Charge induced energy fluctuations in thin organic films: effect on charge transport

Sergey V. Novikov
A.N. Frumkin Institute of Electrochemistry, Moscow, Russia

Effect of static charges on charge carrier transport in disordered organic materials is considered. Long range nature of Coulomb interaction requires to take into consideration a finite thickness of the transport layer. Presence of conducting electrodes significantly modifies properties of organic medium, removes a long range Coulomb divergence, and makes it possible to calculate in finite form statistical properties of organic medium (with nonzero total charge density), relevant for transport characteristics. A special attention is paid to the particular case of charge induced disorder - a disorder originated from the surface charge located at the rough surface of electrode. We present also a generalization of 1D model of charge carrier transport to the case of inhomogeneous energetic disorder that realizes in for charge induced disorder.

I. INTRODUCTION

In recent years a significant attention has been paid to experimental and theoretical study of the charge carrier transport in disordered organic materials (for good reviews see Refs. [1, 2, 3]). The obtained results profoundly changed our understanding of the characteristics of the charge carrier transport in these materials. The essence of a modern paradigm of the charge carrier transport is a close connection between spatial correlation of energy levels $U(\vec{r})$ of transport sites in particular material and its transport properties [4, 5]. The mostly well understood reason for a strong spatial correlation is a presence in the material some particular kind of molecules, e.g. dipolar or quadrupolar molecules [4, 5, 6]. The most important parameter of the theory is the variance $\sigma^2 = \langle U^2 \rangle - \langle U \rangle^2$ which gives a scale of energy fluctuations in the material. For example, in dipolar materials mobility has the following dependence on electric field $E$ and temperature $T$

$$\mu = \mu_0 \exp \left[ -A \left( \frac{\sigma}{kT} \right)^2 + C_0 \left( \frac{\sigma}{kT} \right)^{3/2} - \Gamma \right] \sqrt{\frac{eaE}{\sigma}},$$

where computer simulation for 3D model gives $A = 9/25$, $C_0 = 0.78$, $\Gamma = 2$ [1], while an exact solution for 1D case gives $A = 1$, $C_0 = 2$, $\Gamma = 0$ [4]. The particular kind of mobility field dependence $\mu \propto E^{1/2}$ (a Poole-Frenkel dependence) is a result of slow decay of correlation function $C(\vec{r}) = \langle U(\vec{r})U(0) \rangle \propto 1/r$. This general theory describes well all major features of photoinduced charge transport in disordered organic materials.

Until now a very limited attention has been paid to the influence of charges on the correlation properties of disordered organic materials (the only exception is the paper [7]). These charges may be movable charges flowing through the sample or static charges inserted into the sample, e.g. by the pulse of accelerated electrons. Effect of charged particles on transport properties was mainly considered using the framework of the oversimplified Poole-Frenkel model of the isolated Coulomb trap. This approach totally neglects collective effects which are significant because of the long range nature of the Coulomb potential and, thus, is limited to the case of extremely small concentration of charged particles. This very long range nature of Coulomb interaction requires to include into consideration the finite thickness of transport layer. In the most typical configuration transport layer consists of a film of organic material bounded by highly conductive (metallic) electrodes. We show that contribution of image charges created by these electrodes significantly modifies properties of organic medium. For example, this effect removes a notorious Coulomb divergence and makes possible to calculate in finite form properties (mean carrier energy, its variance, correlation function, etc) of organic medium with nonzero total charge density. Hence, this approach presents a first step in order to understand the influence of finite concentration of carriers on the transport properties of materials (beyond the effect of space charge).

In this paper we limit our consideration exclusively to the case of a single charge carrier moving in the presence of static charge background, thus avoiding a tremendous problem of solving a self-consistent problem of the simultaneous motion of many charges. Additionally, the problem of static charges presents a significant interest by itself, because this very situation may realize in some particular cases, for example in the case of radiation-induced charge generation.

*Electronic address: vanlab@online.ru
It will be shown also that if surface of the conducting electrodes is rough, then surface charge accumulated under voltage applied generates an additional disorder in the bulk of organic transport layer. We will consider its influence on transport properties of the device. At present we have two major approaches to consider charge transport in disordered organic materials. One is a computer simulation of the hopping process, and another is an exact solution for the equilibrium carrier mobility in a simplified 1D model [4].

\[ \mu = \frac{\mu_0}{\epsilon \int_0^\infty dy \exp \left( -ey + \beta^2 |C(0) - C(ay)| \right)} \]  

where \( \epsilon = ea\beta E \), \( \beta = 1/kT \), and \( a \) is a minimal charge-dipole separation. In the most thoroughly studied case - charge transport in dipolar glasses - it was shown that these two approaches give essentially the same results with not very important differences for some numeric coefficients [5]. For this reason we use in this paper the 1D model for evaluation of the transport properties of the devices. Word "devices" instead of "materials" is used on purpose, because for the extremely long ranged Coulomb forces the relevant properties of the transport layer (correlation function etc) depend on the size of the device (on the thickness of transport layer) as well as on microscopic properties of the transport medium. In this case a magnitude of the disorder in some particular domain of transport layer is not a constant but depends on the location of this domain. In other words, charge induced disorder present a case of inhomogeneous energy disorder. In this paper we develop a generalization of the 1D model for this new case.

II. CHARGE TRANSPORT IN 1D INHOMOGENEOUS SYSTEMS

Until now very little is known about 3D charge carrier transport in inhomogeneous random systems. At the same time, the 1D model suggested in Ref. [4] proved to be a useful tool in revealing the dependence of a carrier mobility on electric field and temperature [3]. For this reason it seems to be a reasonable starting point to study charge carrier transport in the framework of the 1D model.

