



On the intrinsic ripples and negative thermal expansion of graphene



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ARTICLE INFO

Article history:

Received 29 July 2014

Received in revised form

28 July 2015

Accepted 7 August 2015

Available online 13 August 2015

Keywords:

Ripples

Negative thermal expansion

Soft phonon modes

ABSTRACT

The intrinsic ripples of suspended graphene have attracted intensive attention due to their influence on the electronic transport and other properties. Negative thermal expansion (NTE), another unconventional phenomenon found in graphene, can be utilized to control the intrinsic ripples in a reversible way, thus opening new perspective for application. In this case, understanding the mutual relation and physical origin of the intrinsic ripples and NTE is crucial, especially since they are both widely observed in other 2D materials. Here we clarify through lattice dynamical analysis that at low temperature the two phenomena are both intrinsic for any 2D crystals with a honeycomb structure (or any monatomic 2D crystals). We find that the intrinsic ripples, generally believed to be caused by thermal fluctuation, have another origin that is the appearance of soft ZA modes near long wavelength limit when the lattice constant is shortened. Moreover, the soft ZA modes and NTE have the same physical origin at low temperature. At finite temperature, NTE is dominantly caused by the “vibrational elongation” effect owing to large out-of-plane fluctuation according to our calculation based on self-consistent phonon theory.

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1. Introduction

Uncovering the nature of its intrinsic ripples [1,2] is one of the most challenging and vital problems concerning suspended graphene. On one hand, its academic interest derives from the Peierls–Landau–Mermin argument, raised almost 80 years ago, about the non-existence of low-dimensional crystalline state [3–5]. On the other hand, the crumpled morphology of a suspended graphene has a profound impact on its physical properties, including electronic transport [6–12], magnetoresistance [13], mechanical strength [14], electromechanical coupling [15] and chemical activity [16,17]. Currently, the spontaneous appearance of ripples in graphene is attributed to several factors, including thermal fluctuations [18,19], spontaneously and/or thermally generated strains [20] and adsorbed OH molecules sitting on random sites [21]. Despite these existing explanations, we believe that the ripple problem for suspended graphene is still far from settled because of many related yet unsolved issues. To name a few of these issues, the

spontaneous ripples found by Meyer et al. [1] in graphene are with a size range of 50 – 100 Å, what factor determines this size and is it controllable? Are the ripples randomly distributed or with a stable pattern? Is the rippled state unique for graphene or is it a common feature for any 2D materials?

Another unusual structural property of graphene is that it possesses NTE coefficient [22], which is also found in graphene oxide [23,24]. Actually, before the experiments, the NTE coefficient of graphene has been predicted and explained by using a theoretical method combining first principle calculation and lattice dynamical analysis [25]. Moreover, it is found that NTE can be used to control the intrinsic ripples in a reversible way [20], which is of great merits for exploration of new tunable graphene-based devices. At this stage, it is natural to think that certain internal relation exists between these two types of exotic structural properties of graphene, which has never been truly understood.

In this work, we try to elucidate the relevance between the intrinsic ripples and the NTE in graphene. By doing so, direct answers or clues to the many unsolved issues concerning the intrinsic ripples are obtained, as well as a deeper understanding of the origin of the ripple formation and the NTE coefficient in graphene. The discussion is divided into two parts: one for low temperature condition where the effect of thermal fluctuation is neglected, and the other for finite temperature condition where thermal fluctuation is significant and even compatible with lattice spacing.

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2. Low-temperature analysis

At low temperature, according to the theory of lattice dynamics in the harmonic approximation [26], the phonon frequencies are determined by

$$\omega_{\mathbf{q}n}^2 = \sum_{\alpha,\beta,k,k'} \varepsilon_{\alpha k}(\mathbf{q}, n) \varepsilon_{\beta k'}(\mathbf{q}, n) D_{\alpha\beta} \left(\frac{\mathbf{q}}{k, k'} \right), \quad (1)$$

