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Bending modes, anharmonic effects, and thermal expansion coefficient in single-layer and multilayer graphene

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We present a simple analytical approach to study anharmonic effects in single-layer, bilayer, and multilayer graphene. The coupling between in-plane and out-of-plane modes leads to negative Grüneisen coefficients and negative thermal expansion. The value of the thermal expansion coefficient depends on the coupling to the substrate. The bending rigidity in bilayer graphene shows a crossover between a long wavelength regime where its value is determined by the in-plane elastic properties, and a short wavelength regime where its value approaches twice that of a single layer.

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I. INTRODUCTION

To realize the full potential of graphene layers in promising applications, such as the design of fast electronic devices or sensitive and accurate molecular detectors, it is important to gain a thorough understanding of the properties of graphene down to the atomic level.[1,2] Perfect graphene is found as a flat honeycomb lattice where carbon atoms form efficient and strong bonds; both experimentally and theoretically, it has been proven that this kind of arrangement results in a material with the largest known in-plane elastic constants to date.[3–5] However, departures from this perfect configuration caused by rippling, corrugation, deformation, etc., are interesting to study since they affect electronic and heat transport and all sorts of mechanical properties.[6–10] In this work, we analyze a simple model based on the theory of elasticity to obtain physical insight into the Grüneisen coefficients and the thermal expansion coefficient of graphene, which can be compared to atomistic models based on *ab initio* density functional theory, which yields a realistic quantitative description of bending modes and corrugations appearing at the atomic scale.[11]

II. SINGLE-LAYER GRAPHENE

We study anharmonic effects using the continuum theory of elasticity. We extend previous analyses[12,13] using the standard theory of free-standing membranes.[6–8,10] The Hamiltonian is[14]

$$\begin{aligned}\mathcal{H}_{\rm el} = \int d^2\vec{\mathbf{r}} \Bigg\{ & \frac{\rho}{2}[(\partial_t u_x)^2 + (\partial_t u_y)^2 + (\partial_t h)^2] \\ & + \frac{\kappa}{2}\left(\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2}\right)^2 \\ & + \frac{\lambda}{2}\left(\partial_x u_x + \partial_y u_y + \frac{(\partial_x h)^2 + (\partial_y h)^2}{2}\right)^2 \\ & + \mu\Bigg[\left(\partial_x u_x + \frac{(\partial_x h)^2}{2}\right)^2 + \left(\partial_y u_y + \frac{(\partial_y h)^2}{2}\right)^2 \\ & + \frac{[\partial_x u_y + \partial_y u_x + (\partial_x h)(\partial_y h)]^2}{2}\Bigg]\Bigg\}, \end{aligned} \tag{1}$$

where ρ is the mass density, $\vec{\mathbf{u}}$ is the two-dimensional (2D) displacement vector, h is the displacement in the out-of-plane direction, κ is the bending rigidity, and λ and μ are 2D elastic Lamé coefficients (for 3D elastic constants, we use the notation c_{ij}). For graphene, we have $\kappa \approx 1$ eV, $\lambda = 2$ eV Å^{-2}, and $\mu = 10$ eV Å^{-2}.[5]

We study the modes associated with the out-of-plane displacements. If we assume that there are no in-plane tensions, $\partial_i u_j = 0$, and we neglect the quartic terms in h, we obtain $\omega_{\vec{\mathbf{q}}} = \sqrt{\kappa|\vec{\mathbf{q}}|^4/\rho}$. This is the well known dispersion relation for out-of-plane flexural modes. We now analyze how these frequencies are modified when the in-plane lattice constant is modified. An isotropic change of the lattice constant by a factor $\bar{u}$ can be included in the Hamiltonian, Eq. (1), by assuming that $\partial_x u_x = \partial_y u_y = \bar{u}$. The effective Hamiltonian for h, expanded to second order, becomes

$$\begin{aligned}\mathcal{H}_{\rm flex} = \int d^2\vec{\mathbf{r}} \Bigg\{ & \frac{\rho}{2}(\partial_t h)^2 + \frac{\kappa}{2}\left(\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2}\right) \\ & + (\lambda + \mu)\bar{u}[(\partial_x h)^2 + (\partial_y h)^2]\Bigg\}. \end{aligned} \tag{2}$$