We are going to find a stationary solution \( c_s(z) \) for the diffusion of a charge carrier in the presence of external electric field \( E \), random potential \( U(z) \), a stationary source of carriers located at \( z = 0 \), and a perfect sink at \( z = L \)

\[ \frac{\partial c}{\partial t} + \frac{\partial J}{\partial z} = I_0 \delta(z), \]  

\[ J(z,t) = -D \left[ \frac{\partial c}{\partial z} + \beta \left( \frac{\partial U}{\partial z} - eE \right) c \right], \quad J(0, t) = 0, \quad c(L, t) = 0, \quad \beta = 1/kT. \]

The most important quantity to calculate is a stationary velocity

\[ v = \frac{I_0 L}{\int_0^L dz c_s(z)}. \]

A direct solution of Eq. (3) gives

\[ v = \frac{L D}{\int_0^L dz e^{-\beta(U(z))} \int_z^L dz' e^{\beta(U(z') - eEz')}}. \]

Unfortunately, to perform the subsequent averaging of \( v \) over random field \( U(z) \) is a difficult task. For this reason we will perform the calculation of the average time \( \langle t_L \rangle \) for the carrier to reach the opposite electrode, where \( t_L = L/v \). One may reasonably assume that functional dependences of \( \langle v \rangle \) and \( L/\langle t_L \rangle \) on the relevant parameters \( (E, T, \text{etc}) \) should be the same. We have

\[ \langle t_L \rangle = \frac{1}{D} \int_0^L dx \int_z^L dz' e^{\beta E(z - z')} \left( e^{\beta |U(z') - U(z)|} \right). \]

If \( U(z) \) is a Gaussian random field, then

\[ \langle t_L \rangle = \frac{1}{D} \int_0^L dz \int_z^L dz' e^{\beta E(z - z')} \exp \left( \beta |U(z')| - |U(z)| + \frac{1}{2} \beta^2 \left( |U(z') - U(z)| - \langle U(z') \rangle + \langle U(z) \rangle \right)^2 \right) \]  

(7)
\[= \frac{1}{D} \int_0^L dz \int_z^L d'z' e^{\beta E(z'-z')} \exp \left( \beta \left( \langle U(z') \rangle - \langle U(z) \rangle \right) + \frac{1}{2} \beta^2 \left[ C(z, z') + C(z', z') - 2C(z, z') \right] \right),\]

\[C(z, z') = \langle U(z)U(z') \rangle - \langle U(z) \rangle \langle U(z') \rangle.\]

In the case of \( L \to \infty \) and a homogeneous random energy \( U(z) \), when \( \langle U(z) \rangle = \text{const} \) and \( C(z, z') \) depends on \( z - z' \) only, this result exactly corresponds to the result of Ref. [4]. Hence, result (9) is a direct generalization of the corresponding result of Ref. [5] to the case of inhomogeneous random potential.

Transformation to new coordinates \( s = z + z', q = z - z' \) reveals an important symmetry of Eq. (7) in the case when \( \langle U(z) \rangle = 0 \)

\[\langle t_L \rangle = \frac{1}{2D} \left( \int_0^L ds \int_0^s dq e^{\beta E} g(s, q) + \int_0^L ds \int_0^{2L-s} dq e^{\beta E} g(s, q) \right), \tag{8}\]

\[g(s, q) = \exp \left\{ \frac{1}{2} \beta^2 \left[ C \left( \frac{s+q}{2}, \frac{s+q}{2} \right) + C \left( \frac{s-q}{2}, \frac{s-q}{2} \right) - 2C \left( \frac{s+q}{2}, \frac{s-q}{2} \right) \right] \right\}. \]

Making an additional transformation \( s \Rightarrow 2L - s \) in the second integral in Eq. (8) we have

\[\langle t_L \rangle = \frac{1}{2D} \left( \int_0^L ds \int_0^s dq e^{\beta E} g(s, q) + \int_0^L ds \int_0^{2L-s} dq e^{\beta E} g(2L - s, q) \right) \tag{9}\]

\[= \frac{1}{2D} \int_0^L ds \int_0^s dq e^{\beta E} \left[ g(s, q) + g(2L - s, q) \right]. \]

(note that \( g(s, q) \) is an even function of \( q \)). The sum \( g(s, q) + g(2L - s, -q) \) in Eq. (8) (and, hence, \( \langle t_L \rangle \)) is invariant under the transformation \( z \Rightarrow L - z, z' \Rightarrow L - z' \), so

\[\langle t_L^- \rangle = \langle t_L^+ \rangle, \tag{10}\]

where \( \langle t_L^- \rangle \) corresponds to carriers generated at \( z = 0 \) and absorbed at \( z = L \), and \( \langle t_L^- \rangle \) corresponds to the reverse process (with the correspondent inversion of the electric field). We will see that in spite of this symmetry the temporal dependence of the photocurrent transient may be very different for these two cases.

III. GENERAL PROPERTIES OF THE CHARGE-INDUCED ENERGY DISORDER

A. Potential energy, generated by random sources

We consider the most simple model of the transport layer - a slab of organic material (infinite in two dimensions) bounded at \( z = 0, L \) by two parallel conducting electrodes having zero potential. Organic medium is modeled by the regular lattice with lattice constant \( a \) and fraction \( c \) of all sites occupied by point charges. Since we are mostly interested in the case \( c \ll 1 \), so the model of the perfect space lattice is not a significant limitation. Lattice sites are also occupied by organic molecules (of dipolar, quadrupolar nature etc), their random positions and orientations produce an intrinsic energy disorder, which we neglect in the most part of the paper, because it is independent of the charge induced disorder, provides an additive contribution to quantities in question (correlation functions etc), and its properties have been extensively studied [4].

