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Bending sound in graphene: Origin and manifestation

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ABSTRACT

It is proved that the acoustic-type dispersion of bending mode in graphene is generated by the fluctuation interaction between in-plane and out-of-plane terms in the free energy arising with account of non-linear components in the graphene strain tensor. In doing so we use an original adiabatic approximation based on the alleged (confirmed *a posteriori*) significant difference of sound speeds for in-plane and bending modes. The explicit expression for the bending sound speed depending only on the graphene mass density, in-plane elastic constants and temperature is deduced as well as the characteristics of the microscopic corrugations of graphene. The obtained results are in good quantitative agreement with the data of real experiments and computer simulations.

1. Introduction

It is well-known that the lattice dynamics of "zero-thickness" crystals has a principal feature, which is not inherent to bulk solids. This is the logarithmic in a 2D lattice area growth of the mean-square atomic displacement at non-zero temperatures (the Peierls–Landau theorem [1]). A more "dangerous" consequence of low dimension, which might appear in 2D crystals, is connected with the classical "membrane" effect [2]: in a suspended (free-standing) state, the dispersion law of the so-called bending (out-of-plane) atomic vibrating mode $\omega_B = \sqrt{\kappa/\rho}q^2$ is quadratic upon the wave-number q; $\kappa > 0$ is the bending rigidity [2] and ρ is the mass density of 2D crystal. Then the mentioned mean-square displacement found using this law may be proportional to the 2D crystal area [3] (see also [4]). Such "membrane" effect should first of all manifest itself in graphene [5] whose comprehensive study was stimulated by work [6].

Meanwhile, the first results of numerical simulation of the normal–normal correlation function for the graphene fluctuating surface [7] showed that for small ($q < 0.1$ Å^{-1}) wave numbers it does not diverge anymore, tending to a saturation (see also papers [8,9] on simulations of the height-height correlation functions for graphene sheets). If so, then actually the eigenfrequencies of long-wave bending vibrations in graphene decrease as $q \to 0$ not faster than linearly in q like those for the in-plane vibrations. Hence, the mean-square atomic displacement in a graphene sheet depends on the sheet area at most logarithmically. However, consequent calculations for large graphene system using a modified Monte Carlo method and molecular dynamics (MD) simulations [10] did not show any saturation of the normal–normal correlation function at least for $q > 0.02$ Å^{-1} (see also [11]) that could indicate a lack of low-frequency sound segment in the graphene bending mode.

Nevertheless, the linear dispersion of the bending mode in graphene at $q \to 0$ was established in the recent papers [12,13]. In [12] this was done within the quantum theory of crystalline membrane with account of cubic interactions between in-plane and out-of-plane displacement fields and a quartic local interaction for the out-of-plane displacements. In [13] starting from a discrete atomistic model of a monolayer crystal with anharmonic coupling of third and fourth orders, a dependence $\omega_B = s_B q$ has been also obtained. It is worth mentioning the work [14], in which the linear dispersion of the bending mode at $q \to 0$ is a result of coupling between structural and electronic degrees of freedom in graphene. The found in [14] $s_B \approx 1$ km/s at 300 K turned out 15–20 times less than the in-plane sound speeds in graphene. Note that close estimate $s_B \approx 1.6$ km/s has been obtained in [15] by analogy between the phonon dispersion curves in graphene and experimental results for graphite.

It is worth mentioning the recent work [16], in which the linear dispersion of the out-of-plane acoustic mode in graphene was obtained by means of classical MD simulations. According to the results of [16], the bending sound speed s_B demonstrates very

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small size effect and changes from 0.4 km/s at 300 K to 0.6 km/s at 2000 K.

Besides, there are experimental facts that give grounds to suggest that $s_B \neq 0$ in graphene. To give a consistent explanation of the temperature dependence of the electron mobility in graphene, it was suggested in [17] that the flexural (out-of-plane) phonons are a major source of electron scattering in suspended graphene. At the same time to match the experimental data the authors of [17] suggested the existence of some (in fact, "frozen") in-plane strain in graphene (see also [18], where the ripples or microscopic corrugations of a graphene sheet are discussed). The presence of these static strains results in the linear dispersion of the bending mode at $q \to 0$. It is worth mentioning that the existence of structural corrugations ("intrinsic microscopic roughening" [19]) of the free-standing graphene with an amplitude $\sim$1 Å and a characteristic wave-length $\approx$50 Å had been observed in the transmission electron microscopy experiments [19–21].

Thus, neither the experimental data nor results of numerical simulation of the structure and phonon spectra of free standing graphene sheet demonstrate any indications of "membrane" effect in the graphene out-of-plane vibrations at $q \to 0$. So, the convincing theoretical arguments in favor of the sound-like long-wave dispersion for the bending vibrations of graphene-like 2D crystals are needed.

Strikingly small value of s_B in comparison with in-plane sound speeds of graphene indicates that the origin of the bending sound differs radically from that of in-plane modes. In the present paper, using transparent physical arguments we show that the long-wave region of the bending mode spectrum must necessarily have linear in wave number dispersion. This result is obtained through the account of the terms represented by products of bilinear combinations of both in-plane and out-of-plane deformations in the graphene elastic free energy. Note that such terms are usually ignored, and their accounting is a key point of our approach to the theory of elastic properties of quasi-2D solids. Using the known values of elastic and structure parameters of graphene, we derive the bending sound speed s_B for arbitrary temperatures without introducing any additional fitting parameters. What matters, the derived formula for s_B is independent of the graphene sample size and is expressed only through its in-plane moduli (and also third-order elastic constants) and temperature. Note that combining results of our approach with result of [12] one can verify that the considered in [12] cubic and quartic terms, which we ignored in the graphene free energy when deriving the expression for s_B, do not change the found expression at least at high temperatures. The corresponding analysis permits also to renormalize the bending rigidity coefficient κ.

