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Effect of van Hove singularities on thermoelectric properties of graphene

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Using the model density of states of free-standing graphene single-sheet graphene, it is shown that van Hove singularities cause divergences of the Seebeck coefficient and the thermoelectric power factor. The results obtained for free-standing graphene are generalized to the case of epitaxial (encapsulated) graphene. Numerical estimates are given for substrates (plates) representing SiC polytypes.

Keywords: electrical conductivity, Seebeck coefficient, thermoelectric power factor, epigraphen, SiC polytypes.

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1. Introduction

Thermoelectric (TE) properties of materials are characterized by the thermoelectric power factor $PF = \sigma S^2$ and the dimensionless product $ZT = (PF/\kappa)T$, referred to as figure of merit in the English literature, where σ is electrical conductivity, S is Seebeck coefficient, T is temperature, κ is total (electron κ_{el} plus phonon κ_{ph}) thermal conductivity. The goal of modern research of bulk (3D) [1] and two-dimensional (2D) [2] materials, their composites, interfaces and nanostructures is to search for objects that have $ZT > 2$. There are no all-purpose methods for such a search, because the values of σ, κ and

$$S = -C_S[d \ln \sigma(\mu, T = 0)/d\mu], \quad C_S = \pi^2 k_{\text{B}}^2 T/3e, \quad (1)$$

where e being elementary charge, k_{B} being Boltzmann constant, μ being chemical potential (Mott formula), are interdependent. Among 2D structures, the most studied, naturally, are the TE properties of graphene (see review in [2] and numerous references given there). Most theoretical studies devoted to TE properties of free-standing graphene single-sheet graphene consider the energy region close to the Dirac point. In this region, the electronic spectrum is quite adequately described by the low-energy approximation of $\varepsilon_{\text{G}}(\boldsymbol{\kappa}) = \varepsilon_{\text{D}} \pm \hbar v_{\text{F}}|\boldsymbol{\kappa}|$, and the corresponding density of states is $\rho_{\text{G}}(\omega) \propto |\omega - \varepsilon_{\text{D}}|$, where ε_{D} is Dirac point energy, $v_{\text{F}} = 3ta/2\hbar$ is Fermi velocity, $\hbar$ is reduced Planck's constant, ω is energy variable, $t \sim 3$ eV is electron hopping energy between p_z-orbitals of neighboring graphene atoms, $\boldsymbol{\kappa}$ is wave vector for electron motion in the graphene plane (x, y), counted from the vector $\mathbf{K}$ of the Dirac point, $a = 1.42$ Å is distance between the nearest neighbors [3]. With the publication of [4], where low-dimensional semiconductor structures with a parabolic electronic spectrum were considered, it became clear that extreme values of the Seebeck coefficient and PF are achieved in cases where the chemical potential falls into the region, where the density of states of the structure under study depends sharply on energy. This statement is also true for graphene. For example, in [5], for graphene with a gap in the interval of $(\varepsilon_{\text{D}} - \Delta, \varepsilon_{\text{D}} + \Delta)$ (gapped graphene) it is shown that the extrema PF occur when $\mu \to \varepsilon_{\text{D}} - \Delta$, $\varepsilon_{\text{D}} + \Delta$. In the case of epitaxial gapless graphene on a semiconductor substrate, the same effect is observed as the chemical potential approaches the bottom of the conduction band and the top of the valence band [6]. Similar effects are also realized in the case of gapless encapsulated graphene, where at least one of the coating layers is semiconductor [7].

In [5–7] a low-energy approximation was used. Meanwhile, in the density of states of free single-layer graphene there are van Hove singularities: $\rho_{\text{G}}(\omega) \to \infty$ at $\omega_\pm = \varepsilon_{\text{D}} \pm t$. Therefore, at $\mu \to \omega_\pm$ TE characteristics of graphene should have special features. This study is devoted to the investigation of such features in free, epitaxial, and encapsulated graphene.

2. Free graphene

Let us consider free-standing single-sheet graphene with the electronic spectrum of the following form

$$\varepsilon_{\text{G}}(\mathbf{k}) = \pm t f(\mathbf{k}),$$

$$f(\mathbf{k}) = \sqrt{3 + 2\cos(k_y a\sqrt{3}) + 4\cos(k_y a\sqrt{3}/2)\cos(3k_x a/2)}, \quad (2)$$

where $\mathbf{k} = (k_x, k_y)$ is measured from the point Γ of the Brillouin zone [3] and it is assumed that $\varepsilon_{\text{D}} = 0$. To describe the TE characteristics of free-standing graphene, we use the following model density of states [3]:

$$\rho_{\text{G}}(x) = \frac{4|x|}{\pi^2 t\sqrt{Z_0}} \mathbf{K}(\pi/2, \bar{k}(x)), \quad (3)$$

