# Supporting Information

## for

# Mapping mechanical properties of organic thin films by force-modulation microscopy in aqueous media

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## Force modulation of the cantilever response

The contact between the AFM tip and the surface can be modeled by Hertzian contact theory. In Hertzian contact models, the applied contact force, $F$, has the following relation with the indentation ($h$):

$$F = \frac{4}{3} E^* \sqrt{R} h^{\frac{3}{2}}, \tag{1}$$

where $R$ is the tip radius and $E^*$ is the reduced Young's modulus. $E^*$ is a function of the Young's moduli of the surface and the tip ($E_s$ and $E_t$), and the Poisson ratio of the surface and the tip ($\nu_s$ and $\nu_t$),

$$E^* = \left( \frac{1-\nu_t^2}{E_t} + \frac{1-\nu_s^2}{E_s} \right)^{-1} . \tag{2}$$

In FMM, the contact of the tip and the surface is modulated, while a higher contact force is applied. One can apply a Taylor series expansion to Equation 1 to determine indentation modulation, $\delta$, for the added force modulation ($F_{ac}$):

$$F_{ac} = \frac{\partial F}{\partial h} \delta + \frac{1}{2} \frac{\partial^2 F}{\partial h^2} \delta^2 + \frac{1}{6} \frac{\partial^3 F}{\partial h^3} \delta^3 \ldots \quad . \tag{3}$$

To stabilize the system, the contact force equilibrates with the force on the cantilever which can be expressed by using the cantilever deflection and the stiffness ($k_c$):

$$F_{ac} = k_c \left( z_0 \sin \omega t - \delta \right), \tag{4}$$

where $z_0$ is the amplitude of the actuation and $\omega$ is the radial frequency of the actuation. Since the sample surface is indented with the applied modulation, the cantilever deflects as much as $u_c$, the difference between the modulation and the indentation:

$$u_c = z_0 \sin \omega t - \delta. \tag{5}$$

When the force modulation is much smaller than the contact force, the first term of Equation 3 is higher than other terms and the contact can be modeled by a linear spring. The stiffness of this spring is called the contact stiffness, $k^*$:

$$\frac{\partial F}{\partial h} = k^* = \sqrt[3]{6FRE^{*2}}. \tag{6}$$

However, the second- and higher-order terms become more prominent when low contact forces are applied. The quadratic term in Equation 3 is

$$\frac{\partial^2 F}{\partial h^2} = \beta = \sqrt[3]{\frac{4R^2E^4}{3F}}. \tag{7}$$

**1. Linear contact regime**

For small modulation amplitudes and high contact forces, the first term of Equation 3 is enough to capture the force modulation, and the force equilibrium can be written as

$$F_{\mathrm{ac}} = k^*\delta = k_{\mathrm{c}}\left(z_0 \sin\omega t - \delta\right). \tag{8}$$

The cantilever deflection, $u_{\mathrm{c}}$, can then be reduced to the following expression:

$$u_{\mathrm{c}} = \frac{k^*}{k^* + k_{\mathrm{c}}} z_0 \sin\omega t. \tag{9}$$

**2. Nonlinear contact regime**

Low contact forces are desired for imaging compliant samples but this causes the second and higher orders of Equation 3 to rise. To understand the force modulation with small nonlinearity, let's assume that the second term in Equation 3 is sufficient. In this case, the force equilibrium is

$$F_{\mathrm{ac}} = k^*\delta + \frac{1}{2}\beta\delta^2 = k_{\mathrm{c}}\left(z_0 \sin\omega t - \delta\right). \tag{10}$$

When the quadratic equation in Equation 10 is solved, δ can be deduced:

$$\delta = \frac{k^* + k_c}{\beta}\left(-1 \pm \sqrt{1 + \frac{2k_c\beta z_0 \sin\omega t}{\left(k^* + k_c\right)^2}}\right). \tag{11}$$

Since a negative δ is not physically meaningful, the positive root is selected and the square root is expanded in a second-order Taylor series:

$$\begin{aligned}\delta &= \frac{k^* + k_c}{\beta}\left(-1 + 1 + \frac{k_c\beta z_0 \sin\omega t}{\left(k^* + k_c\right)^2} - \frac{\left(k_c\beta z_0 \sin\omega t\right)^2}{2\left(k^* + k_c\right)^4}\right) \\ &= \frac{k_c z_0 \sin\omega t}{k^* + k_c} - \frac{k_c^2\beta z_0^2 \left(\sin\omega t\right)^2}{2\left(k^* + k_c\right)^3}.\end{aligned} \tag{12}$$

The cantilever deflection shown in Equation 5 can then be obtained by using this nonlinear indentation:

$$u_c = \frac{k^*}{k^* + k_c} z_0 \sin\omega t + \frac{k_c^2\beta z_0^2 \left(\sin\omega t\right)^2}{2\left(k^* + k_c\right)^3}. \tag{13}$$

Equation 13 can be rewritten by using trigonometric identities:

$$u_c = \frac{k_c^2\beta z_0^2}{4\left(k^* + k_c\right)^3} + \frac{k^*}{k^* + k_c} z_0 \sin\omega t - \frac{k_c^2\beta z_0^2 \cos\left(2\omega t\right)}{4\left(k^* + k_c\right)^3}. \tag{14}$$