# Electron-Induced Rippling in Graphene

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We show that the interaction between flexural phonons, when corrected by the exchange of electron-hole excitations, may drive the graphene sheet into a quantum critical point characterized by the vanishing of the bending rigidity of the membrane. Ripples arise then due to spontaneous symmetry breaking, following a mechanism similar to that responsible for the condensation of the Higgs field in relativistic field theories, and leading to a zero-temperature buckling transition in which the order parameter is given by the square of the gradient of the flexural phonon field.

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*Introduction.*—The discovery of graphene [1–3], the two-dimensional (2D) metallic crystal made of a carbon monolayer, has spurred a flurry of research activity due to its unique electronic properties and potential applications [4]. Its realization can be taken as a nice check of the predicted stability of membranes with crystalline order, in which the fixed connectivity allows for the existence of a low-temperature flat phase [5]. Detailed analyses of this type of membranes have shown that their elastic properties have anomalous momentum dependence, with a rigidity that diverges at long wavelength [6–9]. On top of that, graphene is also a prototype of electronic crystalline membrane, where the mobile electrons are strongly coupled to the elastic degrees of freedom [10,11].

A remarkable and unexpected property observed in graphene is its tendency to develop *ripples*, or long wavelength modulations of the out-of-plane displacements, by which the system *freezes* into a corrugated average configuration [12]. Ripples are expected to have a significant impact on electronic transport in graphene [13].

The origin of graphene's rippling has been heavily debated. In exfoliated graphene, ripples are correlated to some extent with the irregularities of the substrate [14]. But it has been also observed that they may arise in part as an effect intrinsic to the 2D membrane [12]. In this respect, there is evidence that variable length $\sigma$-bonds characteristic of carbon may underlie ripple formation [15]. Other works have focused on the behavior of graphene as an electronic membrane [10,11] in order to investigate the rippling instability.

In this Letter we take farther steps in the study of the role of $\pi$-electrons in the ripple formation mechanism, adopting a self-consistent method supplemented by a renormalization group (RG) approach to the phonon self-energy corrections. The nonperturbative character of this framework allows us to find a critical value of the electron-phonon coupling at which the effective bending rigidity of the membrane vanishes. This effect places the system on the verge of the transition to a new ground state, that proceeds upon the slightest negative tension applied to the sheet. We show that this follows a mechanism similar to that responsible for the condensation of the Higgs field in relativistic field theories, with an order parameter given in this case by the square of the gradient of the flexural phonon field, and leading to a predicted buckled phase consistent with experimental observations.

*Softening of flexural phonons.*—We describe the elastic deformations of a graphene sheet by the vector field $\mathbf{u} = (u_1, u_2, h)$, where $u_1$, $u_2$ represent the in-plane displacement with respect to the equilibrium position and $h$ is the out-of-plane shift. The elastic energy of the membrane is expressed in terms of the strain tensor

$$u_{ij}(\mathbf{r}) = \tfrac{1}{2}(\partial_i u_j + \partial_j u_i + \partial_i h \partial_j h) \tag{1}$$

Coordinate $\mathbf{r}$ runs over the 2D graphene membrane. The bare parameters involved in the continuum elasticity model for graphene are the mass density $\rho$, the bending rigidity ($\kappa \approx 1$ eV) and the in-plane shear ($\mu \approx 9$ eV/Å$^2$) and bulk ($\mu + \lambda \approx 12.6$ eV/Å$^2$) moduli. The action for the phonon fields reads

$$S_{\mathbf{u}} = \frac{1}{2}\int dt d^2 r (\rho(\partial_t \mathbf{u})^2 - \kappa(\nabla^2 h)^2 - 2\mu u_{ij}^2 - \lambda(u_{ii})^2) \tag{2}$$

Respect to other conventional insulating membranes, a novel effect in graphene is that the electronic carriers couple to the displacement of the sheet, in such a way that it gives rise to another source of interaction between the phonon fields [10,11]. We will consider the effect of electrons from the $\pi$ bands of graphene, represented by the field $\Psi(\mathbf{r})$, on the renormalization of elastic parameters. The strongest coupling between electrons and phonons comes from the on-site deformation potential [16],

$$S_{e\text{-ph}} = \int dt d^2 r \Psi^\dagger(\mathbf{r})\Psi(\mathbf{r})(g_{\text{in}}\partial_i u_i + g_{\text{out}}\partial_i h \partial_i h) \tag{3}$$

with general momentum dependent couplings $g_{\text{in/out}}(\mathbf{q})$. Rotational invariance implies that at small momenta $g_{\text{in}}$