The approach developed in the present work allows to reproduce with reasonable accuracy the main results of [16] referencing only to one value of s_B at a certain temperature. Besides, the mean-square out-of-plane displacement for free standing graphene of given linear size is obtained and fluctuation corrugations of graphene are also described. The theory demonstrates quantitative agreement with the experimental data and the results of computer simulations in wide temperature interval. In principle, the results of the paper may also be used for study of the dynamics of graphene-like crystals: silicene, germanene, graphane etc. (see [22–24]).

2. The "sound" segment of the free-standing graphene bending mode

For study of long-wave mechanical vibrations in graphene we use a continuum model of elastic 2D plane in 3D space. Let $\mathbf{r} = (x, y)$ be the radius-vectors of graphene points in equilibrium, $\mathbf{u}(\mathbf{r})$ and $w(\mathbf{r})$ are corresponding in-plane and out-of-plane components of displacement vectors, respectively; $\dot{\mathbf{u}}(\mathbf{r})$, $\dot{w}(\mathbf{r})$ are time-derivatives of $\mathbf{u}(\mathbf{r})$, $w(\mathbf{r})$.

Thereafter the "Hamiltonian" for long-wave mechanical vibration in hexagonal graphene can be written in the form:

$$\boldsymbol{H} = \int d\mathbf{r}\Big\{\frac{\rho}{2}\big[\dot{\mathbf{u}}^2(\mathbf{r}) + \dot{w}^2(\mathbf{r})\big] + \frac{\lambda}{2}\varepsilon_{\alpha\alpha}(\mathbf{r})\varepsilon_{\beta\beta}(\mathbf{r}) + \mu\varepsilon_{\alpha\beta}(\mathbf{r})\varepsilon_{\alpha\beta}(\mathbf{r}) + \frac{\kappa}{2}\big[\nabla^2 w(\mathbf{r})\big]^2\Big\}, \tag{1}$$

where

$$\varepsilon_{\alpha\beta}(\mathbf{r}) = \frac{1}{2}\Big[\frac{\partial u_\alpha(\mathbf{r})}{\partial r_\beta} + \frac{\partial u_\beta(\mathbf{r})}{\partial r_\alpha} + \frac{\partial u_\gamma(\mathbf{r})}{\partial r_\alpha}\frac{\partial u_\gamma(\mathbf{r})}{\partial r_\beta} + \frac{\partial w(\mathbf{r})}{\partial r_\alpha}\frac{\partial w(\mathbf{r})}{\partial r_\beta}\Big] \tag{2}$$

are in-plane components of strain tensor [2] with α, β, γ running x, y (summation in repeating subscripts is implied); ∇ is the 2D gradient, ρ is the 2D mass density, $\lambda > -\mu$ and $\mu > 0$ are Lamé coefficients. In (1) we also included the term with the bending rigidity $\kappa > 0$ which is usually taken into account when considering the flexural effects in membranes [2]. Note that this term for graphene as one-atom-thick 2D layer can not be directly considered in the framework of the elasticity theory for macroscopically "thin" plates [2]. Really, the formal expression for κ in the classical elasticity theory contains the cube of a plate thickness [2] and in application to 2D graphene sheet of "zero" thickness a macroscopic interpretation of the parameter κ becomes problematic. Nevertheless, graphene as quantum 2D lattice of carbon atoms with strong covalent bonds must possess a finite flexural rigidity due to a change of electron hybridization at microscopic bending of graphene [25]. In addition, a certain contribution to κ is attributable to non-linear terms in (2) (below we obtain explicit expression for this contribution using the approach developed in [12]). However, the modeling of bending rigidity for multilayer graphene by formulas of the classical theory of elasticity may be justified [26].

Contrary to many papers on the topic we keep the *quadratic* terms $(\partial u_\gamma(\mathbf{r})/\partial r_\alpha)(\partial u_\gamma(\mathbf{r})/\partial r_\beta)$ in the expression (2) for the strain tensor, which are usually treated as small. This is the key point of our approach.

In the free standing graphene not affected by the action of external forces the strains can have the only oscillation nature (we, surely, disregard the boundary effects). So, in the first order of perturbation theory, the terms of kind

$$\Big[\frac{\partial u_\alpha(\mathbf{r})}{\partial r_\beta} + \frac{\partial u_\beta(\mathbf{r})}{\partial r_\alpha}\Big]\frac{\partial w(\mathbf{r})}{\partial r_\alpha}\frac{\partial w(\mathbf{r})}{\partial r_\beta}, \tag{3}$$

in (1), in fact, will give zero contribution into the free-energy of the long-wave out-of-plane deformations. Indeed, the linear in the in-plane phonons factor in (3) is "rapidly fluctuating" in comparison with the quadratic one related to phonons of the bending branch (cf. the discussion concerning the speeds of the corresponding modes in the Introduction; besides, formally by the dispersion law $\omega_B = \sqrt{\kappa/\rho}q^2$ at $q \to 0$ the speed $d\omega_B/dq \to 0$). Thus, during the period of the "fast" in-plane oscillations the factor $[\partial w(\mathbf{r})/\partial r_\alpha][\partial w(\mathbf{r})/\partial r_\beta]$ in (3) can be considered as constant, and then the average of the linear on the in-plane phonons factor is obviously zero. However, in the second order of perturbation theory the terms (3) give non-zero contribution into the free-energy of the out-of-plane mode (see below in this section).[1] Moreover,

[1] Note, that the above arguments suggest that the free-standing graphene does not undergo an external (for example, from the substrate) stress. The latter can