Can the Poole-Frenkel Model Explain Charge Carrier Transport in Disordered Organic Materials?

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Abstract

Charge carrier transport in materials containing static charges is considered within the framework of the 1D transport model. We show that the mobility dependence on temperature and concentration of charged traps in infinite medium differs drastically from the prediction of the model of isolated charged trap (Poole-Frenkel model). We argue that for transport layer with finite thickness the Poole-Frenkel model can be applied only in the case of very low concentration of static charged centers, thus producing a negligible effect on the mobility field dependence.

1. Introduction

In recent years a significant attention has been paid to experimental and theoretical study of charge carrier transport in disordered organic materials.$^{1-3}$ Quite frequently, experimental results were discussed in terms of the Poole-Frenkel (PF) model of trap-controlled transport with the attractive Coulomb centres serving as traps. If an external uniform electric field E is applied, then the total potential energy of the carrier in a trap is

$$U(\vec{r}) = -e\vec{E}\cdot\vec{r} - \frac{e^2}{\varepsilon r}, \tag{1}$$

where ε is a dielectric constant of the medium. Electric field leads to the decrease of the activation energy for the carrier release from the trap

$$\delta U_{\rm act} = 2\left(\frac{e^3E}{\varepsilon}\right)^{1/2}, \tag{2}$$

thus leading to the estimation for the carrier mean velocity

$$\langle v\rangle \propto \frac{1}{c}\exp\left(\delta U_{\rm act}/kT\right) = \frac{1}{c}\exp\left(\gamma\sqrt{E}\right), \tag{3}$$

where $\gamma = \frac{2}{kT}\left(\frac{e^3}{\varepsilon}\right)^{1/2}$ and c is the concentration of traps.

Early experimental data suggested that mobility $\mu = \langle v\rangle/E$ dependence on E and T may be described by the empirical relation^4

$$\mu = \mu_0 \exp\left[\widetilde{\gamma}\left(\frac{1}{T} - \frac{1}{T_0}\right)\left(\sqrt{E} - \sqrt{E_0}\right)\right], \tag{4}$$

where T_0 and E_0 are some constants. Equation (4) naturally supports an idea of the PF mechanism for the mobility field dependence. Magnitude of the PF coefficient γ in (3) is usually close to the experimental one, though discrepancies of 2-3 times are typical.^{5} Yet for a long time the PF model has been rejected as a valid model of charge transport in organic materials. The main reason for the rejection is the absence of charged traps in such materials in a noticeable concentration.^{5} Recently the PF model was revitalized by Rackovsky and Scher.^{6} They argued that a very low density of Coulomb traps is enough to produce an essentially nondispersive PF charge transport (they estimated that 10^{11}-10^{13} cm^{-3} should be a sufficient density for transport layer with the thickness of 10 μm). Because such low density can easily avoid detection, they suggested that the PF model still can be considered as the true model of the charge transport in disordered organic materials.

Calculation of the PF effect^6 was carried out for the usual case of an isolated Coulomb trap only. In this paper we are going to overcome a scope of an isolated Coulomb trap and present an explicit model of charge carrier transport in charged medium. We will see that the result is in drastic contrast with the case of an isolated Coulomb trap.

2. 1D model of charge transport

Let us consider the 1D diffusion of a single carrier in a random energy landscape $U(z)$ along the direction of the electric field. In this case^7

$$\langle v\rangle = \frac{D}{\int_0^\infty dz\exp(-e\beta Ez)W(z)}, \tag{5}$$

where $W(z) = \langle\exp\left\{\beta\left[U(z) - U(0)\right]\right\}\rangle$, D is a carrier diffusion coefficient, $\beta = 1/kT$, and angular brackets denote statistical averaging.

We consider a potential energy of positively charged carrier (a hole) in a random environment of static charges (located at the sites of regular cubic lattice with the scale a)

$$U(\vec{r}) = \sum_m \eta_m f(\vec{r}, \vec{r}_m). \tag{6}$$

Here source function $f(\vec{r}, \vec{r}_m)$ gives a contribution from the particular source to the total sum (6). Summation in (6) is performed over all lattice points and $\eta_m = 1$ if a positive charge is located at the site m, $\eta_m = -1$ for a negative charge, and $\eta_m = 0$ for the empty site. To avoid unnecessary complications, we consider here the simplest case of macroscopically neutral infinite medium with $c^+ = c^- = c$, where c^+ and c^- are fractions of sites occupied by positive and negative charges, correspondingly, $f(\vec{r}, \vec{r}_m) = e^2/\varepsilon|\vec{r} - \vec{r}_m|$, and

$$\ln W(z) = h_a^3 G(x_0, c),$$

$$G(x_0, c) = \int d\vec{x} \ln\left[1 + 2c\left(\cosh A - 1\right)\right], \tag{7}$$

$$A = \frac{1}{x} - \frac{1}{|\vec{x} - \vec{x}_0|}, \quad \vec{x}_0 = \frac{\varepsilon\vec{z}}{e^2\beta}, \quad h_a = \frac{e^2\beta}{\varepsilon a}.$$