$$\begin{aligned} \left(\frac{\partial^2 \varphi_1(\mathbf{r}_{ij}, \theta_{ijk})}{\partial u_\alpha(\mathbf{0}/k) \partial u_\beta(\mathbf{1}'/k')} \right)_0 &= \left(\frac{\partial \varphi_1}{\partial r_{ij}} \right)_0 \left(\frac{\partial^2 r_{ij}}{\partial u_\alpha(\mathbf{0}/k) \partial u_\beta(\mathbf{1}'/k')} \right)_0 + \sum_{k \neq i,j} \left(\frac{\partial \varphi_1}{\partial \cos \theta_{ijk}} \right)_0 \left(\frac{\partial^2 \cos \theta_{ijk}}{\partial u_\alpha(\mathbf{0}/k) \partial u_\beta(\mathbf{1}'/k')} \right)_0 \\ &+ \left(\frac{\partial^2 \varphi_1}{\partial r_{ij}^2} \right)_0 \left(\frac{\partial r_{ij}}{\partial u_\alpha(\mathbf{0}/k)} \frac{\partial r_{ij}}{\partial u_\beta(\mathbf{1}'/k')} \right)_0 + \sum_{k,l \neq i,j} \left(\frac{\partial^2 \varphi_1}{\partial \cos \theta_{ijk} \partial \cos \theta_{ijl}} \right)_0 \left(\frac{\partial \cos \theta_{ijk}}{\partial u_\alpha(\mathbf{0}/k)} \frac{\partial \cos \theta_{ijl}}{\partial u_\beta(\mathbf{1}'/k')} \right)_0 \\ &+ \sum_{k \neq i,j} \left(\frac{\partial^2 \varphi_1}{\partial \cos \theta_{ijk} \partial r_{ij}} \right)_0 \left[\left(\frac{\partial r_{ij}}{\partial u_\alpha(\mathbf{0}/k)} \frac{\partial \cos \theta_{ijk}}{\partial u_\beta(\mathbf{1}'/k')} \right)_0 + \left(\frac{\partial r_{ij}}{\partial u_\beta(\mathbf{1}'/k')} \frac{\partial \cos \theta_{ijk}}{\partial u_\alpha(\mathbf{0}/k)} \right)_0 \right], \quad (5) \end{aligned}$$

where $\varepsilon_{\alpha k}(\mathbf{q}, n)$ is polarization of the k th atom in the unit cell in the α -axis direction of the n th branch of phonon with wave vector \mathbf{q} , and

$$D_{\alpha\beta} \left(\frac{\mathbf{q}}{k, k'} \right) = \frac{1}{m} \sum_{\mathbf{l}} K_{\alpha\beta} \left(\frac{\mathbf{0}, \mathbf{l}'}{k, k'} \right) e^{-i\mathbf{q}\cdot\mathbf{l}'} \quad (2)$$

is the dynamical matrix. \mathbf{l}'_k is the lattice vector pointing to the unit cell in which atom k' is lying. In Eq. (2)

$$K_{\alpha\beta} \left(\frac{\mathbf{0}, \mathbf{l}'}{kk'} \right) = \left(\frac{\partial^2 U}{\partial u_\alpha(\mathbf{0}/k) \partial u_\beta(\mathbf{l}'/k')} \right)_0, \quad (3)$$

where $U = \sum \Phi_i$ denotes the total potential energy of the system, and Φ_i is the potential energy possessed by the i th atom. The subscript “0” means that the derivative takes value at equilibrium lattice structure, and $u_\alpha(\mathbf{0}/k)$ denotes the α th component of the displacement vector of the k th atom in the 0th unit cell.

A basic character of the vibrational motion of 2D materials is that the restoring force for the out-of-plane motion is caused by changes of bond angles [27]. This means that an effective description of the interatomic potential in this case has to be a multi-body potential. For example, the carbon–carbon potential LCBOPII [28] describes the nearest neighbor interaction between carbon atoms in graphene as a function of the bond length as well as four related bond angles. Describing the system with LCBOPII, the potential energy possessed by the i th atom Φ_i takes the following form [29,30].

