Simulation of hopping in disordered fractal arrays of graphene quantum dots

Ekaterina Morozova
Department of Theoretical Physics, Ulyanovsk State University, Russia
E-mail: kat-valezhanina@yandex.ru

Abstract. Diffusion regimes of charge carriers in artificial quasi-fractal graphene quantum dot (GQD) superlattices forming hexagonal and triangular carpet are investigated. Using the generalized Miller-Abrahams relations for hopping rates we perform Monte Carlo simulation of charge carrier hopping in artificial 2d disordered arrays of armchair GQDs. The variations of the anomalous advection-diffusion parameters as functions of localization radius, electric field intensity, levels of energetic and structural disorder are studied.

1. Introduction
Among graphene nanostructures, graphene ribbons and graphene quantum dots (GQDs) are of particular interest ([1]). GQD’s represent truncated single-layer or several layers of graphene of a size less than 50 nm. They have exceptional properties such as low toxicity, stable photoluminescence, chemical stability and quantum confinement effect. Joung et al. [2] have shown that the low temperature electron transport properties of chemically functionalized graphene can be explained as sequential tunneling of charges through a two dimensional array of graphene quantum dots (GQD) and resistance data exhibit an Efros-Shklovskii variable range hopping arising from structural and size induced disorder.

Graphene sheet and GQDs are convenient systems to construct fractal mesoscopic nanosystems for optoelectronics (diode, sensor, rectenna etc). Fractals display a selfsimilar pattern at various scales. In this work, using the generalized Miller-Abrahams relations for hopping rates we perform Monte Carlo simulation of charge carrier hopping in artificial disordered fractal arrays of GQDs. The variations of the anomalous advection-diffusion parameters as functions of localization radius, electric field intensity, levels of energetic and structural disorder are studied. We consider two types of fractal systems composed of armchair GQDs of hexagonal and triangular shapes. Energy spectra of two example GQDs are shown in Fig. 1. Both GQDs have a bandgap. We consider hopping of excited electrons in the tails of density of states of disordered fractal arrays of GQDs.

2. Monte Carlo algorithm
Monte Carlo simulation of charge carrier hopping in 2D mesoporous samples and spinodal patterns [3] have shown that geometric traps play an important role in charge transport in disordered systems. These traps act independently of thermalization process. Due to this structural disorder, dispersive transport can be observed even at small values of energy disorder.
Figure 1. Energy spectra of hexagonal and trigonal armchair GQDs in the vicinity of the Fermi level calculated using DFT and tight-binding method. Density of states are shown in insets.

In this work, we simulate electron hopping using the generalized Miller-Abrahams relations that can be derived from the representation of superlocalized wave function in fractals. The electrons in fractals at the Fermi level exhibit superlocalization [4, 5] described by wave function

$$|\Psi (r)|^2 \propto \exp \left[ -2(r/a)^\zeta \right],$$  \hspace{1cm} (1)

where $\zeta$ is a superlocalization exponent and $a$ is a localization radius. The probability $W_{ij}$ to hop from an occupied site $i$ to an empty site $j$ with a higher energy is given by the generalized Miller-Abrahams relations:

$$W_{ij} \propto \exp \left[ -2(r_{ij}/a)^\zeta - E_{ij}/kT \right].$$  \hspace{1cm} (2)

Here, $r_{ij}$ is a vector connecting two dots, $E_{ij}$ is an energy difference for the dots. The mean localization time for each transition is defined as

$$\tau_{i \rightarrow j} = \Gamma_0^{-1} \exp \left( \frac{\varepsilon_j - \varepsilon_i}{k_BT} + \frac{eE_{r_{ij}}}{k_BT} + 2 \left( \frac{r_{ij}}{a} \right)^\zeta \right).$$  \hspace{1cm} (3)

These times are used in generation of waiting times $\theta_{jk}$ with pdf

$$p_{\theta_{ij}} (t) = \tau_{ij}^{-1} \exp \left( - \frac{t}{\tau_{ij}} \right).$$  \hspace{1cm} (4)

The hop is realized to the $j$-th QD with the minimal value of $\theta_{ij}$.

Simulated trajectories and the growth of mean square displacement (MSD) for hopping on a fractal hexaflake for different values of localization radius $a$ are demonstrated in Fig. 2. The density of localized states is modeled by Gaussian distribution $\rho(\varepsilon) \propto \exp(-\varepsilon^2/2\sigma^2)$. The level of energetic disorder is $\sigma = 3kT$. The exponents of temporal scaling of MSD clearly indicate the subdiffusive regime of motion. The value 0.825 is related to the walk dimension for the fractal hexaflake. The lower values are related to effect of energetic disorder shortly considered in the next section.
Figure 2. The example of disordered quasi-fractal array of GQDs (left). Disorder is induced by molecular dynamic simulation at room temperature. Right panel show the mean square displacement (MSD) for hopping on the fractal hexaflake. The level of energetic disorder is $\sigma = 3kT$. Subdiffusion exponents (right) depends on $a$ and $\sigma$ and become independent of $\sigma$ for large localization radius $a$.

