Graphene thermal break-down induced by anharmonic bending mode

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Abstract

A novel approach is proposed allowing us to prove, self-consistently, that free-standing graphene reaching a certain temperature loses its mechanical stability resulting in abrupt breakdown, which can be interpreted as melting. Our study is based on the idea of the crucial role of the anomalously soft bending ‘sound’ mode in the jump transition of graphene from the state with relatively small bending fluctuations to a state with fluctuations close in amplitude to the graphene lattice constant. The acme of the developed theory is in establishing a quantitative relationship connecting the graphene elastic moduli of second, third (negative!), and fourth orders at the melting temperature \(T_m\) that permits us to calculate \(T_m\). The results obtained lay a theoretical foundation for an analog of Lindemann criterion for graphene.

Keywords: graphene, anharmonic lattice dynamics, specific phase transitions

(Some figures may appear in colour only in the online journal)

1. Introduction

Creating a consistent theory of melting is still one of the most important problems of statistical physics [1]. The old phenomenological Lindemann criterion (see, for example, [2, 3]), based on an intuitive connection between the average amplitude of thermal vibrations of a three-dimensional (3D) crystal and its melting temperature, allowed us to give semi-quantitative interpretation of experimental data for media of various types—from metals to dielectrics [2, 3].

However, when attempting to build a direct analog of the Lindemann parameter for graphene as a two-dimensional (2D) crystal of ‘zero’ thickness, the specific difficulties arise, which are absent in 3D solids. For example, the logarithmic divergence of the mean-square thermal fluctuations of atomic displacements for a formally infinite 2D lattice (the Peierls–Landau theorem [4]) makes meaningless the usage of the Lindemann criterion in its original form [2] when describing the 2D melting. To avoid this, it was proposed [5] to compare with the lattice constant not the absolute root-mean-square fluctuations of atomic displacements (as in the original Lindemann criterion [2]), but the fluctuations of displacements relative to a certain ‘central’ atom. With this approach, the fluctuations really become finite in the limit of an infinite 2D crystal [5], but the result depends on the number of atomic coordination spheres considered in the model, which makes the calculation of the 2D Lindemann criterion ambiguous [6]. Note that the original concept of [5] is matched to the fundamental principles of the theory of elasticity [7], since both approaches operate with relative displacements of the crystal atoms.

It is significant that the known melting condition of conventional 3D crystals [4], according to which the melting point is determined by the equality of chemical potentials (free energies) of coexisting phases, for graphene as a quasi-2D crystal in 3D space loses meaning [8]. Therefore, as an analog of the graphene ‘liquid’ phase, it was proposed [6, 8] to consider regions of quasi-1D filaments that originate inside the solid graphene when approaching the melting temperature. Besides, in [6, 8], using numerical simulation methods, it was shown that at temperatures preceding the melting of graphene, an increase in the number of the so-called Stone–Wales...
5775 defects with a formation energy of ≈4.6 eV [9, 10] is observed.4

Note that in [5] there was no mention of the possible role of the bending mode in the heat transformations of graphene lattice. Until recently, this mode, by analogy with the bending vibrations of thin plates [7], was attributed to the quadratic dispersion law with respect to the wave number k (see, for example, [12]). However, in our work [13] it was shown that the real dispersion law of the bending mode of graphene in the small k region should contain a ‘sound’—linear in k—segment with anomalously low sound velocity v0 < 1 km s⁻¹ (15–20 times less than the in-plane sound velocities of the graphene layer).5 An important feature of the graphene bending mode is that its ‘sound’ segment has purely fluctuation origin, therefore the velocity of the bending ‘sound’ is a growing function of temperature [13, 15]. On the other hand, the very fact of the existence of a ‘sound’ dispersion of the bending mode at small k makes the divergence of the out-of-plane mean-square fluctuation displacements in graphene not more ‘dangerous’ than logarithmic [13], which leads to the elimination of the ‘catastrophic’—power-type on the 2D sample size—divergences resulting from the membrane model [12].

The development of the ideas of paper [13] made it possible to demonstrate [15] the important contribution of the bending acoustic mode to the graphene thermal expansion. The existence of the extended ‘low-temperature’ region of thermal contraction in graphene [16–19] is mainly due to the ‘soft’ bending mode. At the same time, the effect of the graphene thermal contraction, itself, was consistently described [15] only by going beyond the quasi-harmonic approximation.

In this paper, we show that in addition to the phenomena considered in [13, 15], the anomalously ‘soft’ bending mode play a dominant role in the phase transformation which could be interpreted as a natural analog of graphene melting. We will see that due to the peculiarities of this mode, at a certain temperature graphene abruptly jumps to a state with anomalously large amplitude of out-of-plane fluctuation displacements (Section II), which can be considered as a sign of melting, whatever the nature of the emerging ‘melt’.6 Hereinafter, for definiteness, the corresponding phase transformation is conventionally called ‘melting’. The key point in the very possibility of such a transition, as it turns out, is negativity of the anharmonic third-order elastic moduli of graphene. The modeling of graphene as 2D elastic continuum with certain elastic coefficients allows us not only to introduce the concept of bending ‘sound’ in a consistent way, but also to find a convergent value for the 2D analog of Lindemann criterion (section 3). The numerical results given in section 4 demonstrate the realistic values of characteristic parameters

(1)  
\[ \varepsilon_{\alpha\beta}(u, w) = \frac{1}{2} \left( \partial_\alpha u_\beta(r, t) + \partial_\beta u_\alpha(r, t) + \partial_\alpha u_\gamma(r, t) \partial_\beta w_\gamma(r, t) \right) + \partial_\alpha w_\beta(r, t) \partial_\beta w_\alpha(r, t), \partial_\alpha \equiv \frac{\partial}{\partial r_\alpha}. \]

2. Anharmonic effects and basic principles of the theory of graphene melting

As in our previous studies [13, 15], we simulate graphene as a quasi-2D elastic medium described by quasi-2D local (dependent on time t) strain tensor \( \varepsilon_{\alpha\beta}(r, t) \):7

\[ H(\mathbf{u}, w) = \int d\mathbf{r} \left[ \frac{\rho}{2} (\partial_\alpha u_\beta)^2 + \frac{\kappa}{2} \varepsilon_{\alpha\beta\gamma\delta} \varepsilon_{\gamma\delta} + \mu \varepsilon_{\alpha\beta\gamma\delta} \varepsilon_{\gamma\delta} + \frac{\rho}{2} \left( \partial_\alpha \varepsilon_{\beta\gamma\delta} \varepsilon_{\gamma\delta} + \partial_\beta \varepsilon_{\alpha\gamma\delta} \varepsilon_{\gamma\delta} + \partial_\gamma \varepsilon_{\alpha\beta\delta} \varepsilon_{\delta} \right) \right]. \]

Here \( \rho \) is the 2D mass density of graphene, \( \mu > 0 \) and \( \lambda > -\mu \) (in fact, \( \lambda > 0 \), see [7, 21]) are the 2D Lamé coefficients; \( C_{111} \leq 0 \) and \( C_{112} \leq 0 \) [22–24] are the third order elastic coefficients (we put \( C_{222} = C_{111} \), as in isotropic model) whereas \( a_0 \), \( b_0 \), \( c_0 \), and \( d_0 \) are the fourth order elastic coefficients. Besides, \( \kappa > 0 \) is the so-called bending rigidity and \( \nabla \) is the 2D gradient; \( \mathbf{u} \) and \( \mathbf{w} \) denote the so-called material time-derivatives [25] of the local displacements of material points of graphene as a quasi-2D continuum medium (for more details, see [15]).

From (2) with taking account of (1), it follows that the quantized fields \( \mathbf{u} \) and \( \mathbf{w} \) are formally interacting. However, as shown by detailed analysis in [13, 15], their interaction in graphene is effectively eliminated at each temperature virtually by heat averaging the cross-components like \( \partial_\beta u_\alpha \partial_\gamma u_\beta \partial_\alpha w_\gamma \) and \( \partial_\alpha w_\beta \partial_\beta w_\alpha \partial_\gamma u_\gamma \partial_\delta u_\delta \) (in 2) using the density operator for the harmonic Hamiltonian \( H_0 \) of the ‘fast’ in-plane modes:

\[ H_0 = \int d\mathbf{r} \left[ \frac{\rho}{2} \left( \frac{\partial \mathbf{u}}{\partial t} \right)^2 + \lambda \left( \partial_\alpha u_\beta \partial_\beta u_\alpha \right) + \mu (\partial_\alpha u_\beta \partial_\beta u_\alpha) \right], \]
where \( u_{\alpha\beta} \equiv (\partial_\alpha u_\beta + \partial_\beta u_\alpha)/2 \) is the linear part of the strain tensor (1).