$$\Phi_i = \frac{1}{2} \left[\sum_{j, |\mathbf{r}_{ij}|=a} \varphi_1(\mathbf{r}_{ij}, \theta_{ijk}) + \sum_{j, |\mathbf{r}_{ij}|=\sqrt{3}a} \varphi_2(\mathbf{r}_{ij}) + \sum_{j, |\mathbf{r}_{ij}|=2a} \varphi_3(\mathbf{r}_{ij}) \right], \quad (4)$$

where θ_{ijk} denotes the bond angle between neighboring bond \mathbf{r}_{ij} and \mathbf{r}_{ik} ($k \neq i, j$). $\varphi_1(\mathbf{r}_{ij}, \theta_{ijk})$, $\varphi_2(\mathbf{r}_{ij})$ and $\varphi_3(\mathbf{r}_{ij})$ denote respectively the

nearest neighbor interaction, the second nearest neighbor interaction and the third nearest neighbor interaction. Geometrically, \mathbf{r}_{ij} and θ_{ijk} are both function of $u_\alpha(\mathbf{0}/k)$ and $u_\beta(\mathbf{1}'/k')$ ($\alpha, \beta = 1, 2, 3$). Hence for any 2D lattice structure, the following expansion can always be done concerning the second order derivative of the nearest neighbor interaction $\varphi_1(\mathbf{r}_{ij}, \theta_{ijk})$

where $r_{ij} = |\mathbf{r}_{ij}|$. Eq. (5) expresses the force constants of the phonon vibration by six derivatives of the potential (one should notice that for $k=l$ and $k \neq l$, $\left(\frac{\partial^2 \varphi_1}{\partial \cos \theta_{ijk} \partial \cos \theta_{ijl}} \right)_0$ correspond to two different derivatives). The last five of these derivatives are closely related to the macroscopic mechanical constants of graphene [30].

For the second order derivative of the long-range interactions in graphene, an expansion similar to Eq. (5) can be obtained as

$$\begin{aligned} \left(\frac{\partial^2 \varphi_m(\mathbf{r}_{ij})}{\partial u_\alpha(\mathbf{0}/k) \partial u_\beta(\mathbf{1}'/k')} \right)_0 &= \left(\frac{\partial \varphi_m}{\partial r_{ij}} \right)_0 \left(\frac{\partial^2 r_{ij}}{\partial u_\alpha(\mathbf{0}/k) \partial u_\beta(\mathbf{1}'/k')} \right)_0 \\ &+ \left(\frac{\partial^2 \varphi_m}{\partial r_{ij}^2} \right)_0 \left(\frac{\partial r_{ij}}{\partial u_\alpha(\mathbf{0}/k)} \frac{\partial r_{ij}}{\partial u_\beta(\mathbf{1}'/k')} \right)_0, \quad (6) \end{aligned}$$

where $m = 2, 3$. The expansions in Eq. (5) and Eq. (6) are useful for analyzing the phonon spectrum and related physical properties. For graphene, we find that the first terms on the RHS of Eq. (5) and Eq.

(6) with the form $\left(\frac{\partial \varphi_k}{\partial r_{ij}} \right)_0 \left(\frac{\partial^2 r_{ij}}{\partial u_\alpha(\mathbf{0}/k) \partial u_\beta(\mathbf{1}'/k')} \right)_0$, ($k = 1, 2, 3$) (here-

after called the FOD terms) has a considerable effect on the phonon spectrum and are crucial for the NTE of graphene in low temperature range. Notice that the ground state lattice constant a_0 (here we mean the equilibrium distance between the nearest neighbors) for graphene is determined by

$$\frac{\partial \Phi_i}{\partial a} = \frac{1}{2} \frac{\partial}{\partial a} \left[\sum_{j, |\mathbf{r}_{ij}|=a} \varphi_1(\mathbf{r}_{ij}, \theta_{ijk}) + \sum_{j, |\mathbf{r}_{ij}|=\sqrt{3}a} \varphi_2(\mathbf{r}_{ij}) + \sum_{j, |\mathbf{r}_{ij}|=2a} \varphi_3(\mathbf{r}_{ij}) \right] = 0,$$

where a is the nearest neighbor distance in graphene. To make the sum of this three terms zero, $\left(\frac{\partial \varphi_k}{\partial a} \right)_0$, ($k = 1, 2, 3$) are all nonzero quantities even at ground state, which leads to nonvanishing FOD

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