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Electronic compressibility of graphene: The case of vanishing electron correlations and the role of chirality

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A recent surprising finding that electronic compressibility measured experimentally in monolayer graphene can be described solely in terms of the kinetic energy [J. Martin *et al.*, Nat. Phys. **4**, 144 (2008)] is explained theoretically as a direct consequence of the linear energy dispersion and the chirality of massless Dirac electrons. For bilayer graphene we show that contributions to the compressibility from the electron correlations are restored. We attribute the difference to the respective momentum dependence of the low-energy-band structures of the two materials.

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In an interacting electron system of uniform density, the (inverse) electronic compressibility $\kappa^{-1} \propto \partial\mu/\partial n$ (where μ is the chemical potential and n is the electron density) is a fundamental physical quantity that is intimately related to the strength of interelectron interactions.[1,2] First measured in 1992, the compressibility of a two-dimensional electron gas[3] provides valuable information about the nature of the interacting ground state, particularly in the strong-coupling regime where (in addition to the exchange energy) the Coulomb interaction energy is also known to play a dominant role. In this context, a recent report on the measurement of electronic compressibility in monolayer graphene[4] revealed behavior which was totally unexpected.[5] In this work, scanning single-electron transistor microscopy was used to measure the change of local electrostatic potential (and thereby change in local chemical potential) of a graphene sample when the carrier density was modulated.[5] The observed results for the local inverse compressibility were found to be quantitatively described by the kinetic energy alone and the authors speculated that the exchange and correlation energy contributions to the compressibility either each other cancel out or are negligibly small. This interesting puzzle has remained unsolved because the approximate theoretical schemes adopted by various authors to investigate electron correlations in graphene[6,7] do not find any such cancellations. Similarly, the recently reported Hartree-Fock studies of compressibility[8] in monolayer and bilayer graphene do not consider electron correlations at all and are therefore not in a position to address this important issue.

In this Rapid Communication, we investigate the role of electron correlations in monolayer and bilayer graphene. We show how in monolayer graphene, two fundamental properties of the system, viz., the linear energy dispersion and chirality conspire to allow the exchange and correlation contributions to vanish, just as was observed in the experiment.[5] In bilayer graphene on the other hand, where the low-energy quasiparticles are massive chiral fermions,[9,10] the parabolic dispersion does not allow this vanishing of the two energies, and the kinetic energy retains a dependence on the electron correlation function which manifests in the electron compressibility.

The low-energy charge carriers in monolayer graphene behave as massless Dirac fermions described by the single-particle Hamiltonian $\mathcal{T}_1^{\mathrm{m}} \propto \boldsymbol{\sigma}\cdot\hat{\mathbf{p}}_1$, which is linear in momentum $\mathbf{p}$ and where the subscript refers to the coordinate label of the electron on which it acts. The eigenstates of the Hamiltonian are uniquely labeled by quantum numbers representing the wave vector $\mathbf{q}=\mathbf{p}/\hbar$, the band (conduction/valence) b, valley (pseudospin) ξ, and the z component of the real electron spin σ. The wave functions are of the form, $\psi(\mathbf{r})=e^{i\mathbf{q}\cdot\mathbf{r}}\chi$, where χ is an eight component spinor.[11] A full analytical study of the many-electron system in graphene is clearly an impossible task. However, most of the clues to the puzzle involving the measured compressibility described above can be found at the level of two electrons, which is amenable to a fully analytic solution. We therefore start with a two-electron system where the electrons occupy the states α and β corresponding to the full sets of quantum numbers $(\mathbf{q}_{\alpha,\beta}, b_{\alpha,\beta}, \xi_{\alpha,\beta}, \sigma_{\alpha,\beta})$. We denote by φ the antisymmetric noninteracting two-electron wave function

$$\varphi(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}[\psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2) - \psi_\beta(\mathbf{r}_1)\psi_\alpha(\mathbf{r}_2)].$$

The correlations due to the mutual Coulomb interaction are introduced by multiplying the free-particle wave function by a generic correlation factor F as

$$\Psi = F(\mathbf{r}_1,\mathbf{r}_2)\varphi(\mathbf{r}_1,\mathbf{r}_2).$$

At this stage, a precise definition of F is not necessary. The only requirements are that it should be a real function, and to preserve the antisymmtery of the correlated wave function Ψ it is assumed to be symmetric with respect to exchange of the particle coordinates; i.e., $F(\mathbf{r}_1,\mathbf{r}_2)=F(\mathbf{r}_2,\mathbf{r}_1)$.

