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Organic macromolecule on graphene with structural defects: Estimations of charge transfer and adhesion energy

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The previously proposed model of dengling bonds of an organic macromolecule (MM) adsorbed on an ideal single-layer graphene (SLG) is generalized to the presence of structural defects in SLG: inclusions of two-layer or amorphous graphene. Analytical estimates of the charge transition between MM and the substrate and the adhesion energy are obtained.

Keywords: macromolecule with dangling bonds, single- and bilayer graphene, amorphous graphene.

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1. Introduction

The unique ability to detect absorption of individual molecule found in [1] made graphene one of the most attractive material for resistive gas sensors [2–5], and then for biosensors as well [6–10]. Typical objects for studying in the latter case are macromolecules (MM), which are systems (plaques) with large number of atoms and linear dimensions about hundreds of Å. And neither geometry of such a plaque nor the area of its contact with the substrate are known, yet are strictly fixed. It is clear that direct application of DFT (density functional theory) methods is unacceptable in this case. Therefore, in [11], to describe the energy of interaction (adhesion) of a MM with a single-layer graphene (SLG) a broken bond model was suggested with these bonds considered responsible for the stitching of the MM with the SLG (see Fig. 1 in [11]). Thanks to the simplified scheme of the problem consideration, the authors succeeded in obtaining analytical expressions for the charge transfer between the MM and SLG and for the energy of adhesion. This study makes use of the same MM model, however the graphene substrate is considered non-ideal. Two causes of the deviation from ideal SLG are considered. These are, first, the presence of inclusions of the bilayer graphene (BLG), when a portion of $(1-x)$ of the substrate area is SLG, and a portion of x is BLG. In the following test this structure will be denoted as $\mathrm{S}_{1-x}\mathrm{B}_x$. The second cause is the amorphous inclusions in the ordered monolayer of graphene.

2. Macromolecule on the $\mathrm{S}_{1-x}\mathrm{B}_x$ substrate

Let us consider a substrate composed of SLG and BLG, or a $\mathrm{S}_{1-x}\mathrm{B}_x$ structure. It is worth to note that the situation like this indeed takes place in real device structures (see, for example, [6]). Summarizing the results of [11], where the broken bond model was introduced to describe the interaction between MM and SLG, now we shall take into account that broken bonds of the MM interact not only with the SLG, but also with the BLG. Therefore, instead of Hamiltonian (1) for the MM/SLG system of [11], we write the Hamiltonian for the MM/$\mathrm{S}_{1-x}\mathrm{B}_x$ system as follows

$$H=\sum_{\mathbf{k},J}\varepsilon_J(\mathbf{k})c^+_{\mathbf{k}}c_{\mathbf{k}}+\sum_i\varepsilon_i a^+_i a_i+\sum_{i,\mathbf{k},J}\frac{V^2_{iJ}(c^+_{\mathbf{k}}a_i+a^+_i c_{\mathbf{k}})}{\omega-\varepsilon_J(\mathbf{k})+i0^+},\tag{1}$$

where ω is the energy variable, ε_i is the energy of the i-th broken (vacant) bond of the MM, $\varepsilon_J(\mathbf{k})$ is the law of electron dispersion in $J=\mathrm{SLG}$ or $J=\mathrm{BLG}$, V_{iJ} is the energy of interaction between the i-th bond and the electronic spectrum of SLG or BLG, $c^+_{\mathbf{k}}(c_{\mathbf{k}})$ is the operator of nucleation (annihilation) of SLG or BLG electron in the $|\mathbf{k}\rangle$ state, $a^+_i(a_i)$ are similar operators for the i-th broken bond of the MM. It is easy to show that, due to the adsorption at SLG or BLG the density of states (DOS) of electron on the i-th bond (per one spin projection) is

$$\rho_{iJ}=\frac{1}{\pi}\frac{\Gamma_{iJ}(\omega)}{(\omega-\varepsilon_i-\Lambda_{iJ}(\omega))^2+\Gamma^2_{iJ}(\omega)},\tag{2}$$

where the functions of broadening and shift of the ε_i quasi-level are respectively equal to

$$\Gamma_{iJ}(\omega)=\pi V^2_{iJ}\rho_J(\omega,\ \Lambda_{ij}(\omega)=\frac{1}{\pi}\int\limits_{-\infty}^{\infty}\frac{\Gamma_{iJ}(\omega')d\omega'}{\omega-\omega'}.\tag{3}$$