where $x = \omega/t$, $\mathbf{K}(\pi/2, \bar{k})$ is complete elliptic integral of the first kind,

$$\bar{k}(x) = \sqrt{Z_1(x)/Z_0(x)},$$

$$Z_0(x)=\begin{cases}(1+|x|)^2-(x^2-1)^2/4, & -1\le x\le 1;\\ 4|x|, & -3\le x<-1,\quad 1<x\le 3;\end{cases}$$

$$Z_1(x)=\begin{cases}4|x|, & -1\le x\le 1;\\ (1+|x|)^2-(x^2-1)^2/4, & -3\le x<1,\ 1<x\le 3.\end{cases}$$

According to [8], $\mathbf{K}\approx(\pi/2)(1+\bar{k}^2/4)$ with $\bar{k}^2\ll 1$ (or $|x|\ll 1$) and $\mathbf{K}\approx\ln(4/\sqrt{1-\bar{k}^2})$ with $\bar{k}^2\to 1$ (or $|x|\to 1$), where values of $x_\pm=\pm 1$ determine the positions of the van Hove singularities (graph of the $\rho_{\mathrm{G}}(\omega)$ function is shown in Figure 5 of the review in [3]).

The van Hove feature corresponds to the point M $(2\pi/3a,0)$ of the Brillouin zone of graphene. Assuming $k_x=\kappa_x+2\pi/3a$ and $k_y=\kappa_y$, for small $\boldsymbol{\kappa}$ we have $f(\boldsymbol{\kappa})\approx 1+9\kappa_x^2a^2/2-\kappa_y^2a^2/2$. Thus, point M of the Brillouin zone is a saddle point. With $\kappa_y=0$ we have

$$\varepsilon_{\mathrm{G}}(\kappa_x)\approx\pm t(1+\hbar^2\kappa_x^2/2m_xt),\ \ m_x=\hbar^2/9a^2t, \tag{4}$$

so the reduced effective mass is $m_x^*=m_x/m_e\approx 0.15$, where m_e being mass of a free electron. Electron group velocity $\mathbf{v}=\hbar^{-1}\nabla_\kappa\varepsilon_{\mathrm{G}}(\boldsymbol{\kappa})$ in the direction of x (armchair direction) is equal to $v_x=\pm\hbar\kappa_x/m_x$. Below we will consider the movement of the electron only in the x-direction and will omit the corresponding subscripts of v_x and m_x.

For further analysis, we will use the Boltzmann kinetic equation in the approximation of relaxation time $\tau(\omega)$ (see, for example, [9]) and introduce the differential conductivity:

$$\sigma(\omega)=e^2\rho_{\mathrm{G}}(\omega)v^2(\omega)\tau(\omega)/A_{\mathrm{u.c.}}, \tag{5}$$

where e is elementary charge, $A_{\mathrm{u.c.}}=3\sqrt{3}a^2/2$ is area of the lattice cell of graphene [10,11]. It should be noted that, unlike [10,11], where conductivity was measured in S/m (see [12,13]), here $\sigma(\omega)$ is measured in Siemens, S .

Assume $\tau(\omega)=\tau_0=\mathrm{const}$ for simplicity (option 1) [10–13], which models short-range scattering on uncharged impurities [14]. Due to the fact that $v^2(\mu)=2m(|\mu|-t)$ and $\rho_{\mathrm{G}}(\mu)\approx(8/\pi^2t)\ln[t/(|\mu|-t)]$, where $|\mu|>t$, with $|\mu|\to t+0^+$ $|\mu|\to t+0^+$ we get

$$\sigma(\mu)\approx\frac{2e^2m\tau_0}{\pi^2tA_{\mathrm{u.c.}}}(|\mu|-t)\ln\frac{t}{|\mu|-t},$$

$$S\approx-\mathrm{sgn}(\mu)\frac{C_S}{|\mu|-t},\quad PF\approx\frac{C_1C_S^2}{|\mu|-t}\ln\frac{t}{|\mu|-t}, \tag{6}$$

where $C_1=16e^2m\tau_0/\pi^2tA_{\mathrm{u.c.}}$.

Now assume $\tau(\omega)=C_\tau/\rho_{\mathrm{G}}(\omega)$ (option 2) [10–13]. Then we find that:

$$\sigma(\mu)\approx\frac{2e^2mC_\tau}{A_{\mathrm{u.c.}}}(|\mu|-t),$$

$$S\approx-\mathrm{sgn}(\mu)\frac{2C_S}{|\mu|-t},\quad PF\approx\frac{C_2C_\tau C_S^2}{|\mu|-t}, \tag{7}$$

where $C_2=8e^2m/A_{\mathrm{u.c.}}$. Thus, both approximations for the relaxation time lead to a divergence of the Seebeck coefficient and the TE power factor at $|\mu|\to t+0^+$.