We emphasize that namely the ‘soft’ bending mode may be considered as a factor due to which graphene can most easily lose its stability at high temperatures. As for the ‘hard’ in-plane acoustic fluctuations, we will take them into account as a source of possible temperature dependences of the elastic coefficients of graphene. Given this, the phenomenon of graphene melting can be clarified using shortened Hamiltonian:

\[
H_w = \int d\mathbf{r} \left[ \frac{\alpha}{2} \left( \frac{\partial w}{\partial t} \right)^2 + \frac{\beta}{2} (\nabla w)^2 + \frac{\gamma}{2} (\nabla^2 w)^2 + C_{111}(T) (\nabla w)^4 + C_{111}^{\prime \prime} (\nabla w)^6 + C_{222}^{\prime \prime} (\nabla w)^8 \right],
\]

(4)

which is the ‘bending’ part of the general expression (2). In (4), \( B(T) \) is the temperature-dependent bending modulus of graphene [13, 15]; also, we allowed, beforehand, the possibility of a temperature dependence of the second-order elastic modulus \( C_{111}(T) \), with \( C_{111}(0) = \lambda + 2\mu \). Besides, expression (4) contains a ‘consolidated’ fourth-order elastic modulus \( C_{111} + a_4 + b_4 + c_4 + d_4 > 0 \), the value of which, in principle, can be reconstructed from the results of numerical simulations for graphene [24, 26]. Within the scope of this work, the ‘anharmonic’ elastic moduli \( C_{111} < 0 [22–24, 26] \) and \( C_{111} > 0 [24] \) can be considered as constants. Note, that just the term in (4) with a positive coefficient determined by fourth-order elastic moduli in Hamiltonian (2) ensures the stability of graphene with respect to large bending fluctuations.

A direct calculation of the contribution \( F_w(T) \) based on the Hamiltonian (4) to the total free energy of graphene so far is not real. We have to some extent overcome this difficulty reducing approximately \( H_w \) to some pseudo-harmonic (superscript (p-h)) ‘bending’ Hamiltonian \( H_w^{(p-h)} \). In general terms, the idea of obtaining \( H_w^{(p-h)} \) can be understood by the example of an approximate representation of the anharmonic terms in the integrand in (4) using the following rule:

\[
\langle (\nabla w)^4 \rangle \approx \langle (\nabla w)^2 \rangle^2 \langle (\nabla w)^2 \rangle^2, \langle (\nabla w)^6 \rangle \approx \langle (\nabla w)^4 \rangle^2 \langle (\nabla w)^2 \rangle^2, \langle (\nabla w)^8 \rangle \approx \langle (\nabla w)^6 \rangle \langle (\nabla w)^2 \rangle^2.
\]

(5)

As shown in appendix A, within the framework of the resulting ‘pseudo-harmonic’ problem, the fluctuation averages in (5) are expressed through the powers of the ‘irreducible’ average \( \langle (\nabla w)^2 \rangle \) using the general formula:

\[
\langle (\nabla w)^{2n} \rangle = n! \langle (\nabla w)^2 \rangle^n, n \geq 1.
\]

(6)

In the next section, we obtain a closure condition of the problem in the form of a self-consistent equation for \( \langle (\nabla w)^2 \rangle \).

The derivation of the pseudo-harmonic ‘bending’ Hamiltonian of graphene \( H_w^{(p-h)} \) is given in appendix B; the resulting expression is as follows:

\[
H_w^{(p-h)} = \int d\mathbf{r} \left[ \frac{\rho}{2} \left( \frac{\partial w}{\partial t} \right)^2 + \frac{1}{2} B(Q; T) (\nabla w)^2 + \frac{\kappa}{2} (\nabla^2 w)^2 \right].
\]

(7)

Here, a pseudo-harmonic bending modulus (see (B.20))

\[
B(Q; T) \equiv B(T) + B_0(t)[\eta(T) Q - 3Q^2 + 3Q^3],
\]

(8)

is expressed through the redefined mean square of the gradient of the graphene out-of-plane displacement

\[
Q \equiv \frac{2C_{111}}{3}\langle (\nabla w)^2 \rangle_w
\]

(9)

and a dimensionless ‘controlling’ parameter (which depends on temperature through \( C_{111}(T) \))

\[
\eta(T) \equiv \frac{8C_{111}}{3C_{111}^{\prime \prime}} C_{111}(T).
\]

(10)

It is clear, that in the high-temperature limit of interest, the information about a model parameter \( T_0 \) drops out from (8) and (B.20).

Based on (7), we obtain a dispersion law of the ‘pseudo-harmonic’ bending mode of graphene:

\[
\left[ \omega_B^{(p-h)}(k) \right]^2 = s_B^2(Q; T) k^2 + \frac{\kappa}{\rho} k^4, s_B(Q; T) \equiv \sqrt{\frac{B(Q; T)}{\rho}}.
\]

(11)

For purely harmonic bending mode (i.e. neglecting the terms with \( Q \) in (8)) we return to the dispersion law [13, 15]

\[
\omega_B^2(k) = s_B^2 k^2 + \frac{\kappa}{\rho} k^4
\]

(12)

with the sound velocity \( s_B \equiv \sqrt{B(T)/\rho} \) characterized by the ‘bare’ bending modulus of graphene \( B(T) \).

3. Threshold singularity of the bending mode as a sign of graphene melting

If \( \eta(T) < 1 \), then, as is easily seen from (8), function \( B(Q; T) \) passes through a maximum and a minimum at points \( Q_c = (1 - \sqrt{1 - \eta(T)})/3 \) and \( Q_+ = (1 + \sqrt{1 - \eta(T)})/3 \), respectively. Further, if \( \eta(T) < 3/4 \), then function \( \eta(T) Q - 3Q^2 + 3Q^3 \) has a range of negative values. The latter circumstance is especially important since in this case it is possible to achieve small (in principle, arbitrarily small) values of the ‘pseudo-harmonic’ bending modulus, which is a necessary prerequisite for the implementation of solutions with ‘large’ (−1) values of \( Q \). The abrupt transition from \( Q \ll 1 \) to \( Q \sim 1 \) upon reaching a certain temperature \( T_m \) will be interpreted as a sign of the graphene melting.

It is worth mentioning that the use of the function \( \eta(T) Q - 3Q^2 + 3Q^3 \), which depends on the redefined

}\]

\]
dimensionless variable $Q$, makes it possible to describe the melting phenomenon in the most general form, not limited to the specific numerical values of the elastic moduli of different orders. We will see that the appearance of a ‘special’ (with $Q \sim 1$) solution of a self-consistent equation is of a fundamentally threshold nature. In this case, at the very threshold point the solution with $Q \sim 1$ will correspond to a lower free energy of the graphene bending mode fluctuations than the ‘regular’ (with $Q \ll 1$) solution.

In the framework of the proposed approach, the analysis of the phenomenon of graphene melting can be given, based on the expression for $\left(\nabla w\right)^2$, derived in our works [13, 15]. Replacing the ‘bare’ bending modulus $B(T)$ with the ‘pseudo-harmonic’ one $B(Q; T)$ in accordance with (7), (8) and taking into account (10) and (11), we arrive at a self-consistent equation for finding possible values of $Q$:

$$Q = \frac{hC_{1111}}{6\pi\rho C_{1111}} \int_0^{k_{\text{max}}} \frac{k^3 dk}{\omega_p^{(B)}(k)} \left[ \frac{1}{e^{\eta C_{1111}}(k)/T} - 1 \right]^{\frac{1}{2}},$$  \hspace{1cm} (13)

where $k_{\text{max}} = \sqrt{4\pi\rho/m}$ is the maximum wave-number in the Debye model [13, 15]. Further, since the melting of graphene occurs at a temperature of $\approx 4500$ K, the right-hand side of (13) can be taken in the high temperature limit (as in [13]), and then we obtain the desired self-consistent equation in the form:

$$Q = \frac{C_{1111}T}{6\pi|C_{1111}|\kappa} \ln \left[ 1 + \frac{4\pi\kappa\rho}{mB(Q; T)} \right].$$  \hspace{1cm} (14)

First of all, it is obvious that equation (14) at all temperatures contains the above mentioned ‘regular’ (superscript (R)) solution, $Q^{(R)} \ll 1$ (for details see section 4). In addition, using equation (14), one can determine the threshold for the appearance of the desired ‘special’ (superscript (S)) solution $Q^{(S)} \sim 1$. To do this, it suffices to find the temperature $T_m$ and the value of variable $Q_m^{(S)}$ at the point of tangency of the left and right sides of equation (14). One of the conditions of tangency will be the fulfillment of equality (14) itself, and the second is the equality of the derivatives of the left and right sides of (14) at $T = T_m$ and $Q = Q_m^{(S)}$. As a result, two equations for determining $T_m$ and $Q_m^{(S)}$ will have the form:

$$Q_m^{(S)} = \frac{C_{1111}T_m}{6\pi|C_{1111}|\kappa} \ln \left[ 1 + \frac{4\pi\kappa\rho}{mB(Q_m^{(S)}; T_m)} \right];$$  \hspace{1cm} (15)

$$1 = 1 - \frac{2C_{1111}T_m\rho B'(Q_m^{(S)}; T_m)}{3|C_{1111}|[4\pi\kappa\rho + mB(Q_m^{(S)}; T_m)]B(Q_m^{(S)}; T_m)},$$  \hspace{1cm} (16)

where

$$B'(Q_m^{(S)}; T_m) = \frac{\partial B(Q; T_m)}{\partial Q} \bigg|_{Q_m^{(S)}}.$$  \hspace{1cm} (17)

The temperature $T_m$ at which the ‘special’ solution $Q_m^{(S)}$ abruptly appears could be naturally identified with the melting temperature of graphene.