Let us represent the $\rho_{sub}(\omega,x)$ DOS of electrons for a $\mathrm{S}_{1-x}\mathrm{B}_x$ substrate as follows

$$\rho_{sub}(\omega,x)=(1-x)\rho_{\mathrm{SLG}}+x\rho_{\mathrm{BLG}}(\omega).\tag{4}$$

The expression for the ρ_{SLG} DOS of SLG in a low-energy approximation, when $\varepsilon_{\mathrm{SLG}}(\mathbf{k})\approx\pm(3t/2)|\mathbf{k}|a$, where

a being the distance between the nearest neighbors (n. n.) in the graphene, t being the energy of electron hopping between n. n., is well-known [12] and has the following form:

$$\rho_{\text{SLG}}(\omega) = |\omega|/\xi^2, \quad |\omega| < \xi, \tag{5}$$

where $\xi = \sqrt{\pi\sqrt{3}/4}t \sim t$ is the cutting energy. In the case of AB packing BLG in the same low-energy approximation for l-bands nearest to the Dirac point (where l means „lower") we have

$$\varepsilon^l_{\text{BLG}}(\mathbf{k}) \approx \pm\varepsilon^2_{\text{SLG}}(\mathbf{k})/t_\perp,$$

where $t_\perp \sim 0.4\,\text{eV}$ is the energy of electron hopping between the planes of the BLG [12,13]. Using the result of [14], we can represent the $\rho^l_{\text{BLG}}(\omega)$ as

$$\rho^l_{\text{BLG}}(\omega) = t_\perp/2\xi^2, \quad |\omega| < \xi, \tag{6}$$

where we made use of the same energies of Dirac point $\varepsilon_D = -$ and cutting ξ, as in the case of SLG. For u-bands (where u means „upper"):

$$\varepsilon^u_{\text{BLG}}(\mathbf{k}) \approx \pm\sqrt{t^2_\perp + \varepsilon^2_{\text{SLG}}}. \tag{7}$$

Then, by an analogy with [11], the expression for the corresponding DOS can be written as follows:

$$\rho^u_{\text{BLG}}(\omega) = \begin{cases} |\omega|/\xi^2, & t_\perp \le |\omega| < \xi, \\ 0, & |\omega| < t_\perp. \end{cases} \tag{8}$$

The DOS on the i-th bond (per one spin projection) is

$$\rho_i(\omega, x) = (1-x)\rho_{i\text{SLG}}(\omega) + x\rho_{i\text{BLG}}(\omega), \tag{9}$$

where

$$\rho_{\text{BLG}}(\omega) = \rho^l_{\text{BLG}}(\omega)\Theta(\xi - |\omega|) + \rho^u_{\text{BLG}}(\omega)\Theta(|\omega| - t_\perp)\Theta(\xi - |\omega|),$$

where $\Theta(\ldots)$ — Heaviside function, and

$$\rho_{iJ}(\omega) = \frac{1}{\pi}\frac{\Gamma_{iJ}(\omega)}{(\omega - \varepsilon_i - \Lambda_{iJ}(\omega))^2 + \Gamma^2_{iJ}(\omega)}. \tag{10}$$

According to [11],

$$\Gamma_{i\text{SLG}}(\omega) = \pi V^2_{i\text{SLG}}\rho_{i\text{SLG}}(\omega),$$

$$\Lambda_{i\text{SLG}}(\omega) = (\omega V^2_{i\text{SLG}}/\xi^2)\ln|\omega^2/(\xi^2 - \omega^2)|. \tag{11}$$