The new frequencies of the flexural phonons are

$$\omega_{\vec{\mathbf{q}}} = \sqrt{\frac{\kappa|\vec{\mathbf{q}}|^4 + 2(\lambda + \mu)\bar{u}|\vec{\mathbf{q}}|^2}{\rho}}. \tag{3}$$

The derivative of the phonon frequency with respect to a change in the area of the unit cell $\mathcal{A}$ is

$$\gamma_{\vec{\mathbf{q}}} = -\frac{\mathcal{A}}{\omega_{\vec{\mathbf{q}}}}\frac{\partial \omega_{\vec{\mathbf{q}}}}{\partial \mathcal{A}} = -\frac{1}{2\omega_{\vec{\mathbf{q}}}}\frac{\partial \omega_{\vec{\mathbf{q}}}}{\partial \bar{u}}\bigg|_{\bar{u}=0} = -\frac{\lambda + \mu}{2\kappa|\vec{\mathbf{q}}|^2}, \tag{4}$$

where $\gamma_{\vec{\mathbf{q}}}$ is the Grüneisen parameter. We obtain a negative Grüneisen parameter for all low-frequency flexural modes, which diverge for $|\vec{\mathbf{q}}| \to 0$ as $|\vec{\mathbf{q}}|^{-2}$. This expression is valid for momenta much smaller than the inverse of the interatomic spacing a, $|\vec{\mathbf{q}}| \ll a^{-1}$. This result is consistent with a number of numerical calculations, which show negative Grüneisen coefficients for flexural modes, which tend to diverge at low momenta.[4,5,15,16]

Within the harmonic approximation, the estimate of the Grüneisen parameters in Eq. (4) allows us to obtain the thermal expansion coefficient,[10]

$$\alpha = \frac{k_B}{\mathcal{A}(\lambda+\mu)} \sum_{\vec{\mathbf{q}}} \left(\frac{\hbar\omega_{\vec{\mathbf{q}}}}{2k_BT} \right)^2 \frac{\gamma_{\vec{\mathbf{q}}}}{\sinh^2\left(\frac{\hbar\omega_{\vec{\mathbf{q}}}}{2k_BT}\right)}, \tag{5}$$

where $\mathcal{A}$ is the area of the unit cell and we take into account that the two-dimensional bulk modulus $B = \lambda + \mu$. The sum (in the thermodynamic limit it is replaced by an integral) on the right-hand side of Eq. (5) is divergent at small q, which is a consequence of the inapplicability of the harmonic approximation at small q where renormalization of effective bending rigidity and elastic moduli becomes relevant. The crossover wave vector is[6,10]

$$q^* = \sqrt{\frac{3k_BTY}{8\pi\kappa^2}}, \tag{6}$$

where $Y = 4\mu(\lambda+\mu)/(\lambda+2\mu)$ is the two-dimensional Young modulus. Note that the corresponding phonon frequency lies deep in the classical region:

$$\hbar\omega^* = \frac{3k_BT}{8\pi}\frac{Y}{\sqrt{\kappa^3\rho}} \sim k_BT\sqrt{\frac{m}{M}} \ll k_BT, \tag{7}$$

where m and M are the electron mass and the mass of a carbon atom, respectively. With logarithmic accuracy,

$$\alpha \approx -\frac{k_B}{4\pi\kappa}\int_{q^*}^{q_T}\frac{dq}{q} = -\frac{k_B}{8\pi\kappa}\ln\frac{k_BT}{\hbar\omega^*} \approx -\frac{k_B}{16\pi\kappa}\ln\frac{\kappa^3\rho}{\hbar^2Y^2}, \tag{8}$$

where q_T is the thermal wave vector satisfying the condition $\hbar\omega(q_T) = k_BT$. From the estimation in Eq. (8), we obtain $\alpha \approx -10^{-5}\ \mathrm{K}^{-1}$, a quite good estimation for such an oversimplified model (cf. Refs. 4 and 5). Here we assume that the temperature is smaller than the maximal energy of the flexural phonon, $T_m \approx 15$ THz ≈ 700 K,[4] otherwise one needs to add the factor T_m/T under the argument of the logarithm in Eq. (8).