Parameter h_a is large in a typical situation ($h_a = 20 - 25$ for $a \approx 1$ nm at room temperature). We present result of calculation of (8) for the most interesting case $c \ll 1$ and $c \exp h_a \gg 1$ (details of calculation will be published elsewhere)

$$G(x_0, c) \simeq G_1 + G_2 + G_3, \tag{8}$$

$$G_1 = \frac{4\pi}{3(\ln c)^2} + \frac{8\pi}{3x_0(\ln c)^3}. \tag{9}$$

$$G_2 \approx \frac{8\pi}{(\ln c)^4}\left(1 - \frac{1}{x_0}\right), \quad G_3 \approx 4\pi c x_0. \tag{10}$$

Note the special role of the term G_3: it effectively renormalizes electric field to the value $E_{\text{eff}} = E - E_{\text{cr}}$, $E_{\text{cr}} = 4\pi c\beta e^3/\varepsilon^2 a^3$. If $E < E_{\text{cr}}$, then a nondispersive carrier motion across the transport layer when $\langle v \rangle$ does not depend on L is not possible. This phenomenon was already reported.[8] For the reasonable range of $c = 10^{-8} - 10^{-6}$ term G_1 plays a major role.

In the case of strong disorder

$$\mu \propto \exp\left[-P(c, \beta) + 2(ea\beta EQ)^{1/2}\right] \tag{11}$$

$$P(c, \beta) = \frac{4\pi h_a^3}{3(\ln c)^2}, \quad Q(c, \beta) = -\frac{8\pi h_a^4}{3(\ln c)^3}$$

(here we neglect the difference between E and E_{eff}). We see that a quasi-PF (qPF) mobility dependence indeed arises in the charged medium. For comparison, one can see the result of the numerical calculation of $\mu(E)$ in figure 1.

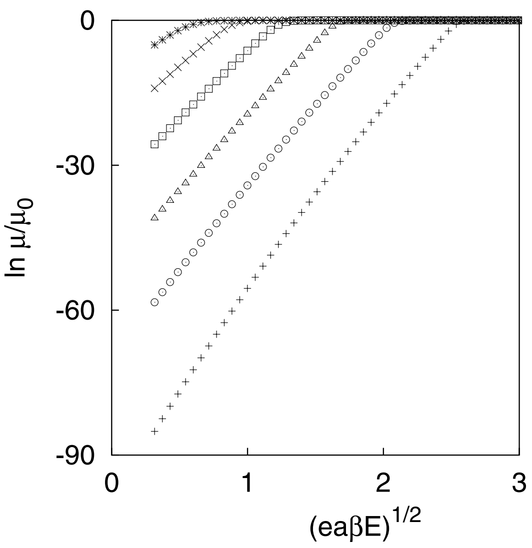

Figure 1: Mobility field dependence calculated by numerical evaluation of $W(z)$. Mobility curve are calculated using (5) for $h_a = 20$ and following values of c (from the top curve downwards): 3×10^{-9}, 1×10^{-8}, 3×10^{-8}, 1×10^{-7}, 3×10^{-7}, and 1×10^{-6}, correspondingly, and $\mu_0 = e\beta D$. For room temperature and $a = 1$ nm $ea\beta E = 1$ for $E \approx 2.5 \times 10^5$ V/cm.

The best test of the validity of equation (11) is to study the dependence of slope S and intercept I of the mobility field dependence $\ln\mu$ vs $(ea\beta E)^{1/2}$ on c and T

$$\frac{I(c, \beta)}{h_a} = \frac{P(c, \beta)}{h_a} = \frac{4\pi}{3}Z^2, \tag{12}$$

$$\frac{S^2(c, \beta)}{h_a} = 4\frac{Q(c, \beta)}{h_a} = \frac{32\pi}{3}Z^3, \quad Z = -h_a/\ln c.$$

Thus, I/h_a and S^2/h_a are functions of the universal parameter Z only and this fact is in a reasonable agreement with the result of numerical calculation (see figures 2,3). Slope of I/h_a vs Z^2 plot should be $4\pi/3 \approx 4.2$. Calculated slope equals to 4.1. Slope of S^2/h_a vs Z^3 plot should be $32\pi/3 \approx 33.5$. the calculated one equals to 35.3, so we have a reasonable agreement.

