

A Unified Guide to Two Opposite Size Effects in Nano Elastic Materials *

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The microstructural variation near surface of nano elastic materials is analyzed based on different potentials. The atomic/molecular mechanism underlying the variation and its effect on elastic modulus are such that the nature of long-range interactions (attractive or repulsive) in the atomic/molecular potentials essentially governs the variation near surface (looser or tighter) and results in two opposite size effects (decreasing or increasing modulus) with decreasing size.

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Recently, the rapid development of nanotechnologies and extensive use of nano materials have made the understanding and characterizing of their mechanical properties become an urgent task. On the other hand, nano materials often exhibit behaviors very different from their conventional counterparts, even their elastic modulus varies significantly when the sample size decreases down to nano-scale. Surprisingly, variations of the modulus are radically different in different nano materials, either decreasing or increasing modulus with decreasing size.^[1–8] Since a small size leads to a large surface to volume ratio, the surface effects are usually considered to take the responsibility for the variations of mechanical properties at nano scale. Different models, such as continuum theories^[4,9–14] and microscopic models^[15–17] have been developed to explain different surface and size effects. However, a unified understanding of the surface effects and the two different size effects still remains open. Obviously, variations of elastic properties of nano materials with decreasing size should be attributed to the reconstruction of the surface layer.

In this Letter, we present a unified interpretation of two opposite size effects of the elastic modulus, i.e. either decreasing or increasing modulus with decreasing size, based on atomic/molecular interactions.

First, let us illustrate the importance of the variation of atomic/molecular spacing near the surface of a nanofilm with a simple example: the (001) surface of *fcc* nanofilm in terms of Lennard–Jones potential,

$$u(r_{ij}) = 4\varepsilon_0 \left[\left(\frac{r_0}{r_{ij}} \right)^{12} - \left(\frac{r_0}{r_{ij}} \right)^6 \right], \quad (1)$$

where ε_0 and r_0 are the two potential parameters.

Now, examine a nanofilm with $2N + 1$ layers and its corresponding bulk lattice constant a_0 . However, to form such a film, the bulk should suffer from a readjustment to achieve a new equilibrium with two free surfaces. Considering the sufficiently large length/width to thickness ratio of the nanofilm, we can

simplify the film as a one-dimensional sample that all atoms distribute uniformly in the length and width directions and all (001) facets atoms remain coplanar after the readjustment. Hence, the spacing of the layers in thickness acts as the only nonuniformity parameter of the nanofilm. We denote the spacing between the i^{th} and the $(i + 1)^{\text{th}}$ layer by d_i , $i = 1, \dots, 2N$. The series of spacing d_i can be determined by solving the force equilibrium equation of a representative atom of each layer in thickness. The results for the cases $N = 3, 6, 20$ and the corresponding curve fitting are shown in Fig. 1. Noticeably, the lattice constant $2d_{20} = 0.97158 \times 2^{2/3}r_0$ is in good agreement with the previously obtained bulk spacing $a_0 = 0.971 \times 2^{2/3}r_0$.^[18] More importantly, it can be seen from Fig. 1 that the spacing near the surface is slightly greater than that in the bulk (about 2%) but decreases rapidly inward, for instance, d_5 is only 0.011% greater than d_6 for the case $N = 20$. Thus, the non-uniform region is a very thin layer near the surface, named as the surface layer later.

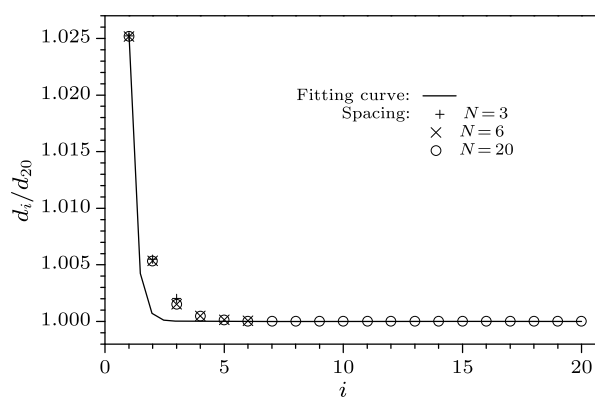


Fig. 1. Spacing of two neighboring layers normalized by d_{20} , for $N = 3, 6, 20$ of nanofilm with Lennard–Jones potential.

