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Elastic and nonlinear stiffness of graphene: A simple approach

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The recent experiment C. G. Lee *et al.* [Science **321**, 385 (2008)] on the Young's modulus and third-order elastic stiffness of graphene are well explained in a very simple approach, where the graphene is described by a simplified system and the force constant for the nonlinear interaction is estimated from the Tersoff-Brenner potential.

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Graphene has received a large number of interests since its discovery.[1,2] Among others, a recent experiment has shown that the graphene has excellent mechnical properties with very large Young's modulus.[3] This experiment also found obvious nonlinear effect for the graphene in the large strain regime. Theoretically, the elastic properties in the graphene can be studied in the continuum mechanics approach[4] or the *ab initio* method.[5] In Ref. 6, Pugno derived the third-order elastic stiffness (TOES) by relating it to the coefficient of thermal expansion.[7] In this Brief Report, we describe the graphene in a simplified system with very simple interaction potential. There are no variable parameters in the potential, where the nonlinear interaction can be deduced from the Tersoff-Brenner (TB) potential.[8,9] The recent experiment for the Young's modulus and the TOES of the graphene are well explained by our model.

Graphene samples in the mechanical experiment[3] usually have a radius larger than 0.75 μm. In this large radius two-dimensional sheet, the number of atoms on the boundary (N_b) is much smaller than that of the inner atoms (N_i). It can be estimated as

$$N_b = \frac{2\pi r}{b},$$

$$N_i = \pi r^2 / \left(\frac{s}{2}\right) = \left(\frac{r}{1.5\sqrt{3}b}\right)\left(\frac{2\pi r}{b}\right),$$

where r is the radius of sample, and $b = 1.42$ Å is the C-C bond length in the graphene. $s = \frac{\sqrt{3}}{2}(\sqrt{3}b)^2$ is the area of the unit cell in the graphene. The ratio of these two numbers is

$$\frac{N_b}{N_i} = 1.5\sqrt{3}b/r \approx 5 \times 10^{-4},$$

where $r = 0.75$ μm is used. It shows that the number of boundary atoms in the sample is about four orders lesser than the inner atoms. As a result, the contribution of the boundary atoms to the total energy is also four orders smaller than the inner atoms. In this sense, we can ignore the contribution of the boundary atoms to the total energy in the graphene. In the following we consider only the inner atoms.

Because of the translational symmetry, all unit cells in the graphene are equivalent to each other. We can consider only one unit cell as a representative of the graphene, as shown in Fig. 1(a), where atoms 4 and 5 are the two nonequivalent carbon atoms in the representative unit cell.

In this Brief Report, the direction with angle $\theta = 0$ directs from atom 4 to 5 in Fig. 1(a). And $\theta = \pi/2$ is the vertical direction which is named armchair direction throughout this Brief Report.

The interaction potential we used includes both linear and nonlinear terms. The linear interaction is the frequently used bond stretching interaction V_l,

$$V_l = \frac{k_l}{2}(b - b_0)^2, \tag{1}$$

where, $b(b_0)$ is the strained (unstrained) C-C bond length in graphene. The force constant $k_l = 305$ Nm^{-1} is taken from Ref. 10, where this potential was applied successfully to explain phonon properties in the carbon nanotubes and graphene layers.

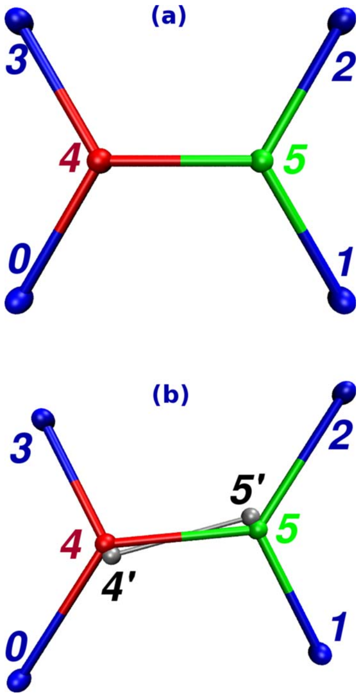

FIG. 1. (Color online) Configuration for the simplified system. (a) is the equilibrium position. (b) is the configuration with strain. The inner atoms 4 and 5 are optimized into new equilibrium position 4′ and 5′ with four outside atoms fixed.

TABLE I. Parameters in the Tersoff-Brenner potential. See text for the meaning of each parameters.