Due to Eq. (7), phonons relevant for the thermal expansion coefficient can be considered to be classical at any temperature. This allows us to repeat the calculation of α, taking into account anharmonic effects. Due to Eq. (2) and the Hellmann-Feynman theorem, the derivative of the free energy $\mathcal{F}$ with respect to the deformation at $\bar{u} = 0$ can be rigorously expressed via the correlation function of out-of-plane displacements:

$$\frac{\partial\mathcal{F}}{\partial\bar{u}} = \left\langle \frac{\partial\mathcal{H}_{\text{flex}}}{\partial\bar{u}} \right\rangle = (\lambda+\mu)\sum_{\vec{q}} q^2\langle|h_{\vec{q}}|^2\rangle, \tag{9}$$

and via the anharmonic self-energy $\Sigma(\vec{q})$:

$$\langle|h_{\vec{q}}|^2\rangle = \frac{k_BT}{\kappa q^4 + \Sigma(\vec{q})}. \tag{10}$$

The latter can be estimated from the condition that at $q = q^*$, both terms in the denominator in Eq. (10) are of the same order of magnitude:[17]

$$\Sigma(q) = A\,(Yk_BT)^{\eta/2}\,\kappa^{1-\eta}q^{4-\eta}, \tag{11}$$

where $\eta \approx 0.85$ is the exponent of renormalization of the bending rigidity. The numerical factor A was calculated within the self-consistent screening approximation;[18] it was also shown that this approximation agrees quite well with the atomistic Monte Carlo simulations. Substituting Eq. (11) into Eq. (10) and further into Eq. (9), one can calculate the thermal expansion coefficient

$$\alpha = -\frac{1}{2(\lambda+\mu)}\frac{\partial^2\mathcal{F}}{\partial T\,\partial\bar{u}} \tag{12}$$

with anharmonic effects taken into account. With logarithmic accuracy, the result coincides with Eq. (8) provided the upper cutoff phonon energy is chosen as $\min(k_BT_m, k_BT)$. Thus, the contribution of the flexural mode to the thermal expansion coefficient is always negative and temperature independent up to $T \approx T_m \approx 700$ K; at higher temperatures, it depends on the temperature logarithmically. This means that the inversion of the sign of the thermal expansion coefficient at high temperature found in atomistic simulations[5] is due to contributions of other phonon modes.

This justifies the use of the quasiharmonic approximation to estimate the contribution of flexural phonons to the thermal expansion. From this point on, we will consider only this approximation.

Finally, from Eq. (3) for the phonon frequencies, we can estimate the momentum q_c for which the value of $\omega^2_{\mathbf{q}}$ becomes negative for negative $\bar{u}$. We obtain $q_c = \sqrt{[(\lambda+\mu)|\bar{u}|]/\kappa}$. For $\bar{u} = -0.04$, we find $q_c \approx 0.6\ \text{Å}^{-1}$.

III. GRAPHENE ON A SUBSTRATE

The flexural modes of graphene on a substrate are modified by the coupling to the substrate. The leading effect at long wavelengths can be analyzed by considering the interaction energy per unit area between the graphene layer and the substrate, $V_{\text{subs}}(h_{\text{subs}})$, where h_{subs} is the distance to the substrate. The dispersion relation for the flexural modes becomes $\omega_{|\vec{\mathbf{q}}|} \approx \sqrt{[\kappa|\vec{\mathbf{q}}|^4 + V''(h_{\text{eq}})]/\rho} = \sqrt{(\omega^0_{\vec{\mathbf{q}}})^2 + \omega_0^2}$, where h_{eq} is the equilibrium distance. We can get an estimate of $V''(h_{\text{eq}})$,

$$V''(h_{\text{eq}}) = \frac{V(h_{\text{eq}})}{d_0^2}, \tag{13}$$

where $V(h_{\text{eq}})$ is the binding energy per unit area of graphene to the substrate, and d_0 is a length scale such that $d_0 \lesssim h_{\text{eq}}$. The binding energy between graphene and the substrate depends on the precise attraction mechanism[19] between the two materials, and it is likely bound by the van der Waals interactions. A reasonable range of values is 5–50 meV Å^{-2}. For $d_0 \approx 2$ Å, we find $\hbar\omega_0 \approx 1$–4 meV. The value of ω_0 provides a cutoff in the expression for the thermal expansion, Eq. (5). This approximation is valid for substrates such that their binding to graphene is not larger than the binding between two graphene layers. The analysis is not applicable to graphene on metals,[16] where the van der Waals interaction is much larger, due to the high polarizability of the metal.[20]

