THERMAL EXPANSION STUDY IN GRAPHENE WITH FIRST PRINCIPLES

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This paper focuses more on thermal expansion. For this dynamical matrix was calculated using VASP software under both simple DFT and DFPT approximation and the phonon frequencies were calculated using phonopy code under harmonic approximation. The linear thermal expansion coefficient (LTEC) of graphene is estimated with DFT in the temperature range between 0 and 1000 K. It is found to be strongly dependent on temperature but remains negative up to 470 K and positive thereafter with a room temperature value of ($- 1.44 \times 10^{-6}$). The negative expansion coefficient is very interesting and is found to be in conformity with experimental results as well as with recent theoretical estimates. There is only qualitative agreement of our results with experimental data and motivates further investigation, primarily on the high negative values of Gruneisen parameters. A detailed calculation has been made for other thermodynamical properties. We present here some results like phonon dispersions, mode Gruneisen parameters and bulk modulus also which are essential ingredients to estimation of thermal expansion.

KEYWORDS : Phonon dispersion, Gruneisen parameter, thermal expansion, Graphene.

INTRODUCTION

Graphene is attracting much interest due to potential applications as a next generation electronic material as well as its unique physical properties [1]. In addition to unique transport properties of pure graphene, much efforts has been devoted to a study of electronic band structure of B or N or B/N codoped graphenes which become interesting new materials [2, 3]. In order to study phonon transport properties of doped graphene we as a first step devote our effort to pure graphene. In particular, graphene has superior thermal and mechanical properties, including high thermal conductivity and extremely high mechanical strength that exceeds 100 GPa, make it a prime candidate material for heat control in high-density, high-speed integrated electronic devices. For such applications, knowledge of the linear thermal expansion coefficient (LTEC) as a function of temperature is crucial.

For calculating LTEC of single layer graphene (SLG), several authors have used various methods [4-9] using various experimental techniques [4-5] and theoretical models [6-9]. D. Yoon *et al.* [8] experimentally estimated the LTEC in the temperature range of 200-400 K by

monitoring graphene samples prepared on silicon substrates covered with a 300-nm-thick SiO_2 layer by mechanical exfoliation of natural graphite flakes.

They obtained temperature-dependent Raman spectra of graphene. N. Mounet *et al*. [6] estimated the LTEC of graphene as a function of temperature by using a first-principles calculation (DFPT) under quasiharmonic approximation and predicted that graphene has a negative LTEC at least up to 2500 K. Alternatively, Y. Magnin *et al*. [8] predicted LTEC of graphene based on fully anharmonic MC simulations based on atomistic potentials predicting different behavior under different model potentials. C. Sevik [9] has done the calculations using DFPT implemented in Vasp predicting almost same behavior as N. Mounet *et. al*.

It is not yet clear whether this discrepancy between theory and experimental data is caused by uncertainties in the accuracy of the experimental measurements, or limitations in the theoretical calculation. Since precise knowledge of the LTEC in a wide temperature range is crucial in designing graphene-based devices and heat management systems, more precise measurements are needed.

Thermal expansion of graphene is hereby predicted under QHA by considering vibrational free energy. As a first step we have reproduced phonon dispersion of graphene which agrees well with theory and experiments.

COMPUTATIONAL DETAILS

Although knowing phonon frequencies, Gruneisen parameters and the bulk modulus (in the present case we define a surface modulus B_s) it is quite straight forward to obtain thermal expansion [10-11],

$$B_s = S \frac{\delta^2}{\delta V^2} = LB \qquad \dots (1)$$

where L is the distance between two sheets, which is helpful to define some fixed long distance and helps in using standard expressions for 3-*d* systems. B_s is easily obtained from energy vs volume curve. But here we determine the LTEC of graphene using first principle calculations.

The vibrational frequencies and corresponding density of states are obtained using PHONOPY [12] code, which can directly use forces calculated on displaced atoms by DFT as implemented in Vienna *ab initio* simulation package (VASP) [13]. The LTEC of graphene is predicted as follows,

$$\alpha(T) = \frac{1}{a(T)} \frac{da(T)}{dT} \qquad \dots (2)$$

where $a(T)$ is the equilibrium lattice parameter corresponding to minimum Helmholtz free energy at any temperature. The *ab initio* calculations are performed using the VASP code which is based on density functional theory. We adopted the Perdew-Burke-Ernzerh of (PBE) exchange correlation (XC) functional of generalized gradient approximation (GGA) in our calculations. The plane wave cut-off energy was set to 750 eV. The 4×4 supercell (consisting of 32 atoms) has been used to simulate the isolated grapheme sheet and sheets are separated by 12Å along perpendicular direction to avoid interlayer interactions. The Monkhorst-pack scheme is used for sampling Brillouin zone. The structure is fully relaxed with Gamma centered $7 \times 7 \times 1$ k-mesh.

