

## Model for the adsorption-induced change in resonance frequency of a cantilever

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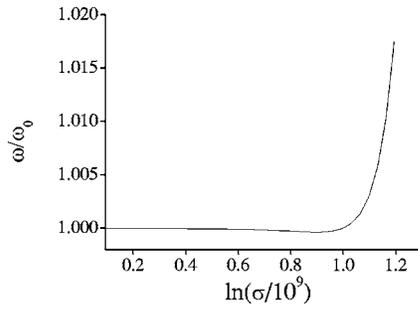


FIG. 2. Variation of the resonance frequency with the adsorbate density for  $E=130$  GPa,  $c=25$  nm,  $a=0.35$  nm,  $A=2.8377 \times 10^{-77}$  J m<sup>6</sup>, and  $B=1.943 \times 10^{-134}$  J m<sup>12</sup>.

$$U_e = \frac{1}{2} \int_l EI \kappa^2 dx. \quad (4)$$

$EI$  in the above equation is the bending stiffness of the cantilever itself. The kinetic energy of the adsorbate-adsorbent system can be expressed as

$$U_k = \frac{1}{2} \int_l (\rho F + 2\sigma m_a) \dot{y}^2 dx, \quad (5)$$

where  $\rho$  is the mass density of the cantilever and the overdots denotes partial derivative with respect to time,  $F$  is the cross section area, and  $m_a$  is the mass of an adatom. Using Eqs. (3)–(5), we can write the Lagrangian  $L$  of the system as follows:

$$L = U_k - U_i - U_e. \quad (6)$$

The vibration equation for the microcantilever thereby can be obtained from  $\partial(\delta L / \delta \dot{y}) / \partial t = \delta L / \delta y$ . Since variations  $\delta U_e = \int_l EI \kappa \delta \kappa dx$  and  $\delta U_i = \int_l (\partial u_i / \partial \kappa) \delta \kappa dx$ , we may expand  $\partial u_i / \partial \kappa$  into Taylor's series with respect to  $\kappa$  and neglect the terms with order higher than one if the small value of  $\kappa$  is considered. Thus the free vibration equation can be approximated by

$$(\rho F + 2\sigma m_a) \ddot{y} = - \left( EI + \left. \frac{\partial^2 u_i}{\partial \kappa^2} \right|_{\kappa=0} \right) \frac{\partial^4 y}{\partial x^4}. \quad (7)$$

$\partial u_i / \partial \kappa|_{\kappa=0}$  does not appear in Eq. (7) because it would appear in the boundary conditions. From the above equation, one may note that due to adsorption on the microcantilever, both the effective mass density and the effective stiffness change. And the fundamental resonance frequency of the microcantilever can be expressed as

$$\frac{\omega}{\omega_0} = \sqrt{\frac{1 + (\partial^2 u_i / \partial \kappa^2)_{\kappa=0} / EI}{1 + 2\sigma m_a / \rho F}}, \quad (8)$$

with  $\omega_0 = \beta \sqrt{EI / \rho F l^4}$ . It is clearly seen that whether the resonance frequency increases or decreases will largely depend on the interaction between the adsorbates and cantilever and that between the adsorbates in addition to the mass of the adsorbates. When the mass of the adsorbates is negligible as compared to that of the cantilever which is true in many cases, the interaction between the adsorbates and the cantilever and that between the adsorbates themselves determine the resonance frequency change. Furthermore, using Eqs. (1) and (2), we can explicitly obtain

$$\left. \frac{\partial^2 u_i}{\partial \kappa^2} \right|_{\kappa=0} \approx \sigma^7 (a+c)^2 \left( B \sigma^6 \left\{ 312 + \frac{42}{[1/4 + (a\sigma)^2]^8} \right\} - A \left\{ 84 + \frac{12}{[1/4 + (a\sigma)^2]^5} \right\} \right), \quad (9)$$

from which it can be concluded that if the repulsive interaction dominates over the attractive one, the resonance frequency of the microcantilever due to adsorption will increase and vice versa.