Let us consider a general case of a potential energy, generated by random sources

\[U(\vec{r}) = \sum_n n_f(\vec{r}, \vec{r}_n, \nu_n). \tag{11}\]

Here source function \( f(\vec{r}, \vec{r}_n, \nu_n) \) describes the contribution from a particular source to the total sum (11) and \( \nu \) is an additional random parameter (or parameters) that may affect the strength of the contribution (e.g., it may be an orientation of dipole in the case of dipolar sources). Note that summation in Eq. (11) is performed over all lattice
points and $\eta_n = 1$ if a real source is located at the site $n$ and $\eta_n = 0$ otherwise. In this paper we need to calculate positional averages of two kinds

$$\langle \langle \eta_n A(\nu_n) \rangle \rangle = \langle \eta_n \rangle \langle A(\nu_n) \rangle = c \langle A(\nu_n) \rangle,$$

(12)

and

$$\langle \langle \eta_m \eta_n A(\nu_m) A(\nu_n) \rangle \rangle = \langle \eta_n^2 \rangle \delta_{mn} \langle A^2(\nu_n) \rangle + \langle \eta_n \rangle (1 - \delta_{mn}) \langle A(\nu_m) \rangle \langle A(\nu_n) \rangle$$

$$= c \delta_{mn} \langle A^2(\nu_n) \rangle + c^2 (1 - \delta_{mn}) \langle A(\nu_m) \rangle \langle A(\nu_n) \rangle.$$

(13)

Double brackets in the left part of Eqs. (12) and (13) denote a simultaneous averaging over positions and parameter $\nu$.

**B. Source function and correlation function for point charges**

In the case of random potential energy generated by randomly located point charges function $f(\vec{r}, \vec{r}_n, \nu_n)$ is proportional to the electrostatic potential of the charge located at $\vec{r} = \vec{r}_n$ (here and later we assume that charge carrier has a positive charge)

$$f(\vec{r}, \vec{r}_n, \nu_n) = e \varphi(\vec{r}, \vec{r}_n),$$

(14)

and $\varphi(\vec{r}, \vec{r}_n)$ obeys a Poisson equation

$$\Delta \varphi = \frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} + \frac{\partial^2 \varphi}{\partial z^2} = -\frac{4\pi e}{\varepsilon} \delta (\vec{r} - \vec{r}_n)$$

(15)

with zero boundary conditions

$$\varphi|_{z=0} = \varphi|_{z=L} = 0.$$

(16)

Hence, $\varphi(\vec{r}, \vec{r}_n)$ is proportional to the Green function of the Laplace equation with the corresponding boundary conditions

$$\varphi(\vec{r}, \vec{r}_n) = -\frac{4\pi e}{\varepsilon} G(\vec{r}, \vec{r}_n).$$

(17)

Green function $G(\vec{r}, \vec{r}_n)$ is calculated in the Appendix and has a form

$$G(\vec{r}, \vec{r}_n) = -\frac{1}{\pi L} \sum_{s=1}^{\infty} \sin \frac{s\pi x}{L} \sin \frac{s\pi x_n}{L} K_0 \left( \frac{s\pi \rho}{L} \right),$$

(18)

where $K_0(x)$ is the Macdonald function and $\rho^2 = (x - x_n)^2 + (y - y_n)^2$.

We consider here a slightly more general case when two types of static charges are present: positive with fraction $c_n^+$ and negative with fraction $c_n^-$ (we assume that these fractions may vary with $n$). Note, that $c_n^+ + c_n^- \leq 1$. Average energy of the charge carrier is

$$\langle U(\vec{r}) \rangle = -\frac{4\pi e^2}{\varepsilon} \sum_n (c_n^+ - c_n^-) G(\vec{r}, \vec{r}_n),$$

(19)

and the correlation function $C(\vec{r}, \vec{r}')$ is

$$C(\vec{r}, \vec{r}') = \langle U(\vec{r}) U(\vec{r}') \rangle - \langle U(\vec{r}) \rangle \langle U(\vec{r}') \rangle = \frac{16\pi^2 e^4}{\varepsilon^2} \sum_n \left[ c_n^+ + c_n^- - (c_n^+ - c_n^-)^2 \right] G(\vec{r}, \vec{r}_n) G(\vec{r}', \vec{r}_n).$$

(20)
C. Uniform distribution of charges

As a simple example we provide a result for the case of uniform charge distribution with $c_+^+, c_-^-$ = const. Here

$$\langle U(z) \rangle = \frac{2\pi e^2 (c^+ - c^-)}{\varepsilon a^3} z(L - z),$$  \hspace{1cm} (21)

and

$$C(\vec{r}, \vec{r}') = C(z, z', \rho) = \frac{8e^4 [c^+ + c^- -(c^+ - c^-)^2]}{\varepsilon^2 a^3 L} \rho \sum_{s=1}^{\infty} 1 \sin \frac{\pi sz}{L} \sin \frac{\pi sz'}{L} K_0 \left( \frac{\pi \rho}{L} \right),$$  \hspace{1cm} (22)

In the particular case $\rho = 0$

$$C(z, z', 0) = \frac{4\pi e^4 [c^+ + c^- -(c^+ - c^-)^2]}{\varepsilon^2 a^3 L} z_-(L - z_+), \quad z_+ = \max(z, z'), \quad z_- = \min(z, z').$$  \hspace{1cm} (23)