Hence, the negative contribution of the flexural modes is reduced at temperatures such that $T \approx (\hbar\omega_0)/k_B \approx 10$–$40$ K. For $k_BT \gg \hbar\omega_0$, the thermal expansion of graphene on a substrate should be similar to that of free-standing graphene. At room temperature and $V(h_{\text{eq}}) \lesssim 50$ meV Å^{-2}, the anharmonic momentum cutoff q^* [see Eq. (6)] is such that $q^* \ll [V(h_{\text{eq}})/\kappa d_0^2]^{1/4}$, and the thermal expansion of graphene should be independent of the substrate.

IV. BILAYER GRAPHENE

In a discrete stack made of weakly coupled slabs, we can expand the interlayer coupling assuming that the displacements vary slowly as a function of the two-dimensional coordinate $\vec{\mathbf{r}}$, $u_{zz}^2 \to (u_{nz} - u_{n+1z}/d)^2$, $u_{xz}^2 + u_{yz}^2 \to |(\vec{\mathbf{r}}_{n+1} - \vec{\mathbf{r}}_{n-1})/2 + \nabla_{\parallel} u_{nz}|^2$, where d is the distance between the layers.

For two layers, an approximate expression is

$$\begin{aligned}
\mathcal{E} &= \sum_{i=1,2} \mathcal{E}_i + \mathcal{E}_{\mathrm{int}}, \\
\mathcal{E}_i &= \int d^2\vec{\mathbf{r}} \left[\frac{\lambda}{2}(u_{ixx} + u_{iyy})^2 + \mu\left(u_{ixx}^2 + u_{iyy}^2 + 2u_{ixy}^2\right) + \frac{\kappa}{2}\left(\partial_{xx}^2 u_{iz} + \partial_{yy}^2 u_{iz}\right) \right], \\
\mathcal{E}_{\mathrm{int}} &= \int d^2\vec{\mathbf{r}} \left\{ \frac{g_1}{2}\left(\frac{u_{1z} - u_{2z}}{d}\right)^2 + \frac{g_2}{2}\left[\left(\frac{u_{1x} - u_{2x}}{d} + \frac{\partial_x u_{1z} + \partial_x u_{2z}}{2}\right)^2 + \left(\frac{u_{1y} - u_{2y}}{d} + \frac{\partial_y u_{1z} + \partial_y u_{2z}}{2}\right)^2\right] \right. \\
&\quad \left. + \frac{g_3}{2}\left[\frac{\partial_x(u_{1x} + u_{2x}) + \partial_y(u_{1y} + u_{2y})}{2}\,\frac{(u_{1z} - u_{2z})}{d}\right]\right\},
\end{aligned} \tag{14}$$

where the Lamé coefficients and bending rigidity in $\mathcal{E}_i$ are the same as in the Hamiltonian for a single layer, Eq. (1). For an infinite three-dimensional stack, the parameters g_1, g_2, and g_3 define a continuum model like the one in Eq. (20) with $c_{33} = g_1/d$, $c_{13} = g_3/d$, and $c_{44} = g_2/d$.

If we assume that $g_2 = 0$, the in-plane and out-of-plane modes are decoupled. The equations of motion for the out-of-plane modes are

$$\begin{aligned}
\rho\partial_{tt}^2 u_{1z} &= -\kappa\left(\partial_{xx}^2 + \partial_{yy}^2\right)^2 u_{1z} - \frac{g_1}{d^2}(u_{1z} - u_{2z}), \\
\rho\partial_{tt}^2 u_{2z} &= -\kappa\left(\partial_{xx}^2 + \partial_{yy}^2\right)^2 u_{2z} - \frac{g_1}{d^2}(u_{2z} - u_{2z}),
\end{aligned} \tag{15}$$

where ρ is the two-dimensional mass density. In momentum space, we obtain two flexural modes, $\omega_+(\vec{\mathbf{k}}) = \sqrt{\kappa/\rho}k^2$, $\omega_-(\vec{\mathbf{k}}) = \sqrt{(\kappa k^4 + 2g_1/d^2)/\rho}$, where $k = |\vec{\mathbf{k}}|$.

