Quadratic flexural acoustic phonons and in-plane sound propagation in graphene

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The discovery of graphene1–4 proved the existence of 2D materials and launched their science and technology. Graphene is already a reality in different industrial products5 that benefit from its fantastic properties. In particular, its mechanical and thermal properties are crucial for many of its current and future applications. For instance, graphene’s uneven strength, stiffness, and lightness6 have been used to make stronger but lighter macroscopic objects, such as tennis rackets, shoes, and so on. Graphene, due to its very high thermal conductivity7, has been already incorporated into electronic devices like mobile phones for efficient heat dissipation.

The understanding of the mechanical, vibrational, and thermal properties of graphene, and in general of any 2D material, is, however, far from trivial. Even the possibility of having crystalline order in 2D has been long questioned8,9. Indeed, the root mean square displacement calculated in the harmonic approximation diverges in the long wave-length limit, which means that the larger the sample of a 2D material the bigger the atomic displacements, which prevents any crystalline order8. Mermin’s theorem9 proves that, even without assuming the harmonic approximation, long-range crystalline order is not possible in a two-dimensional crystal described by a pair potential at $T \neq 0$. Experimentally, however, crystalline order has been observed in suspended graphene10, although it shows ripples that seem to be intrinsic11.

Most of the problems related to the mechanical stability of graphene are caused by the quadratic dispersion of the acoustic out-of-plane (ZA) mode that is obtained in the harmonic approximation. In this approach, phonon frequencies are obtained diagonalizing the $\phi_{ab}/\sqrt{M_a M_b}$ dynamical matrix, where $a$ and $b$ represent both atom and Cartesian indices, $M_a$ is the mass of atom $a$, and $\phi_{ab} = \left[ \frac{\partial^2 V}{\partial R_a \partial \phi_b} \right]_0$ are the second-order force constants obtained as the second-order derivatives of the Born–Oppenheimer potential $V$ with respect to atomic positions $R$. Rotational symmetry, together with the fact that in a strictly two-dimensional system force constants involving an in-plane and an out-of-plane displacement vanish, makes the ZA mode acquire a quadratic dispersion close to zone center12.

The quadratic dispersion also implies the unphysical result that graphene does not propagate sound. The phonon linewidths of the in-plane acoustic longitudinal (LA) and transverse (TA) phonons calculated perturbatively from the harmonic result do not vanish as the momentum decreases13, precisely, because of the $\sim q^2$ dispersion of the ZA modes14. This yields the conclusion that phonons having sufficiently small momentum do not live long enough for vibrating one period and the quasiparticle picture is lost, together with the propagation of...
sound in the plane. For the same reason as well, the thermal conductivity calculated with the perturbative phonon lifetimes\textsuperscript{15,16} does not converge with the sample size\textsuperscript{14}. The application of strain linearizes the dispersion of the ZA phonons and makes the linewidth of the LA and TA phonon modes vanish together with their frequency at small momenta, recovering the phonon picture\textsuperscript{14}.

It has been argued\textsuperscript{12,17–22} that the anharmonic coupling between in-plane and out-of-plane phonon modes renormalizes the dispersion of the ZA phonon modes, providing it with a linear term at small momenta that somewhat cures the pathologies. This conclusion has been drawn by Monte Carlo simulations with empirical potentials\textsuperscript{12,17–19} and by using a membrane continuum Hamiltonian that mimics the interaction among acoustic modes\textsuperscript{20–22}. Anharmonic phonons expected experimentally should be calculated from the phonon spectral function given by the phonon self-energy\textsuperscript{23} (see Supplementary Material\textsuperscript{24}). For low energy modes, such as the ZA mode, dynamical effects can be safely neglected. In this limit the phonon peaks coincide with the eigenvalues of the free energy Hessian $\left[ \frac{\partial^2 F}{\partial R^2} \right]_{\beta} / \sqrt{M_{\rho}^2 M_{\Phi}}$, where $F$ is the free energy calculated including anharmonic effects and $\Phi$ the most probable ionic positions\textsuperscript{23}. As $F$ obeys the same symmetry properties as $V$, a similar $\sim q^2$ dispersion would be expected for the ZA mode even if anharmonic effects are included in the calculation of $F$. Actually, measurements done with helium diffraction show a ZA mode with a quadratic dispersion\textsuperscript{25–27}, though the linearization regime may not be seen and substrate effects may be important. The remaining question is thus whether the ZA modes really have a quadratic dispersion, and, if it is so, how sound waves can exist in graphene.

