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Machine Learning of the Physicothermal Properties of Graphene

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Graphene is the emerging area of nanomaterials due to their prospect for coming generation electronic devices. Various studies of graphene have been carried out to investigate the phonon properties, elastic properties. However, the physicothermal properties such as heat capacity and Grüneisen parameter have been neglected. The Grüneisen parameter is the main physical parameter in thermal expansion mechanisms. These parameters are generally positive for some modes, but they are found to be negative for **q** values in high-symmetry directions. They are found negative for acoustic mode in case of graphene. The Debye model for the specific heat at low temperatures is also taken into account for acoustic branches. The heat capacity of the graphene is also computed. Physicothermal properties investigated by PYTHON program is agreed very close with the result of other researchers.

Графен є новою галуззю наноматеріялів через їхню перспективність для електронних пристроїв майбутнього покоління. Були проведені різні дослідження графену для вивчення фононних властивостей, пружніх властивостей. Однак такими фізико-термічними властивостями, як тепломісткість і Ґрюнайзенів параметер, нехтували. Ґрюнайзенів параметер є основним фізичним параметром в механізмах теплового розширення. Ці параметри, як правило, позитивні для деяких мод, але вони виявляються неґативними для значень **q** у напрямках високої симетрії. Вони виявляються неґативними для акустичної моди у випадку графену. Дебаїв модель для питомої тепломісткости за низьких температур враховується і для акустичних гілок. Також обчислюється тепломісткість графену. Фізико-термічні властивості, досліджені за програмою PYTHON, дуже близькі до результатів інших дослідників.

Key words: Hamiltonian mechanics, harmonic oscillators, heat capacity, thermal properties of graphene.

Ключові слова: Гамільтонова механіка, гармонічні осцилятори, теплоємність, графенові теплові властивості.

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1. INTRODUCTION

For decades, scientists and researchers believed that two-dimensional ($2D$) crystals are thermodynamically unstable. Graphene was the first two-dimensional material that has successfully been exfoliated from bulk graphite in 2004. The graphene structure has interesting features, which is the good reason for studying its thermal properties. Graphene is a monolayer of hexagonally arranged carbon atoms, which has become practically available today [1–3].

The atoms in the $2D$ monolayer graphene are capable of executing oscillations about their equilibrium position (n, l). In oscillating states, the instantaneous position of atoms (n, l) is denoted by $\mathbf{r}(n,l) = \mathbf{x}(n,l) + \mathbf{u}(n,l)$. Thus, the Hamiltonian of the graphene is

$$H = \sum_{nli} \frac{M_n}{2} \dot{u}_i^2(n,l) + \frac{1}{2} \sum_{nli} \sum_{ml'j} \Phi_{ij} \begin{pmatrix} nm \\ l,l' \end{pmatrix} u_i(n,l) u_j(m,l'), \quad (1)$$

where

$$\Phi_{ij} \begin{pmatrix} nm \\ l,l' \end{pmatrix} = \left[\frac{\partial^2 U}{\partial u_i(n,l) \partial u_j(m,l')} \right]_0 . \quad (2)$$

The force constants are defined as $\Phi_{ij} \begin{pmatrix} nm \\ l,l' \end{pmatrix} = -\gamma e_i e_j$, where e_i and e_j are the unit-vector components; it is the force acting on the n^{th} atom in the l^{th} cell along i^{th} direction due to a unit displacement of the m^{th} atom in the l'^{th} cell along j^{th} direction.

The equation of vibrating motion is given by

$$M_n \ddot{u}_i(n,l) = -\sum_{ml'j} \begin{pmatrix} nm \\ l,l' \end{pmatrix} u_j(m,l') . \quad (3)$$

The solution of above equation is modified by the periodicity of lattice with a wave-like solution of type

$$u_i(n,l) = M_n^{-1/2} u_{in} \exp\left[i\{\mathbf{q} \cdot \mathbf{r}(n,l) - \omega(\mathbf{q})t\} \right], \quad (4)$$

where u_{in} is the amplitude of vibration along i^{th} direction of the n^{th} atom, ω is the angular frequency, $\mathbf{q}$ is wave vector, and the factor

$M_n^{-1/2}$ has been chosen for convenience in further calculations [4].