4. Self-consistent calculation of the graphene melting criterion and numerical estimates

The solution of system (15) and (16) is radically simplified due to the following circumstance. As will be shown, the required value $Q_m^{(S)} \approx 0.5$ is many times greater than the coefficient in front of the logarithm on the right-hand side of equation (15). Indeed, taking for estimation $C_{1111} \approx |C_{1111}|$ (we will see this below) and assuming $\kappa \approx 1.5\text{eV}$ [21], $T_m \approx 4500$ K [6, 8], we have $3\pi|C_{1111}|\kappa/(C_{1111}T_m) \approx 36$, i.e. $mB(Q_m^{(S)}; T_m)/(4\pi\kappa\rho) \approx 10^{-17}$. This means that in equation (16) with the highest accuracy one can put $B(Q_m^{(S)}; T_m) = 0$, and therefore $B'(Q_m^{(S)}; T_m) = 0$, as well. From here we get two equalities:

$$\eta(T_m)Q_m^{(S)} - \frac{3}{2}Q_m^{(S)} + \frac{3}{2}Q_m^{(S)^3} = \frac{B(T_m)}{B_0(T_m)},$$

$$\eta(T_m) - 6Q_m^{(S)} + 9Q_m^{(S)^2} = 0.$$  \hspace{1cm} (18)

Thus, one of the conditions for the appearance of the ‘special’ solution of equation (14) is the practical vanishing of the ‘pseudo-harmonic’ bending modulus at the threshold point. This result, in some sense, returns us to the old idea [28] that when approaching the melting point of a crystal, its shear modulus should tend to zero. However, it was later shown [3] that the assumption [28] is inconsistent with the state of affairs in the melting of real crystals. However, using the example of graphene, we have seen that some effective combination of the elastic moduli (including anharmonic ones!) really undergo an extreme softening at the melting point of the material.

If $B(T_m)/B_0(T_m) \ll 1$ (and this is true for graphene, see below), then up to the principal terms, the solutions of equations (18) are as follows:

$$Q_m^{(S)} = \frac{1}{2} + \frac{2B(T_m)}{3B_0(T_m)}, \quad \eta(T_m) = \frac{3}{4} - \frac{2B(T_m)}{3B_0(T_m)}.$$  \hspace{1cm} (19)

Substituting the solution for $\eta(T_m)$ from (19) into (10), we immediately obtain an expression relating the elastic moduli of different orders between themselves at the melting point of graphene:

$$\frac{32C_{1111}}{9|C_{1111}|^2}C_{1111}(T_m) + \frac{8B(T_m)}{3B_0(T_m)} = 1.$$  \hspace{1cm} (20)

Equation (20) implicitly determines the melting temperature $T_m$ of graphene, which can be considered as one of the central results of the paper. If we neglect the small second term on the left-hand side of (20), then to find $T_m$ it is necessary to have information about the temperature dependence of the second-order elastic modulus $C_{111}$ (T). Then, with the known values of the anharmonic constants $C_{111}$ and $C_{1111}$, the value of $T_m$ for graphene can be found from equation (20).

The dependence $C_{111}(T)$ can be established using the results of simulations [29], wherefrom one can determine the value of $C_{111}(T_m)$. Taking $C_{111}(0) \approx 330$ N m$^{-1}$ [17], estimating the change of $C_{111}(T)$ with temperature according to [29] and assuming $T_m \approx 4500$ K [6, 8], we get $C_{111}(T_m) \approx 293$ N m$^{-1}$, which corresponds to a relative
change \([C_{11}(0) - C_{11}(T)]/C_{11}(0) \approx 11\%\). However, given below in this section (see also appendix C) our estimate of such a change is about half as much, which gives \(C_{11}(T) \approx 314\text{ N m}^{-1}\).

Equation (20) is especially important because, as far as the authors know, only the paper [24] reported the calculation of the elastic constants of the fourth (and also the fifth!) order for graphene using the density functional theory (DFT) method. In paper [15], to match our results on the velocity of the moduli for graphene can be obtained by analyzing the results and setting \(T = 0\), referring to data analysis [26], and also retained the notation \(C_{111}\) for the ‘consolidated’ elastic modulus of the fourth order (see above).

In the on-hand, information about fourth-order elastic moduli for graphene can be obtained by analyzing the results of [26] obtained by MD simulations and DFT calculations. As for third-order elastic moduli (we assume \(C_{111} = C_{222}\)), it was actually established in [26] that their possible values in graphene lie in the range from \(-1100\text{ N m}^{-1}\) to \(-1400\text{ N m}^{-1}\) (see the above estimate from [15]). However, the question of fourth order moduli was not discussed in [25]. Meanwhile, based on the Hamiltonian of graphene (2) and considering the uniaxial strain \(\varepsilon\), we can write the following non-linear expression for uniaxial stress (see [24]):

\[
\sigma = C_{11}(0)\varepsilon + \frac{1}{2}C_{111}\varepsilon^2 + \frac{1}{6}C_{1111}\varepsilon^3,
\]

where we put \(T = 0\), referring to data analysis [26], and also retained the notation \(C_{111}\) for the ‘consolidated’ elastic modulus of the fourth order (see above).

In figure 1, as an example, we represent the stress–strain data obtained in [26] by MD simulations (squares) and by DFT method (diamonds) for armchair configuration of graphene edges. Our fittings of these data using equation (21) are shown in figure 1 by corresponding solid curves with parameters: \(C_{11}(0) = 328\text{ N m}^{-1}\), \(C_{111} = -1270\text{ N m}^{-1}\), \(C_{1111} = 960\text{ N m}^{-1}\)(MD) and \(C_{11}(0) = 328\text{ N m}^{-1}\), \(C_{111} = -1470\text{ N m}^{-1}\), \(C_{1111} = 960\text{ N m}^{-1}\)(DFT). In addition, in figure 1 we show a thick curve constructed from equation (21) with the values of the parameters \(C_{11}(0) = 328\text{ N m}^{-1}\), \(C_{111} = -1000\text{ N m}^{-1}\), \(C_{1111} = 900\text{ N m}^{-1}\), which we consider as preferable within the framework of our theory; this curve also falls within the error range (dashed lines) of the experiment [23]. Besides, in figure 1 we also show the DFT data [24] for zigzag configuration (circles); our best fitting of these data by equation (21) (solid line) led to the next values: \(C_{11}(0) = 350\text{ N m}^{-1}\), \(C_{111} = -2450\text{ N m}^{-1}\), \(C_{1111} = 7640\text{ N m}^{-1}\). At last, the dash-dotted line in figure 1 depicts the fitting of the data [24] by equation (21) with \(C_{11}(0) = 315\text{ N m}^{-1}\), \(C_{111} = -1620\text{ N m}^{-1}\), \(C_{1111} = 1000\text{ N m}^{-1}\) (see the corresponding comment in section 5).

Thus, the processing of the simulation stress–strain dependences for graphene (figure 1) shows that the data of [26] are closer to what is predicted by our theory than the data of [24]. Therefore, it can be expected that the estimates of the elastic parameters of graphene at a level of \(C_{11}(0) \approx 330\text{ N m}^{-1}\), \(C_{111} \approx -1000\text{ N m}^{-1}\), \(C_{1111} \approx 900\text{ N m}^{-1}\), can already be used as a basis for describing the phenomenon of graphene melting according to the scheme proposed in this work. Note that with these values of elastic moduli, using formula (10), we obtain \(\eta(0) \approx 0.788\). In addition, taking these estimates, using the above values of the remaining parameters, and setting \(T_0 = 1000\text{ K}\), we find from expressions (8), (B.12) and (B.13): \(B(T_m) \approx 0.448\text{ N m}^{-1}\), \(B_0(T_m) \approx 578\text{ N m}^{-1}\). This implies the following estimate: \(B(T_m)/B_0(T_m) \approx 7.76 \cdot 10^{-4}\), which justifies the inequality used above.