3. Transport layer with finite thickness

Why does the qPF regime (11) differ so significantly from the PF regime (3)? Why does the isolated trap approximation fail to capture mobility dependence on T and c? The answer is that this approximation cannot be applied to the case of charged traps because of the long range of the Coulomb potential. For example, in the case of infinite medium $\langle U^2 \rangle$ diverges because of the contribution from

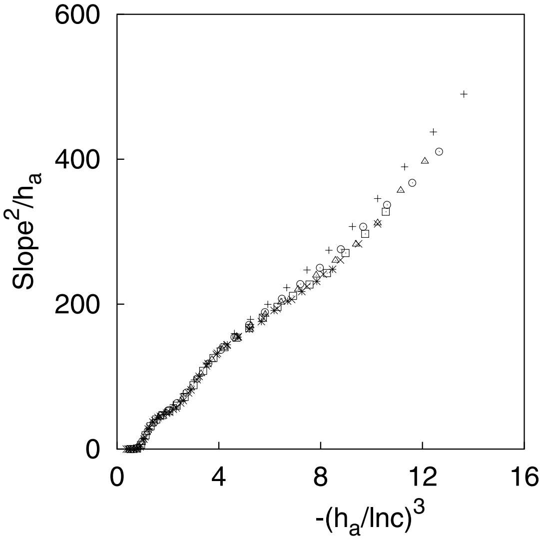

Figure 2: *Dependence of the slope of the mobility field curve, calculated by numerical evaluation of (5), on the universal parameter $Z = -h_a/\ln c$. Data points are calculated for 6 different values of c spanning a range from 3×10^{-9} to 1×10^{-6}. Parameter h_a spans the range from 14 to 40.*

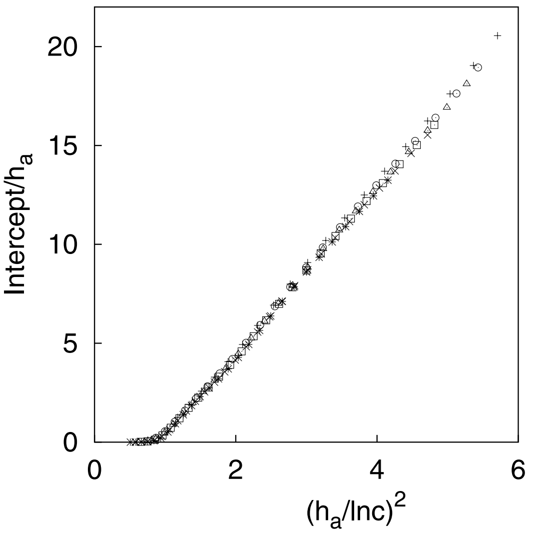

Figure 3: *Dependence of the intercept of the mobility field curve on the universal parameter $Z = -h_a/\ln c$. Parameters are the same as in figure 2.*

large distances; it is a clear indication of huge collective fluctuations of the carrier potential energy in the charged medium. For this reason it's impossible to write the carrier energy in the form (1) and the case of isolated trap and the case of uniformly charged medium for $c \to 0$ are principally different for *an infinite medium*.

What has happened in the case of *finite* medium (a slab of organic material with the thickness L containing static charges and bounded by conducting electrodes)? In this case the distribution of $U(\vec{r})$ is not a uniform random field even for uniform distribution of static charges,[9] our basic equation (5) is not valid anymore, and the calculation of transport properties of the device is a much more formidable task. Here we note only some simple estimations. For a finite L a variance of $U(\vec{r})$ is[9]

$$\sigma^2(z) = \frac{8\pi e^4 c}{\varepsilon^2 a^3 L} z(L-z). \tag{13}$$

We should expect that a particular domain inside the transport layer located at z contributes to the isolated trap PF regime if a fluctuation contribution to the carrier total potential energy is much smaller than the decrease of the activation energy, e.g. $\sigma(z) \ll \delta U_{\rm act}$, or

$$c \ll \frac{E}{E_{\rm i}} \frac{aL}{2\pi z(L-z)}, \quad E_{\rm i} = e/\varepsilon a^2. \tag{14}$$

For typical materials $E_{\rm i} = 5 \times 10^6 - 1 \times 10^7$ V/cm, so for $E = 1 \times 10^4$ V/cm in the bulk of the transport layer at $z \approx L/2$ for $L = 10$ μm and $a = 1$ nm we have $c \ll 10^{-7}$ or $n \ll 10^{14}$ cm^{-3}.