Equation (23) shows that even in the case of uniform charge distribution the resulting energetic disorder is not a homogeneous one: the correlation function does depend on $z, z'$ separately, and not on the difference $z - z'$ only, as it should be for the homogeneous case. Of course, the reason for this phenomenon is an effect of conducting electrodes, which is important for a very long range Coulomb interaction. Magnitude of the disorder induced in a transport layer could be measured by the variance $\sigma^2(z) = C(z, z)$. For the uniform distribution of charges

$$\sigma^2(z) = \frac{4\pi e^4 [c^+ + c^- -(c^+ - c^-)^2]}{\varepsilon^2 a^3 L} z_-(L - z),$$  \hspace{1cm} (24)

it attains a maximum at $z = L/2$ and goes to zero at the electrode surfaces (as it should be, because electrodes have a constant potential).

A direct calculation gives for the time $\langle t_L \rangle$

$$\langle t_L \rangle = \frac{L^2}{D} \int_0^1 d\xi \int_0^1 d\xi' \exp[\lambda S(\xi, \xi')],$$  \hspace{1cm} (25)

$$S(\xi, \xi') = -2\pi \lambda c_2 (\xi - \xi')^2 + 2\pi \lambda c_1 (\xi^2 - \xi'^2) + f(\xi - \xi'),$$

$$\lambda = \frac{\beta e^2}{\varepsilon a}, \quad l = \frac{L}{a}, \quad f = \frac{\varepsilon a^2 E}{e} - 2\pi \lambda c_2 - 2\pi \lambda c_1, \quad c_1 = c^+ - c^-, \quad c_2 = c^+ + c^- -(c^+ - c^-)^2.$$  \hspace{1cm} (26)

Introducing new coordinates $\zeta = \xi + \xi'$ and $\eta = \xi' - \xi$ we have

$$\langle t_L \rangle = \frac{L^2}{2D} \int_0^1 d\eta \exp \left[ \lambda \left( -2\pi \lambda c_2 \eta^2 - f \eta \right) \right] \int_0^{2-\eta} d\zeta \exp \left( -2\pi \lambda c_1 \zeta \eta \right)$$

$$= \frac{L^2}{2D \pi l^2 c_1} \int_0^1 \frac{d\eta}{\eta} \exp \left[ 2\pi \lambda c_1 (\eta - \eta^2) - e\beta E L \eta \right] \sinh \left[ 2\pi \lambda c_1 (\eta - \eta^2) \right].$$

One can see that Eq. (26) is an even function of $c_1$, so charge carrier interacts in the same way with static backgrounds created either by trapped electrons or holes. It is easy to show that this particular property is valid for any charge distribution having symmetry $\langle U(z) \rangle = \langle U(L - z) \rangle$ (spatial symmetry of $C(z, z')$ is not important because it is an even function of $c_1$). We should emphasize that this particular property holds for the Gaussian approximation only.

Let us discuss Eq. (24) in the particular case $c_1 = 0$, i.e. when the medium is neutral. This case was briefly discussed in Ref. [3] for the infinite medium. We have

$$\langle t_L \rangle_n = \frac{L^2}{D} \int_0^1 d\eta (1 - \eta) \exp \left[ \lambda \left( -2\pi \lambda c_2 \eta^2 - f \eta \right) \right] = H(f) + \frac{1}{M} \frac{\partial H}{\partial f},$$  \hspace{1cm} (27)
Finally,

\[ \langle t_L \rangle_n = \frac{L^2}{4\sqrt{\pi DL^2l_c}} \left\{ (A + B)e^{B^2} [\text{erf}(A + B) - \text{erf}(B)] - \frac{1}{\sqrt{\pi}} \left( 1 - e^{-A^2 - 2AB} \right) \right\}, \quad (28) \]

\[ A = \lambda \sqrt{2\pi l_c}, \quad B = f \frac{l}{8\pi c}. \]

The most prominent feature of Eq. (28) is its behavior for \( L \to \infty \). If \( f > 0 \) (i.e., if \( E > E_{cr} \)), then \( \langle t_L \rangle_n \propto L \) and carriers have a well-defined average velocity which does not depend on \( L \)

\[ \langle v \rangle_\infty = eD(E - E_{cr}), \quad E_{cr} = \frac{2\pi \beta e^2 c}{\epsilon^2 a^3}. \quad (29) \]

If \( f < 0 \), then \( \log \langle t_L \rangle_n \propto L \) and average carrier velocity goes to 0. Transition occurs at \( E = E_{cr} \) in full agreement with Ref. [7].

We would like to note a close connection between the case of charge carrier transport in the infinite neutral medium with \( c^+ = c^- \) and the anomalous diffusion of the particle in a 1D random force field, described by the Langevin equation

\[ \frac{dz}{dt} = \frac{1}{\gamma} F(z) + \eta(t), \quad (30) \]

with a thermal noise \( \eta(t) \)

\[ \langle \eta(t) \rangle = 0, \quad \langle \eta(t)\eta(t') \rangle = 2\frac{kT}{\gamma} \delta(t - t'), \quad (31) \]

and a quenched random force \( F(z) \) being a Gaussian white noise

\[ \langle F(z) \rangle = F_0, \quad \langle F(z)F(z') \rangle - F_0^2 = \sigma \delta(z - z'). \quad (32) \]

This problem was discussed thoroughly in Refs. [13, 16] it demonstrates the same transition from the mobile carriers with non-zero average velocity to the immobile ones. The relation between the case \( c^+ = c^- \) (for \( L \to \infty \)) and the problem (28) arises from the identical forms of the corresponding energy-energy correlation functions. In both cases

\[ \langle |U(z) - U(z')|^2 \rangle \propto |z - z'|. \]

A more careful analysis of this relationship will be studied elsewhere.