As already mentioned, from the self-consistent equation (14) at any temperature, one can find a ‘regular’ solution \(Q^R \ll 1\), and then return to the out-of-plane quantity by formula (9):

\[
\sqrt{\frac{\langle (\nabla w^R)^2 \rangle_w}{\langle \nabla w^R \rangle_w}} \equiv \sqrt{\frac{3|C_{111}|}{2C_{1111}} Q^R}.
\]

The temperature dependence of this quantity at the above values of parameters is shown in figure 2 by curve 1(R) (blue). On the other hand, at \(T \geq T_m\), equation (14) contains the aforementioned ‘special’ solution \(Q^S \sim 1\), defining another out-of-plane quantity

\[
\sqrt{\frac{\langle (\nabla w^S)^2 \rangle_w}{\langle \nabla w^S \rangle_w}} \equiv \sqrt{\frac{3|C_{111}|}{2C_{1111}} Q^S}.
\]

In figure 2, curve 1(S) (blue) represents the temperature dependence of the quantity (23) for the above values of the parameters. In addition, curve 2 (red) in figure 2 shows the temperature dependence of the in-plane quantity \(\sqrt{\langle \partial_{\alpha\beta}\partial_{\alpha\beta}u_\alpha u_\beta \rangle_w^R}\) derived by equation (B.13). By the arrow in figure 2 we mark a jump of the out-of-plane-quantity into the state with abnormally large (determined by the value \(Q^S_m \approx 0.5\)) fluctuations at the melting temperature \(T_m = 4950\text{ K}\).

The analysis shows that the ‘regular’ solution of equation (14) at temperature \(T_m\) has the value \(Q^R_m \approx 0.017\), whereas the corresponding value of the ‘pseudo-harmonic’ bending modulus of graphene turns out to be small, but quite finite: \(B(Q^R_m)/T_m \approx 7.93\text{ N m}^{-1}\), so that \(B(Q^R_m)/T_m \approx 1.37 \cdot 10^{-2}\). Considering now equation (22) at \(T = T_m\), substituting in it the found value \(Q^R_m\) and the above numerical estimates for anharmonic elastic moduli, we arrive at the following definition of the out-of-plane ‘Lindemann parameter’ for graphene:

\[
L_m \equiv \sqrt{\frac{\langle (\nabla w_m^R)^2 \rangle_w}{\langle \nabla w_m^R \rangle_w}} = \sqrt{\frac{3|C_{111}|}{2C_{1111}} Q^R_m} \approx 0.176.
\]
The dimensionless quantity $L_w$ can serve as a quantitative characteristic of the melting phenomenon of graphene, similar to the well-known phenomenological melting criterion of Lindemann [2, 3]. A close physical connection of $L_w$ with the usual definition of the Lindemann parameter [2] is evident from the fact that $\sqrt{\left< \left( \nabla w^{(R)} \right)^2 \right>_{w}}$ has the meaning of averaged relative amplitude of bending thermal vibrations of graphene atoms at the threshold of the appearance of the ‘special’ solution of the self-consistent equation (14). Therefore, the estimate given in (24) can be considered, even by the numerical value (close to typical values $\approx 0.25$ for 3D solids [2]), as a direct analog of the Lindemann criterion with respect to the graphene melting.

In addition to (24), it is easy to estimate the averaged relative amplitude of thermal vibrations of atoms in the graphene

**Figure 1.** Stress–strain data for graphene extracted from literature sources. The results obtained in [26] for armchair configuration of graphene edges are shown by squares (MD simulations) and by diamonds (DFT method). Our processing of these data using equation (21) is shown by the corresponding solid lines (the parameter values are in the text). The thick solid curve is constructed according to equation (21) with the following parameter values: $C_{11}(0) = 328 \text{ N m}^{-1}$, $C_{111} = -1000 \text{ N m}^{-1}$, $C_{1111} = 900 \text{ N m}^{-1}$. DFT data from [24] are given by circles; their best fitting according to equation (21) is shown by the corresponding solid curve (the parameter values are in the text), whereas the dash-dotted line depicts the fitting of the data [24] by equation (21) with $C_{11}(0) = 315 \text{ N m}^{-1}$, $C_{111} = -1620 \text{ N m}^{-1}$, $C_{1111} = 1000 \text{ N m}^{-1}$ (the corresponding comment is given in section 5). The dashed lines represent the boundaries of the experimental error [23] (see [22]).

**Figure 2.** Temperature dependences of the out-of-plane quantities derived by equation (22) (curve 1(R), blue) and by equation (23) (curve 1(S), blue). The temperature-dependent in-plane quantity according to equation (B.13) is shown by curve 2 (red). When building these curves we used the following values of elastic parameters: $C_{11}(0) = 328 \text{ N m}^{-1}$, $C_{111} = -1000 \text{ N m}^{-1}$, $C_{1111} = 900 \text{ N m}^{-1}$. The arrow indicates the melting temperature of graphene $T_m$, at which the jump of the out-of-plane quantity occurs into the state with abnormally large fluctuations. Continuations of the ‘regular’ out-of-plane quantity (22) and the in-plane quantity (B.13) into the metastable region (i.e. above $T_m$) are indicated by dotted lines.
plane at the melting threshold introducing the in-plane analog of the ‘Lindemann parameter’:

\[ L_u \equiv \sqrt{\langle \partial_u u_{\beta\lambda}\partial_u u_{\beta\lambda} \rangle_u} \approx 0.164, \]  

(25)

where the thermal average \( \langle \ldots \rangle_u \) is calculated using the in-plane Hamiltonian (3). We note the proximity of the estimates for \( L_0 \) and \( L_u \) and emphasize once again that for the consistent analysis of the melting phenomenon of graphene, it is fundamentally necessary to take into account third- and fourth-order anharmonic invariants for the strain tensor in the elastic Hamiltonian (see (2)).

Let us now dwell on one essential point. As is known [4], the important characteristics of a phase transition are the conditions that the thermodynamic functions of the coexisting phases must satisfy. For example, at the melting point of an ordinary 3D solid, its free energy (specific) must coincide with the free energy of the resulting liquid, but the entropy, expressed through the temperature derivative of the free energy, will experience a jump. Let us show that, according to the theory of 2D melting under consideration, already the graphene free energy itself (or rather, its bending part) should experience a jump at the transition point. Our consideration is based on the following expression for the dimensionless free energy of bending vibrations of graphene per cell (see equation (19) from [15]):

\[ f_m[\xi_\omega; \xi_\omega(Q; T)] = \frac{1}{\xi_\omega} \int_{\xi_\omega}^{\infty} \xi \ln \left\{ 1 - \exp \left[ -\sqrt{\xi^2 + \xi_\omega(Q; T)} \right] \right\}, \]  

(26)

where the following notations are used:

\[ \xi_\omega \equiv \frac{\theta_\omega}{T}, \xi_\omega(Q; T) \equiv \frac{h}{T} \sqrt{\frac{T}{\kappa}} \xi_\omega(Q; T). \]  

(27)

Calculations using formula (26) with the above values of parameters confirm that the free energy corresponding to the ‘special’ root \((f_m^{(S)} = -4.812)\) already at the threshold of its appearance is less than the free energy corresponding to the ‘regular’ root \((f_m^{(R)} = -4.518)\). This means that the transition of graphene to the ‘melting’ state is energetically favorable, although a complete analogy with the thermodynamics of melting of 3D crystals is excluded (see Introduction and section 5).