Using expressions (6), (7) and (3), for $|\omega| < \xi$ we get

$$\Gamma^l_{i\text{BLG}} = \pi(V^l_{i\text{BLG}})^2\rho^l_{\text{BLG}} = \text{const},$$

$$\Lambda^l_{i\text{BLG}}(\omega) = (\Gamma^l_{i\text{BLG}}/\pi)\ln\left|\frac{\xi - \omega}{\xi + \omega}\right|, \tag{12}$$

$$\Gamma^u_{i\text{BLG}}(\omega) = \pi(V^u_{i\text{BLG}})^2\rho^u_{\text{BLG}}(\omega),$$

$$\Lambda^u_{i\text{BLG}}(\omega) = \frac{(V^u_{i\text{BLG}})^2\omega}{\xi^2}\ln\left|\frac{t^2_\perp - \omega^2}{\xi^2 + t^2_\perp - \omega^2}\right|. \tag{13}$$

By making use of the simplification described in [11], and replacing DOS (10) with

$$\rho_{iJ}(\omega) \approx \frac{1}{\pi}\frac{\bar\Gamma_{iJ}}{(\omega - \bar\varepsilon_{iJ})^2 + \Gamma^2_{iJ}}, \tag{14}$$

where $\bar\varepsilon_{oiJ} = \varepsilon_i + \Lambda_{iJ}(\varepsilon_i)$ and $\bar\Gamma_{iJ} = \pi V^2_{iJ}\rho_J(\varepsilon_i)$, we get the following for the charge of the i-th bond $Z_i(x)$:

$$Z_i(x) = (1-x)Z_{i\text{BLG}} + xZ_{i\text{BLG}}. \tag{15}$$

For an undoped graphene, when the Fermi level is $\varepsilon_F = \varepsilon_D = 0$, the charge is $Z_{iJ} \approx (2/\pi)\arctan(\bar\varepsilon_{iJ}/\bar\Gamma_{iJ})$. It is worth noting that a more rigorous treatment of the problem of individual atom adsorption on BLG is presented in [15].

The sum charge transferred from the MM to the substrate is $Z(x) = -\sum_i Z_i(x)$, so in an initially undoped heterogeneous film charge carriers arise with a concentration of $n(x) = |Z(x)|/S$. With $Z(x) < 0$ the charge carriers are electrons, and with $Z(x) > 0$ the carriers are holes. Thus, the SLG conductivity becomes $\sigma(x) = en(x)\mu_{\text{int}}(x)$, where $\mu_{\text{int}}(x)$ being integral mobility of carriers in the $S_{1-x}\text{B}_x$ structure.

As in the case of SLG, the energy of adhesion E_{ads} on the BSL can be represented as a sum of the ion E^{ion}_{adh} and metal E^{met}_{adh} components determined by formulae (10)–(15) from [11]. For a substrate formed by SLG and BLG, we can write the following:

$$E^{ion(met)}_{adh}(x) = \sum_i E^{ion(met)}_i(x)N_i,$$

$$E^{ion(met)}_i(x) = (1-x)E^{ion(met)}_{i\text{SLG}} + xE^{ion(met)}_{i\text{BLG}}, \tag{16}$$

where $N_i = m_i/S$ is the concentration of m_i broken i-bonds per a lattice cell of graphene with an area of $S = 3\sqrt{3}a^2/2$ ($a = 1.42\,\text{Å}$ is the distance between the nearest neighbors in the graphene).

Turning now to numerical estimates, we use the same values of ε_i, $d_i = d = 2.5\,\text{Å}$, $V^{l,u}_{i\text{BSL}} = V_{i\text{SLG}} = 2.7\,\text{eV}$, $\varepsilon_{st} = 3$, $\xi = 3\,\text{eV}$, as in [11]. Results of calculations of charges and components of adhesion energy are summarized in the table below. The main issue that is worth noting as a result of comparing the characteristics of BLG and SLG is the proximity of these characteristics to each other for all considered fragments of the MM, except for the ratio of $z = Z_{i\text{BLG}}/Z_{i\text{SLG}}$ for NO and NH. The point is that for NO and NH $\varepsilon^2_i \sim t^2_\perp$, while for other MM fragments $\varepsilon^2_i \gg t^2_\perp$. In this case $\rho_{i\text{SLG}}(\omega) \sim \rho^u_{i\text{BLG}}(\omega)$, and the contribution of $\rho^l_{i\text{BLG}}(\omega)$ can be ignored, so that $\Gamma_{i\text{SLG}}(\omega) \sim \Gamma_{i\text{BLG}}(\omega)$ and $\Lambda_{i\text{SLG}}(\omega) \sim \Lambda_{i\text{BLG}}(\omega)$. By rewriting expression (15) as follows

$$Z_i(x) = Z_{i\text{SLG}}[1 + x(z-1)], \tag{17}$$

and taking into account that the typical value $x \sim 0.1$ [6], with a good accuracy we get $Z_i(x) \approx Z_{i\text{SLG}}$. Then