In the general case of macroscopically charged medium with \( c_1 \neq 0 \) we can estimate time (31) for strong disorder, when \( 2\pi l^2 |c_1| \gg 1 \). In this case we can retain only the leading exponential term in (28), so

\[ \langle t_L \rangle \approx \frac{L^2}{2Dl^2|c_1|} \left\{ \frac{2\lambda l(\lambda c_2 + l|c_1|)}{2\pi \lambda l(\lambda c_2 + l|c_1|) - e\beta EL} \right\} \exp \left[ \frac{(2\pi \lambda l(\lambda c_2 + l|c_1|) - e\beta EL)^2}{8\pi \lambda l(\lambda c_2 + l|c_1|)} \right]. \quad (33) \]

This expression is valid if

\[ 2\pi \lambda l(\lambda c_2 + l|c_1|) - e\beta EL \gg [2\pi \lambda l(\lambda c_2 + l|c_1|)]^{1/2}. \]

Note, that if \( c_1 \neq 0 \), then \( \log \langle t_L \rangle \propto L^2 \) for \( L \to \infty \), so for a infinite charged medium there is no non-dispersive transport. Field dependence of time (28) is shown in Fig. 4.

The case of the uniform distribution of static charges does realize in the case of radiation-induced charge generation in disorder organic materials. In this particular case movable charges are induced in the material by the pulse of accelerated electrons. In the most typical case electrons have high energy, so concentration of electron-hole pairs (usually, electrons get trapped and holes are movable) created in the bulk of the material is approximately constant and does not decay while going away from electrode. We could expect that the model of uniformly charged material is a reasonable model for description of transport properties in the radiation-induced generation, at least for large times, when concentration of movable charges is much smaller than the concentration of static charges.

A different case of static charges trapped at the close vicinity of the electrode (this case does realize for the radiation-induced generation of charge carriers by the pulse of low energy electrons) will be studied elsewhere.
FIG. 1: Field dependence of $\langle t_L \rangle$ for the case of uniformly charged background with $L/a = 150$, $e^2\beta/\varepsilon a = 20$, $c^- = 0$, and different values of $c^+$: $1 \times 10^{-5}$, $3 \times 10^{-5}$, and $5 \times 10^{-5}$, from upper curve downwards, correspondingly.

D. How valid is the Gaussian approximation?

Particular case of the uniform charge distribution gives us a good possibility to discuss a validity of the Gaussian approximation for the 1D transport model. Gaussian approximation is valid for the main body of the distribution if $\sigma^2(z) \gg U_s^2$, where $U_s = e^2c^{1/3}/\varepsilon a$ is a typical contribution from the single charge source, thus ensuring that the resulting potential energy is not dominating by the single contribution. This inequality leads to

$$\frac{4\pi c^{1/3}}{aL}z(L - z) \gg 1. \tag{34}$$

Hence, the Gaussian approximation is valid in the bulk of the layer if $\pi c^{1/3}L/a \gg 1$, but in the near vicinity of electrode at $z \leq z_b$, $z_b \simeq a/4\pi c^{1/3}$ non-Gaussian effects are significant. If $4\pi c^{1/3} \geq 1 (c \geq 5 \times 10^{-4})$, then for the whole transport layer the main body of distribution has a Gaussian shape.

Nevertheless, a Gaussian shape for the tail of the distribution holds only if a more strong inequality is valid: $\sigma^2(z) \gg U_{max}^2$, where $U_{max} = e^2/\varepsilon a$ is a maximal contribution from the single source. This leads to

$$\frac{4\pi c}{aL}z(L - z) \gg 1, \tag{35}$$

so tail of the distribution is Gaussian in the bulk of the layer if $\pi cL/a \gg 1$, and at the vicinity of electrodes if $4\pi c \geq 1$ (or $c \geq 0.1$). The last condition seems to be difficult to match.

IV. RANDOM POTENTIAL ENERGY, GENERATED BY CHARGED ROUGH METALLIC SURFACE

A. Basic formalism

A typical transport device can be described as a flat capacitor with the region between conducting electrodes filled by an organic material (transport layer with the thickness $L$). If voltage $V_0$ is applied to the capacitor, then surfaces of the electrodes develop a surface charge with the density $Q$ proportional to the electric field $E = -V_0/L$, namely $Q = E/4\pi$. In the ideal case of absolutely flat electrodes’ surfaces the surface charge just maintains this very field...
$E = \text{const}$ in the bulk of organic material, according to the well known formula for a correspondent distribution of the electrostatic potential $\varphi$ in the bulk of the capacitor

$$\varphi(\vec{r}) = \int_S \frac{QdS}{R},$$

where integration is carried out over the electrode surfaces and $R$ is a distance between point $\vec{r}$ and a particular part of the surface. Situation is different in the case of a rough surface of the electrodes (Fig. 2a). In this case we can describe surface of the electrode as a random surface, so the distance $R$ in Eq. (36) fluctuates, thus the resulting potential $\varphi$ is a random function. Hence, a roughness of the electrode surface induces an additional energetic disorder in the bulk of the organic transport layer. We are going to estimate a magnitude of this kind of disorder and its effect on the transport properties of devices. One could immediately note two important properties of this kind of disorder: its magnitude increases with the increase of the electric field on the transport properties of devices. One could immediately note two important properties of this kind of disorder: its magnitude increases with the increase of the electric field $E$ applied to the device, and decreases while going away from the electrodes (so this is another case of inhomogeneous disorder).