We now turn to expression (C.6) (with taking account of (C.7)) that determines the temperature dependence of the second-order elastic modulus (see appendix C) and rewrite this expression in the form:

\[ C_{11}(T) = (\lambda + 2\mu) \left( 1 - \frac{T}{T_\infty} \right), \]  

(28)

where a certain characteristic temperature appears:

\[ T_\infty \equiv \frac{m\mu(\lambda + 2\mu)^2}{\rho(\lambda + 3\mu)C_{11}^{(T)}}. \]  

(29)

Assuming that \( C_{1111} \approx a_1 + b_1 + c_1 + d_1 = 900 \text{ N m}^{-1}, \ C_{1112} \approx C_{111} / 5 \) [30] and estimating the expression in parentheses of (C.7) as \( \approx 2C_{1111} \) we find \( C_{11}^{(T)} \approx 750 \text{ N m}^{-1} \). Further, substituting into (29) the well-known [17] numerical values of the graphene parameters: \( \rho = 7.6 \times 10^{-8} \text{ g cm}^{-2}, \mu \approx 3\lambda \approx 9 \text{ eV Å}^{-2}, m = 2 \times 10^{-23} \text{ g} \) and using the above estimate of \( C_{11}^{(T)} \), we find for the characteristic temperature the value \( T_\infty \approx 82000 \text{ K} \). Processing the results of numerical calculations of the graphene elastic characteristics [29] leads to the values \( T_\infty \approx 40000-53000 \text{ K} \).10

It is useful to note that in energy units, the given estimates for \( T_\infty \) are in order of magnitude consistent with the formation energy \( E_{\text{sw}} \) of the Stone–Wales defect in graphene. Really, besides the value \( E_{\text{sw}} \approx 4.6 \text{ eV} \) [9, 10] indicated in the Introduction, in the literature one can find calculated values from 4.8 eV and 5.2 eV [31] to 5.8 eV [32] and even 6.0 eV [33]. It should be borne in mind that the estimation of \( T_\infty \) should rather be associated not with \( E_{\text{sw}} \), but with the height of the barrier, which separates the ground state of graphene and the state in the presence of the Stone–Wales defect. Taking into account the estimate for this barrier height \( \approx 9-10 \text{ eV} \) [31], we come to the conclusion that it correlates well with the found above value \( T_\infty \). Thus, we see that the proposed model, which considers the fluctuation vibrations of the crystal lattice as the resulting cause of its melting [2, 3], does not contradict the ‘defect’ model of melting [3, 6, 8] (for more details, see section 5).

Note that if we use expression (10), substitute (28) into it at \( T = T_\infty \) and take into account that \( \eta(T_m) = 3/4 \) (we neglect the term with \( B(T_m)/B_0(T_m) \ll 1 \)), then we obtain the relation:

\[ \frac{T_m}{T_\infty} = 1 - \frac{3}{4\eta(0)}. \]  

(30)

This relation directly expresses the graphene melting temperature \( T_m \) through its characteristic temperature \( T_\infty \) and the dimensionless combination of elastic moduli of second, third, and fourth orders at zero temperature (of course, it should be \( \eta(0) > 3/4 \)).

In fact, equation (30) is a simplified analog of formula (20), if in the latter one neglects the small value \( 8B(T_m)/[3B_0(T_m)] \). Table 1 shows the results of self-consistent calculation of the characteristic parameters of graphene using equation (20). Naturally, these results somewhat differ from those obtained from equation (30).

Note the sharp dependence of \( T_m \) on the difference \( \eta(0) - 3/4 \) (see table 1). This means that in order to obtain

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
\( C_{1111} \) & \( \eta(0) \) & \( T_\infty \) & \( T_m \) & \( L_0 \) & \( L_u \) \\
\hline
890 & 0.779 & 81560 & 4030 & 0.164 & 0.148 \\
895 & 0.784 & 81650 & 4490 & 0.170 & 0.156 \\
901 & 0.789 & 81760 & 5040 & 0.178 & 0.165 \\
906 & 0.793 & 81850 & 5490 & 0.183 & 0.172 \\
912 & 0.799 & 81960 & 6030 & 0.190 & 0.180 \\
\hline
\end{tabular}
\end{table}

10 Similar processing of the data [17] gives a much smaller value: \( T_\infty \approx 16000 \text{ K} \).
reliable information about $T_m$, it is necessary to know as accurately as possible the value of $\eta(0)$ (or the value of $\mathcal{C}_{1111}$ for given values of $\mathcal{C}_{11}(0)$ and $\mathcal{C}_{1111}$). This conclusion is in qualitative agreement with the statement [1] that to accurately predict the melting point (of silicon [1]), it is necessary to know the free energies of the solid and liquid phases with very high precision.

5. Discussion and conclusions

The results obtained in this work allow us to associate the melting phenomenon of quasi-2D graphene crystal with the temperature transformation of an anomalously soft bending mode, whose `sound’ dispersion at small wave numbers is entirely determined by fluctuation effects in the ensemble of in-plane oscillations [13]. Although the melting mechanism itself is determined to a decisive degree by the anharmonic properties of the material, however, precisely due to the natural softening of second-order elastic moduli, graphene at a certain (rather high) temperature can enter a new phase, which in principle does not exist at lower temperatures. This transition is of threshold-type; it is characterized by a sharp increase in the root-mean-square deviations of the graphene surface from the flat. At the same time, the new phase (‘melt’) already at the point of its origin turns out to be energetically more favorable than the initial—crystalline—phase.

It is necessary to immediately emphasize the difference between the proposed approach and mechanical single-phase melting models [3] (for example, in the old paper [28], the melting temperature was determined by the condition that the shear modulus of a crystal vanishes). In the proposed approach, the melting point of graphene is associated with the sudden appearance of a new solution of the self-consistent equation for the root-mean-square fluctuations of the bending strain tensor, and not with some limit condition on the regular—‘crystalline’—solution. It is interesting, however, that some effective construction—the ‘pseudo-harmonic’ bending modulus of graphene—still turns out to be very close to zero at the melting point. The melting characteristics of graphene themselves (the melting temperature and the value of the Lindemann constant) naturally depend on its elastic moduli not only of the second, but also of the third and fourth orders. In this case, the analog of the Lindemann constant for graphene calculated in this work turns out to be numerically close to the empirical value ($\approx 0.25$) typical for 3D crystals [2]. It is important to note that all the parameters of the theory, in principle, can be found independently (both from real experiments and using numerical simulation of the elastic characteristics of graphene). Given the fact that the theoretical criterion for the graphene melting includes both harmonic and anharmonic elastic moduli (see equation (24)), it can be argued, that just through the dimensionless combination of these moduli should be expressed the empirical numerical coefficient, which is present in the purely ‘harmonic’ 3D formula of Lindemann [2].

We pay special attention to the following circumstance. As is well known (see, for example, [3]), along with the so-called ‘oscillatory’ models of melting (on which, in fact, the Lindemann formula is based), there are also approaches in which the melting mechanism is associated with the increasing role of intrinsic crystal defects when approaching the melting point. In our approach, we nowhere explicitly used the concept of crystal defects. It is significant, however, that the very form of Hamiltonian (4) indicates the crucial role of multi-phonon processes in the occurrence of conditions for the transition of graphene into a phase with abnormally large fluctuations of the bending component of the strain tensor. Since the formation of defects (in the case of graphene, this may be the already mentioned Stone–Wales defects [9, 10]) is due to precisely multi-phonon processes, the theory proposed in this paper is naturally linked with ideas about the melting of a crystal as the result of its ‘softening’ due to the thermal creation of defects [3, 6, 8].

Note also that although the paper [24] is so far the only source of information on the numerical values of higher order elastic moduli of graphene (up to the fifth inclusive!), it is hardly possible to directly use these values for our purposes. The point is that in order to coordinate the results of the DFT calculations with the concepts of the theory of elasticity, in [24] it was necessary to introduce into the strain energy the terms of the fifth order with the elastic constants $\approx -32\,000$ N·m$^{-1}$. Meanwhile, the break of expression for the elastic energy on the term with negative elastic constants leads to physically unsatisfactory results, since it allows the formal divergence of the components of the strain tensor as a condition of ‘minimum’ of the strain free energy. To eliminate such a divergence, in the expression for the elastic energy one should take into account the sixth-order terms with positive coefficients, which would lead to unnecessarily cumbersome mathematical operations.

The natural way to build a theory, necessarily satisfying the physical requirements of the finiteness of the results and quite mathematically acceptable, is the break of the expansion of the elastic energy density on the fourth-order term over the strain tensor. Thus, we return to Hamiltonian (2) and to all the results obtained above in sections 2–4. In this case, however, it is necessary to select a suitable fourth-order polynomial for the graphene elastic energy density in order to describe quantitatively the DFT calculation of the stress–strain curves obtained in [24]. Thus, the analysis of the DFT data [24] by formula (21), based on such expansion of the elastic energy constants with satisfactory accuracy: $\mathcal{C}_{1111} = -2450$ N·m$^{-1}$, $\mathcal{C}_{1111} = 7640$ N·m$^{-1}$ (see figure 1). The latter value is almost twice as small as $\mathcal{C}_{1111} \approx \mathcal{C}_{2222} \approx 13\,000$ N·m$^{-1}$, obtained in [24] when taking into account also terms of the fifth-order on strain tensor in the elastic energy density. Interestingly, substituting $\mathcal{C}_{1111} = -2450$ N·m$^{-1}$, $\mathcal{C}_{1111} = 7640$ N·m$^{-1}$ together with $\mathcal{C}_{11}(0) = 350$ N·m$^{-1}$ [24] into formula (10), we come to the value $\eta(0) \approx 1.2 > 3/4$ (see the condition at the end of the previous section). This means that, in principle, the results of [24] can be agreed (at least on a qualitative level) with the main conclusions of our theory of graphene melting.

