Thermal Properties of Graphene: A Greens Function Approach

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Abstract: Investigations on the hydrogenation of graphene has gained a significant momentum due to its applications in the fields of hydrogen storage, automobiles, etc. The knowledge on lattice vibrations and hence the thermal properties of hydrogenated graphene (graphane) is important in order to use this material for hydrogen storage applications. This study has reported one of the important thermal properties namely Debye-Waller factor and defect modes of graphane by computing phonon frequency modes by considering atomic interactions up to six neighbors in the framework of Born von Karman formalism and Green's function approach. The estimated defect modes particularly the localized vibrational modes and the values of Debye-Waller factor for a temperature range of 400 to 1300 K have been reported.

Key words: Graphene, defect modes, Debye-Waller factor, graphane, hydrogenation, phonon frequencies

INTRODUCTION

Graphene is a two-dimensional covalently bonded hydrocarbon in which hydrogen (H) atoms are chemically bound to the carbon (C) atoms on alternate sides of the membrane causing a local buckling of the membrane. Slutter and Kawazoe (2003) first predicted Graphene (GA) and it was recently rediscovered by Sofo et al. (2007). With reference to their prediction, GA “hydrogen atoms are chemically bound to the carbon atoms on alternating sides of the membrane” which causes a “local buckling of the membrane”. Flores et al. (2009) has recently reported such deformations for small membrane size (<1 nm). In the recent past many experimental (Ao and Peeters, 2010) and theoretical investigations (Karssemaker and Fasolino, 2011; Flores et al., 2009; Tewary and Yang, 2009) have been carried out on the electronic, thermal properties of hydrogenated graphene i.e., graphane due to its applications in the fields of astronomy (Huang et al., 2009), nuclear industries (Areou et al., 2011) and for designing electronic components (Huang et al., 2011). The theoretical insight of the hydrogenation process of graphene helps to predict the electronic properties of graphene based devices (Bang and Chang, 2010; Soriano et al., 2010). The lattice thermal properties of GA such as thermal conduction, roughness and heat capacity are reported by Neek-Amal and Peeters (2011). Born von Karman formalism was used to compute the phonon dispersion of graphene by considering first, second and third neighbor interactions (Falkovsky, 2008), first and second neighbor interactions with appropriated constraints (Falkovsky, 2007) using the respective force constant values. However, other lattice vibrations based thermal properties such as defect modes and Debye-Waller factor are not reported so far for this system. Hence, in this study, the theoretically calculated results of defect modes and Debye-Waller factor by considering interactions up to six nearest neighbours are reported.

METHOD OF CALCULATION

In recent experiment, Elias et al. (2009) demonstrated the fabrication of GA from a graphene (GE) membrane through hydrogenation which was found to be reversible. Since GA can be derived from GE, as a first step, the phonon frequencies of GE are calculated using Born von Karman formalism considering interactions up to sixth neighbors. The following set of force constants have been assigned for first, second, third, fourth, fifth and sixth neighbor interactions:

- Force constants for first: neighbour interaction: \( A_1, B_{1}, A_2, B_2, C_1 \) and \( D_2 \)
- Force constants for second: neighbour interaction: \( A_3, B_3, C_3, D_3, A_4, B_4 \)
- Force constants for third: neighbour interaction: \( A_5, B_5, A_6, B_6, C_4 \) and \( D_6 \)
- Force constants for fourth: neighbour interaction: \( A_7, B_7, C_7, D_7, A_8, B_8, C_8 \) and \( D_8 \)
- Force constants for fifth: neighbour interaction: \( A_9, B_{10}, C_{10}, D_{10}, A_{11}, B_{11} \) and \( C_{11} \)
- Force constants for sixth: neighbour interaction: \( A_{12}, B_{12}, C_{12}, D_{12}, A_{13} \) and \( B_{13} \)

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With these parameters the dynamical matrix has been constructed and the elements of dynamical matrix D are as follows:

\begin{equation}
D(1,1) = A_1 \cos \beta a_{1} \cos \beta = 2A_2, \quad A \cos \beta a_{1} \cos \beta = 2A_1, \quad A \cos \beta a_{1} \cos \beta = 2A_2, \\
\cos \beta a_{1} \cos \beta = 2A_2, \quad \cos \beta a_{1} \cos \beta = 2A_1, \quad \cos \beta a_{1} \cos \beta = 2A_2, \\
\cos \beta a_{1} \cos \beta = 2A_1, \quad \cos \beta a_{1} \cos \beta = 2A_2, \quad \cos \beta a_{1} \cos \beta = 2A_1, \\
\cos \beta a_{1} \cos \beta = 2A_2, \quad \cos \beta a_{1} \cos \beta = 2A_1, \quad \cos \beta a_{1} \cos \beta = 2A_2
\end{equation}

(1)

\begin{equation}
D(2,2) = 2B_2 \sin \beta a_{2} \sin \beta a_{2} = 2B_1 \sin \beta a_{1} \sin \beta a_{1}
\end{equation}

(2)

\begin{equation}
D(1,5) = 2B_2 \sin \beta a_{2} \sin \beta a_{2} = 2B_1 \sin \beta a_{1} \sin \beta a_{1}
\end{equation}

(3)

\begin{equation}
D(2,5) = B_1 \cos \beta a_{1} \cos \beta a_{1} = 2B_2 \cos \beta a_{2} \cos \beta a_{2}
\end{equation}