The equation of motion in matrix notation is

$$\omega^2(\theta)MU(\mathbf{q}) = D(\mathbf{q})U(\mathbf{q})\,. \tag{5}$$

The condition for non-trivial solution

$$\left|D(\mathbf{q}) - \omega^2(\mathbf{q})MI\right| = 0\,. \tag{6}$$

The elements of dynamical matrix are defined as

$$D_{ij} = \sum\nolimits_{l'} \Phi_{ij}\begin{pmatrix} nm \\ l,l' \end{pmatrix} \exp\left(i\mathbf{q}\cdot\mathbf{r}(nm,ll')\right), \tag{7}$$

The above equation in matrix form is solved by MATLAB program. And the result is investigated along hexagonal Brillouin zone with symmetry points $\Gamma(0,0)$, $M\left(\frac{2\pi}{a\sqrt{3}},0\right)$ [13–15].

2. STUDY OF GRÜNEISEN PARAMETERS OF GRAPHENE

On the basis of oscillator model, Grüneisen predicted that the three important physical properties of a solid, the thermal expansion coefficient, the lattice specific heat, and the compressibility are linked together. To understand the physical importance of the relation, we examine that the frequency of a lattice vibration of specified wave vector changes with the lattice parameter of the solid; this leads to anharmonic effect. For simplicity, we assume that a given change in lattice parameter gives rise to the same relative change of frequency of every mode of vibration. The results of Kamlesh *et al.* were obtained by calculating individual values of the angular frequencies $\omega_{a,\mathbf{q},j}$ for different modes in high-symmetry direction [12, 14, 15]. The Grüneisen parameter for $2D$ nanostructure materials of IV$^{\text{th}}$ group of semiconductor is derived by Xu-Jin Ge *et al.* [21]:

$$\Upsilon(\mathbf{q},j) = -\frac{a_0}{\omega_{a,\mathbf{q},j}}\left[\frac{\partial\omega_{a,\mathbf{q},j}}{\partial a}\right]_{a_0}. \tag{8}$$

It is now clear that, if $\omega_{a,\mathbf{q},j}$ is angular frequency of the solid, corresponding to wave vector $\mathbf{q}$, mode j, a_0 is the equilibrium lattice constant. $\Upsilon(\mathbf{q},j)$ is independent of compressibility and, thus, it has the same value for every modes at low temperature. Thus, at low frequency modes, the variation is negligible for Grüneisen parameter. However, when Grüneisen parameter $\Upsilon(\mathbf{q},j)$ is associated with acous-

TABLE 1. Calculated Grüneisen parameters of graphene for acoustic modes.

Wave vector, **q**	Grüneisen parameter for acoustic mode
0.00	–0.0
0.05	–4.4801
0.10	–8.5944
0.15	–12.1295
0.20	–15.0468
0.25	–17.4116
0.30	–19.3231
0.35	–20.8768
0.40	–22.1518
0.45	–23.2099
0.50	–24.0980
0.55	–24.8514
0.60	–25.4972
0.65	–26.0559
0.70	–26.5433
0.75	–26.9719
0.80	–27.3515

tic modes, it is heavily weighted and tends to a decrease in $\Upsilon(\mathbf{q}, j)$. Grüneisen parameter $\Upsilon(\mathbf{q}, j)$ is the same for modes in the dispersive region of any given branch of acoustic modes and, here, the optic modes can be ignored. The $\Upsilon(\mathbf{q}, j)$ calculated in Table 1 comes from the PYTHON program.

In high-symmetry direction M–Γ, Grüneisen parameter of graphene is determined by acoustic modes:

$$\Upsilon(\mathbf{q}, j) = -a_0 \frac{\sqrt{3}}{4} q_y \left[\cot\left(\frac{\sqrt{3}}{4} q_y a_0 \right) \right]. \tag{9}$$

The Grüneisen parameter plays greater role in finding the dependence of various thermal properties of nanomaterials on different temperature from phonon frequency to thermal conductivity of a nanomaterial [6, 7]. We have shown that the graphene *LA* and *TA* modes have negative Grüneisen parameters (Fig. 1). This negative value is because of the anomalous hardening of phonon modes upon expansion and 2*D* buckled mode. However, the acoustic modes have Grüneisen parameters, which are varying from 0 to –27.35 for graphene corresponding to different wave vector **q**. Such high values of Grüneisen parameters lead to high value of thermal conductivity. These acoustic modes generate highly negative Grüneisen parameters. The other modes such as LA, LO, TA, TO and the remaining transverse modes (ZO) has not dominant effect [12].