 

and $g_{\rm out}$ must coincide. A microscopic analysis shows however that $g_{\rm in/out}(\mathbf{q}) = g(1 - c_{\rm in/out}a^2|\mathbf{q}|^2 + \ldots)$, where $a$ is the C-C distance and $c_{\rm in} \approx 0.3$, $c_{\rm out} \approx 0.1$ in a tight-binding model with up to third-neighbor hopping[17]. Detailed electron-phonon calculations have also shown that $g_{\rm in}$ has very small values $\lesssim 1$ eV at the $K$ point of the Brillouin zone [18].

The energy of the electronic excitations is proportional to the Fermi velocity $v_F$ and (for a given momentum) much larger than that of other modes in the problem. Thus, we can first integrate out the electron degrees of freedom, which leads to a phonon interaction due to the exchange of electron-hole pairs, proportional to the static charge susceptibility $\chi(\mathbf{q}, 0) \sim -|\mathbf{q}|/v_F$ [19]. One may then integrate out the in-plane phonons, and arrive at the action for the flexural modes

$$S = \frac{1}{2}\int \frac{d^2q}{(2\pi)^2}\frac{d\omega}{2\pi}(\rho\omega^2 - \kappa\mathbf{q}^4)h(\mathbf{q},\omega)h(-\mathbf{q},-\omega) - \frac{1}{2}\int \frac{d^2q}{(2\pi)^2}\frac{d\omega}{2\pi}K(q)u(\mathbf{q},\omega)u(-\mathbf{q},-\omega) \quad (4)$$

where $u(\mathbf{q}, \omega)$ stands for the Fourier transform of $\frac{1}{2}P_{ij}\partial_i h\partial_j h$, $P_{ij}$ being the transverse projector [5], and

$$K(q) = 2\mu + \lambda - g_{\rm out}^2|\mathbf{q}|/v_F - \frac{(\lambda - g_{\rm in}g_{\rm out}|\mathbf{q}|/v_F)^2}{2\mu + \lambda - g_{\rm in}^2|\mathbf{q}|/v_F} \quad (5)$$

An electron-induced bulk instability could occur if the pole in the coupling function $K(q)$ would fall inside the first Brillouin zone, leading to a vanishing velocity of in-plane longitudinal phonons. The realization of such an instability is ruled out however in a real graphene system, since experimentally the in-plane integrity of graphene is intact. But even if the coupling $g_{\rm in}(\mathbf{q})$ is not strong enough to destabilize the bulk, exchange of particle-hole pairs can make the flexural phonon coupling function $K(q)$ negative (i.e., attractive), which indicates a potential instability of out-of-plane displacements. The effect of the negative terms in Eq. (5) is only significant at short wavelengths, and vanishes in the limit $\mathbf{q} \to 0$. Then, in order to study the competition between positive and negative couplings in Eq. (5), we may approximate this coupling function by the constant term $K_0$ and the dominant powers of $|\mathbf{q}|$

$$K(q) \approx K_0 + K_1|\mathbf{q}| + K_2|\mathbf{q}|^2 \quad (6)$$

with $-K_1 \propto g^2$ and $-K_2 \propto g^4$.

The resulting interactions tend to enhance or suppress the low-energy rigidity $\kappa$ depending on their repulsive or attractive character. This is encoded into the corrections to the phonon self-energy $\Sigma(\mathbf{q}, \omega)$ represented in Fig. 1. Computing the full propagator of the flexural phonons from the expression $D^{-1}(\mathbf{q}, \omega) = \omega^2 - (\kappa_0/\rho)\mathbf{q}^4 - \Sigma(\mathbf{q}, \omega)$, we find that the dressed bending rigidity $\kappa(\mathbf{q})$ is given by the self-consistent equation

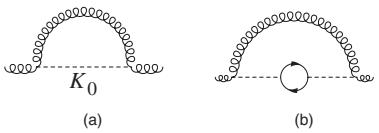


FIG. 1. Lowest order corrections to the self-energy of flexural phonons (represented by a curly line) arising from (a) the four-phonon interaction $K_0$ and (b) the exchange of electron-hole excitations (represented by the bubble with fermion lines).