In this work we show that a quadratic dispersion of the ZA mode in graphene is actually expected for unstrained graphene provided that it is calculated from the anharmonic spectral function, and that it is compatible with well-defined sound waves. To account for anharmonicity at all orders, we apply the self-consistent harmonic approximation (SCHA) in its stochastic implementation (SSCHA)\textsuperscript{23,28,29} making use of a machine learning atomistic potential trained with density functional theory\textsuperscript{30}. We also solve the SCHA equations in a membrane continuum Hamiltonian. The SCHA is a variational method that minimizes the free energy of the system

$$F = \langle T + V + \frac{1}{\beta} \ln \rho_{\mathcal{R} \Phi} \rangle_{\beta \rho_{\mathcal{R} \Phi}}$$

(1)

with respect to a density matrix $\rho_{\mathcal{R} \Phi}$ parametrized with centroid positions $\mathcal{R}$ and effective force constants $\Phi$, which are related to the width of the ionic fluctuations around $\mathcal{R}$ (bold symbols represent vectors or tensors in compact notation). In Eq. (1) $T$ is the ionic kinetic energy, $\beta$ the inverse temperature, and $\langle O \rangle_{\beta \rho_{\mathcal{R} \Phi}} = \text{tr}[\rho_{\mathcal{R} \Phi} O]$ ($O$ is any operator). Our results show that even if the dispersion of the ZA mode obtained from the SCHA phonon spectral function is quadratic in unstrained graphene, the linewidths of the LA and TA modes calculated within the SCHA vanish as expected at small momenta in contrast to the harmonic result.

Figure 1. Lattice parameter of graphene as a function of temperature obtained with the SSCHA using a machine learning atomistic potential. Both quantum (black) and classical (blue) calculations are included. The classical result is calculated setting $\hbar = 0$ in the SCHA free energy. The temperature-independent frozen nuclei (FN) result corresponds to the lattice parameter that minimizes the Born Oppenheimer potential $V$. Results obtained by Rowe et al.\textsuperscript{30} are also included for comparison. The black dashed line corresponds to the quasiharmonic result. In the grey zone harmonic phonons become unstable breaking down the quasiharmonic approximation.

In order to calculate phonon spectra in unstrained graphene at any temperature, we calculate the SCHA stress tensor following the procedure in Ref. \textsuperscript{29} and pick the lattice parameter that sets it to zero at each temperature. The lattice parameter calculated in this way includes anharmonic effects as well as the effect of quantum and thermal fluctuations. In order to properly account for thermal expansion, all the phonon spectra shown in this work that are obtained with the atomistic potential are calculated with the lattice parameter that gives a null SCHA stress at each temperature. The harmonic spectra on the contrary are always calculated at the lattice parameter that minimizes $V$. The temperature dependence of the lattice parameter is shown in Fig. 1. We include the molecular dynamics (MD) results of Rowe et al. obtained with the same potential\textsuperscript{30}, which do not account for quantum effects. For comparison, we also include SSCHA calculations in the classical limit, by making $\hbar = 0$ in $\rho_{\mathcal{R} \Phi}$, and within the quasiharmonic (QH) approximation. We expand our calculations up to 500 K, as below this temperature corrugations seem negligible\textsuperscript{10,34}. The centroid positions in the SCHA calculations are in the plane. Our quantum calculations correctly capture the negative thermal expansion of graphene that has been estimated in previous theoretical works\textsuperscript{19,30}. Our SCHA result shows a larger lattice parameter than the classical result. This is not surprising as classical calculations neglect quantum fluctuations and, consequently, underesti-
Figure 2. Harmonic ZA phonon spectra together with the SCHA phonons obtained diagonalizing \( \Phi_b \) (labeled as “SCHA”) and those obtained from the phonon spectral function (labeled as “Physical”). Results at 0 K (a) and 300 K (b) are shown. (c) and (d) show the frequency divided by the squared momentum. In the panels the dispersion corresponds to the \( \Gamma M \) spectra with the one obtained diagonalizing the SCHA spectral function, the physical phonons are flat. The SCHA ZA frequencies is very clear in Fig. 2(c) and (d), where we show the frequency divided by the squared momentum and the dispersion of the ZA modes obtained from \( \Phi \). Both shifts are bigger when the temperature is increased, but the quadratic behavior of the ZA modes is always recovered regardless of the temperature. In (e) we show the temperature dependence of the frequency shift of the optical \( E_{2g} \) mode calculated within the SCHA and from the phonon spectral function. We include experimental results in graphene\(^{31}\) and graphite\(^{32,33}\). All these calculations are performed with the machine learning atomistic potential.