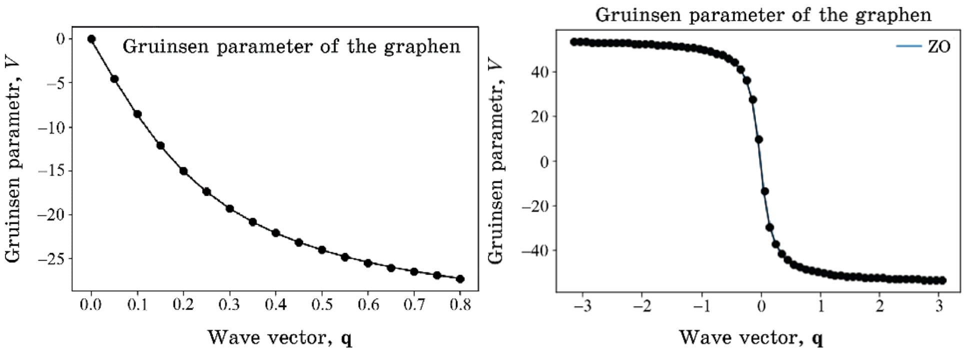

Fig. 1. Variation of Grüneisen parameter with wave vector **q** in high-symmetry direction Γ–M.

3. DEBYE TEMPERATURE VARIATION OF GRAPHENE

The Debye theory agrees with both the classical and the Einstein quantum theories. The quantum considerations are of almost no significance at higher temperature range [5]. The theory gives a quite satisfactory account of the observed variation of the heat capacity in the low-temperature region. The Debye theory of specific heat also treats the atoms of the monolayer graphene as harmonic oscillators, however, incapable of vibrating independently of one another. It rather treats them to be strongly coupled together oscillating relative to their neighbours in the lattice. Therefore, we should consider the vibrational motion of the monolayer graphene as a whole rather than the vibrational motion of a single atom [16, 17].

The Debye formula for heat capacity of graphene as $2D$ material is derived as

$$C = 4R\left(\frac{T}{\theta}\right)^2 \int_0^{\theta/T} \frac{x^3 e^x}{(e^x - 1)^2}\,dx\,; \tag{10}$$

here, $x = \hbar\omega/(k_B T)$.

The value of $R = N_0 k_B$ depends on the units involved, but it is usually stated with S.I. units as $R = 8.314$ J/(mol·K). The parameter θ entering into our present discussion is usually referred to as the Debye temperature. It plays the role of a characteristic temperature of a solid. With the Debye temperature at sufficiently low temperatures T, here, only acoustic modes are excited. In this case, $x >> 1$ and the upper limit of the integration can be extended to infinity. The integral is then deduced in terms of Riemann–Zeta function ζ. The heat capacity of graphene is simulated with the PYTHON program.

The variation of the experimentally measured heat capacity is compared with that computed data (Table 2). This comparison is performed by plotting the heat capacity against the temperature. For determination of the exact variation of Debye temperatures, we have used PYTHON program. In this technique, the specific heat is expressed in terms of Riemann–Zeta function ζ (3). ζ (3) has a special value of the Riemann–Zeta function, which is equal to 1.202056903 [9]. From the calculated heat capacities at different temperatures, heat capacity of pure graphene is determined in terms of Riemann–Zeta function. We make a plot of this function by using the PYTHON program. It is seen from this plot that the heat capacity approaches the zero value as $T \to 0$ K. For higher temperature, heat capacity is not varying abruptly and almost constant $2Nk_B$. It is easily observed from the graph as shown in Fig. 2 that heat capacity for pure graphene reaches a 0.97 J/(g·K) near room temperature. The specific heat at constant volume behaviour of the graphene does not show any anomaly. Figure 2 illustrates the

TABLE 2. Variation of heat capacity with temperature of graphene.