Although the shown value $\mathcal{C}_{1111} = 7640$ N·m$^{-1}$ is almost half the value found in [24], it sharply differs from $\mathcal{C}_{1111} \approx 1000$ N·m$^{-1}$ given in section 4. At first glance, it is difficult to give a rational explanation for this discrepancy.
Meanwhile, it is quite possible that the simulation scheme used in [24] allows satisfactorily describing the stress–strain curves of graphene for relatively small in-plane deformations, whereas for large strains (say, at $\varepsilon > 0.3$), the results of [24] should be treated with caution. The reality of such a possibility is illustrated by the dash-dotted curve in figure 1 (section 4); this curve, constructed by equation (21) with elastic constants $C_{11}(0) = 315$ N m$^{-1}$, $C_{111} = -1620$ N m$^{-1}$, $C_{1111} = 1000$ N m$^{-1}$, satisfactorily fits the DFT data from [24] at $\varepsilon < 0.3$. This means that with more accurate numerical calculations, the values of the anharmonic elastic constants of graphene may be closer to those that appear in the theory of 2D melting proposed in the present paper.

The principal results of our study of 2D melting are:

1. Melting should be regarded as a fundamentally nonlinear phenomenon, since arbitrarily large displacements of atoms from the initial positions are permissible in the disordered phase. Therefore, it seems impossible to create a consistent theory of melting based on a purely harmonic approximation for a crystal (for example, from the requirement that one of its harmonic elastic moduli vanishes at the melting point [28]). Using the example of graphene as quasi-2D crystal with the bending degree of freedom, we substantiated this statement by constructing a self-consistent theory taking into account third- and fourth-order anharmonic effects. In this case, the decisive fact was that the third order elastic constants for graphene are negative;

2. The melting point of graphene is determined by the condition of its jump-like transition into a ‘special’ phase, characterized by abnormally large mean-square bending fluctuations of the strain tensor. On the other hand, a certain effective construction, the ‘pseudo-harmonic’ bending modulus of graphene, reaches an unusually small value at the transition point, which signals the phenomenon of melting. Below the melting point, the theory does not predict any premelting effects, i.e. signs of the existence of a ‘special’ phase (‘melt’), even as metastable one;

3. The presence of anharmonic terms in the elastic Hamiltonian of graphene is equivalent to taking into account multi-phonon processes that can lead to the appearance of structural defects. Therefore, the approach proposed in the present paper can be considered as a theoretical alternative to the model based on the ideas about the main role of intrinsic defects in crystal melting;

4. The most important role of the ‘soft’ bending mode in the mechanism of graphene melting is evidenced by the fact that while ignoring the bending degree of freedom, MD simulations [20] lead to a much overestimated (almost twice compared with the generally accepted value $\approx 4500$ K [6, 8]) melting temperature of graphene. On the contrary, taking into account the bending mode, we can construct a self-consistent theory of 2D melting and obtain a realistic estimate of the melting temperature, as well as find the value of a parameter similar to the well-known 3D Lindemann parameter.

Note that the proposed theory of melting (with specific refinements) can be applied to related 2D crystals: silicene, germanene, etc. In this case, in contrast to the flat (in the ‘undisturbed’ state) free-standing graphene, a planar state of formally free-standing silicene (as well as that of germanene) is unstable owing to the anomalous fluctuations of out-of-plane optical (ZO) mode [35]. This instability caused by the peculiarities of the electron hybridization of silicon atoms results in the formation of slightly buckled structure, in which the neighboring atoms of two sublattices of silicene move apart in the out-of-plane direction at a distance of about 0.45 Å. Surely such a buckling, which exists already at the zero temperature is not related to the phenomenon of 2D melting. The approach proposed in the present paper connects the melting of graphene with a sudden jump in out-of-plane fluctuations of the graphene surface. This result may cause associations with the loss of stability, leading to the buckling of the flat surface of graphene. We emphasize, however, that such ‘buckling’ is purely dynamic—fluctuating—in nature (but not static, as in [34]).

The conceptual statements of the theory formulated in the present work, in principle, can be tried to be extended to 3D crystals. As an important suggestive consideration, we note a well-known experimental fact [36, 37] (see also [23]), according to which third-order elastic moduli in real 3D solids, as a rule, turn out to be negative. In the light of the approach outlined above, this fact could be crucial for the very possibility to realize a thermodynamic condition of the liquid–solid coexistence at the melting point of 3D crystal (the condition having no sense for the case of graphene melting).

Finally, we draw attention to the last question. The self-consistent theory proposed above made it possible to express the fluctuation characteristics of graphene at temperatures up to the melting point through the ‘harmonic’ (temperature-dependent) modulus, as well as third-order and fourth-order elastic constants. Unfortunately, to date, information on fourth-order elastic moduli is practically absent in the literature devoted to graphene (the exception is work [24], but with the remarks noted above); there is also no consensus regarding the values of the third order elastic constants. In this regard, further work on the study of the anharmonic elastic characteristics of graphene and similar 2D compounds is of utmost importance.

Appendix A. Finding some ‘pseudo-harmonic’ averages for the graphene bending mode

Here, considering the mean $\langle (\nabla w)^6 \rangle$ as an example, we outline the path for obtaining formula (6). First of all, we write the

$11$ Here we do not mean the transition of a planar graphene ribbon into a state with the out-of-plane buckling under an in-plane compression (this so-called Euler instability of graphene was considered in [34]). The local deviations of the free-standing graphene shape from the plain are of fluctuation nature and appear as intrinsic ripples (see [13] and references therein).
direct and inverse 2D Fourier transformations of the graphene bending displacement (we omit the temporal argument):

\[
w_k = \frac{1}{\sqrt{3}} \int e^{-i \mathbf{k} \cdot \mathbf{r}} \, d\mathbf{r}, \quad w(\mathbf{r}) = \frac{1}{\sqrt{3}} \sum_k w_k e^{i \mathbf{k} \cdot \mathbf{r} - \mathbf{k} \cdot \mathbf{w}_k},
\]

(A.1)

where \( S \) is the graphene sheet area. Then, let us proceed under the sign of the mean to the 2D Fourier representation (A.1) and take into account that in the pseudo-harmonic approximation the averaging will occur with the Gaussian distribution function

\[
\exp \left[-\frac{1}{T} \sum_k \psi(k) w_k w_{-k} \right]. \quad (A.2)
\]

where \( \psi(k) \) is an amplitude. Then we have:

\[
\langle (\nabla w)^6 \rangle_w = \frac{\rho \beta}{S} \left\{ \sum_{k_1 \ldots k_6} k_1 k_2 k_3 k_4 k_5 \delta_{k_1 + k_2 + k_3 + k_4 + k_5 + k_6} w_{k_1} w_{k_2} w_{k_3} w_{k_4} w_{k_5} w_{k_6} \delta_{k_1 + k_2 + k_3 + k_4 + k_5 + k_6} \right\}_w.
\]

(A.3)

where \( \delta_{k_1 + k_2 + k_3 + k_4 + k_5 + k_6} \) is the Kronecker \( \delta \)-symbol (1 or 0). Eliminating one of the sums with the help of the \( \delta \)-symbol, one can lead the right-hand side of (A.3) to the form:

\[
\frac{4}{S} \left\{ \sum_{k_1 \ldots k_5} k_1 k_2 k_3 k_4 k_5 \delta_{k_1 + k_2 + k_3 + k_4 + k_5} w_{k_1} w_{k_2} w_{k_3} w_{k_4} w_{k_5} \right\}_w
\]

(A.4)

Further, we take into account the fact that with Gaussian averaging a nonzero contribution to (A.4) will be obtained only in cases where each harmonic will be in even degrees. This allows rewriting (A.4) in the form:

\[
\frac{4}{S} \left\{ \sum_{k_1 \ldots k_5} k_1 k_2 k_3 k_4 k_5 \delta_{k_1 + k_2 + k_3 + k_4 + k_5} w_{k_1} w_{k_2} w_{k_3} w_{k_4} w_{k_5} \right\}_w.
\]

(A.5)

Noticing now that \( \langle k_1 k_2 k_3 w_{-k_1 k_2 k_3} \rangle_w = (1/2) \delta_{\gamma \alpha} \langle k_2^2 \rangle_w \langle k_1^2 \rangle_w \), we obtain from (A.5):

\[
\langle (\nabla w)^6 \rangle_w = 3 \left\{ \sum_k k_1^2 \langle k_1^2 \rangle_w \right\} \frac{1}{S} \sum_{k_1 \ldots k_6} k_1 k_2 k_3 k_4 k_5 \delta_{k_1 + k_2 + k_3 + k_4 + k_5 + k_6} w_{k_1} w_{k_2} w_{k_3} w_{k_4} w_{k_5} w_{k_6} \right\}_w.
\]