In Figs. 2 (a)-(d) we compare the harmonic phonon spectra with the one obtained diagonalizing the \( \Phi_b \) as well as with the spectra obtained from the SCHA spectral function, the physical phonons. The main conclusion is that while the dispersion of the ZA modes obtained from \( \Phi \) is linearized, the physical phonons given by the spectral function become close to a quadratic dispersion and approach the harmonic dispersion, as expected by symmetry. This is very clear in Fig. 2(c) and (d), where we show the frequency divided by the squared momentum and the physical phonons are flat. The SCHA ZA frequencies suffer a blue-shift with respect to the harmonic ones, but are red-shifted once the physical phonons are calculated. Both shifts are bigger when the temperature is increased, but the quadratic behavior of the ZA modes is always recovered regardless of the temperature. In Fig. 2 (e) we show the results for the optical \( E_{2g} \) mode. We observe that both SCHA and physical frequencies red-shift with increasing temperature. This is in agreement with experiments\(^{32,33,36}\), as shown in the figure, and theory\(^{37}\). For this mode the difference between the SCHA and physical results is not so crucial.

Even if the anharmonic correction to the phonon spectra may look small in Fig. 2, it has a huge impact on the mechanical and thermal properties of graphene. When calculating the root mean square atomic displacement with the SCHA density matrix as \( \sqrt{\langle |\Phi|^2 \rangle} \), the dramatic divergences with the sample size obtained in the harmonic case are partially suppressed (see Supplementary Material\(^{24}\)), clearly showing the contribution of anharmonicity to the mechanical stability of graphene. The divergences reduce precisely because the SCHA auxiliary phonon frequencies obtained from \( \Phi \) that build \( \rho_{bR} \) are linear at small momenta (see Fig. 2). Thus, even if the phonons obtained from the SCHA spectral function are quadratic, the fact that the density matrix used to compute thermodynamic properties is built with auxiliar linearized phonons makes the divergences reduce.

As shown in Fig. 3, the SCHA calculation dramatically changes the linewidth of the LA and TA modes at small momenta by making them smaller as momentum decreases, in clear contrast to the harmonic result. This happens thanks to the linearization of the SCHA auxiliary acoustic phonons at small momentum. When the ratio between the FWHM and the frequency of the mode is approximately 1, the quasiparticle picture is lost.

\[ \omega / |q| \]
This value is reached in the 0.001-0.002 Å⁻¹ momentum range in the harmonic case. However, when the linewidth is calculated within the SCHA, the ratio never gets bigger than 0.05. These results recover the quasiparticle picture for these modes at any wavevector, guaranteeing that graphene always propagates sound. The momentum range for which the quasiparticle picture is lost in the harmonic approximation can be reached experimentally with Brillouin scattering probes. In fact, for few layer graphene the quasiparticle picture holds in the 0.001-0.002 Å⁻¹ region, in agreement with our calculations. It has been argued previously that strain linearizes the ZA dispersion and makes the linewidths of LA and TA modes vanish at small momenta. We show here that strain linearizes the quadratic ZA physical phonon dispersion in graphene, but, more importantly, we also show that there is no need of strain to have physically well-defined phonon linewidths.

In order to obtain results at very small momenta and reinforce the conclusions drawn with the atomistic calculations with the machine learning potential, we also solve the SCHA equations in a continuum membrane Hamiltonian. This model has been widely used in the literature to describe graphene as an elastic membrane as well as to account for the coupling between in-plane and out-of-plane acoustic modes. The most general rotationally invariant continuum model potential to describe a free-standing 2D membrane up to the fourth-order in the phonon fields has the following form:

\[ V = \frac{1}{2} \int d^2 x \left[ \kappa (\partial^2 h)^2 + C^{ijkl} \partial_i u_j \partial_k h \partial_l h + \frac{C^{ijkl}}{4} \partial_i h \partial_j h \partial_k h \partial_l h + \frac{C^{ijkl}}{2} \partial_i u \cdot \partial_j u \partial_k h \partial_l h + C^{ijkl} \partial_i u_j \partial_k u \cdot \partial_i u + \frac{C^{ijkl}}{4} \partial_i u \cdot \partial_j u \partial_k u \cdot \partial_i u \right]. \] (2)