Characteristics of the AB packing BLG: energies of broken bonds ε_i, charges Z_i, adsorption energies $E^{ion}_{i\mathrm{BLG}}$, $E^{met}_{i1\mathrm{BLG}}$, $E^{met}_{i2\mathrm{BLG}}$, $E^{ads}_{i\mathrm{BLG}}$ (all energy parameters are given in eV) and ratios $z = Z_{i\mathrm{BLG}}/Z_{i\mathrm{SLG}}$, $e_{met} = E^{met}_{i\mathrm{BLG}}/E^{met}_{i\mathrm{SLG}}$ and $e_{ads} = E^{ads}_{i\mathrm{BLG}}/E^{ads}_{i\mathrm{SLG}}$

Fragment of MM →	O_2	NO	NH	CH_2	NH_2	CH_3
ε_i	−1.78	−0.47	−0.32	−1.02	−0.96	−0.96
$Z_{i\mathrm{BLG}}$	−0.125	0.45	−0.33	0.16	0.19	0.19
$E^{ion}_{i\mathrm{BLG}}$	0.015	0.19	0.10	0.02	0.04	0.04
$E^{met}_{i1\mathrm{BLG}}$	0.30	1.10	0.80	0.39	0.46	0.46
$E^{met}_{i2\mathrm{BLG}}$	1.60	1.01	1.23	1.54	1.48	1.48
$E^{ads}_{i\mathrm{BLG}}$	1.92	2.30	2.13	1.95	1.98	1.98
z	1.04	0.67	−0.62	0.80	0.83	0.83
e_{met}	1.00	0.94	1.015	0.99	0.99	0.99
e_{ads}	1.015	0.86	0.94	0.98	0.98	0.98

the conductivity of initially undoped graphene induced by the MM adsorption is $\sigma(x) \approx e n_{\mathrm{SLG}} \mu_{\mathrm{int}}(x)$. It is worth to note the high mobility of carriers in the BLG: thus, for example, in [13] the authors report a value of $\mu_{\mathrm{BLG}} = 40000\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. If $\mu_{\mathrm{SLG}} \approx \mu_{\mathrm{BLG}}$, then the minimum $\mu_{\mathrm{int}}(x)$ arising in the $S_{1-x}B_x$ structure due to the additional scattering on the boundaries of SLG and BLG regions should be expected at intermediate concentrations of x. On the other hand, we have $x|e_{ads} - 1| \ll 1$ (see the table), so the BLG inclusions have a low effect on the adhesion energy.

Noe let us consider the inclusion of an AA packing BLG [16], for which in the low-energy approximation the law of dispersion and the DOS are, respectively:

$$\varepsilon'_{\mathrm{BLG}}(\mathbf{k}) = \pm\left[|\varepsilon_{\mathrm{SLG}}|/\sqrt{3} \pm t_\perp\right],$$

$$\rho'_{\mathrm{BLG}}(\omega) = [|\omega - t_\perp| + |\omega + t_\perp|]/(\xi')^2. \qquad (18)$$

Here $\xi' = \sqrt{\pi/4\sqrt{3}t}$, that takes into account the Fermi speed of $v'_{F\mathrm{BLG}} = v_{F\mathrm{SLG}}/\sqrt{3}$ (primed symbols correspond to the AA packing). In the $(-t_\perp, t_\perp)$ energy interval the DOS of $\rho'_{\mathrm{BLG}}(\omega) = 2t_\perp/(\xi')^2$ is an analogue of $\rho^l_{\mathrm{BLG}}(\omega) = t_\perp/2\xi^2$ for the AB packing (6); with $|\omega| \ge t_\perp$ we get $\rho'_{\mathrm{BLG}}(\omega) = 2|\omega|/(\xi')^2$ — an analogue of the $\rho^u_{\mathrm{BLG}}(\omega) = |\omega|/\xi^2$ DOS (7). With consideration to these correspondences, it is easy to rewrite expressions (12)−(16) for the AA packing. The scheme proposed herein allows considering the trilayer graphene (TLG) as an inclusion in the SLG [16,18,19], by assuming $\rho(x, y) = (1 - x - y)\rho_{\mathrm{SLG}} + x\rho_{\mathrm{BLG}} + y\rho_{\mathrm{TLG}}$.

