Fast-track communication

Hidden Kekulé ordering of adatoms on graphene

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Electronic and transport properties of Graphene, a one-atom thick crystalline material, are sensitive to the presence of adsorbed atoms on its surface. An ensemble of randomly positioned adatoms, each serving as a scattering center, leads to the Boltzmann–Drude diffusion of charge determining the resistivity of the material. An important question, however, is whether the distribution of adatoms is always genuinely random. In this Communication we demonstrate that dilute adatoms on graphene may have a tendency towards a spatially correlated state with a hidden Kekulé mosaic order. This effect emerges from the interaction between the adatoms mediated by the Friedel oscillations of the electron density in graphene. The onset of the ordered state, as the system is cooled below the critical temperature, is accompanied by the opening of a gap in the electronic spectrum of the material, dramatically changing its transport properties.

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When can an apparently random system be considered as ordered? Or can an apparently random ensemble of impurities in a material be correlated enough to force the reconstruction of the electronic band structure in a material? In this Communication we predict that a dilute ensemble of adatoms sprinkled randomly over a graphene monolayer [1,2] can establish long-range correlations between their positions, despite the fact that they may be many graphene unit cell lengths apart. This correlation is strong enough that at a transition temperature it will induce an energy gap in the electronic spectrum despite the fact that, in the “ordered” state, the distribution of adatoms does not show any crystalline structure. It rather resembles the ferromagnetically ordered state of spins of magnetic ions in dilute magnetic semiconductors [3]. The physical mechanism behind this phenomenon is the electronic-mediated interaction between the adsorbents, which prompts their partial ordering into configurations associated with a hexagonal superlattice with a unit cell three times bigger than that of graphene. Since the density, \( \rho \), of adsorbents is low, they occupy a small randomly chosen fraction of the equivalent positions on the superlattice. This ordering pulls the Brillouin zone and thus opens a spectral gap for low-energy electrons. This phenomenon suggests a novel route towards engineering the band structure and controlling transport in graphene-based devices.

Graphene [4,2] is a two dimensional crystal of carbon atoms, which form a honeycomb lattice with two distinct sublattices (A and B). The first Brillouin zone (BZ) has a hexagonal form (the blue area in Fig. 1(A)), and the conduction band touches the valence band in six BZ corners [4] which form two non-equivalent triads of BZ corners, \( \mathbf{K} \) and \( \mathbf{K}' \) connected by the reciprocal lattice vectors, \( \mathbf{G} \) and \( \mathbf{G}' \). Low-energy electronic excitations in the momentum space are located in the vicinities of the points \( \mathbf{K} \) and \( \mathbf{K}' \), i.e. belong to one of the two valleys with the linear ‘Dirac-type’ spectrum, \( E(p) = \pm v_F p \) where \( p \) is the momentum counted from one of the K-points and \( v \approx 10^6 \text{cm/s} \). Both the gapless spectrum and the valley degeneracy follow directly from the symmetries of the honeycomb lattice. In pristine graphene, the honeycomb lattice is stable against spontaneous structural changes.

Recently, several types of adatoms were used to dope graphene in attempts to tailor properties of graphene-based devices [5–8]. Below, we consider theoretically a particular example, Fig. 2(A), of adatoms, such as alkali atoms [9,10], Ca or Al whose stable positions are above the centers of the hexagons. A single adatom of this type preserves rotational and reflection symmetries but breaks the translational symmetry of the lattice. Therefore, it can scatter electrons between valleys. The intervalley scattering generates the Friedel oscillations (FO) of the electron density, which amplitude rather slowly decays when the distance from the adatom [11]. The pattern and period of such FO are determined by the wave vectors \( \mathbf{G} = \pm (\mathbf{K}' - \mathbf{K}) \) transferred upon scattering between the valleys. Due to a peculiar relation of \( \mathbf{K} \), \( \mathbf{K}' \) and the reciprocal lattice...
vectors in graphene, \( \mathbf{K} = \frac{1}{2}(\mathbf{G} + \mathbf{G}') \) and \( \mathbf{K}' = -\frac{1}{2}(\mathbf{G} + \mathbf{G}') \), the FO formed around an adatom have a structure of a charge density wave with the hexagonal lattice pattern and the unit cell extended over three unit cells of graphene. In graphene with zero carrier density \( \rho_v = 0 \), the amplitude of these superlattice oscillations decays as inverse cube of the distance between the adatoms. The oscillations of the electron density induced by one adatom affect other adatoms, thus leading to the pairwise interaction between adsorbents, which is sensitive to their position in the superlattice. In Fig. 2(A and B), we compare the potential landscape for a probe adatom created by several others due to their FO, to stress that its amplitude is substantially enhanced by ordering. Note that the long-range RKKY-type [12] interaction in a low-density ‘gas’ of adatoms as well as the ordering it promotes has little to do with those in dense aggregates of adsorbents. Indeed, the interaction at atomic distances is mediated by local lattice deformations — phonons. Such an interaction decays exponentially as a function of distance between the adatoms, as opposed to the power law \( 1/R^3 \) decay of the electron-mediated coupling.