For $g_2 \neq 0$, the phonon frequencies are obtained from the diagonalization of the 6×6 matrix. It can be split into two 3×3 matrices by using the combinations $\vec{\mathbf{r}}_1 = \pm\vec{\mathbf{r}}_2, u_{1z} = \mp u_{2z}$. The low-energy modes are given by

$$0 = \det \begin{vmatrix} (\lambda + 2\mu)k_x^2 + \mu k_y + \frac{g_2}{d^2} - \rho\omega^2 & (\lambda + \mu)k_x k_y & \frac{g_2 k_x}{2d} \\ (\lambda + \mu)k_x k_y & (\lambda + 2\mu)k_y^2 + \mu k_x^2 + \frac{g_2}{d^2} - \rho\omega^2 & \frac{g_2 k_y}{2d} \\ \frac{g_2 k_x}{2d} & \frac{g_2 k_y}{2d} & \frac{g_2 k^2}{4} + \kappa k^4 - \rho\omega^2 \end{vmatrix}. \tag{16}$$

The out-of-plane displacement couples to the longitudinal acoustical phonons. At low momenta, we have $g_2/d^2 \gg (\lambda + 2\mu)k^2$, $g_2 k^2$, κk^4, and we find

$$\begin{aligned}
\rho\omega^2 &\approx \frac{g_2 k^2}{4} + \kappa k^4 - \frac{g_2^2 k^2/(4d^2)}{(\lambda + 2\mu)k^2 + g_2/d^2} \\
&\approx \kappa k^4 + \frac{(\lambda + 2\mu)d^2}{4} k^4 \\
&\quad \times \left[1 - O\left(\frac{(\lambda + 2\mu)k^2}{g_2/d^2}\right)\right].
\end{aligned} \tag{17}$$

The quartic term in this expression is consistent with the continuum analysis described below. The flexural modes acquire a contribution which is independent of the parameter g_2, and which scales with the three-dimensional bulk modulus and with d^3, as the relation between two- and three-dimensional Lamé coefficients is $\lambda,\mu \propto c_{12}d, c_{66}d$.

For graphene (2D), $\kappa \ll (\lambda + 2\mu)d^2$, so that the second term dominates in Eq. (17). The bending rigidity of a bilayer should be significantly larger than that of a single layer, provided that the interlayer shear rigidity $g_2 \neq 0$. Using again $\lambda = 2$ eV Å^{-2} and $\mu = 10$ eV Å^{-2}, $g_2 = 0.03$ eV, and $d = 3.3$ Å, we find a crossover from a high to a low value of the flexural rigidity at a length $\ell = k^{-1} \approx 55$ Å. Note that the atomistic simulations for finite-size crystallites in Ref. 21 deal with a larger k region giving approximately the same values for the bending rigidity (per layer) for single-layer and bilayer graphene.

The model in Eq. (14) can be generalized to an arbitrary number of layers, as we show in Sec. V. The dispersion of the flexural phonons for systems with a different number of layers is shown in Fig. 1. The figure highlights the two regimes discussed in the bending rigidity of a graphene multilayer: (i) Above a crossover length, of order k_c^{-1}, the bending rigidity is given by the bending rigidity of an individual plane, irrespective of the number of planes. This regime is shown in the top plot where for $\frac{k}{k_c} \gg 1$ all curves coincide irrespective of the number of layers. (ii) Below the crossover length, on the other hand, the bending rigidity is determined by the in-plane elastic constants and it depends on the number of layers, in agreement with the general behavior of elastic plates.[17] This regime is better observed if energy and momentum are rescaled with the number of planes in the multilayer, N, where now all curves become indistinguishable for $\frac{kN}{k_c} \ll 1$ (bottom plot).

By applying an in-plane strain, u, the frequencies in Eq. (17) are reduced by

$$\delta(\rho\omega^2) = -u(\lambda + \mu)k^2. \tag{18}$$

This expression gives a Grüneisen parameter

$$\gamma_k = -\frac{\lambda + \mu}{2[\kappa + (\lambda + 2\mu)d^2]k^2} \approx -\frac{\lambda + \mu}{2(\lambda + 2\mu)d^2k^2}. \tag{19}$$

This value is lower than the corresponding expression for single-layer graphene, so that the negative expansion coefficient is reduced in a graphene bilayer. The analysis probably can be extended to graphite, although the dispersion of the out-of-plane modes will no longer be quadratic.