At the first glance, our estimation is in perfect agreement with the idea of Rackovsky and Scher[6] that the PF-like mobility field dependence in disordered organic materials is delivered by very small concentration of charged traps. More careful analysis reveals, however, that the model of finite charged slab for $c \le 10^{-8}$ can hardly reproduce experimental mobility dependence. Indeed, increase of the magnitude of the disorder leads both to the increase of the mobility variation with the variation of the electric field strength and broadening of the field region where mobility significantly depends on E. For this reason we could expect that the mobility curve for a finite slab, where the magnitude of disorder is decreased in comparison to the infinite case (variance (13) is finite), should be located exactly between the corresponding curve for an infinity layer and the limit line $\mu(E) = \mu_0$. Figure 1 indicates that for $c \le 10^{-8}$ there is no possibility for such mobility field dependence to vary significantly in a field range up to 10^6 V/cm.

Rackovsky and Scher reasonably suggested that a minimum of $N \approx 10 - 50$ encounters with traps is enough for establishing of non-dispersive regime,[6] and then estimated the necessary density as $n \approx (N/L)^3$. This estimation seems to be too optimistic in the case of strong electric field $E = 2 \times 10^6$ V/cm.[5] Here we should expect a quasi-1D carrier motion with the minimal re-trapping at the same site. Carrier effectively interacts with traps located in the domain having volume $V \propto L r^2_{\rm Ons}$, where $r_{\rm Ons} = e^2/\varepsilon kT$ is an Onsager radius, so $n \approx N/L r^2_{\rm Ons} \approx 10^{15}-10^{16}$ cm^{-3} at room temperature, which is several orders of magnitude greater than the estimation suggested by Rackovsky and Scher[6] and does not agree with the equation (14). For such high trap density the PF regime should be transformed to the qPF regime (11).

Microscopically charged medium with $c^+ \neq c^-$ imposes even more severe limitation on the density of static charges than equation (14). Using methods, developed in Ref. 9, it is easy to calculate an average carrier energy in the uniformly charged transport layer bounded by conducting electrodes

$$\langle U(z)\rangle = \frac{2\pi e^2 c_d}{\varepsilon a^3}\, z(L-z), \quad c_d = c^+ - c^-. \qquad (15)$$

Such layer serves as a potential well (or a barrier, depending on the sign of c_d) for a carrier with the depth (height) which depends on L

$$U_{\max} = \langle U(L/2)\rangle = \frac{\pi e^2 c_d L^2}{2\varepsilon a^3}. \qquad (16)$$

Non-dispersive transport could be observed if $U_{\max}/kT \leq 1$, or $c_d/a^3 \leq 10^{11} - 10^{12}$ cm^{-3} for $L \approx 10$ μm.

For these reasons we believe that the model of isolated charged traps may be applied only to the case of extremely small density of charged traps, where the macroscopic carrier mobility very weakly depends on the electric field.

4. Conclusion

The PF-like behaviour of the mobility in charged medium differs significantly from the prediction of the model of isolated Coulomb trap. Slope and intercept of the mobility dependence increase with the increase of concentration of charged traps, and at room temperature increase of c by the order of magnitude from 1×10^{-7} to 1×10^{-6} leads to the decrease of the mobility by 10 orders of magnitude, in agreement with previous numerical results.[8] For 3D transport we should expect a weaker dependence on c because in all known cases (e.g. for charge transport in dipolar[10] or quadrupolar[11] glasses) results of 3D computer simulation suggest that the 1D model essentially retains the true functional dependence of the mobility on relevant parameters, but overestimates numeric coefficients in the exponent of (11) by a factor of 2-3. Still, decrease of the mobility by three orders of magnitude seems to be possible.

Experimental test of the mobility dependence on the concentration of charged traps should be the best test of the result (11). By now there are no experimental data on this dependence. Nonetheless, in charged medium the predicted temperature dependence $I \propto T^{-3}$ and $S \propto T^{-5/2}$ (for a plot of $\ln\mu$ vs $E^{1/2}$) seems to be too strong to describe existing experimental data.

There is still a possibility that the charge mobility affected by the influence of static charges has been observed in experiments. A well known phenomenon is the so-called problem of the first pulse in a time-of-flight method of the mobility measurement, where carriers are generated by the action of laser pulse and then drift across a sample under the action of applied voltage. Quite frequently, parameters of the photocurrent transient obtained for a very first laser pulse immediately after preparation of the transport sample differ significantly from the corresponding parameters, obtained for all subsequent pulses. We can speculate that a very low density of static charges may be present in the sample, but after the first packet of charge carriers sweeps across the sample they are effectively neutralized. Of course, there are other possible explanations. Yet we believe that parameters of the transient obtained for a very first laser pulse deserve careful examination.

Acknowledgements Partial financial support of the International Science and Technology Center (grants 872 and PP-2207) and the Russian Fund for Basic Research (grant 99-03-32111) is acknowledged. This work was partially supported by the University of New Mexico and utilized the UNM-Alliance Roadrunner Supercluster at the Albuquerque High Performance Computing Center.

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