3. The model of continuous time random walks on fractal
Klafter et al. [6] have shown that for particle diffusion and trapping on fractals with heavy-tailed waiting-time distributions, the mean squared displacement behaves as $\langle r^2(t) \rangle \propto t^{\alpha \beta}$, whereas the number of delocalized particles decays according to $S(t) = t^{-\alpha}$. In Refs. [3, 7], structural and energy disorders for dispersive transport in percolative media have been simultaneously taken into account within the Continuous Time Random Walks (CTRW) on a comb structure. This model can be easily generalized for CTRW on fractals. CTRW on a percolation cluster is considered in Ref. [3].

The distribution of the sojourn time averaged over random number of visited sites $l$ in a bounded domain $Q$ is

$$\psi_Q(t) = \sum_{l=0}^{\infty} \psi^l(t)p_l. \quad (5)$$

Here, $\psi$ is the waiting time density for an individual site. After the Laplace transformation,

$$\tilde{\psi}_{br}(t) = \sum_{l=0}^{\infty} [\tilde{\psi}(s)]^l p_l \sim \int_0^\infty \exp \left[ l \ln \tilde{\psi}(s) \right] p(l) \, dl = \tilde{\rho} \left( -\ln \tilde{\psi}(s) \right). \quad (6)$$

For the transform of the integral kernel of the generalized FP-equation [8, 3, 9], we have

$$\tilde{\Phi}(s) = \left[s\tilde{\rho} \left( -\ln \tilde{\psi}(s) \right)\right]^{-1} \left\{1 - \tilde{\rho} \left( -\ln \tilde{\psi}(s) \right)\right\}. \quad (7)$$

To obtain asymptotic behavior at large times, we should consider small $s$, $s \to 0$. Assuming power law distribution of a number of visited sites within the given domain due to fractal distribution of sites,

$$p(s) \sim 1 - c_3s^\beta, \quad -\ln \tilde{\psi}(s) = -\ln \left[1 - s\tilde{\psi}(s)\right] \sim s\tilde{\psi}(s). \quad (8)$$
For the memory kernel, we have

$$\Phi (s) \sim s^{-1} c_\beta \left[ s\tilde{\psi} (s) \right]^{\beta}.$$  \hspace{1cm} (9)

For asymptotic large times, drift-diffusion equation has the form [3],

$$c_\beta \left[ s\tilde{\psi} (s) \right]^{\beta} \left[ \tilde{p} (x, s) - s^{-1} p (x, 0) \right] - \hat{L}_x \tilde{p} (x, s) = 0.$$  \hspace{1cm} (10)

In the multiple trapping model with exponential DoS \( \rho (\varepsilon) = \varepsilon^{-1} \exp (-\varepsilon/\varepsilon_0) \):

$$\Psi (t) = \int_0^\infty \exp \left\{ -\omega_0 t e^{-\varepsilon/kT} \right\} \varepsilon^{-1} \exp \left( -\frac{\varepsilon}{\varepsilon_0} \right) d\varepsilon \approx \frac{\alpha \Gamma (\alpha)}{\omega_0^\alpha} t^{-\alpha}.$$  \hspace{1cm} (11)

As a result, we have

$$\Phi (s) \sim c_\beta \left( \frac{\pi \alpha}{\sin \pi \alpha} \right)^{\beta} \omega_0^{-\alpha\beta} s^{\alpha\beta-1}.$$  \hspace{1cm} (12)

This kernel of the generalized Fokker-Planck equation leads to subdiffusion with dispersion parameter \( \alpha\beta \), where \( \alpha \) is associated with energy disorder, and \( \beta \) is related to walk dimension for a given fractal.

Figure 3. Left panel: MSD for hopping diffusion on the quasi-fractal ensemble of GQDs consisting of Serpinski triangles. Right panel: Variance (centered MSD) along and perpendicular to the applied electric field for different values of electric field.

The application of external electric field can lead to change in subdiffusion exponents. The MSD vs time plots for hopping on a quasi-fractal carpet composed of Sierpinski triangles of GQDs for different values of localization radius \( a \) and different values of electric field are shown in Fig. 3. The density of localized states is modeled by Gaussian distribution \( \rho (\varepsilon) \propto \exp (-\varepsilon^2/2\sigma^2) \) with \( \sigma = 3kT \). In the case of non-zero external field, we divide MSD on longitudinal and transverse directions. The transition to normal diffusion (slope 1 in log-log scale of MSD vs time) occurs due to the quasi-fractal structure, i.e. the maximal scale of Sierpinski triangle is limited and chosen by hand. For longitudinal MSD there is a situation when superdiffusive behavior of biased hopping is observed due to the field-induced amplification of carrier dispersion.
4. Summary
Here, we presented the results of Monte Carlo simulation of electron hopping in artificial disordered fractal arrays of armchair GQDs of hexagonal and triangular shapes. Main aspects of electron transport in mesoscopic fractals can be testified by simulation of hopping in quasi-fractal GQD systems. Anomalous drift-diffusion in two-dimensional semiconductor systems with coexisting energetic and structural disorder can be described as CTRW on a fractal structure. Waiting time distribution is defined by DoS, temperature $T$, number and geometry of empty states accessible within wave function localization domain. Superdiffusive behavior of biased hopping in fractals can be explained by the field-induced amplification of carrier separation.

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