3. Epitaxial and encapsulated graphene

Let us now consider epitaxial graphene (epigraphene), assuming that the substrate is a semiconductor. The Green's function of free graphene $G(\omega,\mathbf{k})$ has the following form: $G^{-1}(\omega,\mathbf{k})=\omega-\varepsilon_{\mathrm{G}}(\mathbf{k})+i0^+$. Then for the Green's function of epigraphene $\tilde{G}(\omega,\mathbf{k})$ we get

$$\tilde{G}^{-1}(\omega,\mathbf{k})=\omega-\varepsilon_{\mathrm{G}}(\mathbf{k})-\Lambda_{\mathrm{sub}}(\omega)+i\Gamma_{\mathrm{sub}}(\omega). \tag{8}$$

Here, the half-width and shift of states of free-standing graphene induced by the substrate are equal to, respectively

$$\Gamma_{\mathrm{sub}}(\omega)=\pi V^2\rho_{\mathrm{sub}}(\omega),$$

$$\Lambda_{\mathrm{sub}}(\omega)=V^2P\int_{-\infty}^{\infty}\frac{\rho_{\mathrm{sub}}(\omega')d\omega'}{\omega-\omega}, \tag{9}$$

where V is matrix element of the graphene−substrate interaction, P is symbol of the main value of the integral [7,8]. Returning to the counting of wave vectors from point M $(2\pi/3a,0)$ of the Brillouin zone of graphene and taking as a guide the scheme of [15,16], for $\kappa_xa\ll 1$ and $\kappa_y=0$ instead of (4) we get

$$\tilde{\varepsilon}_{\mathrm{G}}(\kappa_x)\approx\pm t(1+\hbar^2\kappa_x^2/2\tilde{m}_\pm t),$$

$$\tilde{v}_\pm=v\eta_\pm,\ \ \tilde{m}_\pm\eta_\pm=m, \tag{10}$$

where the coefficient is as follows

$$\eta_\pm\equiv\eta(\pm t)=[1-(d\Lambda_{\mathrm{sub}}(\omega)/d\omega)_{\omega=\pm t}]^{-1}.$$

To find the $\Gamma_{\mathrm{sub}}(\omega)$ and $\Lambda_{\mathrm{sub}}(\omega)$ functions, it is necessary to specify the density of states of the semiconductor substrate $\rho_{\mathrm{sub}}(\omega)$. In the simplest Haldane–Anderson model [17] we have $\rho_{\mathrm{sub}}(\omega)=\rho_{sc}=\mathrm{const}$ for $|\omega-\omega_0|\ge E_g/2$ and $\rho_{\mathrm{sub}}(\omega)=0$ for $|\omega-\omega_0|\le E_g/2$, where ω_0 is energy of the center of the band gap with a width of E_g. Then for the half-width function we get $\Gamma_{\mathrm{sub}}(\omega)=\pi V^2\rho_{sc}$ for $|\omega-\omega_0|\ge E_g/2$, $\Gamma_{\mathrm{sub}}(\omega)=0$ for $|\omega-\omega_0|\le E_g/2$, and the shift function is equal to $\Lambda_{\mathrm{sub}}(\omega)=\rho_{sc}V^2\ln|(\omega-\omega_0-E_g/2)/(\omega-\omega_0+E_g/2)|$. Hence we get

$$\eta_\pm=\left(1+\frac{\rho_{sc}V^2E_g}{(\pm t-\omega_0)^2-(E_g/2)^2}\right)^{-1}. \tag{11}$$

Neglecting the broadening of states (see, for example, [18]) and taking into account only their shift, instead of energy ω we get $\omega'=\omega-\Lambda_{\mathrm{sub}}(\omega)$. Thus, the renormalized energy of the Dirac point is $\varepsilon'_{\mathrm{D}}=-\Lambda_{\mathrm{sub}}(0)$, and positions of the van Hove singularities are $\omega'_\pm=\pm t-\Lambda_{\mathrm{sub}}(\pm t)$.