(4)

\begin{equation}
D(1,3) = D(2,3) = D(2,6) = D(3,1) = D(3,2) = D(3,4) = D(3,5) = 0
\end{equation}

(5)

\begin{equation}
D(4,5) = D(4,6) = D(5,3) = D(5,6) = D(6,1) = D(6,2) = D(6,4) = D(6,5) = 0
\end{equation}

(6)

\begin{equation}
D(2,1) = D(1,2) = D(4,5) = D(5,4)
\end{equation}

(7)

\begin{equation}
D(2,4) = D(1,5) = D(4,2) = D(5,1)
\end{equation}

(8)

\[ \text{D}(4,4) = \text{D}(1,1) \]
\[ \text{D}(5,2) = -\text{D}(2,5) \]
\[ \text{D}(5,5) = \text{D}(2,2) \]
\[ \text{D}(6,3) = -\text{D}(3,6) \]
\[ \text{D}(6,6) = -\text{D}(3,3) \]

Phonon frequencies and eigenvectors are obtained by diagonalising this matrix for 14 wave vector points obtained by uniformly dividing the Brillouin zone. Using the phonon frequencies and eigenvectors, the Green's function values are calculated using the formula:

\[ c_{k,\omega} = \frac{1}{\sqrt{\frac{\omega_m}{\omega}}} \sum_{n} \frac{\epsilon_{n,k} \epsilon_{n,\omega}}{\epsilon_{n,k} - \epsilon_{n,\omega}} \epsilon_{n,k} \epsilon_{n,\omega} \]

(9)

where, \( \omega_m \) is the maximum frequency among all normal modes of the host crystal.

Using these Green function values and the change in dynamical matrix due to the presence of hydrogen, the defect modes are calculated by solving the secular equation:

\[ |\text{I}-g\Omega'| = 0 \]

(10)

Debye-Waller factor is calculated using the formula:

\[ B = \frac{8\pi^2}{3} \langle u_i^2 \rangle \]

(11)

where:

\[ \langle u_i^2 \rangle = -\frac{1}{\hbar} \int \frac{d\omega}{\coth(\hbar\omega/2k_B T)} \hbar \omega \]

(12)

The \( u_i \) values are calculated using the formula:

\[ u_i = [I+g \Omega' (I-\Omega')]^{-1} u_{0i} \]

(13)

where:

\[ u_{0i} \left( \frac{1}{k}, \bar{k} \right) = \frac{\hbar}{\sqrt{2N_m \epsilon_k}} e_{i,\bar{k}}(k,\bar{k}) \exp\left[ i\int_{0}^{1} \right] \]

(14)

**RESULTS AND DISCUSSION**

By considering the hexagonal close packed coordinates of the system of study and applying the modified Morse potential (Belytschko et al., 2002), the force constant values were calculated and are listed in Table 1.
The computed force constant values have been substituted in the dynamical matrix and the phonon frequencies and eigenvectors were calculated by diagonalising the dynamical matrix for 14 representative points obtained by uniformly dividing the Brillouin zone (Balaguru et al., 2002).

In the presence of defects, the individual frequency levels inside the bands of allowed frequencies are shifted by small amounts and a small number of frequencies which normally lie near the band edges can emerge out of the allowed bands into the gap of the forbidden frequencies. Such normal modes are called Localised Vibrational Modes (LVM) and they have frequencies greater than the maximum frequency of the host crystal. LVMs are observed due to light impurities or impurities which are tightly bound to the surrounding atoms.

A special kind of LVM has been identified with the characteristic that its frequency, instead of lying above the maximum frequency of the host crystal falls in the gap of the two host crystal frequencies. Such modes are called gap modes. In addition to these two modes, resonance type mode occurs, for which, the vibrational amplitude of defect atom is very much higher compared to that of host crystal atoms.

Greens function approach was adapted to estimate the defect mode present in graphene and calculated resonance and gap modes are given in Table 2. The maximum phonon frequency mode of graphene falls at 1600 cm⁻¹ (Maultzsch et al., 2002; Zimmermann et al., 2008; Mohr et al., 2007) and the estimated defect modes after the hydrogenation of graphene falls in the range of 1600.62 to 6182.82 cm⁻¹. Since all these modes are greater than the maximum frequency of the host system, all the listed modes in Table 2 are called as localized vibrational modes.

There are neither other theoretical nor experimental results available to compare our results with them. The computed Debye-Waller factor values were estimated at various temperatures and are shown in Fig. 1. It increases with temperature as expected.
As there are no reported works for GA, the results are compared with that of GE (Tewary and Yang, 2009).

The Debye-Waller factor for GA was found to be much smaller compared to that of GE (Tewary, 2007). This may be due the presence of H in GA and this in-turn generated the defect modes. There are three types of defect modes namely: resonance, gap and localized. Due to the onset of resonance modes, the H atom vibrates with more amplitude by suppressing the amplitude of vibration of the surrounding C atoms. More results in this direction for GA are welcome to check the validity of the present study.

CONCLUSION

The defect modes namely localized vibrational modes, gap modes and resonance modes of Graphane have been computed employing Green’s function technique and scattering matrix formalism. This particular study also supports the fact that lattice defects can perturb the thermal properties of low dimensional materials. The computed values of Debye-Waller factor also support the influence of hydrogen induced defect modes in Graphane.

REFERENCES


