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STATISTICAL MOMENT DETERMINATION OF THERMODYNAMIC PROPERTIES OF BILAYER GRAPHENE

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Abstract: *Thermodynamic properties of bilayer graphene are investigated using the statistical moment method (SMM) taking into account the anharmonic effects of the lattice vibrations. The nearest neighbor distance, thermal expansion coefficient, and specific heat at the constant volume of the bilayer graphene are calculated as a function of the temperature, using three different interatomic potentials. We discuss the temperature dependence of the thermodynamic quantities of the graphene and bilayer graphene and compare our calculated results with those of the experimental results and of the other theories.*

I. INTRODUCTION

Graphene is a network of carbon atoms positioned in a beehive-like shape with 0.142 nm a long carbon-to-carbon distance. It is a new material successfully produced in the recent years, and there have been many theoretical and also experimental studies about graphene [1 ÷ 5]. One hopes that graphene with its special properties can replace Silicon in the future electronic technology.

In the present study, the thermodynamic properties of bilayer graphene are investigated by SMM [6, 7].

II. THEORY

II.1. Free energy of bilayer graphene

To derive the temperature dependence of the thermodynamic properties of bilayer graphene, we use the statistical moment method. This method allows us to take into account the anharmonicity of thermal lattice vibrations on the thermodynamic quantities in the analytic formulations.

The essence of the SMM scheme can be summarized as follows : for simplicity, we derive the thermodynamic quantities of bilayer graphene, taking into account the higher (fourth) order anharmonic contributions in the thermal lattice vibrations going beyond the quasi-Hamonic (QH) approximation. The basic equations for obtaining thermodynamic quantities of the given system are derived in a following manner : the equilibrium thermal lattice expansions are calculated by the force balance criterion and then the thermodynamic quantities are determinded for the equilibrium lattice spacings. The anharmonic contributions of the thermodynamic quantities are given explicitly in terms of the power moments of the thermal atomic displacements.

For the evaluation of the anharmonic contributions to the free energy ψ, we consider a quantum system, which is influenced by supplemental forces α_i in the space of the generalized coordinates q_i. For simplicity, we only discuss monatomic metallic systems and hereafter omit the indices l on the sublattices. Then, the Hamiltonian of the crystalline system is given by:

$$\widehat{H} = \widehat{H}_0 - \sum_i \alpha_i \hat{q}_i, \tag{1}$$

where $\widehat{H}_0$ denote the crystalline Hamiltonian without the supplementary forces α_i and upper huts represent operrators. The supplementary forces α_i are acted in the direction of the generalized coordinates q_i. The thermodynamic quantities of the anharmonic crystal (harmonic Hamiltonian) will be treated in the Einstein approximation. One can get the Helmholtz free energy of the system in the following form [6].

$$\psi = U_0 + \psi_0 + \psi_1 \tag{2}$$

where ψ_0 denotes the free energy in the harmonic approximation and ψ_1 the anharmonic contribution to the free energy. The Helmholtz free energy of our system can be derived from the Hamiltonian H of the following form:

$$\widehat{H} = \widehat{H}_0 - \lambda \widehat{V} \tag{3}$$

where $\widehat{H}_0$ denote the Hamiltonian of the harmonic approximation, λ the parameter and $\widehat{V}$ the anharmonic vibrational contributions. Following exactly the general formalism in the SMM formulation [6, 7], one can get the free energy ψ

$$\psi = U_0 + \psi_0 - \int_0^{\lambda} \langle \widehat{V} \rangle_{\lambda} d\lambda \tag{4}$$

where $\lambda\widehat{V}$ represents the Hamiltonian corresponding to the anharmonicity contribution. Then the free energy of bilayer graphene is given by :

$$\psi = \psi_0 + U_0 + 3N \left(\int_0^{\gamma_2} \left\langle u^2 \right\rangle^2_{\gamma_1,\beta=0} d\gamma_2 + \int_0^{\gamma_1} \left\langle u^4 \right\rangle_{\beta=0} d\gamma_1 + \int_0^{\beta} \left\langle u^3 \right\rangle d\beta \right). \tag{5}$$

We obtained the expresion of free energy of bilayer graphene

$$\begin{aligned}
\psi &= \psi_0 + U_0 + 3N \Bigg\{ \frac{\theta^2}{k^2} \left(\gamma_2 \cdot x^2 cth^2 x - \frac{2}{3}\gamma_1 \left(1 + \frac{xcthx}{2} \right) \right) \\
&+ \frac{\theta^3}{k^4} \left[\frac{2}{3}\gamma_2^2 \left(1 + \frac{xcthx}{2} \right) xcthx - 2 \left(\frac{\gamma_1^2}{2} + \gamma_1\gamma_2 \right) \left(1 + \frac{xcthx}{2} \right) (xcthx + 1) \right] \\
&+ \frac{\theta^4}{k^6} \left[\left(\frac{4}{27}\gamma_2^3 - \frac{4}{3} \left(\frac{\gamma_1^2}{3} + \gamma_1^2\gamma_2 + \gamma_1\gamma_2^2 \right) \right) \left(1 + \frac{xcthx}{2} \right)^2 \right] \\
&+ \left[\frac{\sqrt{2}(\gamma_1 + \gamma_2)\theta^2\beta}{k\sqrt{3k(\gamma_1 + \gamma_2) - \beta^2}} (xcthx - 1) + \frac{2\sqrt{2}(\gamma_1 + \gamma_2)^2\theta^3\beta}{3k\sqrt{3k(\gamma_1 + \gamma_2) - \beta^2}} \left(1 + \frac{xcthx}{2} \right)^{\frac{3}{2}} \right] \Bigg\}
\end{aligned} \tag{6}$$

