Ising instability of a Holstein phonon mode in graphene

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We study the thermal distribution of phonons in a honeycomb lattice. Due to the two electronic bands there are two out-of-plane phonon modes with respect to the two sublattices. One of these modes undergoes an Ising transition by spontaneously breaking the sublattice symmetry. We calculate the critical point, the renormalization of the phonon frequency and the average lattice distortion. This transition might be observable in doped graphene by Raman scattering and transport experiments.

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Transport measurements have revealed many interesting properties of the two-dimensional material graphene.[1–6] More recently, Raman scattering has become an additional experimental method to study physical properties of graphene.[7–10] It provides a deeper insight into the elastic properties of the honeycomb lattice of carbon atoms and the related electron-phonon interaction. Since the latter is important also for some of the unusual transport properties, these results are of great value for a better understanding of graphene.

Recent experiments on hydrogenated graphene (graphane) have revealed additional Raman spectral lines due to hydrogen atoms,[10] indicating that there is an important electron-phonon interaction between the conduction electrons and the lattice formed by the hydrogen atoms. Another mechanism that might change the band structure is the graphene-substrate interaction in epitaxial graphene, which can lead to a band opening due to breaking the graphene sublattice symmetry.[11] These results indicate that doping can alter the properties of graphene by changing the band structure as well as by modifiying the elastic properties due to phonons.

Theoretical studies of the electron-phonon interaction in graphene at zero temperature came to a mixed conclusion. Although the electron-phonon coupling is remarkably strong in terms of a renormalization of the lattice vibrations, its effect on transport properties is rather weak.[5,12] In particular, the out-of-plane optical mode (ZO phonon) has almost no effect on transport at all.[13] Some experiments also provide evidence that transport properties are not much affected by phonons.[14] This requires a better understanding of the electron-phonon interaction and its consequences for the transport properties.

In this Brief Report we will explain that the ZO phonon mode can play an important role by spontaneously breaking the chiral (sublattice) symmetry of graphene. This effect is accompanied by an Ising transition which is associated with a softening of the optical phonon mode.

Model. The dynamics of phonons of a honeycomb lattice is complex and can be described by a number of phonon modes.[5,12,13,15,16] For simplicity, we focus here on optical phonons, coupled to the electrons by a Holstein interaction.[13] Then in a tight-binding description, electrons coupled to optical (Einstein) phonons at frequency ω_0 are described by the Holstein Hamiltonian as

$$H = \omega_0 \sum_{\mathbf{r}} b^\dagger_{\mathbf{r}} b_{\mathbf{r}} + \sum_{\mathbf{r},\mathbf{r}'} h_{\mathbf{r},\mathbf{r}'} c^\dagger_{\mathbf{r}} c_{\mathbf{r}'} + \alpha \sum_{\mathbf{r}} f(b_{\mathbf{r}} + b^\dagger_{\mathbf{r}}) c^\dagger_{\mathbf{r}} c_{\mathbf{r}}. \tag{1}$$

Here $c^\dagger_{\mathbf{r}}$ ($c_{\mathbf{r}}$) are the electron creation (annihilation) operators and $b^\dagger_{\mathbf{r}}$ ($b_{\mathbf{r}}$) are the phonon creation (annihilation) operators. Usually the Holstein model has a linear electron-phonon coupling $f(x) = x$. However, geometric constraints can enforce a mirror symmetry, where the coupling should be symmetric with respect to out-of-plane distortions in the two directions. This effect can be taken into account by a quadratic coupling $f(x) = x^2$.[17]