Fig. 2 illustrates an example of hidden structural ordering of adatoms sprinkled over graphene. Without mosaic coloring (or a superlattice mesh) it would be difficult to distinguish the ordered configuration of adatoms (Fig. 2(D)) from a disordered state (Fig. 2(C)). With the help of colors, one can identify a triple-size unit cell of the superlattice, with three non-equivalent adatom positions (red, blue, and green) between six carbons, which resembles a hexagonal Kekulé-type [13] lattice [14,10]. The FO-mediated interaction \( V_{ij} \) between two adatoms \( i \) and \( j \) depends on whether they occupy equivalent (same color) positions on the superlattice, or not. This consideration maps the problem of hidden Kekulé mosaic ordering of adsorbents onto the three-state Potts model [15] with a random in strength ‘ferromagnetic’ coupling of species.

To estimate critical temperature of the hidden ordering, one has to evaluate the function \( V_{ij}(\mathbf{r}_i - \mathbf{r}_j) \), where \( \mathbf{r}_i \) and \( \mathbf{r}_j \) are adatoms locations. We use the technique developed for the studies dealing with disorder in graphene [16,17,11] and describe electrons by the four-component Bloch function \( \psi \) (taking into account its sublattice composition and valley degeneracy) and the \( 4 \times 4 \) Hamiltonian,

\[
H = v(\mathbf{p} \cdot \sigma)\mathcal{P}_z + \lambda \hbar v\alpha \sum_{\mathbf{r}_i} (\mathbf{u}_i \cdot \Pi) \delta(\mathbf{r} - \mathbf{r}_i).
\]

Here, Pauli matrices \( \sigma_{x,y,z} \) act on sublattice indices and \( \mathcal{P}_{x,y,z} \) on the valley indices of \( \psi \) [16,17,11]. The first term in Eq. (1) is a familiar Hamiltonian for Dirac-type electrons in pristine graphene. The second accounts for the intervalley scattering of electrons by adatoms, with \( \lambda \) being the dimensionless coupling constant (realistically, \( \lambda < 1 \) since \( h/v_\alpha \) is of the order of the bandwidth in graphene). Unit two-component vector \( \mathbf{u}_i = (\cos \frac{2\pi m_i}{3}, \sin \frac{2\pi m_i}{3}) \)

-Fig. 2. Kekulé mosaic ordering of adatoms of the same chemical element on graphene lattice. Panels (A) and (B) show the potential landscape that an extra atom would see in the presence of four atoms already shown. Coloring of the atoms is introduced to reveal their position within the Kekulé superlattice, as shown in panels (C) and (D). From a comparison of (A) and (B) one can see that adatoms placed on unicolor tiles enhance the potential landscape forcing other atoms to occupy tiles of the same color. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

specifies which of the three non-equivalent positions the \( i \)th adatom occupies on the superlattice, with \( m_i = -1, 0 \) and \( -1 \) (red, blue, and green hexagons).

Using thermodynamic perturbation theory and the standard RKKY approach [12] we express the interaction between adsorbents mediated by electrons as

\[
V_g = 2(\lambda \hbar v\alpha)^2 \text{Tr} \int_{-\infty}^{\infty} \frac{d\tau}{2\pi} \mathbf{u}_i \cdot \Pi G(\mathbf{r}_i - \mathbf{r}_j, \tau)
\]

\[
	imes (\mathbf{u}_j \cdot \Pi) G(\mathbf{r}_j - \mathbf{r}_i, -\tau),
\]

Fig. 1. (A) Brillouin zone of graphene in the reciprocal space is shown as a blue hexagon. The two valleys \( \mathbf{K} \) and \( \mathbf{K}' \) are situated in the six corners of the hexagon, which are identified via reciprocal lattice translations generated by vectors \( \mathbf{G} \) and \( \mathbf{G}' \). (B) Brillouin zone folding due to the ordering transition. The folding leads to the identification of the valley points \( \mathbf{K} \) and \( \mathbf{K}' \) with the \( \Gamma \)-point in the center of the Brillouin zone. (C) The energy surface in the folded Brillouin zone. Due to the interaction between the valleys a gap opens in the spectrum. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

\[
G(\mathbf{r}, \tau) = -\frac{1}{4\pi} \frac{v\tau + i\hbar \alpha \sigma \cdot \mathbf{r}}{(v\tau^2 + r^2)^{3/2}},
\]

where \( \tau \) is imaginary time and \( G(\mathbf{r}, \tau) \) is the zero-temperature Green function of Dirac-like electrons. Strictly speaking the Eq. (2) is valid at \( T = 0 \). However one can use it as long as \( T < \hbar v_\alpha / 2 \). The, trace \( \text{Tr} \) is taken over the sublattice and valley indices. The electron spin degeneracy is accounted for by the overall factor
of \(2\). The resulting electron-mediated ‘ferromagnetic’ interaction between adatoms at a distance \(|r_i - r_j| \gg a\),

\[
V_{ij} = - J \frac{\mathbf{u}_i \cdot \mathbf{u}_j}{|r_i - r_j|^3/2}, \quad \mathbf{u}_i \cdot \mathbf{u}_j = \cos \frac{2\pi (m_i - m_j)}{3},
\]

has a long-range tail, \(V \propto |r_i - r_j|^{-3}\). The typical interaction energy scale, \(J\) is the interaction strength at a mean distance between the nearest neighbors, \(\sim \rho^{-1/2}\) (recall that \(\rho \ll a^{-2}\)).