Temperature, K	Heat capacity with Riemann–Zeta function, ζ (3)	Heat capacity, J/(g·K)
0	0	0
40	0.0165000625919003·zeta(3)	0.0198
80	0.0660002503676014·zeta(3)	0.0793
120	0.148500563327103·zeta(3)	0.1785
160	0.264001001470406·zeta(3)	0.4958
200	0.412501564797509·zeta(3)	0.7140
240	0.594002253308412·zeta(3)	0.9718
280	0.808503067003117·zeta(3)	1.2693
320	1.05600400588162·zeta(3)	

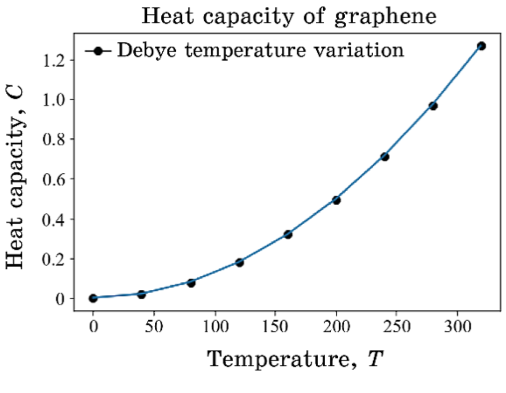

Fig. 2. Debye temperature variation at low temperatures.

higher order of agreement with other researchers [8–10].

4. CONCLUSIONS

Based on the discussion above, it is important to note that the physicothermal properties, such as Grüneisen parameter, are strongly dependent on wave vector and Debye temperature, as well as on phonon polarizations [10, 11]. We evaluate it along high-symmetry directions for acoustic modes because this mode play main role in thermal expansion. We find that the Grüneisen parameter of graphene $2D$ materials is negative for low-frequency phonons near Γ. This is happening because the lower acoustic modes are excited at low temperatures. The computed Grüneisen parameters of the LA and TA branches are highest for graphene with similar results. The study of monolayer graphene under quasi-harmonic approximation gives the negative values of Grüneisen parameters, which will be further used in determination of thermal expansion coefficients and thermal conductivity of nanomaterials. Figure 2 illustrates that the order of the agreement between the Debye curve and the experimental curve for graphene is remarkable [17]. This is, of course, what we should expect of the Debye approximation at sufficiently low temperatures. Long-wavelength acoustic modes are just the modes, which may be treated as in elastic continuum concept of Debye theory. Notwithstanding the great success of the Debye theory, precise measurements in the low-temperature region show certain deviations from the theoretical predictions. Debye model for the heat capacity of graphene has been remarkably successful in describing the simulations in the low-temperature range. This conclusion is supported by the work of Pop *et al.* [18].

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PROGRAM ORGANIZATION

Appendix A. PYTHON Program of the Grüneisen Parameter of Graphene

```
import matplotlib.pyplot as plt
import numpy as np
import math
# #vj = gamma
```

```
a = 2.47
vj = 8.98
points=np.arange(-np.pi, np.pi, 0.1)
def solve(fun):
  op = []
  for i in points:
    op.append(fun(i))

  return op
def v(qx):
  return (((-
a)*math.sqrt(3))/2)*(math.sqrt(11*vj))*(np.arctan(math.sqrt(3)*qx*a))
v = solve(v)
plt.plot(points,v)
plt.ylabel(“Grüneisen parameter V”)
plt.xlabel(“Wave vector (q)”)
plt.plot(points, v, color= ‘k’, linewidth=1, marker=‘o’)
plt.suptitle(‘Grüneisen Parameter of the Graphene’, x=0.50, y=0.98)
plt.legend([‘ZO’])
plt.show()
```

Appendix B. Python Program of the Heat Capacity of Graphene

```
import math
import numpy as np
import matplotlib.pyplot as plt
from __future__ import division
from sympy import *
x, T=symbols(‘x T’)
integrate(((x*x*x)*exp(x))/((exp(x)-1)*(exp(x)-1)), (x, 0, oo))

C=[]

T=[0,40,80,120,160,200,240,280,320]

for i in T:
  calC=(2*zeta(3)*8.31*4*i*i)/(2539*2539)
  C.append(calC)
plt.ylabel(“Heat Capacity(C)”)
plt.xlabel(“Temperature (T)”)
plt.plot(T, C, color= ‘k’, linewidth=1,  marker = ‘o’)
plt.suptitle(‘HEAT CAPACITY OF GRAPHENE’, x=0.50, y=0.98)
plt.legend([‘Debye temperature variation’])
plt.plot(T, C)
plt.show()
```

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