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The thermodynamics of electrons and the thermoelectric transport in epitaxial graphene on the size-quantized films

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HIGHLIGHTS

- We studied the thermodynamics of epitaxial graphene on size-quantized films.
- We showed that in such a system there are kinks of conductivity.
- We showed that in such a system there are thermoelectric power peaks.
- We compared our system with cases of 2D and 3D substrates.

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ABSTRACT

We investigated the thermodynamic parameters (chemical potential, heat capacity and thermodynamic potential) and a thermoelectric transport in an epitaxial graphene on the size-quantized metal and semiconductor films within the framework of simple analytical model. We considered limiting cases of high and low temperatures. We showed that the chemical potential of epitaxial graphene is smaller than the chemical potential of isolated graphene at the same carrier concentration. Conversely, the heat capacity of the epitaxial graphene is greater than the heat capacity of the isolated graphene. We investigated a conductivity and thermopower of the epitaxial graphene. We showed that in such system there are the kinks of conductivity and peaks of thermoelectric power. These peaks are several times greater than those of isolated graphene. We compared our system with cases of 2D and 3D substrates.

1. Introduction

The symmetry of graphene crystal lattice and the valence of carbon atoms leads to unique spectrum for electron excitations [1]. Indeed, the study of the band structure of graphene shows that graphene is semimetal with linear energy spectrum carrier near K points of Brillouin zone [2]. This spectrum leads to the different unique properties of graphene [2,3–11]. Currently, graphene is actively discussed even for such practical applications as purification of natural gas [12] and water desalination [13]. Thus, graphene is a promising material for various practical applications. The study of epitaxial graphene (EG) is one of the main questions in the physics of graphene [14–26]. The properties of EG sheets are interesting for several reasons. First of all, graphene on the surface of metals and semiconductors can be considered as an effective contact for devices. On the other hand, in order to make full use of the properties of graphene in electronics, it is necessary to vary the structure, chemical composition, morphology, etc., that can be done using a suitable substrate. In addition, there is the limiting of the real application of free graphene in the electronics. We are talking about the absence of the energy gap in the energy spectrum of the carriers. The opening of the band gap in the spectrum of graphene is an actual problem in the physics of graphene. There are many experimental studies of the electronic properties of EG, for example, see papers [14–19] and works of group of Walter de Heer.[1]

In this paper, we will investigate the thermodynamics and thermoelectric transport in a single-layer graphene formed on the

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[1] http://www.graphene.gatech.edu.

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surface of a size-quantized metal and a semiconductor films within the framework of theoretical model. To our knowledge, such a system has not yet been investigated experimentally. It must be emphasized that this system can become very interesting for applications since it has some interesting properties, which was predicted recent (see, for example, [25,26]).

2. The model of graphene formed on substrate

We investigate the monolayer graphene (MG) formed on the substrate within the framework of a simple model. In this model, the MG on the substrate is represented as carbon atoms adsorbed on this substrate and arranged in a hexagonal structure. Such model was first proposed by Davydov [20] to study of the electronic states of epitaxial graphene. In Refs. [20–26], this model was applied to different cases: epitaxial graphene on metal, epitaxial graphene on semiconductor, epitaxial graphene on size-quantized film etc. This model is as follows. A quasi-level of single carbon atom adsorbed on the substrate surface (adatom) is shifted and broadens. This is due to hybridization of atom with substrate. In the framework of Anderson–Newns model, Hamiltonian of system "adatom-substrate" can be written as follows [27,28]:

$$H = \sum_{\boldsymbol{p},\sigma} \varepsilon(\boldsymbol{p}) c^{+}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + E_a \sum_{\sigma} a^{+}_{i\sigma} a_{i\sigma} + \vartheta a^{+}_{i\uparrow} a_{i\uparrow} a^{+}_{i\downarrow} a_{i\downarrow} + \frac{V}{\sqrt{N}} \sum_{\boldsymbol{p},\sigma} \left(c^{+}_{\boldsymbol{p}\sigma} a_{i\sigma} + h.\,c. \right), \tag{1}$$