(A.6)

It should, however, be noted that formula (A.6) is strictly correct only in the macroscopic limit \( (S \to \infty) \). Indeed, in the derivation of (A.6), we discarded averages like

\[
\frac{1}{S} \left\{ \sum_{k_1} k_1^2 \langle k_1^2 \rangle_w \right\}_w \left\{ \sum_{k_2} k_2^2 \langle k_2^2 \rangle_w \right\}_w.
\]

[38] (see also [39, 40]). In terms of the quantities introduced above, the theorem [38] reads as follows:

\[
F_w(T) \leq F_w^{(p-h)}(T) + \langle H_w - H_w^{(p-h)} \rangle_w. \quad (B.3)
\]

We will consider the right-hand side of inequality (B.3) as a functional of variable \( E_k \equiv \omega_B^{(p-h)}(k) \) and find its minimum by this variable using expressions (4), (B.1) and (B.2).
Representing the ‘pseudo-harmonic’ free energy $F_{\rho}^{(p-h)}(T)$ in explicit form [2], one can write the right-hand side of (B.3) as a functional of $E_k$:

$$J\{E_k\} \equiv \sum_k \left[ \frac{E_k}{2} + T \ln \left( 1 - e^{-E_k/T} \right) \right] + \langle H_w - H_w^{(p-h)} \rangle_w.$$

(F.4)

Further, when calculating the averages in (B.4), we take into account that

$$\left\langle \left( \nabla w \right)^2 \right\rangle_w = \int \left\langle \left( \nabla w \right)^2 \right\rangle_w \, dr = S \left\langle \left( \nabla w \right)^2 \right\rangle_w , n \geq 1,$$

(B.5)

and then instead of (B.4) we get:

$$J\{E_k\} = T \sum_k \ln \left[ 2 \sinh \left( \frac{E_k}{2T} \right) \right] + \frac{\mu}{2} \sum_k \left[ B(T) k^2 + \kappa k^4 - \rho E_k^2 \right] \left\langle |w_k|^2 \right\rangle_w \ + S \left[ \frac{\mu}{2} \left\langle \left( \nabla w \right)^4 \right\rangle_w + \frac{\kappa}{2} \left\langle \left( \nabla w \right)^6 \right\rangle_w + \frac{\rho}{2} \left\langle \left( \nabla w \right)^8 \right\rangle_w \right].$$

(B.6)

Since the averaging in (B.6) is carried out with the pseudo-harmonic Hamiltonian (B.1), the formula (6) takes place (see appendix A).

Thus, the averages appearing in (B.6) can be expressed in terms of the only quantity:

$$q \equiv \frac{1}{2} \left\langle \left( \nabla w \right)^2 \right\rangle_w = \frac{1}{2} \sum_k k^2 \left\langle |w_k|^2 \right\rangle_w.$$

(B.7)

where (see [15])

$$\left\langle |w_k|^2 \right\rangle_w = \frac{\hbar^2}{2\rho E_k} \coth \left( \frac{E_k}{2T} \right).$$

(B.8)

Now, taking into account (6), (B.7) and (B.8), we lead (B.6) to the form:

$$J\{E_k\} = T \sum_k \ln \left[ 2 \sinh \left( \frac{E_k}{2T} \right) \right] + \frac{\mu}{2} \sum_k \left[ B(T) k^2 + \kappa k^4 - E_k \right] \coth \left( \frac{E_k}{2T} \right) \ + S \left[ \frac{\mu}{2} \left\langle \left( \nabla w \right)^4 \right\rangle_w + \frac{\kappa}{2} \left\langle \left( \nabla w \right)^6 \right\rangle_w + \frac{\rho}{2} \left\langle \left( \nabla w \right)^8 \right\rangle_w \right].$$

(B.9)

After that, varying (B.9) over $E_k$ and equating the result to zero, we arrive at the equation:

$$\frac{\partial J\{E_k\}}{\partial E_k} = \frac{\mu}{2} \left\{ B(T) + 2C_{111}\langle \nabla w \rangle^4 + 4C_{111}\langle q \rangle^2 + \kappa k^4 \right\} = 0,$$

(B.10)

which provides a minimum (more exactly, an extremum) of the functional $J\{E_k\}$.

As a result, we obtain from (B.10) the dispersion equation for the bending mode in the framework of the ‘pseudo-harmonic’ problem:

$$\rho \omega_p^{(p-h)}(k)^2 = \left\{ B(T) + 2C_{111}\langle \nabla w \rangle^4 + 4C_{111}\langle q \rangle^2 + \kappa k^4 \right\} = 0,$$

(B.11)

Here, the parameter $q$ defined by (B.7) contains integrated information about the spectrum $\omega_p^{(p-h)}(k) \equiv E_k/\hbar$, and, of course, the coefficient at $k^2$ in (B.11) is assumed to be positive. It is easy to verify that equation (B.11) exactly matches the dispersion law (11) of the ‘pseudo-harmonic’ bending mode of graphene. More sophisticated consideration shows that the extremals of $J\{E_k\}$ obtained in this way give precisely the minima if the quantities found from (B.7) and (B.11) satisfy the additional condition

$$1 + \frac{1}{4\rho} \frac{2C_{111}(T) + 6C_{111}q + 12C_{111}\langle q \rangle^2}{\langle \nabla w \rangle^2} > 0,$$

which is definitely satisfied in our task.

For reference purposes, we give the expression for the ‘bare’ bending modulus [13, 15]:

$$B(T) = \frac{1}{4} \left( 3\lambda + 5\mu + \frac{3C_{111} + C_{111}}{4} \right) \langle \partial_\alpha u_\beta \partial_\alpha u_\beta \rangle_w.$$

(B.12)

Here, the thermal average found using the in-plane harmonic Hamiltonian (3) is as follows:

$$\langle \partial_\alpha u_\beta \partial_\alpha u_\beta \rangle_w = \frac{(\lambda + 3\mu)\rho}{3m/\mu(\lambda + 2\mu)} \left[ 1 + \frac{1}{2} \frac{\kappa k^4}{m/\mu(\lambda + 2\mu)} \right] \int_0^{\theta_{\parallel}/T} \frac{t^2 dt}{e^t - 1}$$

(B.13)

with $m$ as an atomic mass (in the case of graphene it is the mass of $^{13}$C) and the in-plane Debye temperature

$$\theta_{\parallel} = 2\hbar \sqrt{\frac{2\pi m(\lambda + 2\mu)}{m(\lambda + 3\mu)}} \approx 2670 \text{ K}.$$  

(B.14)

On the other hand, the out-of-plane Debye temperature of graphene is (see [15]):

$$\theta_w \equiv \frac{4\pi \hbar}{m} \sqrt{\frac{\kappa}{\rho}} \approx 2040 \text{ K}.$$  

(B.15)

Here, however, it is necessary to dwell on the question of the temperature range of applicability of the ‘pseudo-harmonic’ approximation (B.11). We show that at ‘low’ temperatures (below, we will specify this definition), taking into account the anharmonic term $(\lambda + 2\mu)(\nabla w)^4/8$ in (4) will only affect the coefficient at $k^4$ in the dispersion equation (12), but will not affect the velocity of bending sound $s_B$. It is easy to verify that when taking into account the mentioned anharmonic term, the equation of motion for the bending mode will take the form:

$$\frac{\partial^2 w}{\partial t^2} = s_B^2 \frac{\partial^2 w}{\partial \alpha^2} - \frac{\kappa}{\rho} \frac{\partial^2 w}{\partial \alpha \partial \beta} + \frac{\lambda + 2\mu}{\rho} \frac{\partial^2 w}{\partial \alpha \partial \beta} + \frac{\lambda}{\rho} \frac{\partial^2 w}{\partial \beta^2}.$$

(B.16)

Suppose now that in a graphene sample there is a single bending wave with the wave vector $k$, frequency $\omega$, and amplitude $w_k$:

$$w(r, t) = w_k \cos(\mathbf{k}r - \omega t).$$

(B.17)

Substituting (B.17) into (B.16) and omitting terms with triple harmonics, we obtain instead of (12) the dispersion law of the bending mode with taking account of the nonlinear contribution (self-action):

$$\omega^2_k = s_B^2 k^2 + \frac{\kappa}{\rho} k^4 + \frac{3(\lambda + 2\mu)}{16\rho} w_k^2 k^4.$$  

(B.18)
Thus, the inclusion of anharmonic terms in the ‘bending’ Hamiltonian of graphene does not lead to the modification of the long-wave—‘sound’—part of the bending mode spectrum at low temperatures. However, the role of the last term in \((B.18)\) will increase with increasing temperature due to the natural growth of the mean square amplitude of the graphene bending mode. On the other hand, at finite temperatures, harmonics with different (including large) wave numbers will be excited in graphene. As a result, the anharmonic terms of the form (see \((B.18)\))

\[
\sim \frac{\lambda + 2\mu}{\rho} k^2 \sum_{k, \neq k} k^2 w_k^2,
\]

will appear in the dispersion equation of the bending mode; at that, the short-wave harmonics give the main contribution to the sum in \((B.19)\). The terms of the form \((B.19)\) after thermodynamic averaging of the sum will lead to the modification of the ‘sound’ part of the of graphene bending vibrations, which, in fact, is reflected in equation \((B.11)\). Such a modification, however, can effectively manifest itself only at sufficiently high temperatures\(^{12}\).