Specifically, we examine the elastic modulus of an

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fcc nanofilm. Under uni-axial stress state, the elastic modulus E in the $\langle 100 \rangle$ direction is calculated analytically, as shown in Fig. 2. In order to justify the analysis, the elastic moduli E in the $\langle 100 \rangle$ direction for different thicknesses, $N = 6, 15, 30$, are also numerically calculated using molecular statics (MS), see Fig. 2. Obviously, the analytical results of E agree well with the numerical ones. One significant issue in the understanding of the mechanism underlying the size effect is to split the effect of the less coordination number, as reported in Refs. [15,16], from that of the looser surface lattice on elastic modulus. For this sake, a virtual uniform nanofilm with d_N ($N = 20$) is examined and its modulus in the $\langle 100 \rangle$ direction E^0 is calculated accordingly, also see Fig. 2. In this case, the decrease of the normalized modulus E^0/E_∞ with decreasing thickness results from the less coordination number of the surface only, where E_∞ is the corresponding bulk value as N approaches to infinite, as reported in a simple cubic lattice.^[15] However, from Fig. 2 one should note that the modulus of the film with a looser surface E/E_∞ decreases much more rapidly than E^0/E_∞ . Therefore, we can conclude that although both less coordination number and looser surface layer contribute to the reduction of the elastic modulus of the film, the looseness of the surface layer reduces the modulus more pronouncedly. In addition, this tendency agrees well with the previous numerical results.^[8] Thus, in the following, we focus on the lattice spacing in the surface layer only.

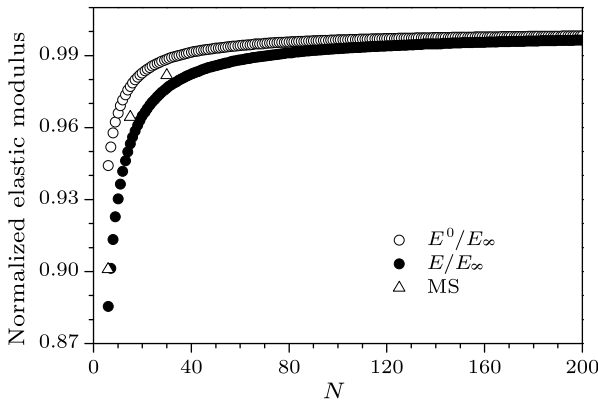


Fig. 2. Comparison of the variations of normalized elastic modulus in the $\langle 100 \rangle$ direction as a function of N with uniform (open circle), looser (closed circle) surface layers and MS results (triangle).

Now, one may ask why the surface layer with L-J potential becomes looser and whether the surface layer is always looser. To answer these questions, let us separate an infinite bulk medium into two semi-infinite bodies to create a new planar surface. As a result, the atomic lattice near the surface will be differentiated from the original uniform bulk lattice, either expanding outward owing to repulsive force or shrinking inwards owing to the attractive force, resulting from all inside atoms of the semi-infinite body. To illustrate the surface state clearly, let us examine a long one-dimensional chain of $N + 1$ atoms with spacing a .

After adopting a pair potential $u(r_{ij})$ and taking the superposition of energy for the atomic system, where r_{ij} is the distance between atoms i and j , the total potential energy of the atomic chain is

$$u_{\text{tot}} = \frac{1}{2} \sum_{i=1}^{N+1} \sum_{j \neq i}^{N+1} u(r_{ij}) \approx \frac{1}{2} (N+1) 2 \sum_{n=1}^{N/2} u(na). \quad (2)$$

The latter approximation works, provided that the chain is long enough ($N \gg 1$) or the chain is a large circle. The equilibrium lattice constant a_0 can be determined by means of the minimization of the total potential energy with respect to a :

$$\begin{aligned} \frac{du_{\text{tot}}}{da} &\approx (N+1) \sum_{n=1}^{N/2} n \frac{\partial u(x)}{\partial x} \Big|_{x=na_0} \\ &= (N+1) \sum_{n=1}^{N/2} nu'(na_0) = 0, \end{aligned} \quad (3)$$

where $u'(x)$ denotes the derivative of function u with respect to its argument x . Equation (3) can be rewritten such that the nearest force $-u'(a_0)$ (positive indicating repulsive force as usual) at equilibrium state can be expressed by a certain sum of the long range interactions ($n \geq 2$) as

$$-u'(a_0) = \sum_{n=2}^{N/2} nu'(na_0). \quad (4)$$

On the other hand, for the one-dimensional case, the one-side force acting on a representative atom i from all unilateral atoms can be written as

$$\mathbf{f}_i = - \sum_{j=i+1}^{i+N/2} \frac{\partial u(r_{ij})}{\partial \mathbf{r}_i} = - \sum_{j=i+1}^{i+N/2} \frac{\partial u(r_i - r_j)}{\partial \mathbf{r}_i} \mathbf{e}_r, \quad (5)$$

where \mathbf{e}_r is the unit vector of the position vector \mathbf{r} . Note that positive \mathbf{f}_i denotes the repulsive force acting on atom i , and vice versa. Since $r_{ij} = r_i - r_j$ can be rewritten as na in a one-dimensional chain, the one-side force \mathbf{f}_i acting on the representative atom i in the bulk with uniform lattice spacing a_0 can be written as

$$\begin{aligned} \mathbf{f}_i &= - \sum_{n=1}^{N/2} u'(na_0) \mathbf{e}_r \\ &= -u'(a_0) \mathbf{e}_r - \sum_{n=2}^{N/2} u'(na_0) \mathbf{e}_r. \end{aligned} \quad (6)$$