The conventional approach to determine the properties of a coupled system of phonons and electrons is based on a self-consistent evaluation of the self-energy (Migdal approximation).[18,19] The latter provides an effective (or renormalized) energy and its imaginary part provides an effective scattering rate. Such a static approximation might be insufficient in a two-dimensional system, since it does not take into account thermal fluctuations.[9] Therefore, we include thermal fluctuations in our approach. To this end, we replace the phonon operators $b_{\mathbf{r}}, b^\dagger_{\mathbf{r}}$ by their quantum averages $b_{\mathbf{r}} \approx \langle b_{\mathbf{r}} \rangle \equiv u_{\mathbf{r}}$ and $b^\dagger_{\mathbf{r}} \approx \langle b^\dagger_{\mathbf{r}} \rangle \equiv u^*_{\mathbf{r}}$, and replace the phonon term in the Holstein Hamiltonian by $f(v_{\mathbf{r}}) = f(u_{\mathbf{r}} + u^*_{\mathbf{r}})$. In this approximation we can keep thermal fluctuations but ignore quantum fluctuations of the phonons. The electrons, on the other hand, are studied in full quantum dynamics. This reduces the grand-canonical ensemble at inverse temperature β to a functional integral with respect to thermal fluctuations of the lattice distortions $v_{\mathbf{r}}$ and a trace with respect to the electrons. After performing the trace over the electrons we get the partition function

$$\mathrm{Tr}\, e^{-\beta H} \approx \int \det(\mathbf{1} + e^{-\beta h}) e^{-\beta S_0} \mathcal{D}[v] \equiv Z, \tag{2}$$

with the phonon dispersion

$$S_0 = \frac{\omega_0}{2} \sum_{\mathbf{r}} \vec{v}^2_{\mathbf{r}}. \tag{3}$$

It is convenient to introduce a sublattice representation for the tight-binding Hamiltonian h, since the graphene unit cell

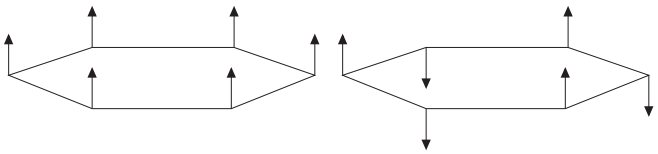

FIG. 1. The two out-of-plane modes: the μ' mode (left-hand figure) and the m mode (right-hand figure). The arrows indicate the distortions of the carbon atoms according to Eq. (9).

contains two atoms, each of them having one π orbital. This gives a two-component wave function, and the electronic Hamiltonian can be expressed by 2×2 (Pauli) matrices whose matrix elements refer to the A and B sublattices:

$$h_e = \begin{pmatrix} -\mu & \hat{t} \\ \hat{t}^T & -\mu, \end{pmatrix} \equiv h_1\sigma_1 + h_2\sigma_2 - \mu\sigma_0, \tag{4}$$

with $h_1 = (\hat{t} + \hat{t}^T)/2, h_2 = i(\hat{t} - \hat{t}^T)/2$, and with the chemical potential (bare Fermi energy) μ. In case of the honeycomb lattice $\hat{t}$ is a matrix that connects nearest-neighbor sites on the lattice

$$\hat{t}_{\mathbf{r},\mathbf{r}'} = t \sum_{j=1}^{3} \delta_{\mathbf{r}',\mathbf{r}+\mathbf{a}_j}, \tag{5}$$

where $\mathbf{r}$ is on sublattice A and $\mathbf{r} + \mathbf{a}_j$ is on sublattice B. Thus $\hat{t}$ describes an electronic hop from sublattice B to sublattice A and vice versa for $\hat{t}^T$.

The linear electron-phonon coupling reads in this sublattice representation as (spatial dependence of the distortions are implictly assumed)

$$h_{e\text{-ph}} = \alpha \begin{pmatrix} v_\mathrm{A} & 0 \\ 0 & v_\mathrm{B} \end{pmatrix} = \psi\sigma_0 + \phi\sigma_3, \tag{6}$$

where $\psi = \alpha(v_\mathrm{A} + v_\mathrm{B})/2$ and $\phi = \alpha(v_\mathrm{A} - v_\mathrm{B})/2$. For quadratic coupling this reads

$$h_{e\text{-ph}} = \alpha \begin{pmatrix} v_\mathrm{A}^2 & 0 \\ 0 & v_\mathrm{B}^2 \end{pmatrix} = \frac{1}{\alpha}[(\psi^2 + \phi^2)\sigma_0 + 2\psi\phi\sigma_3]. \tag{7}$$

