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Thermal Expansion and Deformation of Graphene *

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Taking into consideration short-atomic-range interactions and anharmonic effects, we calculate the thermal expansion coefficients, Gruneisen parameters, the elastic modulus of graphene varying with temperature and the phonon frequency. The anharmonic effects associated with the graphene deformation are also discussed. The results show that the value of thermal expansion coefficient is negative in the moderate temperature range, and it becomes positive when the temperature grows to be higher than a certain value. The change rate of elastic modulus with respect to temperature and pressure are calculated, and phonon frequencies are estimated. In the process of graphene thermal expansion, it is accompanied with the change of bond length and the rotation around the axis normal to the plane. Our results indicate that the effects due to the bond change are more significant than that of the rotation. We also show that if anharmonic effects are ignored, the thermal expansion coefficient and the Gruneisen parameters are zero, and the elastic modulus and the phonon frequency are constant. If anharmonic effects are considered up to the second term, these values will vary with temperature, and become closer to the experimental value. The higher the temperature is, the more significant the anharmonic effects become.

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The graphene preparation and properties have been widely studied in experiments due to the unique performance and promising prospects. Researchers[1–3] have reported the methods of using the vapor deposition and hydrothermal deposition to prepare graphene and investigated morphology and electrochemistry properties of graphene. Theoretically, the electric conductivity properties of graphene have been studied from the first principle, and the finite difference time domain method and effective medium theory have also been applied.[4–6] The surface fluctuation of multi-layer graphene has been investigated with the method of molecular dynamics.[7] Based on the density function,[8] the absorption of Au, Ag and Cu to the defect graphene of unilateral and bilateral systems was studied for investigating the charge transfer and electronic structure properties. In 2011, the state density simplified model was proposed with the application of the Anderson model to graphene,[9] and then it was generalized to amorphous graphene for the description of absorption and state density.[10] The thermodynamics properties, e.g., the elasticity and the phase transition of the GaP and ThO_2 were investigated by using the density functional method, and their anharmoinc properties were also discussed.[11,12] However, the graphene thermodynamic properties are relatively less studied, and its anharmonic effects are poorly known. The graphene thermal expansion has been investigated with the simple harmonic approximation within the density function theory in Ref. [13]. The results show that the thermal expansion coefficient (TEC) is negative, and it grows with the temperature within the range 0–2250 K. The numerical results based on the Monte-Carlo simulation[14] show that TEC is a constant $(4.8 \pm 1.0) \times 10^{-6}\,\mathrm{K}$ in the range of 0–300 K. The experiment[15] reports that TEC is $-7 \times 10^{-6}\,\mathrm{K}^{-1}$ at the temperature $T = 300\,\mathrm{K}$, and the value becomes positive, i.e., $5 \times 10^{-6}\,\mathrm{K}^{-1}$ when $T > 1000\,\mathrm{K}$. In Ref. [16] the TEC is calculated to be $-6 \times 10^{-6}\,\mathrm{K}^{-1}$ at 300 K, and to be $2\times10^{-6}\,\mathrm{K}^{-1}$ in a high temperature region by using the nonequilibrium Green function. From the first principle of molecular dynamics,[17] the TEC is calculated to be $6.5 \times 10^{-6}\,\mathrm{K}^{-1}$. In the Harrison bond-orbit calculation,[18] the TEC is $-5.41\times10^{-6}\,\mathrm{K}^{-1}$, here only the first anharmonic term is used and the short interactions between atoms are ignored. This calculation shows that the TEC value is negative with large uncertainty, and the elastic modulus is a constant value though it has an evidently anharmonic character. The calculation in Ref. [19] indicates that Yang's modulus for the graphene varies with the temperature, while the relations are not given. In these investigations, the anharmonic vibration is not considered, and the second anharmonic term is disregarded. Therefore it results in some differences from the experimental values. In this Letter, by taking into consideration short range interactions of atoms, and anharmonic terms up to the second order, we relate the graphene TEC and elastic modulus to temperature. The Gruneisen parameters and phonon efficiency are estimated, and the graphene deformation characters are investigated.