$$\kappa(\mathbf{q}) = \kappa_0 + \frac{1}{8\pi^2}\int d^2p \sin^4(\phi_{q,p})\frac{K(|\mathbf{q}-\mathbf{p}|)}{|\mathbf{q}-\mathbf{p}|^4}\frac{|\mathbf{p}|^2}{\sqrt{\rho\kappa(\mathbf{p})}}. \quad (7)$$

We note that Eq. (7) amounts to the sum of a vast class of diagrams from multiple iteration of first-order self-energy corrections in the phonon propagator. Solutions in different regimes of the couplings can be seen in Fig. 2(a). We observe that, for a sufficiently large value $g^*$ of the deformation potential, $\kappa(\mathbf{q})$ vanishes at a certain momentum, bouncing back for smaller values of $|\mathbf{q}|$. In this picture, $g^*$ plays the role of critical coupling above which we would find negative values of the bending rigidity, suggesting a flexural instability in the system. In this situation, a RG analysis may be also pertinent in order to capture the low-energy scaling of the couplings $K_n$.

The RG scheme proceeds by progressive integration of energy shells, starting from a high-energy cutoff $E_c = \sqrt{\kappa_0/\rho}q_c^2$, to approach the low-energy regime. The bare couplings $K_n$ are then corrected to lowest order by the exchange of two flexural phonons given by the diagram in Fig. 3(a), which shows a logarithmic dependence on the cutoff $q_c$. This can be absorbed into a renormalization of the effective couplings, leading to the scaling with the running cutoff $q_c \to 0$

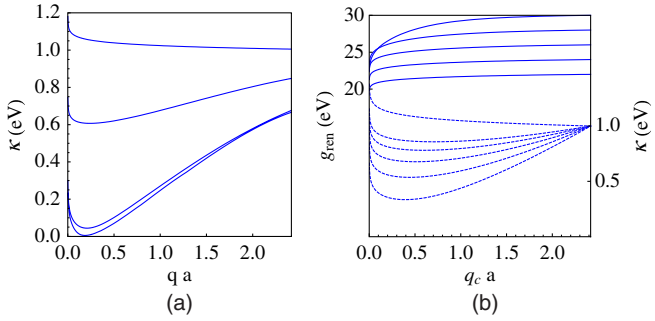


FIG. 2 (color online). (a) Effective momentum dependence of $\kappa$ obtained from Eq. (7) for $\kappa_0 = 1.0$ eV, $K_0 = 20.5$ eV/Å$^2$, and values of the deformation potential $g$ equal (from top to bottom) to 0, 10, 23.06, and 23.16 eV (the last solution already has a small imaginary part). (b) Scaling of $\kappa$ (dashed lines) and the renormalized deformation potential $g_{\rm ren}$ (full lines) in the RG approach, for bare values of $g$ equal to 0, 22, 24, 26, 28, and 30 eV. The lowest flow of $\kappa$ corresponds to the largest value of $g$, with couplings already close to the regime where $K_i/16\pi\sqrt{\rho\kappa^3} \sim 1$. $a$ is the C-C distance.

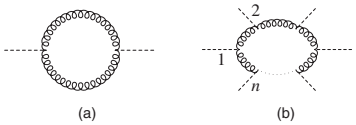


FIG. 3. (a) Exchange of flexural phonons (curly lines) leading to logarithmic cutoff-dependence of the interactions $K_0$, $K_1$ and $K_2$. (b) Generic form of the diagrams building up the series of the $\sigma$ field (dashed lines) in the effective potential.

$$q_c \frac{\partial K_n}{\partial q_c} = \frac{3}{64\pi} \sum_{i+j=n} \frac{K_i K_j}{\sqrt{\rho}\kappa^{3/2}}. \tag{8}$$

A scaling equation can be also written for the rigidity $\kappa$, as the self-energy diagrams in Fig. 1 display a logarithmic dependence on the cutoff $q_c$,

$$q_c \frac{\partial \kappa}{\partial q_c} = -\frac{3}{16\pi} \sum_{n=0}^{2} q_c^n \frac{K_n}{\sqrt{\rho\kappa}}. \tag{9}$$