RESULTS AND DISCUSSION

As a preliminary step we obtained phonon dispersion of pure graphene using DFPT and force sets method shown in figure 1. The phonon dispersion curve is similar for both methods. As the DFPT approach is really time consuming and requires heavy computation, we stick to Force sets method for further calculations. We have compared the phonon dispersion curve obtained by VASP (GGA-PBE) as compared to that given by Zhang *et al* in fig. 1. The phonon dispersion curves have been obtained by simulating the graphene sheet for directions between the high-symmetry Γ point and a large number of points on the line. The phonon dispersion curve is in good agreement with reference [14] where they have compared the phonon dispersion curve using VASP and REBO potential for pure graphene. Our phonon dispersion curve is also fairly in agreement with experimental studies [15-16] as shown in fig. 1
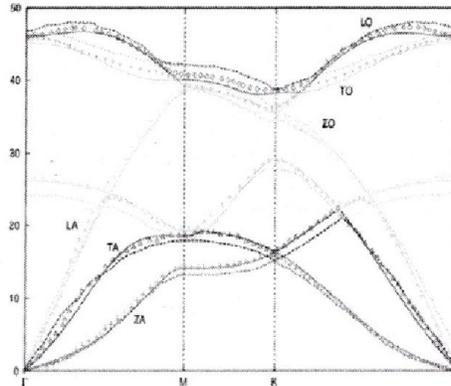
Fig. 1. Phonon Dispersion curve for pure graphene (solid lines) as compared to that in Ref. [14] (symbols), Ref. [15] dashed lines and Ref. [16] dotted-dashed lines. LA (LO), TA (TO) and ZA (ZO) are longitudinal, transversal and out-of-plane acoustical (optical) branches respectively.
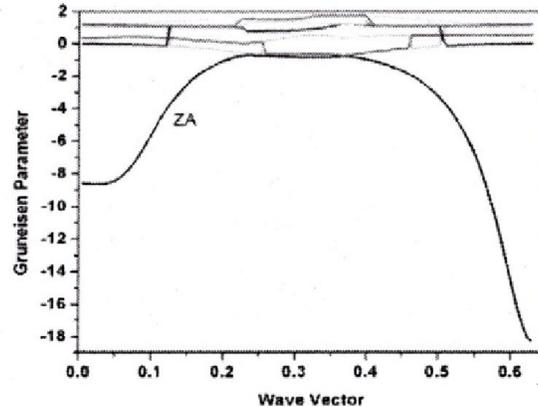
Fig. 2. Mode dependent Gruneisen parameter

Phonon dispersion curve obtained by DFPT method is also similar but the DFPT approach is a time consuming process compared to force-sets approach.

The Gruneisen parameter plays an important role in thermal expansion of a material. The mode dependent Gruneisen parameter has been obtained for various phonon branches corresponding to different *q*-values. The Gruneisen parameter corresponding to lowest transverse acoustic mode is negative in the whole region. Thus total Gruneisen parameter is negative in the low temperature region and becomes positive at high temperature region. The surface bulk modulus calculated here is 902.4 Gpa

We obtained the behavior of LTEC for pure grapheme using DFT under quasiharmonic approximation. Although the room temperature value of LTEC is smaller than that determined by Mounet *et. al.* [6] of the order of -1.44×10^{-6} and this can be explained by the existence of more negative Gruneisen parameters corresponding to the lowest transverse parameters corresponding to the lowest transverse acoustic (ZA) modes in graphene, shown in Fig. 3. The experimentally measured values in the temperature range 200-400 K are strikingly different when compared with the theoretical values obtained by Mounet *et al.* [6]. However, due to the strong anharmonic character of graphene structure, which is not taken into account in QHA calculations, a prominent difference may arise. On the other hand, the LTEC values predicted by Y. magnin *et al.* [8] considering model potential approach gives a variety of results depending upon the potential considered.
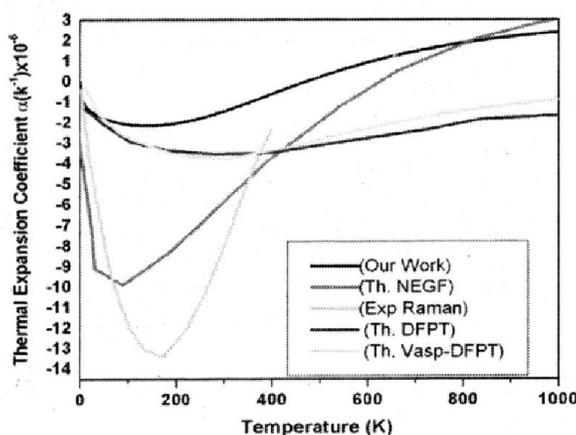
Fig. 3. Temperature dependence of LTEC.

CONCLUSION

We have presented a full first-principles study of grapheme at the GGA-PBE level using the quasiharmonic approximation to derive the thermal expansion coefficient of pure grapheme. The ingredients that enter into its calculation, like phonon frequencies are in very good agreement with experimental data, all the phonon dispersions are well reproduced. The thermal expansion coefficient is negative in low temperature region and becomes positive at high temperatures and is in well agreement with available theoretical and experimental data. The gruneisen parameters are comparable to other calculations but the negative values dominate up to moderate temperatures resulting in negative values of LTEC. The good agreement of thermal expansion calculated here for pure graphene using VASP-phonopy software with various theoretical and experimental data inspires us to go further into similar

calculations for B and N doped graphene as well as BN co-doped graphene, which is our primary aim. However there is significant difference in numerical values of LTEC which indicates need for reassuring of our values of Gruneisen parameters.

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