where E_a is the adsorbate's orbital energy in the vacuum, ϑ is the intraadsorbate Coulomb repulsion, $c^{+}_{\boldsymbol{k}\sigma}$ ($c_{\boldsymbol{k}\sigma}$) is creation (annihilation) operators for substrate electrons for quantum state $|\boldsymbol{p}\sigma\rangle$, $a^{+}_{i\sigma}$ ($a_{i\sigma}$) is creation (annihilation) operators for adsorbate's electrons, V is the hybridization potential (in this paper we assume that the hybridization potential does not depend on the $|\boldsymbol{p}\sigma\rangle$), N is the number of surface atoms in substrate, $\sigma = \pm 1$ is spin quantum number. Next, we will consider only single spin state, i.e. $\sigma = 1$. In the Anderson–Newns model for the Green function of single adatom, we have

$$G^{0}_{i}(\varepsilon) = (\varepsilon - \varepsilon_a - \Lambda(\varepsilon) - i\Gamma_c(\varepsilon))^{-1}, \tag{2}$$

where ε_a is the energy of adatom quasi-level, $\Gamma_c(\varepsilon) = \pi |V|^2 \rho_B(\varepsilon)$ denotes the half-width of adatom level, $\Lambda(\varepsilon) = \pi^{-1} P \int_{-\infty}^{\infty} (\varepsilon') d\varepsilon' / (\varepsilon - \varepsilon') \Gamma_c$ is the level shift function, $\rho_B(\varepsilon)$ is the density of states (DOS) of substrate, "P" denotes the principle value of the integral. Below, $\varepsilon_a = 0$ is accepted. An electron exchange occurs between carbon adatom arranged in the hexagonal structure. Thus, the Brillouin zone of MG on the substrate is formed. To determine the Green's function of the system perturbed owing to the electron exchange, the Dyson equation is used in the approximation where only the direct exchange between the nearest neighboring atoms is taken into account

$$G_{ij} = G^{0}_{i} \delta_{ij} + \sum_{l} G^{0}_{i} t_{il} G_{lj}, \tag{3}$$

where $t_{il} = t$ is the in-plane hopping energy ($t \approx 2.8$ eV). In view of the symmetry of the graphene crystal lattice and $G^{0}_{i} = G_0$, the Fourier transform of the Dyson equation gives

$$G^{-1}_{\boldsymbol{q}}(\varepsilon) = G^{-1}_{0}(\varepsilon) - tf(\boldsymbol{q}) - i\gamma, \tag{4}$$

where

$$f(\boldsymbol{q}) = \nu_b \sqrt{3 + 2\cos\left(\sqrt{3} q_x a\right) + 4\cos\left(\sqrt{3} q_x a/2\right)\cos\left(3 q_y a/2\right)},$$

$a \approx 1.42$ Å is the carbon–carbon distance, $\boldsymbol{q}$ is the two-dimensional wave vector of electrons of graphene, ν_b is the band index: $\nu_b = +1$ corresponds to the conduction band and $\nu_b = -1$ corresponds to the valence band, γ is a small residual scattering rate (scattering on phonons, impurity atoms, defects of the crystal lattice, etc.). The energy spectrum near the Dirac point with the coordinate $\boldsymbol{Q} = \left(2\pi/3a,\ 2\pi/3\sqrt{3}\,a\right)$ is given by the expression: $tf(\boldsymbol{k}) = \nu_b 3ta|\boldsymbol{k}|/2 = \nu_b \upsilon_F \hbar |\boldsymbol{k}|$, where $\boldsymbol{k} = \boldsymbol{q} - \boldsymbol{Q}$.