3. Macromolecule on the SLG with amorphous inclusions

Amon various deviations of graphene from the ideal structure [20], we shall consider the amorphous SLG, or the a-SLG, that, as known [21], contains pentagons, hexagons and heptagons of carbon atoms [21]. It is worth noting that the a-SLG, which is interpreted here as a defect inclusion, is of immediate interest for applications as an interphase coating or an inoculum for the processes of atomic layer deposition [21]. In the following text we use the model of [22,23], according to which the DOS $\rho_{am}(\omega)$ for a-SLG in the low-energy approximation has the following form:

$$\rho_{am}(\omega) = \sqrt{\omega^2 + \Delta^2}/\xi^2, \quad |\omega| < \xi, \qquad (19)$$

where the Δ energy characterizes the amorphization and the Dirac point is adopted as the energy zero. It can be easily seen that DOS (19) at $\Delta = 0$ becomes equal to (5). The dependence (19) in the range of $(-t, t)$ is qualitatively matched with the results of numerical calculations (see, for example, Fig. 2 in [21], Fig. 3 in [24], Fig. 6 in [25]). Here, for $\rho_{am}(\omega)$ (as well as for $\rho_{\mathrm{SLG}}(\omega)$) we use a simplified expression as compared to [22,23], the background for which is presented in section 2 of the Annex to [11]. It is worth to emphasize that DOS (19) reflects the main feature of the a-SLG, i.e. the increase in the density of states in the neighborhood of the Dirac point. It is interesting to note that the graphene disordered as a result of high concentration of vacancies has its DOS form similar to (19) [26–28].

By making use of (19), we get the functions of broadening $\Gamma_{am}(\omega) = \pi V^2_{am}\rho_{am}(\omega)$ and shift

$$\begin{aligned}\Lambda_{iam}(\omega) = \frac{V^2_{iam}}{\xi^2}\Bigg[\sqrt{\omega^2 + \Delta^2}\Bigg(&\mathrm{Arsh}\,\frac{\omega\xi + \Delta^2}{\Delta|\xi - \omega|} \\ &+ \mathrm{Arsh}\,\frac{\omega\xi - \Delta^2}{\Delta|\xi + \omega|}\Bigg) - 2\omega\,\mathrm{Arsh}\,\frac{\xi}{\Delta}\Bigg], \qquad (20)\end{aligned}$$

where V_{iam} is the matrix element of interaction between the i-th bond of the MM and the a-SLG. With $\Delta = 0$, the $\Lambda_{iam}(\omega)$ becomes the function of shift for SLG (see formula (5) in [11]). By using the same simplifications as above for the charge on the i-th bond, we get

$$Z_{iam} \approx \frac{2}{\pi} \arctan \frac{\bar{\varepsilon}_{iam} - \varepsilon_F}{\Gamma_{iam}(\varepsilon_i)}, \qquad (21)$$

where $\bar{\varepsilon}_{iam} = \varepsilon_i + \Lambda_{am}(\varepsilon_i)$. For further estimates we assume $V_{iam} = V_{\text{SLG}} = V$, $\varepsilon_F = 0$ and use the same values of other parameters, as above. Let us introduce as a dimensionless characteristic of the amorphism degree the parameter $\delta = \Delta/\xi$ and relative units $e_i = \varepsilon_i/\xi$, $\upsilon = V/\xi$ and consider the special cases.