In order to evaluate the two-particle energy we have to normalize the wave function Ψ. A straightforward calculation yields

$$\|\Psi\|^2 = \langle\Psi|\Psi\rangle = \int d\mathbf{r}_1 d\mathbf{r}_2 F(\mathbf{r}_1,\mathbf{r}_2)^2 \Big\{1 - \tfrac{1}{2}\delta_{\xi_\alpha\xi_\beta}[1 + b_\alpha b_\beta \cos(\theta_\alpha - \theta_\beta)]\cos Q\Big\},$$

where $Q=(\mathbf{q}_\beta-\mathbf{q}_\alpha)\cdot(\mathbf{r}_1-\mathbf{r}_2)$, and $\theta_{\alpha,\beta}$ are the polar angles of the momenta $\mathbf{q}_{\alpha,\beta}$. Evaluation of the expectation value of the kinetic part of the Hamiltonian $T^{\mathrm{m}}=\langle\Psi|\mathcal{T}_1^{\mathrm{m}}+\mathcal{T}_2^{\mathrm{m}}|\Psi\rangle$ leads to the expression

$$\begin{aligned} T^{\mathrm{m}} = \tfrac{1}{2}\hbar v_F \int d\mathbf{r}_1 d\mathbf{r}_2 F \Bigg\{ & \tfrac{1}{4} i \delta_{\sigma_\alpha\sigma_\beta}\delta_{\xi_\alpha\xi_\beta}[e^{\mathrm{i}Q}Z^1_{\alpha\beta}(1 + b_\alpha b_\beta e^{-\mathrm{i}(\theta_\beta-\theta_\alpha)}) + e^{\mathrm{i}Q}Z^2_{\beta\alpha}(1 + b_\alpha b_\beta e^{\mathrm{i}(\theta_\beta-\theta_\alpha)}) + e^{-\mathrm{i}Q}Z^1_{\beta\alpha}(1 + b_\alpha b_\beta e^{\mathrm{i}(\theta_\beta-\theta_\alpha)}) \\ & + e^{-\mathrm{i}Q}Z^2_{\alpha\beta}(1 + b_\alpha b_\beta e^{-\mathrm{i}(\theta_\beta-\theta_\alpha)})] - i b_\beta\left(\cos\theta_\beta \frac{\partial F}{\partial x_1} + \cos\theta_\beta \frac{\partial F}{\partial x_2} + \sin\theta_\beta \frac{\partial F}{\partial y_1} + \sin\theta_\beta \frac{\partial F}{\partial y_2} + 2\mathrm{i}q_\beta F\right) \\ & - i b_\alpha\left(\cos\theta_\alpha \frac{\partial F}{\partial x_1} + \cos\theta_\alpha \frac{\partial F}{\partial x_2} + \sin\theta_\alpha \frac{\partial F}{\partial y_1} + \sin\theta_\alpha \frac{\partial F}{\partial y_2} + 2 i q_\alpha F\right)\Bigg\}, \end{aligned}$$

where F stands for $F(\mathbf{r}_1,\mathbf{r}_2)$, v_F is the Fermi velocity, and $Z^j_{\alpha\beta}$ is shorthand for

$$\begin{aligned} Z^j_{\alpha\beta} = {} & (b_\beta e^{\mathrm{i}\theta_\beta} + b_\alpha e^{-\mathrm{i}\theta_\alpha})\frac{\partial F}{\partial x_j} - i(b_\beta e^{\mathrm{i}\theta_\beta} - b_\alpha e^{-\mathrm{i}\theta_\alpha})\frac{\partial F}{\partial y_j} \\ & + i q_\beta F(b_\beta + b_\alpha e^{\mathrm{i}(\theta_\beta-\theta_\alpha)}). \end{aligned}$$