In the above equations (5) and (6), k, γ_1, γ_2 and β are defined by:

$$k = \frac{1}{2}\sum_i \left(\frac{\partial^2 \varphi_{i0}}{\partial u_{i\beta}^2}\right)_{eq} \equiv m\omega^2,\ \gamma_1 = \frac{1}{4}\left(\frac{1}{12}\sum_i \left(\frac{\partial^4 \varphi_{i0}}{\partial u_{i\beta}^4}\right)_{eq}\right),$$

$$\gamma_2 = \frac{6}{4}\left(\frac{1}{12}\sum_i \left(\frac{\partial^4 \varphi_{i0}}{\partial u_{i\beta}^2 \partial u_{i\gamma}^2}\right)_{eq}\right), \beta = \sum_i \left(\frac{\partial^3 \varphi_{i0}}{\partial u_{jx}\partial u_{jy}\partial u_{jz}}\right)_{eq} \tag{7}$$

II.2. Thermodynamic quantities of bilayer graphene

The lattice constant a at temperature T can be determined from experiment or the minimum condition of the free energy of the bilayer graphene. Using the approximation expresion of free energy (6) for the bilayer graphene:

$$\psi \simeq \psi_0 + U_0 + \frac{N\theta^2}{k^2}\left(\gamma_2 \cdot x^2\, \mathrm{c}\, th^2 x - \frac{2}{3}\gamma_1\left(1 + \frac{x\, \mathrm{c}\, thx}{2}\right)\right) \tag{8}$$

and from the minimization condition of the free energy of the bilayer graphene with respect to the lattice constant, we obtain the following equation:

$$\frac{d\psi}{da} = 0$$

or

$$3N\theta \frac{xcthx}{2k}\frac{dk}{da} + \frac{N}{2}\sum_i \frac{d\varphi_{i0}}{da} + N\theta^2 \frac{1}{k^2}\left\{x^2\, \mathrm{c}\, th^2 x \cdot \frac{d\gamma_2}{da} - \frac{2}{3}\left(1 + \frac{x\, \mathrm{c}\, thx}{2}\right)\frac{d\gamma_1}{da}\right\}$$

$$+N\theta^2 \frac{1}{k^3}\left\{-\gamma_2\left(x^2\, \mathrm{c}\, th^2 x + \frac{x^3 cthx}{sh^2 x}\right) + \gamma_1\left(\frac{4}{3} - \frac{x\, \mathrm{c}\, thx}{2} + \frac{x^2}{sh^2 x}\right)\right\}\frac{dk}{da} = 0 \tag{9}$$

Using the MAPLE program, Eq.(9) can be solved, we find the values of the lattice constant $a(T)$. We assume that the linear thermal expansion coefficient α of the bilayer graphene at temperature T can be written as:

$$\alpha\,(T_2) = \frac{a\,(T_2) - a\,(T_1)}{a_0\,(T_2 - T_1)} \tag{10}$$

On the other hand, the internal energy E of the system is given by:

$$E = \psi + TS \tag{11}$$

where entropy S is defined by: $S = -k_B\left(\frac{\partial \psi}{\partial \theta}\right)$. Then, the specific heat at constant volume C_v is obtained from the derivative of internal energy E with respect to the temperature T and is given by:

