THERMODYNAMIC PROPERTIES OF GRAPHENE IN THE LINEAR APPROXIMATION OF ITS ENERGY DISPERSION RELATION

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Abstract

This paper presents the thermodynamic properties of graphene via its partition function. The energy dispersion relation for the first nearest neighbour hopping is approximated to its linear term and was used to model a partition function for the single layer graphene. The specific heat, Helmholtz free energy and entropy of graphene were calculated and their temperature dependence was shown.

1.   Introduction

Graphene is the first example of a truly two dimensional crystal. The electronic properties of graphene are exceptionally novel. For instance, the low-energy quasi-particles in graphene behave as massless chiral Dirac fermions, which have led to the experimental observation of many interesting effects similar to those predicted in the relativistic regime. Graphene also has immense potential to be a key ingredient of new devices, such as single molecule gas sensors, ballistic transistors and spintronic devices [1]. High in-plane thermal conductivity is due to covalent sp^2 bonding between carbon atoms, whereas out-of-plane heat flow is limited by weak van der Waals coupling [2]. The strong and anisotropic bonding and the low mass of the carbon atoms give graphene and related materials unique thermal properties. Herein, we seek to solve some of the thermodynamic properties by using a modeled partition function and establish their temperature dependence.

2. Theoretical Analysis

a. Linearization of Energy Dispersion of Graphene Around The Dirac Points

The energy dispersion relation of graphene is given by

$$E = \sqrt{1 + 4\cos\left(\frac{\sqrt{3}}{2}k_x a\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)} \tag{1}$$

Let the E-k relation written in terms of α and β

$$E(\alpha,\beta) = \sqrt{1 + 4\cos\alpha\cos\beta + 4\cos^2\beta} \tag{2}$$

Using Taylor series to expand the relation around the Dirac points

$$E \approx E(\alpha_c,\beta_c) + \frac{\partial E}{\partial\alpha}\Big|_{\alpha_c,\beta_c}(\alpha - \alpha_c) + \frac{\partial E}{\partial\beta}\Big|_{\alpha_c,\beta_c}(\beta - \beta_c) + \ldots \tag{3}$$

Where $\alpha_c = 0$ and $\beta_c = \frac{2\pi}{3}$ are the Dirac points

Approximating up to the linear part

$$E(\alpha_c,\beta_c) = 0$$

$$\frac{\partial E}{\partial\alpha} = \frac{\frac{1}{2}(-4\sin\alpha)\cos\beta}{\sqrt{1 + 4\cos\alpha\cos\beta + 4\cos^2\beta}} = \frac{-2\sin\alpha\cos\beta}{\sqrt{1 + 4\cos\alpha\cos\beta + 4\cos^2\beta}}$$

At β_c

$$\frac{\partial E}{\partial\alpha} = \frac{\sin\alpha}{\sqrt{2 - 2\cos\alpha}} \tag{4}$$

But $2\sin\alpha = 2\sin\frac{\alpha}{2}\cos\frac{\alpha}{2}$ and $1 - \cos\alpha = 2\sin^2\frac{\alpha}{2}$

Substitute these into eqn. (4) and at α_c

$$\frac{\partial E}{\partial\alpha} = \cos\frac{\alpha}{2} = 1 \tag{5}$$

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$$\frac{\partial E}{\partial \beta} = \frac{\frac{1}{2}(-4\cos\alpha\sin\beta - 8\sin\beta\cos\beta)}{\sqrt{1 + 4\cos\alpha\cos\beta + 4\cos^2\beta}} \tag{6}$$

At α_c

$$\frac{\partial E}{\partial \beta} = \frac{-2\sin\beta(1 + 2\cos\beta)}{1 + 2\cos\beta} \tag{7}$$

At β_c, $\frac{\partial E}{\partial \beta} = -2\sin\beta = -\sqrt{3}$

$$E = k_x - i\sqrt{3}k_y \tag{8}$$

Since $\alpha = \frac{a\sqrt{3}}{2}k_x$ and $\beta = \frac{a}{2}k_y$

Then at the Dirac points, eqn. (3) becomes

$$E = \left(\frac{a\sqrt{3}}{2}k_x - 0\right) - i\sqrt{3}\left(\frac{a}{2}k_y - \frac{2\pi}{3}\right) \tag{9}$$

$$E + \frac{2\pi\sqrt{3}}{3} = \frac{a\sqrt{3}}{2}(k_x - ik_y) \tag{10}$$

We assume that $E = E + \frac{2\pi\sqrt{3}}{3}$ and $k = \frac{a\sqrt{3}}{2}(k_x - ik_y)$

Therefore, the linearization of energy dispersion of graphene results

$$E = a|k| \tag{11}$$

b. Thermodynamic properties of Graphene

In order to obtain all thermodynamic quantities of graphene, we concentrate, at first, on the calculation of the partition function Z.