It should be noticed that each of the two phonon modes couples linearly to σ_3. The out-of-plane modes ψ and ϕ break the chiral symmetry of h_e. Due to the rescaled phonon modes Eq. (3) becomes

$$S_0 = \sum_{\mathbf{r}} \left(\omega_\psi \psi_\mathbf{r}^2 + \omega_\phi \phi_\mathbf{r}^2\right), \quad \omega_\psi = \omega_\phi = \omega \equiv \frac{\omega_0}{\alpha^2}. \tag{8}$$

Eventually, the combined electronic Hamiltonian $h = h_e + h_{e\text{-ph}}$ reads

$$h = h_1\sigma_1 + h_2\sigma_2 + (\mu' - \mu)\sigma_0 + m\sigma_3, \tag{9}$$

where $\mu' = \psi$, $m = \phi$ for linear coupling and $\mu' = (\psi^2 + \phi^2)/\alpha$, $m = 2\psi\phi/\alpha$ for quadratic coupling (See Fig. 1).

Z of Eq. (2) serves as a generating function that allows us to get, for instance, the static electronic Green's by differentiation of $\ln Z$ as

$$G_{\mathbf{r},\mathbf{r}'} = \frac{1}{Z} \int (\mathbf{1} + e^{-\beta h})^{-1}_{\mathbf{r},\mathbf{r}'} e^{-\beta S} \mathcal{D}[\phi, \psi], \tag{10}$$

with $S = S_0 - \beta^{-1} \ln\det(\mathbf{1} + e^{-\beta h})$. It is important to notice that $e^{-\beta S} = e^{-\beta S_0} \det(\mathbf{1} + e^{-\beta h})$ is a non-negative function. Therefore, $e^{-\beta S}/Z$ is a probability density for the phonon field. Then the static one-particle Green's function can be rewritten as an average $\langle \cdots \rangle_\mathrm{ph}$ with respect to the distribution $e^{-\beta S}/Z$:[20]

$$G_{\mathbf{r},\mathbf{r}'} = \left\langle (\mathbf{1} + e^{-\beta h})^{-1}_{\mathbf{r},\mathbf{r}'} \right\rangle_\mathrm{ph}. \tag{11}$$

Without an electron-phonon interaction the distribution of lattice vibrations is $\exp(-\beta S_0)$ such that the average lattice distortion vanishes: $\langle\phi\rangle_\mathrm{ph} = \langle\psi\rangle_\mathrm{ph} = 0$. A nonzero $\langle\mu'\rangle_\mathrm{ph}$ presents a shift of the Fermi energy, whereas a nonzero $\langle m\rangle_\mathrm{ph}$ would break the sublattice symmetry. An interesting question is whether or not a coupling to electrons can create a nonzero average distortion. From the symmetry point of view this should not be the case for m because the system is invariant under the transformation $m \to -m$. This is a consequence of the fact that the distribution $e^{-\beta S}/Z$ is invariant under the unitary transformation $U = (\sigma_1 + \sigma_2)/\sqrt{2}$:

$$UhU^\dagger = h_1\sigma_2 + h_2\sigma_1 + (\mu' - \mu)\sigma_0 - m\sigma_3. \tag{12}$$

This means for h in Eq. (9) an exchange of h_1 with h_2 and a sign change $m \to -m$. Since the system is assumed to be isotropic, only the sign change remains. This is the invariance under a Z_2 (Ising-like) transformation, where $\langle m\rangle_\mathrm{ph} \neq 0$ represents a typical problem of spontaneous symmetry breaking.

From now on we focus on the case with linear coupling, which is relevant for graphene on a substrate. The quadratic coupling would give similar results because the mechanism of spontaneous symmetry breaking is identical for both couplings.

