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Theory of low-field hopping mobility in organic solids with energetic and positional disorder

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The influence of superimposed energetic and positional disorder on the field dependence of drift mobility in disordered organic solids is considered for the first time analytically by an Effective Medium theory. We find that the negative field dependence of the drift mobility at low fields is a genuine property of the nondispersive hopping transport in three-dimensional disordered organic solids and caused by positional disorder.

1 Introduction The field dependence of charge mobility in hopping transport materials at low electric fields still remains a debated issue though it bears on the fundamental nature of charge hopping transport in organic materials. In general, mobilities of charge carriers typically increase with electric field in a Poole-Frenkel fashion, i.e. $\ln\mu \propto \sqrt{E}$. However, in low field region negative field dependences have been observed in various organic materials [1, 2]. Computer simulations [1, 3] reproduced such an effect and suggested that the decrease of charge mobility with increasing electric fields at low fields is due to the influence of positional disorder.

In the present work an Effective Medium approach (EMA) developed in [4–8] has been successfully applied to consider the influence of superimposed energetic and positional disorder on the electric field dependence of charge-carrier hopping mobility in disordered organic solids.

2 Low-field charge-carrier drift mobility A self-consistent theory based on the effective medium approach based on a two-site cluster approximation was recently formulated [5] to describe nondispersive charge carrier transport in disordered 3D organic systems. A set of three transcendental equations have been derived that allow the calculation of three effective parameters, namely W_e^+, W_e^- and W_e, which describe the effective jump rates along–, opposite–, and normal to the electric field direction, respectively, for arbitrary electric field $\boldsymbol{E} = \{E,0,0\}$. The effective drift mobility μ_e by definition is

$$\mu_{\mathrm{e}} = a\left(W_{\mathrm{e}}^{+} - W_{\mathrm{e}}^{-}\right)E^{-1}, \tag{1}$$

where a is an average distance between neighboring hopping sites. Let us consider a disordered organic system with superimposed independent energetic and positional disorder. In this case [8] the two-site

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transition rates $W_{12}^{+}(W_{21}^{-})$ and the effective transition rates $W_e^{+}(W_e^{-})$ along (opposite) to the electric field direction can be written

$$W_{12}^{+} = W_{12}Q_{12}^{+},\ W_{21}^{-} = W_{21}Q_{21}^{-}\sqrt{b^2 - 4ac},\ W_e^{+} = W_eQ_e^{+},\ W_e^{-} = W_eQ_e^{-}. \tag{2}$$

Here $W_{12}(W_{21})$ and W_e are energetic disorder components of the two-site- and effective transition rates, respectively, in zero electric field. Effective rate W_e was calculated in Ref. [4, 5]. Values $Q_{12}^{+}(Q_{21}^{-})$ and $Q_e^{+}(Q_e^{-})$ are positional disorder components of the two-site- and effective transition rates, respectively, along (opposite) to the electric field direction. Effective rates $Q_e^{+}(Q_e^{-})$ and Q_e (in zero electric field) can also be calculated in the framework of the EMA method [5]. At relatively weak electric fields when $\eta = (Q_e^{+} + Q_e^{-})/2Q_e > 1$ and $\delta = (Q_e^{+} - Q_e^{-})/2Q_e < 1$ in iteration approximation one obtains [8]

$$Q_e^{+} = \frac{\left\langle Q_{12}^{+}(Q+2Q_e)^{-1}\right\rangle}{\left\langle (Q+2Q_e)^{-1}\right\rangle},\ Q_e^{-} = \frac{\left\langle Q_{21}^{-}(Q+2Q_e)^{-1}\right\rangle}{\left\langle (Q+2Q_e)^{-1}\right\rangle}, \tag{3}$$

where $Q = \left(Q_{12}^{+} + Q_{21}^{-}\right)/2$. Angular brackets in Eqs. (3) denote positional configuration averaging. When accounting for energetic and positional disorder the general expression (1) for the drift mobility transforms to

$$\mu_e = \mu_{e0}\left(Q_e^{+} - Q_e^{-}\right)\lambda^{-1}, \tag{4}$$

where $\mu_{e0} = ea^2W_e/k_BT$ is the zero-field effective drift mobility determined solely by the energetic disorder, and $\lambda = eaE/k_BT$.

Further theoretical treatment requires choosing an expression for the two-site transition rates $W_{12}^{+}\left(W_{21}^{-}\right)$ as well as functions describing energetic and positional disorder. Let us use the two-site transition rates based, without loss of generality of results [8], on the Marcus jump-rate expressions [9]

$$W_{12}^{+} = W_1\exp\left[-\frac{\varepsilon_{21}-\varepsilon_E}{2k_BT} - \frac{(\varepsilon_{21}-\varepsilon_E)^2}{16E_ak_BT}\right],\ W_{21}^{-} = W_1\exp\left[-\frac{\varepsilon_{12}-\varepsilon_E}{2k_BT} - \frac{(\varepsilon_{12}-\varepsilon_E)^2}{16E_ak_BT}\right], \tag{5}$$

where $\varepsilon_{ji} = \varepsilon_j - \varepsilon_i$, $\varepsilon_E = eaE$. To take into account the positional disorder we use the approach suggested by Gartstein and Conwell [10], i.e., we choose $W_1 = W_0\exp(-E_a/k_BT)\exp(\xi)$. Here E_a is the polaron activation energy, ξ is parameter of positional disorder and it changes uniformly within the range $-\xi_0 \le \xi \le \xi_0$. Energetic disorder is described by a Gaussian distribution with the width σ. The result of calculation of drift mobility reads as follows