For a canonical ensemble that is mechanical and continuous, the canonical partition function is defined as [3]

$$Z = \int e^{-\tau E(k_x k_y)} dk_x dk_y \tag{12}$$

Where $\tau = \frac{1}{K_B T}$

As we calculated in equation (11), the linear approximation of E is

$$E(k_x k_y) = a|k|$$

Therefore,

$$Z = \int e^{-a\tau k} dk_x dk_y \tag{13}$$

Assuming a circular symmetry instead of the hexagonal lattice,

$$\int dk_x dk_y = 2\pi \int_0^q k\,dk = \pi q^2 \tag{14}$$

$$Z = 2\pi \int e^{-a\tau k} k\,dk = \frac{-2\pi}{a}\frac{\partial}{\partial\tau}\int e^{-a\tau k}\,dk = \frac{2\pi}{a}\frac{\partial}{\partial\tau}\left[\frac{e^{-a\tau k}}{a\tau}\right] \tag{15}$$

$$Z = \frac{-2\pi}{a^2\tau^2}[a k\tau e^{-a\tau k} + e^{-a\tau k}]_0^q \tag{16}$$

$$Z = \frac{2\pi}{a^2\tau^2}\{1 - aq\tau e^{-a\tau q} - e^{-a\tau q}\} \tag{17}$$

Eqn. (17) is the approximate partition function for a monolayer graphene

The area of the lattice can be calculated using the reciprocal lattice vectors. The vectors are [4]

$$\overrightarrow{b_1} = \left(\frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a}\right) \text{and} \overrightarrow{b_2} = \left(\frac{2\pi}{\sqrt{3}a}, \frac{-2\pi}{a}\right) \tag{18}$$

The determinant of the reciprocal lattice vectors is equal to the area of the lattice

$$\pi q^2 = \begin{vmatrix} i & j & k \\ \frac{2\pi}{\sqrt{3}a} & \frac{2\pi}{a} & 0 \\ \frac{2\pi}{\sqrt{3}a} & \frac{-2\pi}{a} & 0 \end{vmatrix} \tag{19}$$

$$q = \frac{2\pi}{a}\left(\frac{2\pi}{\sqrt{3}}\right)^{\frac{1}{2}} \tag{20}$$

The specific heat is defined in terms of partition function as [3]

$$C = 2K_B T\frac{d\ln Z}{dT} + K_B T^2\frac{d\ln Z}{dT} \tag{21}$$

But $\tau = \frac{1}{K_B T}$, then C becomes

$$C = -2K_B\frac{d\ln Z}{dT} + K_B\frac{\partial}{\partial\tau}\left(\tau^2\frac{d\ln Z}{dT}\right) \tag{22}$$

$$\ln Z = \ln\left(\frac{2\pi}{a^2}\right) - 2\ln\tau + \ln(1 - aq\tau - e^{-aq\tau}) \tag{23}$$

$$\frac{dlnZ}{d\tau} = -\frac{2}{\tau} + \frac{a^2 q^2 \tau}{e^{aq\tau} - aq\tau - 1} \tag{24}$$

$$\frac{dlnZ}{d\tau} = -\frac{2}{\tau} - \frac{a^2 q^2 \tau}{1 + aq\tau - e^{aq\tau}} \tag{25}$$

Therefore,

$$C = -2K_B \left(-2 - \frac{a^2 q^2 \tau}{1 + aq\tau - e^{aq\tau}}\right) - K_B \frac{\partial}{\partial \tau}\left(2\tau + \frac{a^2 q^2 \tau^3}{1 + aq\tau - e^{aq\tau}}\right) \tag{26}$$

$$C = K_B \left(2 - \frac{\omega^2 - \omega^2 e^\omega - \omega^3 e^\omega}{(1 + \omega - e^\omega)^2}\right) \tag{27}$$

where $\omega = aq\tau$

The Helmholtz free energy is related to the partition function as [3]

$$A = -KTlnZ \tag{28}$$

$$A = -\tau lnZ \tag{29}$$

Therefore,

$$A = K_B \tau (ln(\frac{2\pi}{a^2 \tau^2}(1 + \omega - e^\omega) - \omega) \tag{30}$$

The entropy is related to the partition function as [3]:

$$S = KT \frac{\partial lnZ}{\partial T} + KlnZ \tag{31}$$

$$S = \frac{1}{\tau} \frac{\partial lnZ}{\partial \tau} \frac{d\tau}{dT} + KlnZ \tag{32}$$

$$S = K_B \left(2 - \frac{\omega^2}{1 + \omega - e^\omega} + ln\left(\frac{2\pi}{a^2 \tau^2}\right)(1 + \omega - e^\omega) - \omega\right) \tag{33}$$