To be specific, we present numerical estimates for the graphene formed on polytypes of silicon carbide. For the bands of allowed states containing 4 electrons, we obtain $\rho_{sc}=4/W\sim 0.3\,\mathrm{eV}^{-1}$, where widths of these bands are $W\sim 12\,\mathrm{eV}$ [19,20]. Considering the limit of weak coupling between the graphene and the substrate, assume $V=1\,\mathrm{eV}$,

Parameters of SiC and epigraphene polytype: degree of hexagonality D, band gap E_g, electron affinity χ; energy of the center of the band gap ω_0, boundaries of the valence band E_V and conduction band E_C, Dirac point ε'_D and singularities of van Hove $\omega'_\pm$ (relative to the Dirac point of free-standing graphene ε_D); factor $\eta_\pm$. All energy quantities are given in eV

Polytype → Parameter ↓	$8H$	$21R$	$6H$	$15R$	$27R$	$4H$
D	0.25	0.29	0.33	0.40	0.44	0.50
E_g	2.86	2.96	3.00	3.06	3.13	3.23
χ	3.58	3.52	3.45	3.33	3.27	3.17
$-\omega_0$	0.51	0.50	0.45	0.37	0.34	0.29
$-E_V$	0.92	0.98	1.05	1.16	1.23	1.33
E_C	1.94	1.98	1.95	1.90	1.90	1.90
ε'_D	0.75	0.70	0.62	0.49	0.44	0.36
$-\omega'_-$	3.86	3.90	3.93	3.98	4.02	4.08
ω'_+	4.31	4.36	4.35	4.35	4.36	4.38
η_-	0.86	0.85	0.86	0.86	0.86	0.86
η_+	0.88	0.88	0.88	0.87	0.87	0.87

so that $\rho_{sc}V^2 \sim 1\,\text{eV}$. Then, we take into account that $\omega_0 = \chi + E_g/2 - \phi_G$, where χ is electronic affinity, E_g is band gap of the SiC polytype [21], $\phi_G = 4.5\,\text{eV}$ is work function of free-standing graphene [22]. The calculation results are presented in the table, from which it follows, first, that in the series of polytypes considered, arranged in increasing order of the degree of hexagonality D, equal to the relative number of SiC atoms located in hexagonal positions, significantly changing are only the values of ω_0 and ε'_D. Second, the energies of ω'_- and ω'_+ are quite far from the energies of the band gap edges $E_V = -\omega_0 - E_g/2$ and $E_C = -\omega_0 + E_g/2$. In other words, van Hove singularities do not overlap with the divergences arising at the boundaries of the band gap [7,8]. And finally, the coefficients $\eta_\pm$ are almost the same for all polytypes. Thus, for epigraphene, formulae (6) and (7) are valid, with m replaced by $m_\pm$.

Let us now turn to the single-layer graphene encapsulated between coating layers 1 and 2. It is easy to show (see, for example, [7,8]) that the Green's function of the encapsulated layer $\hat{G}(\omega, \mathbf{k})$ can be represented as expression (8), where the $\Gamma_{\text{sub}}(\omega)$ and $\Lambda_{\text{sub}}(\omega)$ functions describing the effect of the presence of a substrate, are replaced by the $\Gamma_1(\omega) + \Gamma_2(\omega)$ and $\Lambda_1(\omega) + \Lambda_2(\omega)$ sums describing the resulting effect of coating layers 1 and 2, and introduce the parameters $E_{g1,2}$ and $\omega_{01,2}$ of the coating layers. In the simplest case of identical coating layers, when $\Gamma_1(\omega) = \Gamma_2(\omega) \equiv \Gamma(\omega)$ and $\Lambda_1(\omega) = \Lambda_2(\omega) \equiv \Lambda(\omega)$, the results obtained can be used for epigraphene by assuming $\Gamma_{\text{sub}}(\omega) = 2\Gamma(\omega)$ and $\Lambda_{\text{sub}}(\omega) = 2\Lambda(\omega)$.

4. Conclusion

In this study, we have shown that van Hove singularities are manifested at $|\mu| \to t$ as divergences in the $S(\mu)$ and $PF(\mu)$ dependences, whereas $\sigma(\mu) \to 0$ (this is referred to the Drude conductivity, not the quantum conductivity). It should be noted that in the case of epigraphene it is more correct to talk about van Hove special features rather than singularities, because consistent consideration of the $\Gamma_{\text{sub}}(\omega)$ broadening leads to extrema rather than divergences. Further, it is demonstrated that both relaxation time approximations ($\tau(\omega) = \tau_0 = \text{const}$ and $\tau(\omega) \propto \rho_G^{-1}(\omega)$) give the same divergences. It should be emphasized that a high level of electronic doping, meeting the condition of $\mu \to \omega'_+$ and corresponding to the charge carrier density of $5.5 \cdot 10^{14}\,\text{cm}^{-2}$, was really achieved for the graphene formed on $6H$–SiC(0001) by ytterbium intercalation and potassium adsorption [23]. Also, it should be noted that there is growing interest in the role of van Hove singularities in the physics of twisted two-layer graphene [24,25], three-layer graphene [26] and the graphene/h-BN superlattice [27].

Conflict of interest

The author declares that he has no conflict of interest.

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