Let us calculate the potential distribution inside a capacitor having rough metallic electrodes. Surface of one electrode obeys an equation $z = h_0(x, y)$, and another one $z = L + h_L(x, y)$, where $h_0(x, y)$ and $h_L(x, y)$ are random functions and $h_0, h_L \ll L$. We define the locations of the average electrode planes in such a way that $\langle h_0, L \rangle = 0$. We are going to study variation of the potential for $z \gg h$.

Inside the capacitor we should solve a Laplace equation

$$\Delta \varphi = \frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} + \frac{\partial^2 \varphi}{\partial z^2} = 0$$

with potential $\varphi$ obeying the boundary conditions

$$\varphi|_{z=h_0(x,y)} = 0, \quad \varphi|_{z=L+h_L(x,y)} = V_0.$$  

We are going to find a correction for the potential distribution inside a capacitor which is resulted from the roughness of the electrode surfaces

$$\varphi(\vec{r}) = -Ez + \delta \varphi(\vec{r}).$$

Calculation of the first order correction to the potential distribution with $\delta \varphi \propto h$ is performed in Appendix A.

The energy-energy correlation function has a form (note that $\langle \delta \varphi(\vec{r}) \rangle = 0$)

$$C(\vec{r}_1, \vec{r}_2) = e^2 \langle \delta \varphi(\vec{r}_1) \delta \varphi(\vec{r}_2) \rangle $$

$$= \frac{1}{4\pi^2} \int d\vec{k} e^{i\vec{k}(\vec{r}_1 - \vec{r}_2)} \frac{1}{\sinh^2 kL} \left[ U_0^2 \Omega_0(k) \sinh k(L - z_1) \sinh k(L - z_2) + U_L^2 \Omega_L(k) \sinh k z_1 \sinh k z_2 \right],$$

$$U_j = eE \langle h_j^2 \rangle^{1/2}, \quad \Omega_j(\vec{r}_1 - \vec{r}_2) = \frac{1}{\langle h_j^2 \rangle} \langle h_j(\vec{r}_1) h_j(\vec{r}_2) \rangle, \quad \Omega_j(k) = \int d\vec{\rho} e^{-i\vec{k}\vec{\rho}} \Omega_j(\vec{\rho}), \quad j = 0, L.$$  

(here $\vec{k}$ and $\vec{\rho} = (x, y)$ are 2D vectors). We can simplify equation (40) in a situation when the surface correlation function $\Omega(\vec{\rho})$ has a single length scale $l$ (surface correlation length). In a very common situation $l \gg \langle h^2 \rangle^{1/2}$ (this is so, for example, for the so called naturally rough metal surfaces [17, 18]). If $z \ll L$, then significant domain in integral (40) is $kl \sim 1$. If $z_1, z_2, l \ll L$ (we consider a vicinity of one electrode), then we can simplify equation (40)

$$C(\vec{r}_1, \vec{r}_2) \approx \frac{U_0^2}{4\pi^2} \int d\vec{k} \Omega_0(k) \exp(i\vec{k}(\vec{r}_1 - \vec{r}_2)) - k(z_1 + z_2),$$

so if $z_1, z_2 \gg l$, then

$$C(\vec{r}_1, \vec{r}_2) \propto U_0^2 l^2 \int d\vec{k} \exp(i\vec{k}(\vec{r}_1 - \vec{r}_2)) - k(z_1 + z_2)) = \frac{U_0^2 l^2(z_1 + z_2)}{[(z_1 + z_2)^2 + l^2]^{3/2}}.$$  

This universal behavior takes place when a large area $S \gg l^2$ of the electrode gives a contribution to the distribution of the potential. Such regime is observed for $z_1, z_2 \gg l$ only, because essential area $S \propto z^2$. Note, that in this very case we should expect that the distribution of $\delta \varphi$ has approximately a Gaussian form (because many independent areas of the surface give contributions to the resulting distribution). In the opposite case, when $z_1, z_2 \ll l$, then $C(\vec{r}_1, \vec{r}_2) \approx U_0^2$. 

B. What should we expect to observe in experiments?

We can calculate time \( \langle t_L \rangle \) for the case of rough electrodes using Eq. (7). For the most interesting case \( l \gg \langle h^2 \rangle^{1/2} \), results are shown in Fig. 3. The most important feature of the mobility dependences is an abrupt decrease of the carrier velocity when \( E \) reaches a critical value. Using a saddle-point method one can show that \( E_{\text{crit}} \propto l/e\beta \langle h^2 \rangle \).

To the best of our knowledge, such abrupt drop of the mobility has not been observed in experiments. Quite possibly, \( E_{\text{crit}} \) is so high that it cannot be reached because of the dielectric breakdown of the layer. If \( l = 15 \text{ nm} \), \( \langle h^2 \rangle^{1/2} = 1.8 \text{ nm} \), then \( E_{\text{crit}} \approx 2 \times 10^6 \text{ V/cm} \). This field is indeed high, but it could be reached for layers of high quality (see Ref. 19). Another possible reason of the discrepancy could be a failure of the 1D model in this particular case. Finally, our approach totally neglects a correlation between rate of the charge carrier injection from some electrode’s area and its profile. We may expect that our approach is valid for rather “smooth” rough surfaces, where we cannot expect a significant variation of the injection rate over electrode surface. Anyway, we believe that a careful study of charge transport in high quality layers with simultaneous control (by the use of scanning tunneling microscope) of the roughness of the electrodes could confirm (or disprove) our results.