In previous calculations only the ψ mode was taken into account, whereas the ϕ mode has been neglected by assuming $\phi = 0$.[12,13] Indeed, a solution with $\langle\phi\rangle = 0$ always exists due to the symmetry in Eq. (12). However, spontaneous symmetry breaking is possible. This would be associated with an instability of the $\langle\phi\rangle = 0$ solution. Although the symmetry-breaking solution is not available from a simple perturbation theory, the latter can be employed to analyze the stability of the symmetry-preserving solution. For this purpose we evaluate the shift of the phonon frequency $\alpha^2\omega_\psi \to \omega_0 + \delta\omega_0$, $\alpha^2\omega_\phi \to \omega_0 + \delta\omega_3$ for $\mathbf{q} = 0$ (i.e., at the Γ point of the Brillouin zone). In second-order perturbation theory in α (Refs. 5,12, and 13) this gives for our model $\delta\omega_0 \sim -\mathrm{const}/\beta$ and

$$\delta\omega_3 = -\frac{\alpha^2}{2\pi\beta t^2} \ln\left[\frac{\cosh(\beta t\Lambda) + \cosh(\beta\mu)}{1 + \cosh(\beta\mu)}\right], \tag{13}$$

where $\Lambda = 2\sqrt{\pi}$ is the momentum cutoff. Thus the renormalization of ω_0 of the ψ mode vanishes at low temperatures. The situation is different for the ϕ mode. Although $\delta\omega_3$ also decreases with decreasing temperature, it has a nonzero value in the limit of zero temperature (cf. Fig. 2). Then the solution $\phi = 0$ is stable (unstable) if $\omega_0 + \delta\omega_3 \geqslant 0$ (<0). An unstable situation with negative renormalized phonon frequency of a different mode was also found by Castro Neto *et al.*[5]

In order to find a stable solution for $\omega_0 + \delta\omega_3 < 0$ we must go beyond perturbation theory. One possibility is to extend the second-order calculation by a partial resummation of the perturbation series to all orders of α. This would provide a self-consistent calculation for the phonon modes. However, it is more convenient here to use a saddle-point (SP) approximation

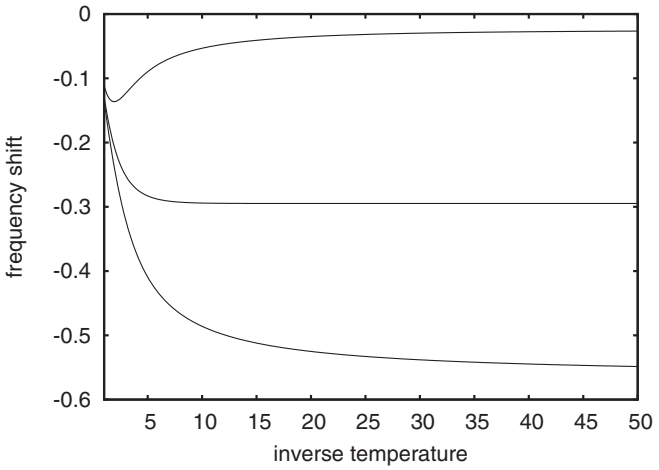

FIG. 2. Frequency shift $\delta\omega_3/\alpha^2$ in units of $1/t$ vs inverse temperature βt for $\mu/t = 0,3,6$ (from bottom to top) from Eq. (13).

for the ϕ,ψ integration in Eqs. (2) and (10). This calculation can be extended to include fluctuations around the SP solution. The latter allows us to analyze the stability of the SP solution, to identify possible instabilities, and to determine the phonon dispersion.