Having in mind these arguments we estimated possible shortcomings of the used quasi-harmonic approximation. To this end we introduced the auxiliary temperature-dependent factor \(T(T_0 + T)\) with controlling parameter \(T_0\) in equation \((8)\). Varying \(T_0\) in the interval from the room to the Debye temperature \(\theta_0\) \((B.15)\) we revealed that result of our calculations at \(T > \theta_0\) visibly did not change if \(T_0 < \theta_0/2 \approx 1000\,\text{K}\).

All the calculations presented here have been performed using the following simple interpolation formula for a ‘pseudo-harmonic’ bending modulus as a factor at \(k^2\) in \((B.11)\):

\[
B(q; T) \equiv B(T) + \frac{T}{T + T_0} \left[2C_{11}(T)\xi^2 + 3C_{111}\xi^2 + 4C_{1111}\xi^2\right]
\]

with the value of \(T_0 = 1000\,\text{K}\). It is worth mentioning that near this temperature the thermal expansion coefficient of graphene changes sign from negative to positive \([15, 17, 18]\).

**Appendix C. Calculating the temperature dependence of \(C_{11}(T)\)**

To calculate the temperature dependence of the ‘harmonic’ elastic modulus \(C_{11}(T)\) (see \((4)\)) we proceed from the general expression \((2)\), in which we specially select the terms, resulting in contributions \(\sim (\nabla w)^4\) under the integral. For convenience, we first break \((1)\) into two contributions (in-plane and out-of-plane ones):

\[
\varepsilon_{\alpha\beta} = u_{\alpha\beta} + w_{\alpha\beta},
\]

\[
u_{\alpha\beta} = \frac{1}{2} \left( \partial_{\alpha} u_{\beta} + \partial_{\beta} u_{\alpha} + \partial_{\alpha} u_{\gamma} \partial_{\beta} u_{\gamma} \right),
\]

\[
w_{\alpha\beta} = \frac{1}{2} \partial_{\alpha} w \partial_{\beta} w.
\]

\[
(C.1)
\]

The resulting dependence \(C_{11}(T)\) is obtained both from terms of type \(u_{\alpha\beta}w_{\alpha\beta}w_{\gamma\gamma}\) and from terms of type \(u_{\alpha\beta}w_{\alpha\beta}w_{\gamma\gamma}\).

Let us first write the contributions of interest to us, derived from the terms of the second and third orders in \(\varepsilon_{\alpha\beta}\) under the integral in \((2)\):

\[
\left( \frac{\lambda + \mu}{\rho} \right) w_{\alpha\beta} w_{\beta\gamma} + \frac{C_{111}}{4} \left( 2u_{\alpha\beta} w_{\alpha\beta} w_{\gamma\gamma} + u_{\alpha\gamma} w_{\alpha\gamma} w_{\beta\beta} \right)
\]

\[
+ \frac{C_{1111}}{12} \left( 2u_{\alpha\alpha} w_{\beta\beta} w_{\gamma\gamma} + u_{\gamma\gamma} w_{\alpha\alpha} w_{\beta\beta} \right).
\]

\[
(C.2)
\]

From the fourth order terms on \(\varepsilon_{\alpha\beta}\) under the integral in \((2)\) we get the following construction:

\[
\left\{ \left( \frac{\lambda + \mu}{\rho} \right) w_{\alpha\beta} w_{\beta\gamma} + \frac{C_{111}}{4} \left( 2u_{\alpha\beta} w_{\alpha\beta} w_{\gamma\gamma} + u_{\gamma\gamma} w_{\alpha\gamma} w_{\beta\beta} \right) + \frac{C_{1111}}{12} \left( 2u_{\alpha\alpha} w_{\beta\beta} w_{\gamma\gamma} + u_{\gamma\gamma} w_{\alpha\alpha} w_{\beta\beta} \right) + c(2u_{\alpha\alpha} w_{\beta\beta} w_{\gamma\gamma} + 4u_{\alpha\gamma} w_{\alpha\gamma} w_{\beta\beta} + 6d_{\alpha\gamma} w_{\alpha\gamma} w_{\beta\beta} \right) \cdot
\]

\[
(C.3)
\]

The next step consists in averaging expressions \((C.2)\) and \((C.3)\) over the ‘fast’ in-plane fluctuation oscillations of graphene (see \([13, 15]\)). It should be noted that non-zero averages in \((C.2)\) arise from bilinear contributions contained in \(u_{\alpha\beta}\), while in \((C.3)\)—from linear contributions contained in each of the two factors of type \(w_{\alpha\beta}\). In addition, we will neglect the averages of the type \(\langle \partial_{\alpha\beta} u_{\gamma\delta} \partial_{\alpha\beta} u_{\gamma\delta} \rangle\) as quantities of the next order of smallness. Then, collecting the terms resulting from the averaging \((C.2)\) and \((C.3)\), taking into account the equalities \(\langle \partial_{\alpha\beta} u_{\gamma\delta} \partial_{\alpha\beta} u_{\gamma\delta} \rangle = \langle \partial_{\beta\gamma} u_{\alpha\beta} \partial_{\beta\gamma} u_{\alpha\beta} \rangle = \langle \partial_{\alpha\beta} \partial_{\alpha\beta} u_{\gamma\delta} \rangle\)\(^{12}\)\([13, 15]\) and omitting the intermediate actions, we find the resulting contribution \(\sim (\nabla w)^4\) to the density of the graphene ‘bending’ Hamiltonian \((4)\)

\[
\frac{1}{8} \left\{ \left( \frac{\lambda + 2\mu}{\rho} \right) \left[ 2C_{1111} - C_{111} \right] + \frac{1}{6} \left( \frac{23}{12} a_4 + \frac{9}{4} d_4 \right) 
\]

\[
+ \frac{7}{3} c_4 + 3d_4 \right\} \left( \partial_{\alpha\beta} u_{\beta\gamma} \partial_{\alpha\beta} u_{\beta\gamma} \right) \langle \nabla w \rangle^4.
\]

\[
(C.4)
\]

In the high-temperature limit of interest to us, from \((B.13)\) it follows:

\[
\langle \partial_{\alpha\beta} u_{\beta\gamma} \partial_{\alpha\beta} u_{\beta\gamma} \rangle = \frac{\rho (\lambda + 3\mu)}{\mu(\lambda + 2\mu)} T.
\]

Finally, comparing expression \((C.4)\) with the general form of the corresponding contribution to \((4)\) and taking into account \((C.5)\), we arrive at formula

\[
C_{11}(T) = \lambda + 2\mu - C_{111}^{(T)} \frac{\rho (\lambda + 3\mu)}{\mu(\lambda + 2\mu)} T.
\]

\[
(C.6)
\]

where we have designated:

\[
C_{111}^{(T)} = |C_{1111}| - \frac{1}{2} |C_{1112}| - \frac{1}{12} \left( \frac{23}{12} a_4 + \frac{9}{4} d_4 + \frac{7}{3} c_4 + 3d_4 \right).
\]

\[
(C.7)
\]

Immediately note, that by the ‘minus’ sign in the right-hand side of \((C.6)\), we especially emphasized the fact that \(C_{11}(T)\)\(^{12}\) The reasoning given here resembles the arguments of work \([41]\), in which the attenuation of the high-intensity sound in a lined acoustic duct was studied using the harmonic linearization method \([42, 43]\). It is useful to note that, as shown in \([13]\), the contribution of \(-t^2\) to the dispersion law of the bending mode due to the term \(\sim (\lambda + 2\mu) (\nabla w)^4\) also takes place at finite temperatures. This, in fact, means that the terms of the form of \((B.19)\), which have anharmonic origin, can manifest themselves only in the high-temperature limit. This question, however, requires more study.
falls with temperature, as it follows, for example, from [17, 29].

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