$D^{(e)}$ (eV)	S	β (Å^{-1})	$R^{(e)}$ (Å)	$R^{(1)}$ (Å)	$R^{(2)}$ (Å)	δ	a_0	c_0	d_0
6	1.22	2.1	1.39	1.7	2	0.5	0.00020813	330	3.5

The nonlinear interaction we applied has the form

$$V_{nl} = \frac{k_{nl}}{3}(b - b_0)^3 \tag{2}$$

and the constant k_{nl} can be evaluated from the commonly used TB potential. Similar expansion has also been done in Refs. 11 and 12.

In the TB potential, the energy is expressed as

$$V_B(r) = V_R(r) - \bar{B}_{ij} \cdot V_A(r).$$

V_R and V_A are the repulsive and attractive energy

$$V_R(r) = \frac{D^{(e)}}{S-1} e^{-\sqrt{2S}\beta(r-R^{(e)})} f_c(r),$$

$$V_A(r) = \frac{D^{(e)}S}{S-1} e^{-\sqrt{2/S}\beta(r-R^{(e)})} f_c(r)$$

with the cutoff function $f_c(r)$,

$$f_c(r) = \begin{cases} 1 & r < R^{(1)} \\ \frac{1}{2}\left\{1 + \cos\left[\frac{\pi(r - R^{(1)})}{R^{(2)} - R^{(1)}}\right]\right\} & R^{(1)} < r < R^{(2)} \\ 0 & r > R^{(2)}. \end{cases}$$

The many-body coupling parameter is

$$\bar{B}_{ij} = \frac{1}{2}(B_{ij} + B_{ji}),$$

$$B_{ij} = \left[1 + \sum_{k \neq ij} G(\theta_{ijk}) f_c(r_{ik})\right]^{-\delta}.$$

The angle function $G(\theta_{ijk})$ is

$$G(\theta_{ijk}) = a_0\left\{1 + \frac{c_0^2}{d_0^2} - \frac{c_0^2}{d_0^2 + [1 + \cos(\theta_{ijk})]^2}\right\}.$$

All parameters in the TB potential are listed in Table I. The ratio of k_{nl}/k_l can be estimated from the TB potential as following.

(1) In the equilibrium structure of the graphene, all of the angles equal to $\frac{2}{3}\pi$. So the angle function $G(\theta_{ijk})$ can be simplified

$$G(\theta) = a_0\left\{1 + \frac{c_0^2}{d_0^2} - \frac{c_0^2}{d_0^2 + \left[1 + \cos\left(\frac{2}{3}\pi\right)\right]^2}\right\} \approx 0.037547.$$

(2) Due to the small value of $G(\theta)$, we have

$$B_{ij} \approx 1,$$

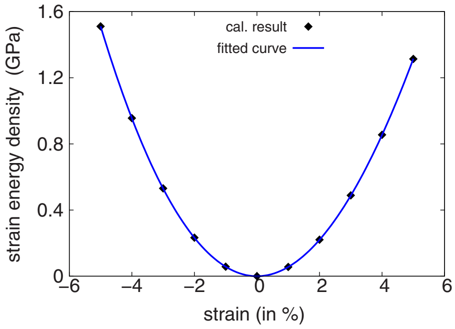

FIG. 2. (Color online) The strain energy vs strain. Strain energy at $\epsilon = -5\%$ is about 15% higher than that at $\epsilon = 5\%$ implicating the nonlinear interaction. The fitted function is $E(\epsilon) = \frac{1}{2}Y\epsilon^2 + \frac{1}{3}D\epsilon^3$ with $Y = 1.131$ TPa and $D = -2.360$ TPa.

$$\bar{B}_{ij} \approx 1.$$

(3) Because $R^{(2)} = 2$ Å in the cutoff function is about 40% larger than the equilibrium bond length 1.42 Å in the graphene, we simply set

$$f_c(r) \approx 1.$$

(4) We expand the exponent function in the repulsive and attractive energy in terms of $r - R^{(e)}$,

$$V_R(r) = \frac{D^{(e)}}{S-1} e^{-\sqrt{2S}\beta(r-R^{(e)})} \approx \frac{D^{(e)}}{S-1}\left[1 - x + \frac{1}{2}x^2 - \frac{1}{6}x^3\right],$$

$$V_A(r) = \frac{D^{(e)}S}{S-1} e^{-\sqrt{2/S}\beta(r-R^{(e)})}$$

$$\approx \frac{D^{(e)}}{S-1}\left[S - x + \frac{1}{2S}x^2 - \frac{1}{6S^2}x^3\right]$$

with $x = \sqrt{2S}\beta(r - R^{(e)})$.