3. The substrate density of states and shift function

We assume that the film lies in the plane XY. For the electron energy of the conduction band of the film, we have:

$$E(p) = (2m)^{-1}\left(p_x^2 + p_y^2\right) + \varepsilon_i, \tag{5}$$

where $p = (p_x, p_y)$ is the two-dimensional momentum of electrons in film, m is the electron effective mass, ε_i is the electrons energy along the OZ axis. Further, we will use for the lateral potential the hard box approximation, i.e. $\varepsilon_i = \pi^2\hbar^2 i^2 / 2m_{\perp} L_2$, $m_{\perp}$ is the electron effective mass along the OZ axis, L is the film thickness. For the spectral function, we have

$$A(\varepsilon, p) = \frac{\chi}{\left(\varepsilon - \varepsilon_i - (2m)^{-1}\left(p_x^2 + p_y^2\right)\right)^2 + \chi^2}, \tag{6}$$

where χ is the residual scattering in the substrate. To get the DOS, it is necessary to integrate Eq. (6) over the two-dimensional phase space of the conduction band

$$\rho_{CB}(\varepsilon, \varepsilon_i) = \pi^{-1} \int A(\varepsilon, p) d^2\boldsymbol{p} = \frac{mS_1L_1}{\pi^2\hbar^2 L}\left(\frac{\pi}{2} - \arctan\frac{\varepsilon_i - \varepsilon + \Delta}{\chi}\right), \tag{7}$$

where Δ is the half-width of the band gap in a semiconductor substrate (we consider the intrinsic and direct-gap semiconductors), $S_1 = 3\sqrt{3a^2/4}$ is the film area corresponding to one atom of graphene, L_1 is the interaction length of graphene with the substrate (length of $2p_z$ orbital of carbon atom). Similarly, for the valence band, we have

$$\rho_{VB}(\varepsilon, \varepsilon_i) = \frac{mS_1L_1}{\pi^2\hbar^2 L}\left(\frac{\pi}{2} - \arctan\frac{\varepsilon_i + \varepsilon + \Delta}{\chi}\right). \tag{8}$$

For the total DOS, we obtain

$$\rho(\varepsilon) = \sum_i \left(\rho_{CB} + \rho_{VB}\right)(\varepsilon, \varepsilon_i) = \frac{mS_1L_1}{\pi^2\hbar^2 L} \times \sum_i \left[\pi + \arctan\frac{\varepsilon - \varepsilon_i - \Delta}{\chi} - \arctan\frac{\varepsilon + \varepsilon_i + \Delta}{\chi}\right]. \tag{9}$$

The S_1L_1/L factor in these formulas has the following origin. The function $\rho(\varepsilon)$ in $\Lambda(\varepsilon)$ and $\Gamma_c(\varepsilon)$ is the substrate DOS corresponding to one atom of graphene (this is why $S = S_1$ in Eqs. (7) and (8). In other words, this is DOS, corresponding to the region of substrate, with which graphene atom interacts. If we introduce the L_1, then, obviously, the volume of 3D substrate corresponding to one graphene atom is equal to S_1L_1. The corresponding DOS of 3D metal ($\Delta = 0$!) at $\chi = 0$ is $S_1L_1\sqrt{2}\,m^{3/2}\sqrt{|\varepsilon|}/(\pi^2\hbar^3)$. On the other hand, we have

$$\frac{\pi\hbar}{\sqrt{2m}L}\sum_{i=0}^{\infty}\left\{\mathrm{arctg}\left(\frac{\varepsilon - \varepsilon_i}{\chi}\right) + \frac{\pi}{2}\right\}_{\substack{L\to\infty \\ \chi\to 0}} = \sqrt{|\varepsilon|}.$$

Using this expression, we can obtain from Eq. (9) the correct expression for the DOS of 3D metal. In this paper, we consider the simply case when point $\varepsilon = 0$ (zero energy in substrate electronic DOS) coincides with the Dirac point. Moreover, we assume that $L_1 \approx 2$ Å. When $\chi \to 0$, we have