$$C_V = k_B \frac{\partial E}{\partial \theta} \tag{12}$$

III. NUMERICAL RESULTS AND DISSCUSION

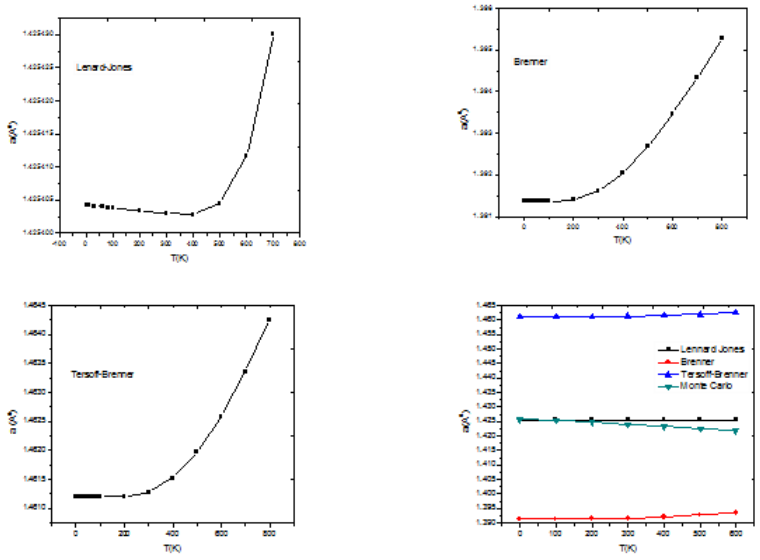

Fig. 1. The temperature-dependent minimum carbon-to-carbon distance calculated by statistical moment method and by other methods.

We use three different inteatomic potentials in order to study two-dimensional graphene: Lennard Jones potential[3], Brener[1] and Tersoff Brener[4,5] and then the SMM caculated results which are demonstrated in these figures below: Fig.1 shows that in the low temperature, if the heat increases, the carbon-to-carbon distance will slightly decrease, and in the high temperature, the distance is a monotonically increasing function of temperature. These results we get are similar to the results calculated by Monte Carlo method [2].

Fig.2 shows that in the low temperature, the thermal expansion coefficient α of graphene is negative, and positive in the high temperature. α is negative in the range 10k to 400k of temperature with Lennard Jones potential, 10k to 90k with Brener potential, and 10k to 100k with Tersoff-Brener potential. Based on Monte Carlo method, we also get α negative in the range 10k to 700k of temperature [2]. Clearly, by using the statistical moment method we get the same thermal expansion coefficient in the low range of temperature when we compare with other methods. α is negative in the low range of temperature, because the carbon-to-carbon distance decreases if the temperature increases which as a result makes two-dimensional graphene shrink.

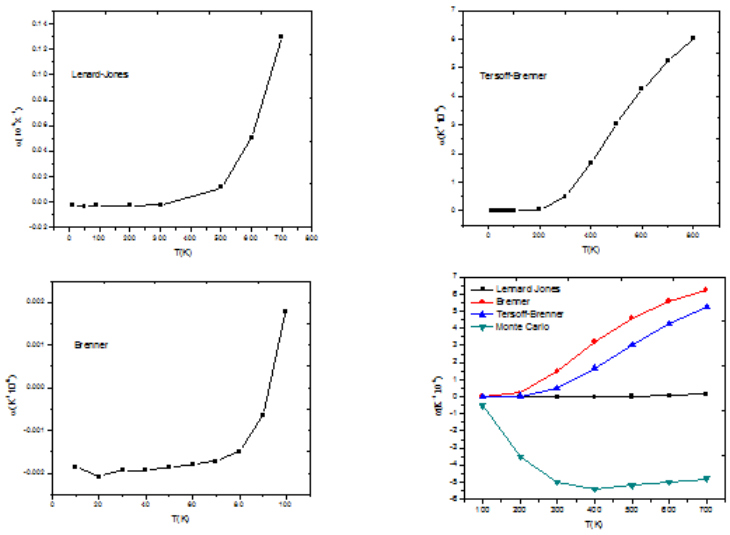

Fig. 2. The temperature-dependent thermal expansion coefficient calculated by statistical moment method and by other methods.

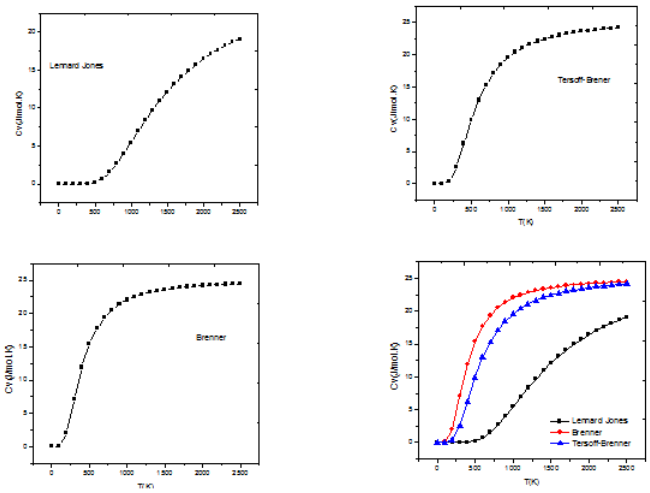

Fig. 3. specific heat capacity at constant volume Cv calculated by statistical moment method.

Fig.3 shows that specific heat capacity at constant volume depends strongly on the temperature below 900K with Brener and Tersoff Brener potentials, and 400K to 2000K with Lennard Jones potential. In the high temperature, specific heat capacity at constant volume depends slightly on temperature. In conclusion it should be noted that

the statistical moment method really permits an investigation of temperature dependece of bilayer graphene. The SMM results are in good agreement with other caculations and experiments. This research is funded by NAFOSTED, grant number 103.01-2011.16.

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