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Sergei V. Novikov

David H. Dunlap

Vasudev M. Kenkre

Paul Ernest Parris

Missouri University of Science and Technology, parris@mst.edu

et. al. For a complete list of authors, see https://scholarsmine.mst.edu/phys_facwork/1384

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Essential Role of Correlations in Governing Charge Transport in Disordered Organic Materials

S. V. Novikov,^{1,2} D. H. Dunlap,² V. M. Kenkre,² P. E. Parris,³ and A. V. Vannikov¹

¹*A. N. Frumkin Institute of Electrochemistry, Moscow, Russia*

²*Center for Advanced Studies, Department of Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico 87131*

³*Department of Physics, University of Missouri-Rolla, Rolla, Missouri 65401*

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The transport of photoinjected charges in disordered organic films is often interpreted using a formula based on a Gaussian disorder model (GDM) that neglects spatial correlations due to charge-dipole interactions, even though such correlations have recently been shown to explain the universal electric field dependence observed in these systems. Based on extensive computer simulations of a 3D disorder model that includes such correlations, we present a new formula for analyzing experiments that accurately describes transport in these materials. [S0031-9007(98)07626-1]

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Recent efforts by a number of workers [1–7] have increased our understanding of nearly universal features of photoinjected charge transport in many disordered organic materials, including molecularly doped polymers [8,9], low molecular weight organic glasses [10,11], and certain polyconjugated polymers [12,13]. In particular, it is now recognized that the Poole-Frenkel (PF) dependence [8–12],

$$\mu \propto \exp(\gamma\sqrt{E}), \quad (1)$$

of the drift mobility μ on electric field E observed in these materials results from slowly varying spatial fluctuations in the potential energy of a charge migrating through the material. Such energetic fluctuations can arise [1] from a random distribution of molecules in the medium possessing permanent electric dipole moments; a carrier's interaction with the latter provides a significant contribution U_d to the total site energy. More importantly, the energy correlation function [1,3]

$$C(r) = \langle U_d(0)U_d(r) \rangle \sim \sigma_d^2 a/r \quad (2)$$

decays very slowly with intersite separation r . Here, $\sigma_d = \langle U_d^2 \rangle^{1/2}$ is the rms width of the dipolar energetic disorder, and a is a minimal charge-dipole separation. In a previous Letter [3], an analytical result equivalent to (1) was derived for carriers diffusing along one spatial dimension through a medium with correlations as in (2). This same behavior was also observed in 3D charge transport simulations [4]. Moreover, very recent studies on both 1D and 3D systems suggest that this mechanism producing PF behavior is stable under additional sources of disorder less correlated than those that arise from dipoles [5,6], and indicate that the PF factor γ in (1) is insensitive to all but the dipolar component of the disorder.

These recent advances raise questions regarding the way materials have been experimentally characterized in the past. Most measurements in the last decade have been interpreted using an uncorrelated Gaussian disorder model, developed and extensively studied by Bäessler and co-workers prior to the recent recognition of the impor-

tance of spatial correlations [14]. In the GDM, transport occurs through hops among localized states characterized by a Gaussian distribution of site energies, with hopping rates obeying an asymmetric detailed balance relation [14]. Numerical simulations capture well many features of experiment; its Gaussian density of states (DOS) leads to a temperature dependence $\ln \mu \propto -(T_0/T)^2$ routinely observed, and the GDM reproduces low temperature transitions between dispersive and nondispersive photocurrents. However, site energies are distributed *independently*, with no correlations occurring over any length scale. Consequently, and consistent with recent work, the field dependence of the GDM agrees with (1) only over a very narrow range at high fields ($E > 3 \times 10^5$ V/cm) [15]. Nonetheless, the nondispersive mobility within this limited range has often been empirically characterized in a form

$$\mu = \mu_0 \exp[-(2\hat{\sigma}/3)^2 + C(\hat{\sigma}^2 - \Sigma^2)\sqrt{E}] \quad (3)$$

widely used in recent years to analyze experiment. In Eq. (3), C is a constant determined from simulation, $\hat{\sigma} = \sigma/kT$ is the width of the DOS relative to kT , and Σ describes the spatial disorder. In analyzing data it is usually assumed that μ_0 , σ , and Σ completely characterize any given material, with σ representing the width of the DOS due to all sources of energetic disorder. Values of these three parameters have been obtained and tabulated for many organic solids.