We should expect that a significant effect of the roughness could be observed for weaker electric field if we consider a temporal behavior of the photocurrent \( I(t) \) for the time-of-flight experiments. At present we cannot produce any analytic or simulation results for \( I(t) \). Anyway, we may safely suppose that:

1) Transport should be more dispersive in the case of rough electrodes in comparison to the case of smooth electrodes, just because of the increase of disorder. Additionally, this increase should lead to the decrease of mobility.

2) If a rough electrode serves as an injector, we should expect an unusual transformation of the temporal behavior of the photocurrent \( I(t) \) with the increase of the electric field \( E \). Typical distribution of sites’ energies in this case is shown in Fig. 2b. In a weak field region we should expect a transient of the usual kind (Fig. 2c). In strong field region, with the increase of the magnitude of the disorder near the injecting electrode, transient should transform to the form shown in Fig. 2d. A reason for the development of the region where current increases with \( t \) is carriers’ acceleration when they move to the region with smaller disorder. This kind of photocurrent transformation with the increase of \( E \) was indeed observed in Ref. 20.

3) We noted previously a principal symmetry of the equation (7), so \( \langle t_L^- \rangle = \langle t_L^- \rangle \) even when electrodes have very different degree of roughness (compare the left and right electrode in Fig. 3a). But if we consider a temporal behavior of the current \( I(t) \), it could be very different for these two cases. For not so small \( E \), if a smooth electrode serves as injector, we should expect a usual form of \( I(t) \) (see Fig. 3a), but if a rough electrode serves as injector, we should expect the form shown in Fig. 3d.

V. CONCLUSIONS

We suggested a new approach for calculation of statistical properties of disordered organic materials with nonzero charge density. Explicit consideration of the finite transport layer bounded by conducting electrodes removes a long range Coulomb divergence and gives finite values for the relevant characteristics of the device (correlation function etc). We presented a generalization of the 1D model of the charge carrier transport in disordered organic matrices to the case of inhomogeneous disorder. This approach permitted us to calculate transport properties of matrices with charge induced disorder. A similar approach permits us to calculate an energy-energy correlation function for the transport layer bounded by rough conducting electrodes. We expect that the roughness of the electrode surface should lead to the unusual temporal behavior of the photocurrent transient (appearance of the region where current increases with time) in the case of strong electric field.

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APPENDIX A: CALCULATION OF THE GREEN FUNCTION FOR THE LAPLACE EQUATION

Taking into account a geometry of the problem, we may write

\[
G(\vec{r}, \vec{r}_n) = \frac{1}{4\pi^2} \int \! d\vec{k} e^{i\vec{k} \cdot \vec{r}} G_k(z, z_n),
\]

(A1)
where \( \vec{k} \) and \( \vec{\rho} = (x - x_n, y - y_n) \) are 2D vectors, and function \( G_k(z, z_n) \) obeys an equation

\[
\frac{d^2 G_k}{dz^2} - k^2 G_k = \delta(z - z_n), \quad G_k(0, z_n) = G_k(L, z_n) = 0, \quad G_k(z, z_n) = G_k(z_n, z).
\] (A2)

A direct calculation gives

\[
G_k(z, z_n) = -\frac{\sinh k z - \sinh k(L - z_+)}{k \sinh k L}, \quad z_+ = \max(z, z_n), \quad z_- = \min(z, z_n).
\] (A3)

We would like to note another useful expression for \( G_k(z, z_n) \) which is based on the series of the eigenfunctions of the operator \( \partial^2 - k^2 \)

\[
G_k(z, z_n) = \sum_{s=1}^{\infty} \frac{\psi_s(z) \psi_s(z_n)}{\lambda_s}, \quad \lambda_s = -k^2 - \left( \frac{\pi s}{L} \right)^2, \quad \psi_s(z) = \sqrt{\frac{2}{L}} \sin \left( \frac{\pi s z}{L} \right).
\] (A4)

From Eq. (A4) it immediately follows that

\[
\varphi(\vec{r}, \vec{r}_n) = \frac{4e}{\varepsilon L} \sum_{s=1}^{\infty} \sin \frac{s \pi z}{L} \sin \frac{s \pi z_n}{L} K_0 \left( \frac{s \pi \rho}{L} \right),
\] (A5)

where \( K_0(x) \) is the Macdonald function. Last expression is useful to show behavior of \( \varphi(\vec{r}, \vec{r}_n) \) for \( \rho \gg L \). Presence of metallic electrodes transforms the usual Coulomb decay to the exponential one

\[
\varphi(\vec{r}, \vec{r}_n) \approx \frac{4e}{\varepsilon L} \sin \frac{\pi z}{L} \sin \frac{\pi z_n}{L} \sqrt{\frac{L}{2 \rho}} \exp \left( -\frac{\pi \rho}{L} \right), \quad \rho \gg L,
\] (A6)

thus removing a nasty long range Coulomb divergence.