Due to the linearity of $\mathcal{T}^{\mathrm{m}}$ in the momentum operators, only the first-order derivatives appear in the integrand. Terms in T^{m} of the form

$$\int d\mathbf{r}_j F\frac{\partial F}{\partial x_j} = \frac{1}{2}\int d\mathbf{r}_j \frac{\partial}{\partial x_j}F^2,$$

clearly vanish due to the antisymmetry of the integrand. Most of the terms left after the volume integration cancel each other as a consequence of the spinor structure of the single-particle wave functions, which is a direct manifestation of the chirality of the electrons. The only surviving terms sum to

$$T^{\mathrm{m}} = \hbar v_F(b_\alpha q_\alpha + b_\beta q_\beta)\|\Psi\|^2,$$

that is, the kinetic-energy expectation value $\langle\mathcal{T}^{\mathrm{m}}\rangle$ is simply the sum of the single free-particle kinetic energies,

$$\langle\mathcal{T}^{\mathrm{m}}\rangle = \frac{T^{\mathrm{m}}}{\|\Psi\|^2} = \hbar v_F(b_\alpha q_\alpha + b_\beta q_\beta) = T_0^{\mathrm{m}} = \frac{\langle\varphi|\mathcal{T}^{\mathrm{m}}|\varphi\rangle}{\|\varphi\|^2},$$

and does not depend on the correlation function F at all. We expect similar cancellations for higher electron numbers, although analytical expressions become intractable already at the level of three electrons.

Complete cancellation of correlation contributions to the kinetic energy (never observed in conventional electron systems) creates an unusual situation as we shall now describe. In the thermodynamic limit, the potential energy (per particle) $\mathcal{V}$ is usually expressed in the form

$$\langle\mathcal{V}\rangle = n\int d\mathbf{r}[g(r) - 1]V_{\mathrm{Coul}}(r),$$

where n is the single-particle number density, V_{Coul} is the Coulomb potential and $g(r)$ is the pair-correlation function which, for $\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2$, is given by

$$g(|\mathbf{r}|) = \frac{N(N-1)}{\|\Psi\|^2 n^2}\int d\mathbf{r}_3 \ldots d\mathbf{r}_N |\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N)|^2,$$

where N is the total number of electrons. The energy functional (per particle) $\mathcal{E}^{\mathrm{m}}$ is now

$$\mathcal{E}^{\mathrm{m}} = t_0^{\mathrm{m}} + n\int d\mathbf{r}[g(r) - 1]V_{\mathrm{Coul}}(r),$$

where $t_0^{\mathrm{m}}=T_0^{\mathrm{m}}/N$ is the kinetic energy per particle. Its variation with respect to $g(r)$, an essential step in determining the optimal $g(r)$, would yield an unusual Euler-Lagrange equation, $V_{\mathrm{Coul}}(r)=0$, which is clearly not the case in graphene.[12] To resolve this dilemma we note that the energy functional $\mathcal{E}^{\mathrm{m}}$ is actually not bounded below: we can choose correlations such that the potential energy takes arbitrarily large negative values. This implies that to determine the optimal $g(r)$ the energy functional derived above is not sufficient and additional physical constraints, for example, that $g(r)$ should correspond to the correct number of states in each band, would be necessary. Clearly, determination of the optimal pair-correlation functions for massless Dirac fermions in graphene is a nontrivial problem.[13] However, we believe that the expression for the functional $\mathcal{E}^{\mathrm{m}}$ is of the correct form; i.e., once the correct pair-distribution function $g(r)$ is found, one could evaluate the correct energy from the above form of the energy functional.