Although Eq. (3) does describe time-of-flight data, provided μ_0 , σ , and Σ are viewed simply as fitting parameters, recent theoretical work casts doubt on whether the σ extracted from experiment using (3) represents the actual width of the full DOS. In the 1D analysis of Ref. [3], e.g., a particle moving in a correlated random potential of width σ is predicted to yield

$$\mu = \mu_0 \exp[-\hat{\sigma}^2 + 2\hat{\sigma}\sqrt{eaE/kT}]. \quad (4)$$

Use of (4) would lead to a different estimate of σ if applied to data, and to a different dependence of the PF factor on σ and T . The use of Eq. (4) for analysis of experimental data has been hindered by the reasonable

doubt about its applicability to 3D case. Indeed, in 1D case the transport path is always the same, while in 3D case it is not fixed and, moreover, there is a possibility that the dominant transport paths may change with E and T in a way that would alter the essential field dependence.

Thus motivated, we have performed extensive numerical simulations on a simple 3D *correlated* disorder model (CDM). The CDM shares some features with the GDM. However, important differences exist that critically affect the interpretation of experiment. Moreover, in contrast to the GDM, essential transport properties of the CDM are insensitive to the way detailed balance is included in the hopping rate; the same PF field dependence occurs with symmetric (“small polaronlike”) rates or asymmetric (“Miller-Abrahams”) rates [16]. These and other results of the simulation verify essential predictions of 1D analyses and quantify the relation between basic features of measured mobilities and microscopic parameters that govern them. On the basis of these simulations, detailed below, we propose the following empirical relation

$$\mu = \mu_0 \exp \left[- \left(\frac{3\hat{\sigma}_d}{5} \right)^2 + C_0 \left(\hat{\sigma}_d^{3/2} - \Gamma \right) \sqrt{\frac{eaE}{\sigma_d}} \right], \quad (5)$$

describing nondispersive mobility in correlated (e.g., dipolar) media, where $C_0 = 0.78$, and $\Gamma = 2$. In (5), the parameter μ_0 may have additional temperature dependence due to other less correlated sources of energy disorder or polaron effects. Experience with the GDM suggests that Γ characterizes geometrical disorder and thus should depend upon transport site concentration. We now describe our numerical studies leading to Eq. (5), the main result of the present Letter.

The CDM treats carrier hopping among sites arranged on a cubic lattice of cell spacing a , but differs from the GDM in the way site energies are determined. In the current dipolar CDM, an independently and randomly oriented dipole of moment p is placed at each lattice site, and the energy of a carrier at a given site is then the sum (calculated using the Ewald method [17])

$$U_m = - \sum_{n \neq m} \frac{e\vec{p}_n \cdot (\vec{r}_n - \vec{r}_m)}{\epsilon |\vec{r}_n - \vec{r}_m|^3} \quad (6)$$

of its interaction with dipoles at all sites except its own. The site energy distribution for this model has been extensively studied, and shown to be approximately Gaussian, with a width [18,19]

$$\sigma_d = 2.35ep/\epsilon a^2. \quad (7)$$

However, unlike the GDM, the many long-range contributions comprising (6) introduce correlations in the distribution of site energies, making this a correlated version of the GDM with the particular kind of correlations described by (2).

Our numerical implementation of the dipolar CDM starts with a simple cubic lattice of $50 \times 50 \times 50$ sites,

from which an extended transport layer is formed by periodic continuation. To determine the mobility, we have performed Monte Carlo simulations using both Miller-Abrahams and small-polaron-like hopping rates that fall off with distance as $\exp(-2\alpha r)$. We take $2\alpha a = 10$, as in Ref. [14]. For each field strength the mobility $\mu = v/E$ is calculated from the average carrier velocity v . Except where noted, data presented below are evaluated with transport layer thickness $L = 2000$ lattice planes (sufficient to obtain a nondispersive equilibrium mobility). To compare with the GDM, we have followed the same procedure with uncorrelated Gaussian site energies. In Fig. 1 we present field-dependent mobilities for the CDM using Miller-Abrahams rates for a wide range of $\hat{\sigma}_d$, along with a curve showing typical behavior of the GDM. With Miller-Abrahams hopping rates [16], the rate for hops down in energy is independent of energy mismatch, causing the drift velocity to saturate and giving a mobility that reaches a maximum before decreasing as E^{-1} at high fields ($E \gtrsim ea/\sigma$). In Figs. 2 and 3 we present data showing the effect of different hopping rates on the GDM and the CDM, respectively.