We assume the graphene system under study composed of N atoms, sited at the hexagon lattice. The mean interaction energy per atom has been calculated in Ref. [18] with the Harrison bond-orbit method, while the short range interaction is not considered. A revised calculation with this interaction[20] shows that the mean interaction energy takes the form

$$\varphi = -V_2\Big[1 + \frac{9R}{V_2 d^{12}} + 5\beta_2\Big(\frac{V_1}{V_2}\Big)^2\Big], \qquad (1)$$

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where V_1 is the metalation energy, V_2 is the covalence energy, which is inversely proportional to the atomic separation d, i.e., $V_2 = 3.26\frac{\hbar^2}{md^2} = \frac{B}{d^2}$, with m being the mass of free electron, $\beta_2 = 2/3$, and $R = 0.154\times10^4(\hbar^2/2m)a_0^{10}$ with a_0 being the Bohr radius. To expand $\varphi(d)$ around the equilibrium position d_0, one can obtain the harmonic coefficient ε_0, anharmonic coefficients $\varepsilon_1$andε_2 up to the second term.

It is well known that the crystal has no thermal expansion under the simple harmonic approximation in the solid state theory, thus the linear thermal expansion coefficient is zero. If the anharmonic atomic vibration is considered, the average displacement of atomic vibration has been given in Ref. [21]. Then one can obtain the linear expansion coefficient α_l at high temperature

$$\alpha_l = \frac{1}{d_0}\Big[\frac{3\varepsilon_1 k_{\rm B}}{\varepsilon_0^2 - 3\varepsilon_2 k_{\rm B}T} - \frac{9\varepsilon_1\varepsilon_2 k_{\rm B}^2 T}{(\varepsilon_0^2 - 3\varepsilon_2 k_{\rm B}T)^2}\Big], \quad (2)$$

where $k_{\rm B}$ is the Boltzmann constant. Gruneisen parameter $\gamma_{\rm G}$ is related to the temperature as

$$\gamma_{\rm G} = -\frac{\varepsilon_1 d_0}{\varepsilon_0}\Big\{1 - \frac{3\varepsilon_1 k_{\rm B}T}{d_0\varepsilon_0^2} \cdot \Big[1 + \frac{3\varepsilon_2 k_{\rm B}T}{\varepsilon_0^2} + \Big(\frac{3\varepsilon_2 k_{\rm B}T}{\varepsilon_0^2}\Big)^2\Big]\Big\}. \quad (3)$$

If the temperature is very low, the vibration is frozen to the ground state, thus the contribution from the crystal lattice to the thermal capacity tends to zero. When the temperature grows, the contribution from electrons should be considered, and α_l should include a term proportional to ηT, and the coefficient can be obtained by applying the Gruneisen theorem to the thermal capacity of electrons.

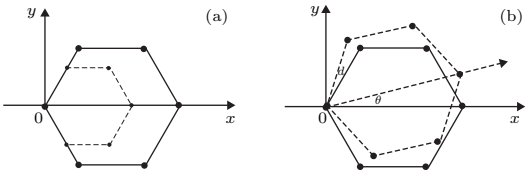

Fig. 1. Schematic illustration of graphene deformation in the process of thermal expansion.

The dependence of graphene elastic modulus B on the temperature and the rate of pressure change can be obtained by using relations $B = \varepsilon_0 d_0^2/\Omega$, $d = d_0(1+\alpha_l T)$ and $\varepsilon_0 = M\omega^2$, where Ω is the cell area, and d is the bond length. Noting the relation of angular frequency ω to the temperature as given in Ref. [22], one has

$$\frac{dB}{dT} = -\frac{2\varepsilon_0 d_0^2}{\Omega}\Big\{\alpha_l - k_{\rm B}\Big(\frac{15\varepsilon_1^2}{\varepsilon_0^3} - \frac{3\varepsilon_2}{\varepsilon_0^2}\Big) \cdot \Big[1 + k_{\rm B}T\Big(\frac{15\varepsilon_1^2}{\varepsilon_0^3} - \frac{3\varepsilon_2}{\varepsilon_0^2}\Big)\Big]^{-1}\Big\}, \quad (4)$$

$$\frac{dB}{dp} = 2\gamma_{\rm G}, \quad (5)$$

which show that if the anharmonic terms are excluded ($\varepsilon_1 = \varepsilon_2 = 0$), the elastic modulus for graphene is a constant. It is such that the anharmonic terms make it temperature-dependent.

In the thermal expansion, the deformation of graphene falls into two types, bond length changes (see Fig. 1(a)) and the rotation around the axis perpendicular to the plane (see Fig. 1(b)). These two kinds of deformation can be expressed with two harmonic coefficients ε_0 and ε_0', which describe the bond changes and the rotation around the axis, respectively. If only there is the change of bond length, one has $\varepsilon_0' = 0$, $\varepsilon_0/\varepsilon_0' = \infty$. If the change of bond length dominates the deformation, one has $\varepsilon_0 > \varepsilon_0'$, while if the rotation dominates the deformation, one has $\varepsilon_0 < \varepsilon_0'$.