Here \( u(x) \) and \( h(x) \) are the in-plane and out-of-plane displacement fields, respectively, and \( x \) is the 2D position vector in the membrane. \( \kappa \) is the bending rigidity of the membrane, \( \Omega \) is the area of the membrane, and the tensor \( C^{ijkl} = \lambda \delta^{ij} \delta^{kl} + \mu (\delta^{ik} \delta^{jl} + \delta^{il} \delta^{jk}) \) contains the Lamé coefficients \( \lambda \) and \( \mu \) and Kronecker deltas. We have calculated the parameters by fitting them to the atomistic potential, which yields \( \lambda = 4.3 \) eVÅ⁻², \( \mu = 9.3 \) eVÅ⁻², \( \kappa = 1.5 \) eV and \( \rho/h^2 = 1097 \) eVÅ⁻⁴. This continuum model only accounts for acoustic modes. The harmonic acoustic frequencies given by Eq. (2) are \( \omega_{ZA}(q) = \sqrt{\kappa/\rho q^2}, \omega_{LA}(q) = \sqrt{(\lambda + \mu)/\rho q}, \) and \( \omega_{TA}(q) = \sqrt{\rho \kappa}, \) \( \rho \) being the mass density of the membrane. The thermal expansion is included in this formalism by changing the in-plane derivatives as \( \partial_i u_j \rightarrow \partial_i u_j + \delta^j_i \delta a, \) with \( \delta a = (a - a_0)/a_0, \) \( a_0 \) being the lattice parameter that...
minimizes $V$. We perform the SCHA variational minimization numerically with the potential in Eq. (2).

The results obtained in this rotationally invariant membrane are shown in Fig. 4. All conclusions drawn with the atomistic model are confirmed and put in solid grounds. Again the ZA phonons obtained from the auxiliary SCHA force constants get linearized at small momenta. These results are consistent with the anharmonic linearization obtained for this mode in previous calculations\textsuperscript{20–22}. However, when the phonons are calculated from the Hessian of the SCHA free energy (due to the low frequencies of the ZA modes this static approximation is perfectly valid as shown in the Supplementary Material\textsuperscript{24}), the ZA phonon frequencies get basically on top of the harmonic values recovering a quadratic dispersion. This means that the physical phonons have a quadratic dispersion for small momenta in an unstrained membrane, as it is expected by symmetry. We also show that accounting correctly for the thermal expansion is crucial to recover the $\sim q^2$ behavior as shown in Fig. 4(b). The membrane potential is able to capture the negative thermal expansion at small temperatures (see Supplementary Material\textsuperscript{24}). It is important to remark that if the rotational symmetry of the potential is broken, e.g. by neglecting the last three terms in Eq. (2)\textsuperscript{20–22}, the quadratic phonon dispersion (see Fig. 4(b)) is not recovered and the mechanical properties of graphene are not correctly estimated. This underlines the importance of keeping all terms in Eq. (2), which is not usually the case\textsuperscript{20–22}, to properly describe graphene’s mechanical and vibrational properties. We also calculate the linewidths of the LA and TA modes in the membrane model in the harmonic and SCHA cases (see. Fig. 3). Again, the results show how the quasiparticle picture is lost in the harmonic case, while it is completely recovered in the SCHA. The linewidths calculated in the atomistic case and within the membrane model are surprisingly close. This means that the simple empirical coefficients that parametrize the membrane potential capture all the anharmonicity that affects acoustic modes in graphene.

In conclusion, we show that anharmonic effects are crucial to make sound propagate in graphene. Moreover, we determine that, despite the relevance of anharmonic effects, the out-of-plane acoustic modes should show a quadratic dispersion experimentally. We estimate anharmonic effects within the self-consistent harmonic approximation both with an atomistic machine learning potential and with a membrane model, obtaining consistent results in both cases. These conclusions can be extrapolated to any strictly 2D material and will have a large impact on the understanding of their mechanical, vibrational, and thermal properties.

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