After substituting the equilibrium condition (4) into the one-side force expression (6), one can obtain an alternative expression of the one-side force as

$$\mathbf{f}_i = \sum_{n=2}^{N/2} (n-1) u'(na_0) \mathbf{e}_r. \quad (7)$$

This means that the one-side force from the semi-infinite chain acting on a representative atom in bulk

can be determined exclusively by a certain sum of the long range atomic/molecular interactions of a pair potential from $n \geq 2$ and this can serve as a helpful guide to judge what size effects may appear. More specifically, provided that all derivatives $u'(na_0) > 0$ for ($n \geq 2$), i.e. all $n \geq 2$ atoms are in the range of attraction-dominated pair interaction, the one-side force must be positive, namely a repulsive force, and then push the surface lattice looser. At first sight, this result seems to be slightly abnormal. As a matter of fact, the repulsive one-side force results from the surplus of the repulsive force due to the nearest interaction ($n = 1$), $-u'(a_0) = \sum_{n=2, \dots, N/2} nu'(na_0)$, to the long interactions from all other atoms ($n \geq 2$), namely $\sum_{n=2, \dots, N/2} u'(na_0)$.

To examine how the guide works, we examine the Lennard-Jones potential with long range attractive interaction. According to Eq. (7) its one-side force is $f_i = 0.02417(4\varepsilon_0/r_0)$, i.e. repulsive. For an infinite uniform *fcc* lattice being separated into two semi-infinite bodies by a (001) plane, the one-side force can also be calculated with Eq. (7) and it is $0.6841(4\varepsilon_0/r_0)$, also repulsive but much greater. Consequently, the lattice near the free surface for an *fcc* lattice with Lennard-Jones potential must be looser than the bulk.

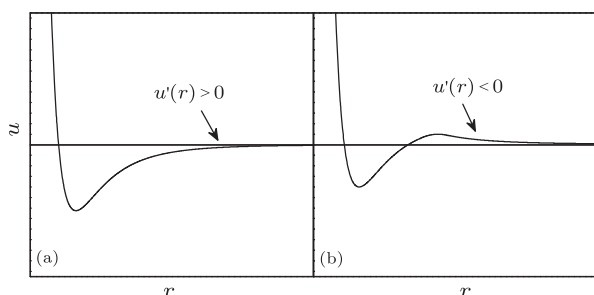


Fig. 3. Two kinds of potential energy profiles. The predominant long range interaction is (a) attractive and (b) repulsive.

More generally speaking, all Mie-type potentials

$$u(r) = \varepsilon_0 \left[\frac{k}{l-k} \left(\frac{r_0}{r} \right)^l - \frac{l}{l-k} \left(\frac{r_0}{r} \right)^k \right], \quad (8)$$

where ε_0 is the energy when distance $r = r_0$, l and k are the power indices of repulsive and attractive interactions respectively, and $l > k$, show similar predominant long range attractive pair interaction $u'(na) > 0$ for $n \geq 2$, as shown in Fig. 3(a), and must also lead to a repulsive one-side force in bulk, according to Eq. (7).

Thus, when would attractive one-side force and tighter surface lattice appear in materials? This would need some predominant long range repulsive interaction and imply an increasing potential with decreasing distance at long range. Obviously, this would be against the existence of a minimum energy, necessary for a stable equilibrium state. To balance the two tendencies, such potentials showing attractive one-side force in bulk should present a certain minimum relevant to the equilibrium state $a = a_0$ as well as a maxi-

imum to guarantee the existence of some predominant repulsive long range interactions $u'(na) < 0$, as shown in Fig. 3(b). However, what potentials in reality could present such a feature? Because of the importance of this matter in surface effect, we apply the above guide to other potentials.

Buckingham potential with Coulomb interaction is such a potential with long range repulsive interactions

$$u(r_{ij}) = \frac{q_i q_j}{r_{ij}} + A \exp\left(\frac{-r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^6}, \quad (9)$$

where r_{ij} is the distance between two ions, q_i is the charge of ion i , and A , ρ and C are potential parameters.^[6] The first term in Eq. (9) represents the long range Coulomb interaction.