Let us now turn our attention to the compressibility as defined in the introduction. To that end we first evaluate the variation $\delta_n\mathcal{E}^{\mathrm{m}}$ of $\mathcal{E}^{\mathrm{m}}$ with respect to n:

$$\begin{aligned}\delta_n\mathcal{E}^{\mathrm{m}} = \frac{\partial t_0}{\partial n}\delta n + \delta n\int d\mathbf{r}[g(r)-1]V_{\mathrm{Coul}}(r)\\ + n\int d\mathbf{r}V_{\mathrm{Coul}}\frac{\delta g(r)}{\delta n}\delta n.\end{aligned}$$

From this we can read the derivative as

$$\frac{\partial\mathcal{E}^{\mathrm{m}}}{\partial n} = \frac{\partial t_0}{\partial n} + \int d\mathbf{r}[g(r)-1]V_{\mathrm{Coul}} + n\int d\mathbf{r}V_{\mathrm{Coul}}\frac{\delta g(r)}{\delta n}.$$

The compressibility will then be proportional to

$$\frac{\partial^2\mathcal{E}^{\mathrm{m}}}{\partial n^2} = \frac{\partial^2 t_0}{\partial n^2} + 2\int d\mathbf{r}V_{\mathrm{Coul}}\frac{\delta g(r)}{\delta n} + n\int d\mathbf{r}V_{\mathrm{Coul}}\frac{\delta(\delta g(r)/\delta n)}{\delta n^2}.$$

We therefore need to make an assumption or estimation of the functional derivative $\delta g(r)/\delta n$. The pair-correlation function is a many-body quantity, so its exact evaluation is impossible. Also, it is not possible to calculate functional derivatives numerically, and any analytical approximation will necessarily obscure the true functional dependence that we require. In conventional two-dimensional electron systems, $g(r)$ varies only slightly as a function of density except at very low densities where it starts to develop a prominent peak as a precursor to Wigner crystallization.[14] Therefore, we appeal to previous work, which shows that there are no phase transitions (such as Wigner crystallization) as the density of the graphene system is varied[15] and so we expect that the functional variation of $g(r)$ with the density will be negligible in this system. Alternatively, we could consider a slightly less stringent condition $\int d\mathbf{r}V_{\mathrm{Coul}}\frac{\delta g(r)}{\delta n}=0$, which implies that the interaction energy depends linearly on the density of Dirac electrons. Under either of these assumptions, the compressibility is described entirely by the kinetic energy

$$\frac{\partial^2\mathcal{E}^{\mathrm{m}}}{\partial n^2} = \frac{\partial^2 t_0}{\partial n^2},$$

in accordance with the experimental observation.[5] In arriving at this striking result, there are two basic properties of monolayer graphene that play crucial roles: the linear energy dispersion and chirality of massless Dirac electrons.

This immediately invites the question: What happens in bilayer graphene,[9,10] where the low-energy charge carriers behave as massive chiral fermions and as such the Hamiltonian is quadratic in momentum operators near the charge neutrality point. The single-particle Hamiltonian is $\mathcal{T}_1^{\mathrm{b}} = -\frac{1}{2m^*}(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}_1)\sigma_x(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}_1)$ where m^* is the effective electron mass generated by the inter layer coupling, and has the spectrum $\epsilon_\alpha=(\hbar q_\alpha)^2$ associated with it. Evaluating the expectation value of an arbitrary two-particle wave function as in the monolayer case, an intermediate expression for the kinetic part of the two-particle energy is