The SP approximation is based on the variational equation $\delta S = 0$, where the SP equation reads

$$\beta\omega\phi_j = \frac{\partial}{\partial\phi_j}\ln[\det(\mathbf{1} + e^{-\beta h})] \quad (j = 0,3), \tag{14}$$

with $\phi_0 = \psi$ and $\phi_3 = \phi$. Now we assume that the SP solution ψ,ϕ is uniform in space. Thus our SP solution is a mean-field approximation. This allows us to diagonalize the argument of the trace term in Eq. (14) using a Fourier representation. Moreover, we now approximate the Hamiltonian h_e by its low-energy Dirac behavior $h_e \sim k_1\sigma_1 + k_2\sigma_2$. Then the eigenvalues of h are $\lambda_\pm = \psi - \mu \pm \sqrt{\phi^2 + t^2k^2}$ and the SP equations read

$$\omega\psi = -1 - \int_0^\Lambda \frac{\sinh[\beta(\mu-\psi)]}{D(\psi,\phi)}\frac{k\,dk}{2\pi}, \tag{15}$$

$$\omega\phi = \int_0^\Lambda \frac{\phi}{\sqrt{\phi^2 + t^2k^2}}\frac{\sinh(\beta\sqrt{\phi^2 + t^2k^2})}{D(\psi,\phi)}\frac{k\,dk}{2\pi}, \tag{16}$$

with

$$D(\psi,\phi) = \cosh[\beta(\mu-\psi)] + \cosh(\beta\sqrt{\phi^2 + t^2k^2}). \tag{17}$$

The integration in Eq. (16) can be performed and gives

$$\omega\phi = \frac{1}{2\pi\beta t^2}\phi\ln\left[\frac{\cosh(\beta\sqrt{\phi^2 + t^2\Lambda^2}) + \cosh(\beta\bar{\mu})}{\cosh(\beta\phi) + \cosh(\beta\bar{\mu})}\right], \tag{18}$$

with the renormalized chemical potential $\bar{\mu} = \mu - \psi$.

If the mean-field solution $\phi = 0$ is unstable, we have to find a solution $\phi \neq 0$ of Eq. (18). This can be obtained from a quadratic equation after an expansion of Eqs. (15) and (18) for small ϕ and $\bar{\mu}$. Then the equation for ϕ reads

$$\frac{\partial S}{\partial\phi} = \Omega\phi + \Gamma\phi^3 + C\bar{\mu}^2\phi = 0, \tag{19}$$

with the coefficients

$$\Omega = \omega - \frac{1}{\pi\beta t^2}\ln\cosh(\beta t\sqrt{\pi}),$$

$$C = \frac{\beta\tau^2}{8\pi t^2}, \quad \Gamma = \frac{\beta}{8\pi t^2}\left(1 - \frac{\tau}{\beta t\sqrt{\pi}}\right),$$

with $\tau = \tanh(\beta t\sqrt{\pi})$. Besides the vanishing mean-field solution $\phi = 0$, there are now the two nonvanishing solutions

$$\phi_\pm = \pm\frac{1}{\sqrt{\Gamma}}\sqrt{-\Omega - C\bar{\mu}^2}. \tag{20}$$

The power law with exponent $1/2$ is the result of the mean-field approximation. Due to the Ising-like symmetry of Eq. (12), the exponent should be $1/8$ instead of $1/2$.[21] However, this incorrectness may only be important very close to the transition point.

In a small vicinity around the Dirac point $\bar{\mu} = 0$, the SP equation (15) can be linearized and gives for small ϕ a renormalized Fermi energy

$$\bar{\mu} \approx \frac{\mu + 1/\omega}{1 - \ln(2)/\pi\beta\omega t^2}. \tag{21}$$

According to the discussion of Eq. (13), a mean-field solution $\phi = 0$ is unstable when $\Omega + C\bar{\mu}^2 < 0$. For $\beta t \gg 1$ we have

$$\Omega + C\bar{\mu}^2 \sim \omega - \frac{1}{\sqrt{\pi}t} + \frac{\ln 2}{\pi\beta t^2} + \frac{\beta\bar{\mu}^2}{8\pi t^2}. \tag{22}$$

It should be noticed here that with decreasing temperature $\Omega + C\bar{\mu}^2$ *decreases* at the Dirac point $\bar{\mu} = 0$ but it *increases* sufficiently away from the Dirac point. Thus, at sufficiently low temperatures a symmetry-broken mean-field solution exists only in a small vicinity of the Dirac point.