To calculate the harmonic coefficient ε_0' and anharmonic coefficients ε_1', ε_2', let θ be the angle for the system turning around the axis, and the tiny rotation is regarded as a perturbation. The expression of V_2 has been given in Refs. [23,24] while the calculation of V_2 is approximated up to the second order of $\cos\theta$ expansion. In our calculation, we take the expansion up to the fourth order, i.e., $\cos\theta \approx 1 - \theta^2/2 + \theta^4/24$. One has

$$\delta V_2 = \Big(\frac{\sqrt{2}}{3}V_{sp\sigma} + \frac{2}{3}V_{pp\sigma}\Big)\theta^2 - \Big(\frac{\sqrt{2}}{36}V_{sp\sigma} + \frac{1}{6}V_{pp\sigma}\Big)\theta^4, \quad (6)$$

where $V_{sp\sigma} = \langle s|V_2|p\rangle$, $V_{pp\sigma} = \langle p|V_2|p\rangle$ and $V_{ss\sigma} = \langle s|V_2|s\rangle$ are the matrix elements for V_2 sandwiched between the atomic wave functions $|s\rangle$ and $|p\rangle$. Their values are $V_{ss\sigma} = -4.9885\,{\rm eV}$, $V_{sp\sigma} = 5.3663\,{\rm eV}$, $V_{pp\sigma} = 8.3896\,{\rm eV}$. To replace V_2 in Eq. (1) with the relation $V_2' = V_2(d) + \delta V_2(\theta)$, one has the mean interaction energy, φ', for atoms with perturbation included. Then one can obtain the harmonic coefficient $\varepsilon_0' = (1/d_0^2)(\partial^2\varphi'/\partial\theta^2)_{\theta=0}$, the first $\varepsilon_1' = (1/6d_0^3)(\partial^3\varphi'/\partial\theta^3)_{\theta=0}$ and the second $\varepsilon_2' = (1/24d_0^4)(\partial^4\varphi'/\partial\theta^4)_{\theta=0}$. They are

$$\varepsilon_0' = -\frac{2}{3d_0^2}\Big(\frac{\sqrt{2}}{3}V_{sp\sigma} + \frac{2}{3}V_{pp\sigma}\Big)\Big[1 - \frac{10}{3}\Big(\frac{V_1}{V_{20}}\Big)^2\Big],$$
$$\varepsilon_1' = 0,$$
$$\varepsilon_2' = \frac{1}{3d_0^4}\Big(\frac{\sqrt{2}}{36}V_{sp\sigma} + \frac{1}{6}V_{pp\sigma}\Big)\Big[1 - \frac{10}{3}\Big(\frac{V_1}{V_{20}}\Big)^2\Big], \quad (7)$$

which relate ε_0 and ε_0' to d_0. Since d_0 is dependent on the temperature, the graphene deformation is temperature dependent.

Applying the relation of the harmonic coefficient to the vibration efficiency, one arrives at the realization that frequencies for the longitudinal (LO) and transverse phonon (TO) are equal if the wave vector $q = 0$, and frequencies for the transverse acoustic (TA) and transverse optical (TO) phonon are equal if the wave vector $q = 2\pi/d_0$. They are given by[24]

$$\nu_{\rm LO}(0) = \nu_{\rm TO}(0) = \frac{1}{2\pi}\sqrt{\frac{8(\varepsilon_0 + 8\varepsilon_0')}{3M}},$$
$$\nu_{\rm TA}(2\pi/d_0) = \frac{1}{2\pi}\sqrt{\frac{12\varepsilon_0'}{M}},$$

$$\nu_{\rm TO}(2\pi/d_0) = \frac{1}{2\pi}\sqrt{\frac{8(\varepsilon_0+\varepsilon_0'/2)}{3M}}. \quad (8)$$

Using the parameter values given in Ref. [24], i.e., $d_0 = 1.42\times10^{-10}$ m, $|V_{20}| = 12.32$ eV, $V_1 = 2.08$ eV and $R = 10.08$ eV (10^{-10} m),[12] then one obtains $\varepsilon_0 = 3.25715\times10^2$ J·m^{-2}, $\varepsilon_1 = -1.92015\times10^{13}$ J·m^{-3} and $\varepsilon_2 = 4.91197\times10^{23}$ J·m^{-4}. Using these results, one obtains the linear expansion coefficient of graphene in terms of temperature from Eq. (2) by taking into consideration electronic contributions, and the numerical results are listed in Table 1. To compare with other calculations and experimental values, we show the results in the table quoted from Refs. [14–18]. We also compare the results obtained with the anharmonic terms up to the first (a) and the second order (b) as indicated in the table. Figure 2 shows these results for comparison.