$$\mu_e = \mu_{e0}Q_e\frac{X_e^{+} - X_e^{-}}{\lambda}, \tag{6}$$

where

$$X_e^{\pm} = \frac{M^{\pm}}{N^{\pm}}\frac{\ln A^{\pm}}{\xi_0 - \frac{1}{2}\ln A^{\pm}},\qquad A^{\pm} = \frac{N^{\pm}\exp(\xi_0) + 2Q_e}{N^{\pm}\exp(-\xi_0) + 2Q_e}, \tag{7}$$

$$M^{\pm} = \exp\left\{\pm\frac{\lambda}{2}\left(1 + 4x^2d\right) - dx^2\right\},\ N^{\pm} = \exp\left(\pm 2x^2d\lambda - dx^2\right)\cosh\left(\frac{\lambda}{2}\right). \tag{8}$$

Here $x = \sigma/k_BT$, $d = k_BT/16E_a$. From Eq. (6) with devoid of positional disorder $(\xi_0 \to 0)$ for arbitrary energetic disorder in very low-field range one has $\ln\mu_e \propto E^2$ and in a broad range of higher fields one obtains $\ln\mu_e \propto E$ which are in agreement with results of recent computer simulations [11] at a low density of charge carriers with using the Miller-Abrahams jump rates. But with accounting in (6) the energetic correlation effects, as it was proposed in [5, 8], one obtains the dependence $\ln\mu_e \propto \sqrt{E}$.

3 Role of diffusion motion of carriers We suggest a simple method to extract the true drift mobility μ_e from the experimentally accessible apparent mobility μ_a obtained by the time-of-flight (TOF) measurement. Thickness of a sample under investigation can be expressed as $L = L_1 + L_2$, where $L_1 = \mu_e E\tau$ is a drift length of charge carriers and $L_2 = \sqrt{6(k_BT/e)\mu_e\tau}$ is their diffusion length. Then the TOF technique gives an apparent mobility $(\mu_a = L/E\tau)$, which can be written as follows

$$\mu_e = \mu_a \left[\left(1 + 3\frac{k_BT}{eLE} \right) - \sqrt{\left(1 + 3\frac{k_BT}{eLE} \right)^2 - 1} \right]. \tag{9}$$

It is easy to see that when $eLE >> 3k_BT$ (drift-control transport regime) then $\mu_e \cong \mu_a$, i.e., the experimentally measured mobility is the true drift mobility. In case when $eLE << 3k_BT$ the charge transport is diffusion-controlled. The electric field $E_{cr} = 3k_BT/eL$ can be considered as a critical field at which a transition from a diffusion-controlled to a drift-controlled transport regime takes place. It should be noted that a rather similar result was obtained by Cordes et al. [12] for a one-dimensional energetic disordered system. It is easy estimate that E_{cr} is far below the experimentally important field range typically employed in TOF measurements.

4 Results and conclusion Figure 1 shows a comparison of calculated field dependences of the apparent μ_a (curves 1 and 2) and drift μ_e mobility (curves 1' and 2') in an organic material with positional disorder. At very weak positional disorders μ_a (not μ_e) indeed has a minimum at very low fields due to the diffusion motion. Drift mobility μ_e shows a minimum at considerably higher fields which are relevant to the TOF experiment but only due to strong positional disorder.

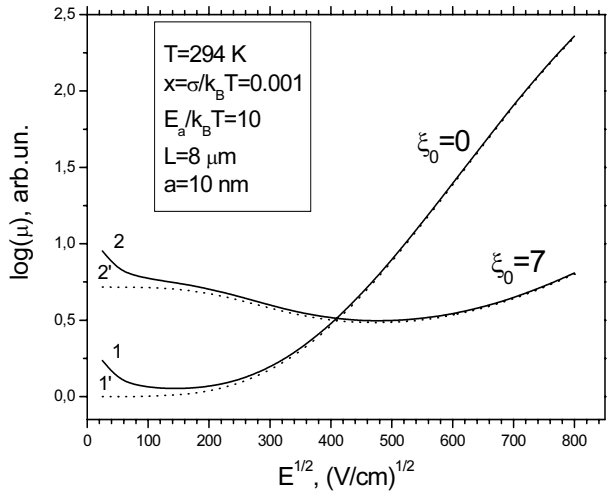

Fig. 1 Field dependences of the apparent charge mobility μ_a calculated using Eqs. (9) and (6) accounting for the diffusion for both very weak and strong positional disorders (curves 1 and 2, respectively). The effective drift mobility μ_e calculated by Eq. (6) is given by curves 1' and 2' for comparison. Here *a* is equal to the average length of conjugated segments in conjugated polymers.

Our EMA results are similar to that obtained by percolation theories [13, 14]. A qualitative explanation for the negative field dependence of charge mobility in 3D hopping organic system with large positional disorder is that the field tends to eliminate the faster detour percolation routes as the latter could include jumps against field direction due to more favorable intersite coupling. At high electric fields the carrier jumps against the field are completely eliminated and charge transport becomes a quasi-1D [8]. Our results are in good agreement with both computer simulations [1, 10] and experimental results [1, 2].

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