To evaluate the critical temperature, \(T_c\), we modeled the ordering transition numerically. We used the cluster Monte Carlo algorithm [18] to compute statistical moments

\[
M_{2n} = \sum_{\mathbf{r}_1,\ldots,\mathbf{r}_n} \sum_{\mathbf{r}_1,\ldots,\mathbf{r}_n} e^{-\beta \sum_{ij} V_{ij}},
\]

for 10 realizations of quenched Poissonian distributions of \(N = 2 \times 10^4\) adatoms. The ordering transition can be detected by a sudden rise of the order parameter \(M = \sqrt{M_2}\), from \(M(T < T_c) = 0\) to \(M(T > T_c) = 1\) accompanied by decrease of \(\eta = M_4/M_2^2\), from \(\eta(T < T_c) = 2\) (set by the central limit theorem for a large number of uncorrelated clusters) to \(\eta(T > T_c) = 1\). Results of the numerical analysis are presented in Fig. 3. The transition temperature turned out to be

\[
T_c \approx 8J \sim 4\lambda^2 (a^2 \rho)^{3/2} \frac{\hbar v_F}{a}.
\]

For example, for \(\lambda \sim 1\), just 1% coverage of graphene by adatoms should generate \(T_c\) in the room temperature range.

Since the mobility of adatoms on graphene strongly depends on temperature, the higher the adsorbent density \(\rho\), the higher \(T_c\) is, and the quicker the self-organization should establish upon cooling. Note that the aggregation of adsorbents, such as discussed in Refs. [19,20], would be a much slower process in a dilute system. At \(T < T_c\) the proposed partial ordering suppresses adatoms diffusion leading to a further slowdown of aggregation.

The value of \(T_c\) may also depend on the concentration \(\rho_c\) of electrons (or holes) in graphene. Finite carrier density leads to the additional modulation of the FO, with the period twice as small as the electron Fermi wavelength \(\sim \rho_c^{-1/2}\) [11]. For \(\rho_c \gtrsim \rho\) these modulations would make the sign of the interaction between adatoms random and, thus, eliminate the ordering. Therefore it seems to be possible to control hidden ordering of adsorbents electrically, by filling or depleting the flake with carriers—the method already in use to fine-tune the ferromagnetic transition temperature in thin films of dilute magnetic semiconductors [21].

The self-organization of an apparently random ensemble of adatoms into a Kekulé-type ordered state drastically changes electronic spectrum in graphene. Adatoms that preferentially occupy one of the three equivalent positions in the supercells over a length scale \(L \gg \sqrt{1/\rho}\) can Bragg scatter electrons between the two valleys coherently. This implies the Brillouin zone folding in Fig. 1(B and C): all of the points \(K\) and \(K'\) of the original BZ are projected onto the \(\Gamma\)-point of a smaller BZ corresponding to the superlattice with a triple unit cell. Simultaneously, a gap, \(\Delta\), opens in the electronic spectrum

\[
\varepsilon(p) = \pm \sqrt{(vp)^2 + \Delta^2}, \quad \Delta = \lambda a^2 \rho \frac{\hbar v_F}{a}.
\]

To derive Eq. (5), one can substitute the second term of the Hamiltonian in Eq. (1) by its average, for example, for all adatoms positioned on yellow hexagons, and diagonalize the resulting matrix, \(H = \sigma \cdot \mathbf{p} + v_F a \rho \mathbf{p}\).

One can think of several ways to experimentally detect the hidden Kekulé mosaic order. One is to use the angle-resolved photo-emission spectroscopy (ARPES). The latter technique is not only a natural method to reveal the formation of the spectral gap. It can also provide a direct evidence of the BZ folding. Indeed, ARPES measures simultaneously the energy and all three momentum components of the photo-emitted electrons. While at low energies only the vicinity of the BZ corners \(K\) and \(K'\) can be seen in pristine graphene [22,23], the Bragg scattering by the self-organized adsorbents generates an ARPES signal also at the \(\Gamma\)-point of the BZ in Fig. 1(A). Another signature of the Kekulé ordering would be a bright appearance of the D peak in the phonon Raman scattering [24]: the excitation of a BZ phonon forbidden by momentum conservation in pristine graphene. Finally, the gap in the electronic spectrum would dramatically affect charge transport in graphene. This may offer numerous opportunities for graphene-based electronics.

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