Table 1. The linear expansion coefficient $\alpha_l(10^{-6}{\rm K}^{-1})$ in terms of temperature. Values in (a) and (b) rows are our results calculated with the anharmonic terms up to the first and second orders, respectively.

T (K)	0	300	600	1000	1100	1200	1300
(a)	0	−7.06	−7.06	−7.063	−7.063	−7.063	−7.063
(b)	0	−6.64	−4.11	−1.000	−0.017	1.063	2.255
Ref. [14]		−4.8					
Ref. [16]		−6					
Ref. [17]		−6.5					
Ref. [18]		−5.41					
Experiment[15]		−7					

Table 2. The Gruneisen parameter $\gamma_{\rm G}$ at different temperatures, and rows a and b are our results obtained with the first and second anharmonic terms, respectively.

T(K)	100	300	500	1000	1500	1600	1700	2000
(a)	1.396	1.398	1.400	1.404	1.409	1.409	1.410	1.413
(b)	1.396	1.399	1.402	1.408	1.417	1.417	1.419	1.423
Ref. [18]	2.1							
Ref. [13]	2							

Our calculation shows that the values of TEC for graphene are negative in a wide temperature region. If the temperature grows larger than 1132 K, the values become positive. The temperature dependence is consistent with the experimental measurement in Ref. [15]. To improve the calculation in Ref. [18] we take into consideration short-range interactions, and the anharmonic effects up to the second term. Our result at $T = 300$ K is closer to the experimental value than other theoretical results. If the temperature grows larger than 300 K, the expansion coefficient increases linearly, and this indicates that the second anharmonic term plays an important role in the high temperature region. As is expected, the thermal expansion coefficient will be zero if the anharmonic effects are not taken into consideration ($\varepsilon_1 = \varepsilon_2 = 0$). If the first anharmonic term is included, the calculation gives the negative values, which is inconsistent with the experimental data in Ref. [15]. To explain the measurements, the calculation needs to go to the second anharmonic term.

The negative expansion coefficient of graphene can be explained as follows: according to the Gruneisen theorem, the thermal expansion coefficient is inversely proportional to Gruneisen parameters, whose temperature behavior is the results due to the interactions of the transverse and longitudinal acoustic vibration in the planar layers. If the temperature becomes very low, the transverse acoustic vibration dominates the contributions, thus the so-called film effects take place. This causes the area of the planar layer to decrease with the increase of temperature.[25,26] From Eq. (3), one can obtain the Gruneisen parameter $\gamma_{\rm G}$, and its values at different temperatures are listed in Table 2. For comparison, we give the results calculated with the anharmonic terms up to the first (row (a)) and second order (row (b)), respectively.

Our results show that the Gruneisen parameter $\gamma_{\rm G}$ is zero if anharmonic terms are not taken into consideration. If the anharmonic term is included in the calculation, the parameter $\gamma_{\rm G}$ will be approximated to be a constant value. If the anharmonic effects are considered up to the second order, the value gradually grows between 1.396 and 1.423 with the increase of temperature. These values are different from those constant values as given in Ref. [13,18], where the short range interactions of atoms and the second anharmonic term are not considered.

To input the graphene unit cell area $\Omega = 1.746254\times10^{-20}$ m^2 into Eqs. (4) and (5), one obtains the elastic modulus, pressure variation dB/dT and $\partial B/\partial p$ relations. They are shown in Figs. 3(a) and 3(b) in terms of temperature, respectively.

The results in the plot show that the elastic modulus is a constant if anharmonic effects are not considered. If the first and second anharmonic terms are included in the calculation, dB/dT are negative with values varying in the range of -2.54646×10^{-2}–-0.58504×10^{-2} N/m·K, and it grows with temperature, while $\partial B/\partial p$ is positive with the values varying from 2.7978 to 2.8324, and it grows gradually with the temperature. Our calculation improves the constant result as given in Ref. [18], i.e., $dB/dT = -1.21\times10^{-2}$ N/m·K.