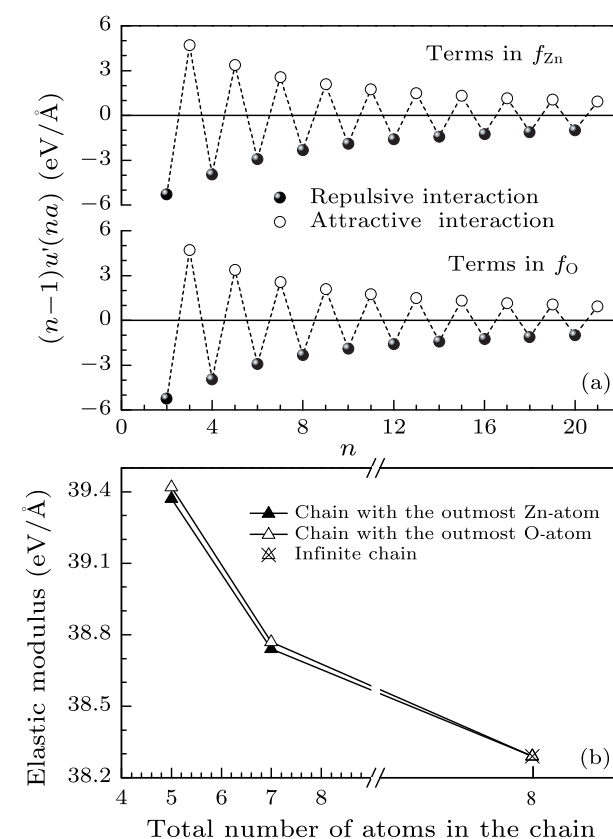


Fig. 4. (a) Terms in the summations of Eq. (7) for f_O and f_{Zn} . (b) Elastic modulus of ZnO chain as a function of the total number of atoms in the chain.

Now, we examine a one-dimensional ZnO chain with this potential to check if our guide still works. According to Eq. (7), the two one-side forces f_O and f_{Zn} acting on O-atom and Zn-atom are calculated. Because of the predominate negative terms resulting from the long range Coulomb repulsive interaction (closed circles in Fig. 4(a)) in the summations, $f_O = -2.730 \text{ eV/Å}$ and $f_{Zn} = -2.697 \text{ eV/Å}$ respectively, namely attractive as the guide anticipates, and the atom near the free surface would shrink inwards, not as claimed by Leach^[19] and Trimble *et al.*^[20] always tend to expand outwards for pair potentials. To justify this issue, the spacing of a semi-infinite one-

dimensional ZnO chain is calculated accordingly. The outermost spacing does become less than that in bulk and the general tendency of the spacing variation near the surface is also shrinking, although some oscillations appear near the surface. As a result, the surface layer could be stiffer, and the corresponding elastic modulus would increase with the decreasing sample size, e.g. the length of the chain, provided that the effect of less coordination number of surface on elastic modulus is minor. We calculate the modulus of the one-dimensional ZnO chain, defined as the ratio of the force to the strain, to check if the above guide works. The results of the linear fitting of the force-strain curves for infinite one-dimensional, 7-atom and 5-atom ZnO chains are shown in Fig. 4(b). These results do justify the inverse size dependence of ZnO, similar to the previous molecular dynamics (MD) as well as molecular statistical thermodynamics (MST) simulations of ZnO nanorods.^[6,7,21] Thus, the multi-fold cross check clearly validates the inverse size dependence of elastic modulus in ZnO with Buckingham potential including long range Coulomb interaction. As an practical example, for the case of an infinite rocksalt ZnO lattice, the one-side forces f_{O} and f_{Zn} are calculated to be equal to $-1.249 \text{ eV}/\text{\AA}$ and $-1.160 \text{ eV}/\text{\AA}$ respectively, once again attractive forces as shown in the one dimensional ZnO chain.

Furthermore, many-body potentials such as the Finnis–Sinclair potential in Cu^[22] are examined and its one-side force f_i is also calculated as before. The force f_i is $-0.4409 \text{ (eV}/\text{\AA})$ in a one-dimensional Cu chain, and $-1.095 \text{ (eV}/\text{\AA})$ in an infinite *fcc* lattice. Hence, the surface layer would be tighter than the bulk (also see Ref. [20]), and result in the increasing modulus with decreasing size.^[8] The insight of the attractive force leading to the tighter surface layer in the case is found to result from the long range repulsive pair interaction, as well as the cohesive many-body interaction caused by the electron redistribution.

In conclusion, the difference in long-range interactions (attractive or repulsive) in a wide range of atomic/molecular pair potentials result in two kinds of surface layer (looser or tighter surface layer) and lead

to two kinds of size dependence of elastic modulus (decreasing or increasing modulus with decreasing size) in nano materials, as shown by Eq. (7). For many-body Finnis–Sinclair potentials, there is not such a concise expression of the guide, but still the long range repulsive interaction along with the electron redistribution effect leads to the tighter surface layer.

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