With $|e_i| \ll \delta^2 \ll 1$ we get $\lambda_{am}(e_i) \equiv \Lambda_{iam}(\varepsilon_i)/\xi \approx -2e_i\upsilon^2 \ln(2/\delta)$ [22] and $\gamma_{am}(e_i) \equiv \Gamma_{am}(\varepsilon_i)/\xi = \pi\upsilon^2\delta \times (1 + e_i^2/2\delta^2)$. Then, in the first order for e_i the charge on the i-th MM bond is

$$Z_{iam} \approx \frac{2}{\pi} \arctan \frac{e_i[1 - \upsilon^2 \ln(2/\delta)]}{\pi\upsilon^2\delta}. \qquad (22)$$

In the mode of weak bond of the MM with the a-SLG, when $\upsilon \ll 1$ and $L(\delta) \equiv 1 - \upsilon^2 \ln(2/\delta) > 0$, an increase in δ leads to a decrease in $|Z_{iam}|$ and with $\delta_0 = 2\exp(-1/\upsilon^2)$ we get $Z_{am} = 0$. In the mode of strong bond, when $\upsilon \gg 1$ and $L(\delta) < 0$, sign of the charge changes, but again: the growth of δ decreases the $|Z_{iam}|$. In the case when $e_i \to \mp 1$ remaining within the interval of $(-1, 1)$, we have $\lambda_{am}(e_i) \to \mp\upsilon^2\sqrt{1+\delta^2} \ln[2/\delta(1 \pm e_i)]$ [11], so

$$Z_{iam} \approx \pm \frac{2}{\pi} \arctan \frac{\ln[2/\delta(1 \pm e_i)]}{\pi}. \qquad (23)$$

It follows therefrom that an increase in the amorphism degree a-SLG results in a decrease in the charge on the MM. Since the ion component of the adsorption energy $E_i^{ion} \propto Z_i^2$ and metal component $E_i^{met} \propto |Z_i|$ [11], then for the considered cases the adhesion energy decreases with growth of the amorphism degree a-SLG. It should be noted that the dependence $Z_{iam}(\delta)$ is non-monotonous, because the $\Lambda_{iam}(\omega)$ function in the $(-\xi, \xi)$ interval has positive and negative extremes, respectively, in the intervals of $-\xi < \omega^* < 0$ and $0 < \omega^* < \xi$ (see Fig. 1 in [11,12]).

As in [11], our understanding is that the charge transferred from the MM to the substrate is $Z_{am} = -\sum_i Z_i$, so the conductivity of a-SLG is $\sigma_{am} = en_{am}\mu_{am}$, where $n_{\text{SLG}} = |Z_{am}|/S$ (S is the area of the lattice cell of graphene) and μ_{am} are concentration and mobility of charge carriers, respectively. Currently, it is known [21] that $\mu_{am} \sim 1{-}10\,\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ (in the air at room temperature) and a length of Anderson localization [29] of about $\ell \sim 10\,\text{nm}$, i.e. a-SLG is an insulator. Thus, the resulting conductivity of SLG with inclusions of a-SLG is approximately equal to $\sigma(x) \approx en_{\text{SLG}}\mu_{\text{SLG}}(1 - x)$. It is worth noting that free-standing a-SLG was obtained in 2020 [30].

To estimate the energy of MM adhesion on a-SLG, formulae (11)−(13) of [11] can be used. Actually, in (12) and (13) the r_{ai}^2 term should be replaced with $(r_{ai}^{-2} - \ell^{-2})$. However, since $r_{ai}^{-2} \gg \ell^{-2}$, the results of [11] can still be used.

4. Conclusion

In this study within the model of broken bonds ε_i we have proposed a scheme to take into account defect inclusions in the SLG. This scheme allowed us to estimate the transfer of charge $Z = -\sum_i Z_i$ between the MM and the substrate, and the adhesion energy determined by Z_i and delocalization of electrons of initially broken i-bonds. Unfortunately, to the best of our knowledge, there is no corresponding experimental information. Moreover, it is worth to emphasize that experimental data even for gas molecules composed of a few atoms adsorbed on real carbon structures are contradictory to a great extent (see discussion of this situation in [31]). Even more questions are caused by the description of carrier mobility on substrates with defect inclusions. The development of appropriate theoretical schemes is just beginning [32,33]. Thus, to create rather a simple (working) model of a graphene-based biosensor, additional experimental and theoretical studies are needed.

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Conflict of interest

The author declares that he has no conflict of interest.

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