**APPENDIX B: FIRST ORDER CORRECTION TO THE POTENTIAL DISTRIBUTION FOR A TRANSPORT LAYER BOUNDED BY ROUGH ELECTRODES**

To solve Eq. (37) let us make a transformation of variables

\[
X = x, \quad Y = y, \quad Z = L(z - h_0) / (L + h_L - h_0),
\] (B1)

so the boundary conditions (38) transform to

\[
\varphi|_{Z=0} = 0, \quad \varphi|_{Z=L} = V_0.
\] (B2)

In new variables \((X, Y, Z)\) the Laplace equation (37) has a form

\[
\frac{\partial^2 \varphi}{\partial X^2} + \frac{\partial^2 \varphi}{\partial Y^2} + \frac{\partial^2 \varphi}{\partial Z^2} \left[ \left( \frac{\partial Z}{\partial x} \right)^2 + \left( \frac{\partial Z}{\partial y} \right)^2 \right] + 2 \left( \frac{\partial^2 \varphi}{\partial X \partial Z} \frac{\partial Z}{\partial x} + \frac{\partial^2 \varphi}{\partial Y \partial Z} \frac{\partial Z}{\partial y} \right) + \frac{\partial \varphi}{\partial Z} \left( \frac{\partial^2 Z}{\partial x^2} + \frac{\partial^2 Z}{\partial y^2} \right) = 0.
\] (B3)

We will seek a solution of Eq. (B3) by the perturbation theory (a formal small parameter being \( h \))

\[
\varphi = \sum_n \varphi_n, \quad \varphi_n \sim O(h^n), \quad \varphi_0 = V_0 Z / L, \quad \varphi_n|_{Z=0} = \varphi_n|_{Z=L} = 0, \quad n \geq 1.
\] (B4)

Our main goal is to calculate a leading term for the correlation function \( C(r_1, r_2) = e^2 \langle \delta \varphi(r_1) \delta \varphi(r_2) \rangle \). For this reason we should calculate \( \varphi_1 \) only.

Equation for an every term \( \varphi_n \) has a general structure

\[
\Delta \varphi_n = J_n,
\] (B5)
where the source $J_n$ depends on $\varphi_k$, $0 \leq k \leq n - 1$. Solution of Eq. (B3) is

$$\varphi_n(\vec{r}) = \int d\vec{r}_1 G(\vec{r}, \vec{r}_1) J_n(\vec{r}_1), \tag{B6}$$

here $G(\vec{r}, \vec{r}_1)$ is the Green function for the Laplace operator with zero boundary conditions (B4).

The source term for the first order correction is

$$J_1 = \frac{V_0}{L} \left[ \left( 1 - \frac{Z}{L} \right) \Delta_\perp h_0 + \frac{Z}{L} \Delta_\perp h_L \right], \quad \Delta_\perp = \frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2}, \tag{B7}$$

so

$$\varphi_1(\vec{r}) = \frac{V_0}{4\pi^2L} \int d\vec{k}_1 \int_{-L}^{L} dZ_1 e^{i\vec{k}_1(\vec{r} - \vec{r}_1)} k^2 G_k(Z, Z_1) \left[ \left( 1 - \frac{Z_1}{L} \right) h_0(\vec{r}_1) + \frac{Z_1}{L} h_L(\vec{r}_1) \right]. \tag{B8}$$

Calculation of the integral (B8) gives

$$\varphi_1(\vec{r}) = -\frac{V_0}{4\pi^2L} \int d\vec{k} \int_{-L}^{L} dZ_1 e^{i\vec{k}(\vec{r} - \vec{r}_1)} k^2 G_k(Z, Z_1) \left[ \left( 1 - \frac{Z_1}{L} \right) h_0(\vec{r}_1) + \frac{Z_1}{L} h_L(\vec{r}_1) \right] \tag{B9}$$

$$= -\frac{V_0}{4\pi^2L} \int d\vec{k} e^{i\vec{k}\vec{r}} \left[ \left( 1 - \frac{Z}{L} \right) - \frac{\sinh k(L - Z)}{\sinh kL} \right] h_0(\vec{k}) + \left( \frac{Z}{L} \right) - \frac{\sinh kZ}{\sinh kL} h_L(\vec{k}). \tag{B10}$$

The total first order correction to the potential distribution (here we are going back to the original coordinates) is

$$\delta \varphi = \varphi - \langle \varphi \rangle = -\frac{V_0}{L} \left[ \left( 1 - \frac{z}{L} \right) h_0(x, y) + \frac{z}{L} h_L(x, y) \right]$$

$$+ \frac{V_0}{4\pi^2L} \int d\vec{k} e^{i\vec{k}\vec{r}} \left[ \left( 1 - \frac{z}{L} \right) - \frac{\sinh k(L - z)}{\sinh kL} \right] h_0(\vec{k}) + \left( \frac{z}{L} \right) - \frac{\sinh kz}{\sinh kL} h_L(\vec{k}). \tag{B11}$$
FIG. 2: (a) Transport layer bounded by rough electrodes (note the different roughness of the left and right electrode). (b) A typical distribution of the random energy $U(z)$ in the bulk of a transport layer induced by the rough surface of the electrodes in the case of significant difference in their roughness. According to Eq. (10) $\langle t_1 \rangle = \langle t_2 \rangle$, but time dependence of the photocurrent may be quite different for these two cases. (c,d) Typical time dependence of the photocurrent in the time-of-flight experiment when a smooth electrode serves as an injector (c), or a rough one serves as an injector (d).
FIG. 3: Field dependence of $\langle t_L \rangle$ for $L/a = 100$, $\langle h_0^2 \rangle^{1/2}/a = 5$, $\langle h_L^2 \rangle^{1/2} = 0$, in the case of quadrupolar glass with $\sigma_q \beta = 2$ bounded by rough metallic electrodes with different values of $l_0/a$: 50, 25, 10, 5, from the right curve to the left, correspondingly. Surface correlation function was chosen in the form $\Omega_0(\vec{\rho}) = \exp \left( -\rho^2/2l_0^2 \right)$, which is suitable for a naturally rough metal surface [17]. If $a = 1$ nm and $\sigma_q = 0.1$ eV, then $e a E/\sigma_q \approx 1$ for $E = 1 \times 10^6$ V/cm.