.7 GPa (Bruker Test Sample). For completeness we provide the viscosity coefficient, the loss tangent and the retardation time.

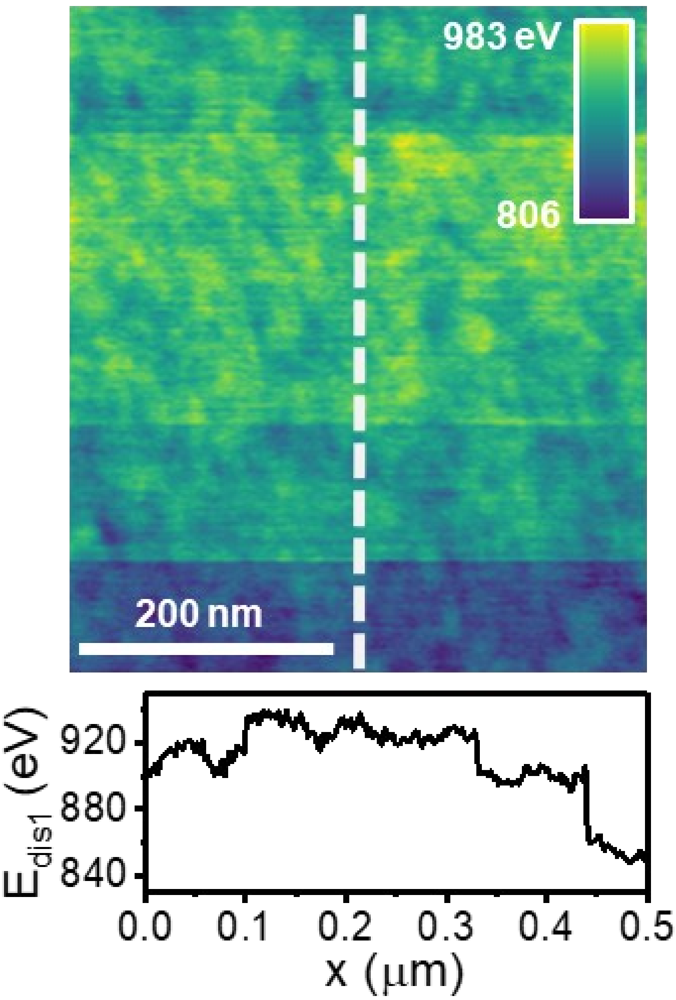
Figure S1. (a) Young's modulus, (b) viscous coefficient, (c) loss tangent and (d) retardation time on a PS sample of nominal elastic modulus value of 2.7 GPa. The Young's modulus has been calculated considering a ν_s=0.34. (e) The extracted nanomechanical values are shown. The measurement parameters are A_{01} = 81 nm, A_1 = 65 nm, f_{01} = 68.070 kHz, k_1 = 2.77 N m^{-1}, Q_1 = 208, A_2 = 1.2 nm, f_{02} = 432.333 kHz, k_2 = 142 N m^{-1}, R = 12 nm.



E (GPa)	tan ρ	τ (μs)	η_{com} (Pa s)
2.75 ± 0.16	0.028 ± 0.009	0.06 ± 0.02	204 ± 73

Energy dissipation map of a LDPE sample

Figure S2. Energy dissipation map of the 1st mode on LDPE. The map was acquired simultaneously with the data shown in Fig. 4.


983 eV
806
200 nm
920
880
840
E_{dis1} (eV)
0.0
0.1
0.2
0.3
0.4
0.5
x (μm)

Influence of the humidity on the bimodal AFM data

Nanomechanical parameters extracted from two bimodal AM-FM experiments performed on a PS-b-PMMA sample with humid air (RH=22%) and in a dry N_2 atmosphere (RH<3 %).

Table S1. PS-b-PMMA viscoelastic properties at two relative humidity.

Measurement condition	PS-b-PMMA block	E_{eff} (GPa)	tan ρ	τ (μs)	η_{eff} (Pa s)
Air	PS	2.1 ± 0.25	0.11 ± 0.02	0.22 ± 0.03	460 ± 65
	PMMA	2.6 ± 0.30	0.07 ± 0.02	0.15 ± 0.03	350 ± 65
N_2 flow	PS	2.1 ± 0.2	0.09 ± 0.03	0.19 ± 0.06	423 ± 130
	PMMA	2.6 ± 0.2	0.03 ± 0.02	0.07 ± 0.05	200 ± 120