(5) Finally, the total binding energy is

$$\begin{aligned} V_B(r) &\approx V_R(r) - V_A(r) \\ &\approx \frac{D^{(e)}}{S-1}\left[(1 - S) + \frac{S-1}{2S}x^2 - \frac{1}{6}\frac{(S+1)(S-1)}{S^2}x^3\right] \\ &\equiv V_0 + \frac{1}{2}k_l(r - R^{(e)})^2 + \frac{1}{3}k_{nl}(r - R^{(e)})^3, \end{aligned}$$

where $V_0 = D^{(e)}$. The vanish of the first-order term in this final expression indicates that our above approximations are physically correct.

(6) Applying parameters in Table I, we obtain the value of k_{nl}/k_l,

$$\frac{k_{nl}}{k_l} = -\frac{1}{2} \times \frac{S+1}{S} \times \sqrt{2S}\beta \approx -3 \text{ Å}^{-1}.$$

So, the nonlinear constant is $k_{nl} = 915$ N m^{-1} Å^{-1}.

In the mechanical experiments on the graphene, the sample is stretched by force and the boundary is then fixed to measure the relation between the force and the strain. Similarly, as shown in Fig. 1, the system is strained (with strain ϵ)

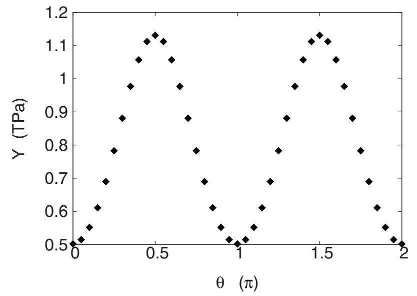

FIG. 3. Young's modulus of the graphene.

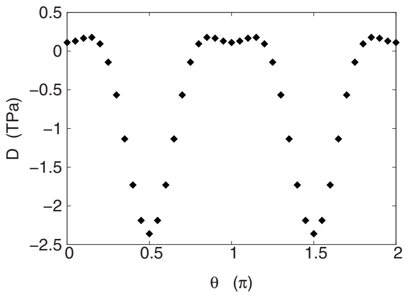

FIG. 4. The third-order stiffness D in the graphene.

in a particular direction [Fig. 1(b)]. Then the outer four atoms 0, 1, 2, and 3 are fixed, which simulates the experimental conditions. The two inner atoms 4 and 5 can move freely to achieve a new configuration 4′ and 5′ with minimum energy $E(\epsilon)$. This optimized configuration is the equilibrium position for the system under strain.

Figure 2 shows the relation between the density of strain energy and the strain. The strain in this figure is added along $\theta=\pi/2$ direction with the value in $[-5\%,5\%]$, which is also the magnitude of strain added in the experiment.[3] The nonlinear effect can be clearly seen from this figure since $E(-5\%)$ is about 15% higher than $E(5\%)$. Fitting this curve by function $E(\epsilon)=\frac{1}{2}Y\epsilon^2+\frac{1}{3}D\epsilon^3$, we can get the Young's modulus $Y=1.131$ TPa and the TOES $D=-2.360$ TPa.

Figure 3 is the dependence of the Young's modulus on the direction angle θ. The average value over θ is about 0.83 TPa. We assume that the experimental measured Young's modulus value 1.0 ± 0.1 TPa is an average over θ. This assumption can be qualitatively understood in terms that the atomic force microscope tip touches the center of the circular graphene sample; thus generating strains equally in all radial directions. Our calculation is in good agreement with this experimental result. As shown in Fig. 4, the average value for TOES D is about -1.3 TPa, which is comparable with the corresponding experimental value -2 ± 0.4 TPa. Our result is a little smaller due to the simplicity of our model, which may underestimate the nonlinear interaction in the system. The main reason for the underestimation is that the interaction V_l can dominate the total interaction in graphene. However, there are some other weaker interactions in the graphene, such as twisting interaction. As these weaker interactions are neglected in present model, the V_l with force constant k_l underestimates the linear interaction. Consequently, the nonlinear force constant from $k_{nl}=3k_l$ will underestimate the nonlinear interaction in the system. In conclusion, we calculate the Young's modulus and TOES of the graphene with a simplified system and very simple interaction without any variable parameters and explain the recent experimental results nicely.

We further remark that a large piece of graphene can be regarded as a thin plate. In a plate, the nonlinear effect of the third order arises from terms in the elastic energy which are cubic in the strains.[13] This nonlinear effect leads to a nonlinear equation of motion for the system, which indicates the coupling between different phonon modes. In the graphene, the nonlinear interaction has exhibited itself in different phenomena. As a direct result of the nonlinear interaction, the Raman G mode shows a redshift with the increase in temperature.[14] Very recently, the nonlinear interaction in carbon nanotubes is confirmed to be the origin of the intrinsic localized mode, which leads to the Stone-Wales defect under axial tension.[15] This effect should exist in the graphene.

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