$$\begin{aligned}T^{\mathrm{b}} = {}&\tfrac{1}{2}(\epsilon_\alpha+\epsilon_\beta) - \int d\mathbf{r}_1 d\mathbf{r}_2\frac{\hbar^2 F}{4m^*}e^{-\mathrm{i}Q}\bigg\{iq_\beta\bigg([\cos\theta_\beta+\cos(2\theta_\alpha-\theta_\beta)]\frac{\partial F}{\partial x_1} + [\sin\theta_\beta+\sin(2\theta_\alpha-\theta_\beta)]\frac{\partial F}{\partial y_1}\bigg)\\ &+ iq_\alpha\bigg([\cos\theta_\alpha+\cos(\theta_\alpha-2\theta_\beta)]\frac{\partial F}{\partial x_2} + [\sin\theta_\alpha-\sin(\theta_\alpha-2\theta_\beta)]\frac{\partial F}{\partial y_2}\bigg)\bigg\} - \int d\mathbf{r}_1 d\mathbf{r}_2\frac{\hbar^2 F}{4m^*}e^{\mathrm{i}Q}\bigg\{iq_\alpha\bigg([\cos\theta_\alpha+\cos(\theta_\alpha-2\theta_\beta)]\frac{\partial F}{\partial x_1}\\ &+ [\sin\theta_\alpha-\sin(\theta_\alpha-2\theta_\beta)]\frac{\partial F}{\partial y_1}\bigg) + iq_\beta\bigg([\cos\theta_\beta+\cos(2\theta_\alpha-\theta_\beta)]\frac{\partial F}{\partial x_2} + [\sin\theta_\beta+\sin(2\theta_\alpha-\theta_\beta)]\frac{\partial F}{\partial y_2}\bigg)\bigg\}\end{aligned}$$

where we have already excluded terms containing mixed second derivatives of F which are identically zero on integration, and those which trivially sum to zero. The integrals of terms with single derivatives of F are finite, and the prefactors (coming from the pseudospinor part of the products of wave functions in the expectation value) do not cancel each other as they did in the monolayer case, but constructively sum to a finite result. This noncancellation is a feature of the sublattice structure of the electronic wave function in bilayer graphene, resulting from the quadratic nature of the low-energy dispersion relation. On evaluation of the remaining integrals, and after some elementary algebra, the energy functional is found to be

$$\begin{aligned}\mathcal{E}^{\mathrm{b}} = t_0^{\mathrm{b}} + \langle\mathcal{V}\rangle + \frac{\hbar^2}{8m^*}\frac{\tilde{F}^2}{\|\Psi\|^2}\cos(\theta_\alpha-\theta_\beta)\\ \times[(q_\alpha^2+q_\beta^2)\cos(\theta_\alpha-\theta_\beta)-2q_\alpha q_\beta]\end{aligned}$$

where $\tilde{F}$ is the Fourier transform of the correlation function. We can easily see that there is a nonzero contribution from the electron correlations to the kinetic energy in this functional, and therefore taking the derivatives with respect to n yields a compressibility which depends nontrivially on them. It is clear that this additional term will also be present in the many-body energy as its integral over momentum is manifestly finite. We would also expect that for bilayer graphene where the excess electron density is high enough that the Fermi energy is in the energy range where the linearity of the spectrum is restored, that the effect of the correlations in the energy functional will again be suppressed. Quantitative computation of this term requires precise knowledge of the radial dependence of F, and the relation between $F(r)$ and $g(r)$.[16] Both of these issues are beyond the scope of the present Rapid Communication, however, as indicated in our present results for bilayer graphene, experimental observation of a shift in compressibility from the pure kinetic-energy contribution would provide a way to directly determine the strength of electron correlations in that system.

To conclude, we have demonstrated that in monolayer graphene, the electron correlations analytically vanish from the two-particle kinetic energy. This and the negligibility of $\delta g(r)/\delta n$ lead to the absence of the electron correlation function in the compressibility, as seen in recent experiments.[5] Conversely, the restoration of a quadratic band structure in bilayer graphene means that the correlations are present in the kinetic-energy functional and compressibility in this case. Our work strongly suggests that quantitative agreement between the single-particle theory and the experimental results in monolayer graphene has its origin in the fundamental properties (and in particular, the linear band structure) of this system. Also, the experimental system exhibits nonhomogeneity of the charge distribution, so a full many-body calculation of the compressibility would have to include this detail. However, the cancellation of the correlation function from the monolayer two-particle energy functional is independent of the energy of the electrons, and will therefore persist in the inhomogeneous system.

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