As a numerical example, we take  $E=130$  GPa,  $c=25$  nm, and parameters  $a=0.35$  nm,  $A=2.8377 \times 10^{-77}$  J m<sup>6</sup>, and  $B=1.943 \times 10^{-134}$  J m<sup>12</sup> as have been used by Dareing and Thundat.<sup>11</sup> The width in the cantilever in the present model can be taken as  $w=1/\sigma$ . These parameters' values may also well approximate those in the experiment of Wang *et al.*<sup>10</sup> where the resonance frequency of a 50 nm thick cantilever rapidly increases and then comes to a stable value with a net increase about 1.6% when exposed to oxygen. Such phenomenon may be the result of continuous adsorption of oxygen till its arrival at a certain balance. We have calculated the resonance frequency  $\omega$  as a function of  $\ln(\sigma/10^9)$  since  $t \propto \ln \sigma$  generally holds true as far as the adsorption dynamics is concerned. The results are plotted in Fig. 2 where the equilibrium value or maximum of  $\sigma$  has been chosen as  $3.3 \times 10^9$ /m. From the figure, it can be seen that the resonance frequency increases by about 1.8% when the adatom density reaches its maximum. It is worthwhile to point out that under the monolayer adsorption, the mass of the oxygen adatoms can still be reasonably neglected for the above selected dimension of the cantilever though accounting for it would decrease the difference between the experimental value and the predicted one. There are other experiments<sup>2,5</sup> that reported the adsorption-induced resonance frequency increases with the same order of magnitude. So the present model may be reasonable, though the results may largely depend on the equivalent value of  $\sigma$  and it is reasonably selected in the present work.<sup>11</sup>

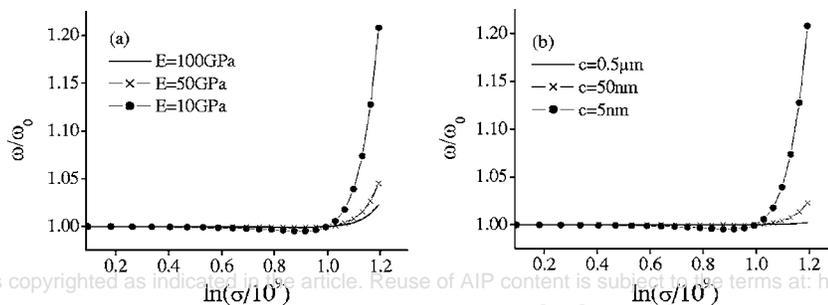


FIG. 3. Variation of the resonance frequency with adsorbate density for (a)  $c=25$  nm and  $E$  equal to 100, 50, and 10 GPa, respectively, and (b)  $E=50$  GPa and  $c$  equal to 500, 50, 5 nm respectively.

The present model also predicts results with certain implications for applications of resonant behavior of cantilevers, e.g., mechanical characterization of nanostructures as Cuenot *et al.*<sup>12</sup> have used atomic force microscopy to measure the elastic modulus of nanotubes by tapping mode. According to Fig. 3, where the resonance frequencies as a function of  $\ln(\sigma/10^9)$  for different values of  $E$  and  $c$  with the rest of parameters' values selected as before have been portrayed, the smaller the size or relatively lower modulus of the cantilever, the larger the contribution of the adsorption to the total resonance frequency. It means that, if adsorption occurs to the nanostructures, it would result in large error in measuring the resonance frequency of the pure structures and thereby the elastic modulus. Nevertheless, such features may help to improve the sensitivity in biological or chemical detections. It is noteworthy that the conclusion is based on the neglect of the adsorbates' mass, which may be not true for some small-dimensioned nanostructures, say, several nanometers in thickness or adsorbates with large mass, e.g., macromolecules and in such cases adsorption-induced resonance frequency should be calculated according to Eq. (8). Finally it is easy to find that the present model is applicable to the occasions when only one surface of the cantilever accommodates adsorbates provided that  $\partial^2 u_i / \partial \kappa^2|_{\kappa=0}$  is replaced by its half in Eq. (8).

In conclusion, a model is proposed to explain the effect of adsorption on the resonance frequency of a cantilever by

taking into account the interaction between the adsorbates and the cantilever surfaces. The model can produce results comparable to some experimental observations and also predict results with meanings for some applications of resonant cantilevers.

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