V. MULTILAYERED GRAPHENE: CONTINUUM MODEL

The elastic energy of a slab which is isotropic in the xy plane can be written as

$$\mathcal{E} = \int_{-h/2}^{h/2} dz \int d^2\vec{\mathbf{r}} \left[\frac{c_{12}}{2}(u_{xx} + u_{yy})^2 + \frac{c_{33}}{2}u_{zz}^2 + c_{13}(u_{xx} + u_{yy})u_{zz} + c_{66}\left(u_{xx}^2 + u_{yy}^2 + 2u_{xy}^2\right) + 2c_{44}\left(u_{xz}^2 + u_{yz}^2\right) \right], \tag{20}$$

where we use the notation c_{ij} for the elastic constants instead of Lamé coefficients.

We assume that the slab is sufficiently narrow so that the stresses at the top and bottom surface do not differ much. The boundary conditions are[14]

$$\begin{aligned} 0 = \sigma_{zz} &= c_{33}u_{zz} + c_{13}(u_{xx} + u_{yy}), \\ 0 = \sigma_{xz} &= 2c_{44}u_{xz}, \\ 0 = \sigma_{yz} &= 2c_{44}u_{yz}. \end{aligned} \tag{21}$$

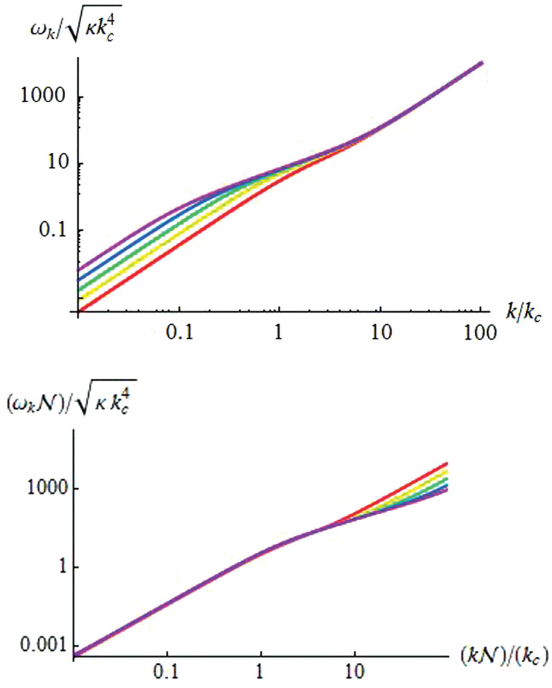

FIG. 1. (Color online) Log-log plot of the dispersion of the flexural modes in graphene multilayers ($k_c^2 = \frac{\kappa}{[(\lambda+2\mu)d^2]}$). Top panel: From bottom to top: 2, 4, 8, 16, and 32 layers. Bottom panel: as in the top graph, with k and w_k rescaled to the number of layers, N.

From these equations, we obtain

$$\begin{aligned} u_{zz} &= -\frac{c_{13}(u_{xx} + u_{yy})}{c_{33}}, \\ u_x &= -z\partial_x u_z, \\ u_y &= -z\partial_y u_z, \\ u_{xx} + u_{yy} &= -z\left(\partial_{xx}^2 u_z + \partial_{yy}^2 u_z\right). \end{aligned} \tag{22}$$

Finally, the frequencies of the flexural modes are given by

$$\rho\omega^2 = \frac{h^2}{12}\left[\lambda + 2\mu - \frac{c_{13}^2}{c_{33}}\right]k^4. \tag{23}$$

This expression does not depend on the value of c_{44}, but the value of this parameter must be different from zero in order for Eq. (21) to be valid, in agreement with the analysis carried out earlier for the bilayer.

VI. CONCLUSIONS

We have used classical elasticity theory to set up an analytical model to describe the role of anharmonicity in the anomalous thermal expansion of very few layers of graphene. While flexural modes explain the negative sign of α at very low T, we find that the change to positive values in graphite at high temperature cannot be explained by anharmonic effects originating on these modes alone. For a bilayer, a crossover between long and short wavelengths has been found from a Landau-like analysis. Finally, the evolution from a single layer to a large stack of weakly interacting layers has been described, and the frequencies for the corresponding bending modes have been obtained.

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