A most refined approach then consists in supplementing the solution of Eq. (7) with the RPA-like scheme encoded in Eq. (8) (the corrections deriving from (9) are actually a subset of those accounted for by (7)). In the RG approach, the electron-phonon couplings get a momentum-dependence that can be obtained from the scaling of the couplings $K_i$, leading to renormalized values of the deformation potential $g_{\mathrm{ren}}$ shown in Fig. 2(b). The important point is whether the critical $g^* \approx 23.1$ eV predicted from (7) can be reached upon renormalization of the couplings down to the scale $10^{-1}a^{-1}$ where $\kappa$ vanishes in Fig. 2(a). We can see from Fig. 2(b) that the critical value $g_{\mathrm{ren}} \approx 23.1$ eV can be found at the low momentum scale starting from a bare deformation potential $g \gtrsim 25$ eV. It is then reassuring that the scaling approach can produce renormalized couplings at $q \sim 10^{-1}a^{-1}$ that are consistent with the input required to find the instability in the self-consistent approach. This has otherwise the capability of producing a more accurate correction to the bending rigidity $\kappa$ on top of the RG effect. We stress finally that $g_{\mathrm{ren}}$ corresponds to the observable quantity to be measured in transport experiments. In this respect, it is interesting to note that the critical value of $\approx 23.1$ eV falls within the estimates recently obtained from a detailed fit of experimental results of the resistivity, over a wide range of doping and temperature of the graphene layer [20].

*Spontaneous symmetry breaking.*—At vanishing $\kappa$, the elastic properties computed from the $h$ field develop severe infrared divergences, reflecting that the theory is then quantized around an unstable (flat) classical solution. The standard technique to compute the configuration of stable equilibrium of the system is the minimization of the effective action $S_{\mathrm{eff}}(h)$ [21]. While symmetry breaking has been described before in the statistical mechanics of polymerized membranes [22], here we deal with the computation of the effective action of the quantum theory at zero temperature. This can be accomplished by introducing first an auxiliary field $\sigma$ with gaussian fluctuations to decouple the four-phonon interaction in (4), allowing us to express the interaction term as

$$S_{\mathrm{int}} = \frac{1}{2} \int \frac{d^2q}{(2\pi)^2} \frac{d\omega}{2\pi} \sigma_{\mathbf{q},\omega} (\sigma_{-\mathbf{q},-\omega} - 2\sqrt{K} u(-\mathbf{q}, -\omega)). \tag{10}$$

The field $h$ has to be decomposed into an average field $h_{\mathrm{av}}$ and quantum fluctuations $\tilde{h}$. The effective action $S_{\mathrm{eff}}(h_{\mathrm{av}})$ is obtained by integrating over $\tilde{h}$ [23], what can be accomplished exactly in the formal limit of a large number of dimensions $d$ of the ambient space containing the membrane.

At large $d$, the effective action is built from diagrams with just one loop of fluctuating $\tilde{h}$ fields, as represented in Fig. 3(b). In the case of static field configurations $u_{\mathrm{av}}(\mathbf{q}, \omega) = \delta(\omega) u_{\mathrm{av}}(\mathbf{q})$ and $\sigma_{\mathbf{q},\omega} = \delta(\omega)\sigma_{\mathbf{q}}$, we get the contribution to the effective action

$$iS^{(1)}_{\mathrm{eff}}(\sigma) = \sum_{n=2}^{\infty} \frac{1}{n} \frac{K_0^{n/2}}{(2\pi)^n} \int_{|\mathbf{q}_i|<\Delta} \prod_{i=1}^{n} \frac{d^2q_i}{(2\pi)^2} \sigma_{\mathbf{q}_i} \delta\Big(\sum \mathbf{q}_i\Big) \times \int_{|\mathbf{p}|>\Delta} \frac{d^2p}{(2\pi)^2} \frac{d\omega_p}{2\pi} \sin^2(\phi_{p,q_i}) \frac{p^{2n}}{(\rho\omega_p^2 - \kappa p^4)^n}. \tag{11}$$

We focus here on the field configurations as $\Delta \to 0$ and the momentum of $\sigma_{\mathbf{q}}$ goes to zero, since this is the regime where terms with higher powers of the field become increasingly infrared divergent.