To input $d_0 = 1.42\times10^{-10}$ m, the mass of carbon atom $M = 1.995017\times10^{-26}$ kg, V_1, V_2 and $V_{sp\sigma}$ into Eq. (7), one obtains parameters of rotation $\varepsilon_0' = 0.41744\times10^2$ J·m^{-2}, $\varepsilon_1' = 0$ and $\varepsilon_2' =$

0.00205×10^{23} J·m^{-4}, and the ratios of bond length ε_0, ε_1 and ε_2. They are $\varepsilon_0/\varepsilon_0' \approx 8.477$, $\varepsilon_2/\varepsilon_2' \approx 156$. This indicates that the deformation of graphene in the thermal expansion is mainly determined by the variation of the bond length, which is dominated by the anharmonic effects. To substitute ε_0, ε_0' and M into Eq. (8), one obtains $v_{\rm LO}(0) = v_{\rm TO}(0) = 4.8283\times10^{13}$ Hz if the wave vector $q = 0$, and $v_{\rm TA}(2\pi/d_0) = 3.5639\times10^{13}$ Hz, $v_{\rm TO}(2\pi/d_0) = 2.5231\times10^{13}$ Hz at $q = 2\pi/d_0$. Our values are close to the experimental value 2.376×10^{13} Hz,[27] but twice those given in Ref. [24], i.e., $\nu_{L0} = \nu_{T0}(0) = 2\times10^{13}$ Hz, $\nu_{\rm TA}(2\pi/d_0) = 10^{13}$ Hz and $\nu_{T0}(2\pi/d_0) = 1.5\times10^{13}$ Hz.

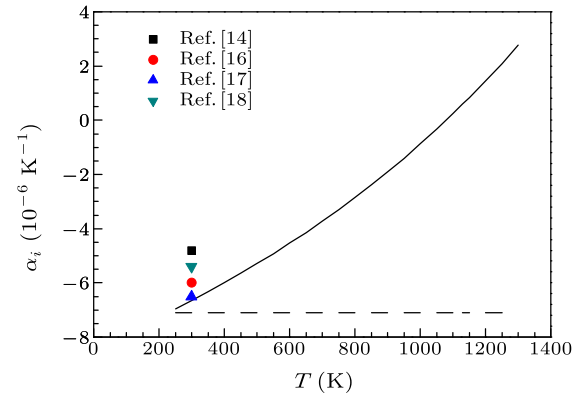

Fig. 2. The linear expansion coefficient in term of temperature. The curve and dashed lines are the results calculated with the anharmonic terms up to the first and second orders, respectively.

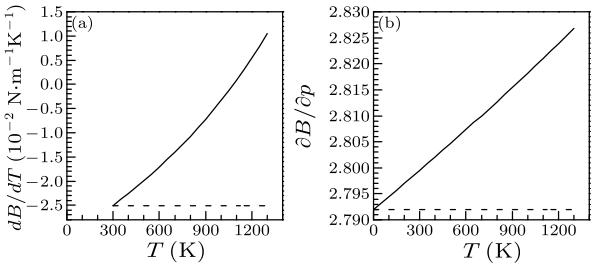

Fig. 3. (a) The elastic modulus of graphene depending on the temperature, (b) the pressure variation depending on the temperature. The dashed and curved lines are our results obtained with anharmonic effects up to the first and second terms, respectively.

In summary, we have calculated the thermal expansion coefficient, Gruneisen parameters, elastic modulus in terms of temperature, and phonon frequency for graphene. In our calculation, we have taken into consideration the atomic short-range interactions and the anharmonic effects, and the results are close to the experimental values. We have shown that in the simple harmonic approximation, the thermal coefficient and Gruneisen parameters are zero. If the anharmonic effects are considered up to the first order, the thermal expansion coefficient, Gruneisen parameters and the variation of elastic modulus with respect to the temperature, and pressure are constant. To include the anharmonic terms up to the second term, their values vary with the temperature, and the thermal expansion coefficient is negative in the moderate temperature range. If the temperature grows larger than a given value, e.g., 1132 K, the value of the thermal expansion coefficient becomes positive. The elastic modulus variation with temperature is in the range of -2.546×10^{-2}–-0.585×10^{-2} N/m·K, and the elastic modulus variation with pressure in the range of 2.7978–2.8324. The phonon frequency of graphene is in the range of 2.4×10^{13}–4.7×10^{13} Hz, which is close to the experimental value. In the process of thermal expansion, it is accompanied with the bond length variation and the tiny rotation around the axis normal to the plane. Our results indicate that the anharmonic effects of bond length are more significant than that of rotation. If the temperature becomes higher, the anharmonic effects of graphene atom vibration becomes more significant.

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