For the case $\Omega + C\bar{\mu}^2 < 0$ we must replace $\phi = 0$ by one of the solutions of Eq. (20). Inserting the proper solution into the expression of the renormalized phonon frequency $\partial^2 S/\partial\phi^2$, we obtain always a non-negative frequency

$$\omega_\phi = \alpha^2\frac{\partial^2 S}{\partial\phi^2} \approx \alpha^2|\Omega + C\bar{\mu}^2|[1 + \Theta(-\Omega - C\bar{\mu}^2)], \tag{23}$$

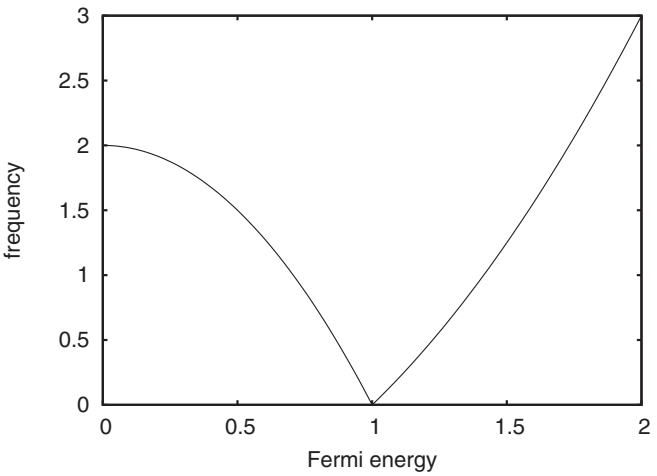

FIG. 3. Renormalized frequency ω_ϕ of the ϕ mode (in arbitrary units) vs. Fermi energy $\bar{\mu}$ (in units of $\sqrt{-\Omega/C}$) from Eq. (23).

where $\Theta(\cdots)$ is the Heaviside function. The behavior of the renormalized phonon frequency is depicted in Fig. 3. This frequency vanishes as a function of the renormalized Fermi energy at the critical point $\mu_c = \sqrt{-\Omega/C}$, provided that $\Omega < 0$. For $\bar{\mu}^2 < \mu_c^2$ we have spontaneous symmetry breaking with $\langle\phi\rangle_{\rm ph} \neq 0$ and for $\bar{\mu}^2 \geqslant \mu_c^2$ a symmetric phase with $\langle\phi\rangle_{\rm ph} = 0$. The softening of the phonons at the critical point should be observable in Raman scattering. Symmetry breaking, on the other hand, may appear in the form of a staggered carbon configuration as in epitaxial graphene[11] or in graphane[10] and should be observable in transport measurements as a metal-insulator transition. However, large fluctuations of ϕ can destroy the gap even for $\langle\phi\rangle_{\rm ph} \neq 0$, similar to the case of a quenched random gap.[22–24]

The values of the model parameters can be compared with experimental data and band-structure calculations. The electronic hopping parameter is $t \approx 2.7$ eV (Ref. 5) and the bare phonon frequency is $\omega_0 \approx 0.1$ eV.[25] With Eq. (22) we need $\alpha > 1.3\sqrt{t\omega_0}$ to observe the Ising transition. This would require $\alpha > 0.7$ eV. Although there is no reliable estimate for α in graphene [e.g., $\alpha \approx 0.5$ eV (Ref. 12)], we can reduce ω_0 for a given coupling constant α by doping with noncarbon atoms (e.g., with hydrogen,[10] oxygen,[26] fluor,[27] NO_2,[28] or organic molecules[29]) to satisfy the transition criterion.

In conclusion, we have found that in the Holstein model for graphene an out-of-plane phonon mode can spontaneously break the sublattice symmetry if the electron-phonon coupling is $\alpha > 1.3\sqrt{t\omega_0}$, leading to a spatially fluctuating gap whose mean value is nonzero. This effect is accompanied by an Ising transition. Although it is not clear whether this can be observed in pristine graphene, doping with noncarbon atoms might provide conditions to create such a transition.

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