3.   Results and Discussion

We have used the analytical results of the thermodynamic properties (specific heat, Helmholtz free energy and entropy) relation for graphene to obtain the numerical data for different values of reduced temperature $\mu = \frac{1}{\tau} = K_B T$ as shown in figure1-3 below. Before we proceed to discuss the main results, we discuss the behaviour of the specific heat in the region of lower temperatures. The specific heat remains unchanged at certain temperatures $\mu = 0 - 2.33$, but increases linearly beyond this point. In this lower temperature region the partition function can be approximated by

$$Z(\tau) = \frac{2K_B \pi}{a^2 \tau^2} \tag{34}$$

Which yields $C = 2K_B$

Therefore the reduced specific heat is

$$\frac{C}{K_B} = 2 \tag{35}$$

We can say that this limit follows the Dulong-Petit law of ultra-relativistic ideal gas [5].

We should mention that in the numerical results, for all the thermodynamic properties of graphene in the linear approximation of its energy dispersion relation, all thermal quantities are plotted against the reduced temperature ($\mu = K_B T$). In figure 1, there is a linear increase beyond temperature ($\mu_0 = 2.33$). From figure 2, we can see that the Helmholtz free energy decreases as expected. In the case of entropy (figure 3), we observed that it increase with temperature without any abrupt change
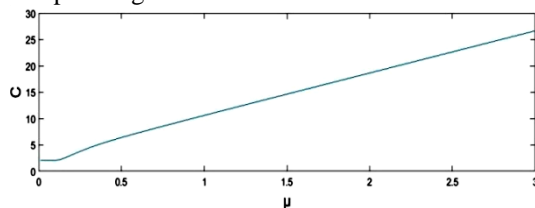

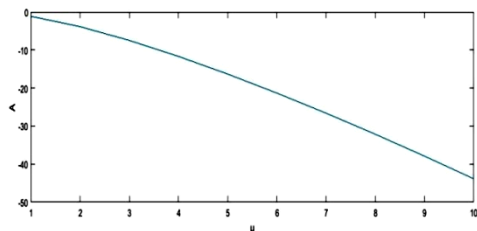Fig.1. Variation of specific heat C with reduced temperature μ

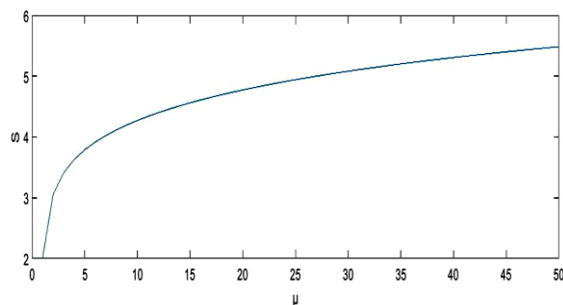Fig.2. Variation of Helmholtz free energy (A) of graphene with reduced temperature μ

Fig.3. Variation of Entropy S of graphene with reduced temperature μ

5. Conclusion

We have presented a well detailed study of the finite temperature behaviour of some thermodynamic quantities of graphene through its modeled partition function. All our results are in good agreement with previous experimental data. The variation of heat capacity of graphene with temperature is in conformity with the experimental results and its unchanged value at lower temperatures has been experimentally shown by Sarita Mann et al. The increasing value of entropy fairly explains the increasing disorder [6]. Also the free energy with increase in temperature expectedly decreases as previous studies.

References
[1] D. S. L. Abergel, V. Apalkov, J. Berashevich, K. Zieg and T. Chakraborty properties of Graphene: "A theoretical perspective", Advance in physics, Vol. 59, No. 4 2010, pp. 261-482.
[2] Eric P, Vikas V, and Ajit K. R. "Thermal properties of graphene: Fundamentals and applications" *MRS Bulletin, vol. 37, pp. 1273-1281 (2012)*
[3] Udayanandan K. M, Sathish R. K and Augustine A. Role of Partition Function in Statistical Mechanics: www.physedu.in, vol. 30, No. 2
[4] H. S. Philip Wong and Deji Akinwande, "Carbon Nanotube and Graphene Device Physics", Cambridge University Press, (2011).
[5] Santos V, Maluf R V and Almeida C A S 2014 Ann. Phys., NY349 402–10
[6] Sarira M, Puja R, Ranjan K, Garija S. D and Jindal V. K, "Thermodynamics of pure and doped (B, N) graphene " DOI: 1601.05896.