The perturbative series has to be summed first in (11) to obtain a sensible result in the limit $\Delta \to 0$. After factoring out the volume of the space, we obtain the contribution to the effective potential

$$iV^{(1)}_{\mathrm{eff}}(\sigma_0) = \int \frac{d^2p}{(2\pi)^2} \frac{d\omega_p}{2\pi} \Big( -\frac{\sqrt{K_0}}{2\pi} \sigma_0 \frac{p^2}{-\rho\omega_p^2 + \kappa p^4} + \log\Big(1 + \frac{\sqrt{K_0}}{2\pi} \sigma_0 \frac{p^2}{-\rho\omega_p^2 + \kappa p^4}\Big)\Big), \tag{12}$$

where $\sigma_0 \equiv (\Delta/2\pi)^2 \sigma(\mathbf{q} \to 0)$. Performing now the loop integration, we get from the sum of the zero-loop and the one-loop effective potential

$$V_{\mathrm{eff}}(h_{\mathrm{av}}, \sigma_0) = \frac{1}{8\pi^2} \Big( -\sigma_0^2 + 2\sqrt{K_0} \frac{\Delta^2}{(2\pi)^2} u_{\mathrm{av}}(\mathbf{q} \to 0)\sigma_0 \Big) + \frac{1}{8\pi^2} \frac{K_0}{16\pi\sqrt{\rho}\kappa^{3/2}} \times \sigma_0^2 \Big( \log\Big( \frac{\sqrt{K_0}}{8\pi\sqrt{\rho\kappa}} \frac{\sigma_0}{E_c} \Big) + \frac{1}{2} \Big). \tag{13}$$

Quite remarkably, Eq. (13) exactly reproduces the structure of the effective potential for a relativistic scalar field theory in $3 + 1$ dimensions [21]. This means that our model actually follows the same mechanism of symmetry breaking characteristic of a Higgs field in particle physics.

In close analogy with the analysis of Ref. [24], the slightest tension in our model will add to the potential a term proportional to $\gamma u_{\mathrm{av}}(\mathbf{q} \to 0)$, destabilizing the minimum at the origin for $\gamma < 0$. The mode $\sigma_0$ can be integrated by the saddle-point method, showing that $V_{\mathrm{eff}}$ will get then the typical "mexican-hat" shape as a function of $u_{\mathrm{av}}$, implying a minimum with $\nabla h_{\mathrm{av}} \neq 0$. Quantizing now the theory around this configuration leads to fluctuations $\tilde{h}$ which get a positive effective tension, in the same fashion as the physical Higgs field develops positive mass square. This is the way in which the elastic properties can be finally computed getting rid of infrared divergences.

We find therefore that there is a buckling transition between the regimes of positive and negative tension in graphene. The nature of the critical (tensionless) theory is less clear, as there is still controversy about whether a scalar field theory may undergo symmetry breaking starting with a massless scalar field. Anyhow, in a typical experimental setup, graphene is held in place by a scaffold or a substrate, which induces certain amount of tension in the membrane. This has been estimated to be of the order of $\sim 1$ eV/nm$^2$ [10]. In our analysis of the symmetry breaking, a negative tension $\gamma$ shifts the minimum of the effective potential to $(\Delta/2\pi)^2 u_{\mathrm{av}}(\mathbf{q} \to 0) = -\gamma/2K_0$. This quantity turns out to be of the order of $\sim 10^{-4}$ with the above estimate. Assuming that $(\Delta/2\pi)^2$ scales in inverse proportion to the volume of the space, we obtain that the average values of $|\nabla h_{\mathrm{av}}|$ must be of the order of $\sim 10^{-2}$, which is consistent with the typical aspect ratio of ripples in graphene.

In the tensionless limit, our model also shares with massless scalar field theories in $3 + 1$ dimensions the intriguing feature that the effective potential becomes complex beyond a certain value of the field. This kind of instability has led to speculate about the possibility that the absolute minimum of the effective potential may be away from the origin in the critical theory [24]. We hope that the connection between buckling and the Higgs condensation may shed light into this question, while carrying out experiments at the low-energy scale of graphene.

*Conclusion.*—We have seen that the interaction between flexural phonons mediated by particle-hole excitations may place the graphene sheet very close to a quantum critical point characterized by the strong suppression of the bending rigidity of the membrane. The same effect can be expected from other degrees of freedom which couple to the lattice deformations, such as absorbed impurities. The effective potential of the zero-temperature theory displays then a mechanism of symmetry breaking that parallels that of the Higgs field in particle physics, the role of order parameter being played in graphene by the square of the gradient of the flexural phonon field. We have found that the system must be unstable towards a buckling transition that is the analogue of Higgs condensation, showing another way to employ graphene as a test ground of fundamental concepts in theoretical physics.

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