The main difference between the two models is the range of fields over which PF behavior occurs. In the CDM, which has the proper correlations, PF behavior occurs down to low fields and persists over a wide field range. In the GDM, the mobility at low fields is almost parabolic when plotted versus \sqrt{E} (see Fig. 1). This suggests, as confirmed in Fig. 2, that at low-to-intermediate fields the GDM is better described by a $\ln \mu \propto E/kT$ law, rather than by (1). Indeed, such a linear field dependence is analytically exact for one-dimensional models with

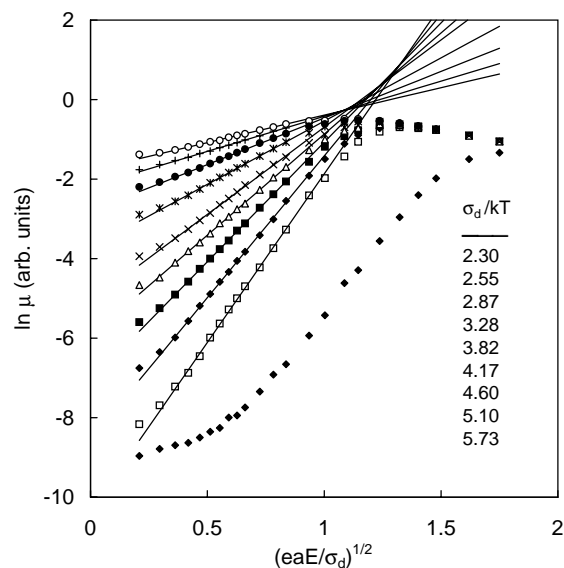


FIG. 1. Field-dependent mobility of the CDM for different values of $\hat{\sigma}_d$ (from top curve downward). The lowest curve is the mobility for the GDM for $\hat{\sigma} = 5.10$. If $\sigma_d = 0.1$ eV and $a = 10 \text{ \AA}$, then $eaE/\sigma_d \approx 1$ for $E = 10^6$ V/cm.

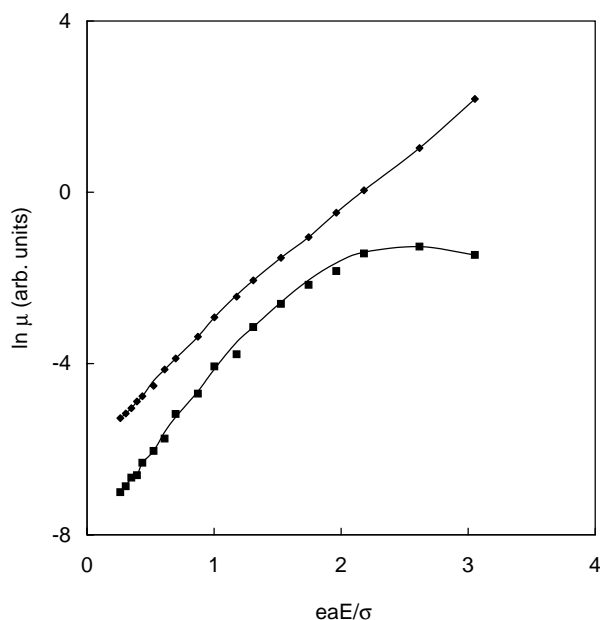


FIG. 2. Field-dependent mobility for the GDM for $\hat{\sigma} = 4.17$ and two different types of hopping rate: Miller-Abrahams (squares) and symmetric (diamonds).

uncorrelated Gaussian disorder. Moreover, a nearly linear field dependence is also consistent with simple scaling arguments. The mobility in energetically uncorrelated media is limited by the slow rate of carrier release from deep sites, rates that would exponentially depend on the (linear) decrease in energy difference between neighboring sites along the field. Indeed, the limited PF behavior of the standard GDM arises from a crossover between the nearly linear E dependence of $\ln \mu$ at low fields and the E^{-1} dependence of μ at high fields, a mechanism that critically requires Miller-Abrahams rates. This viewpoint is supported by the top curve in Fig. 2, which shows no PF dependence in the GDM when symmetric rates are used.

In the CDM, by contrast, we note a PF region at low-to-intermediate fields (see Fig. 3), which, aside from a slight vertical shift, is the same for both rates. Thus, the PF behavior commonly observed in dipolar materials can be considered a robust feature, associated more with long-range fluctuations of the potential characteristic of the medium and less upon the details of electron-phonon coupling constants or of particular hopping rates they produce. This viewpoint was expressed in earlier analytical studies for the 1D version of this model, where it was argued that the relatively low energy difference between neighboring sites in a correlated potential renders the particular form of hopping rate unimportant [3,20].

To characterize the CDM empirically, we have fit the simulation data to a trial function that generalizes the GDM and 1D results, Eqs. (3) and (4). Specifically, we assumed that the dependence of μ on E and T , for moderate fields, has the form

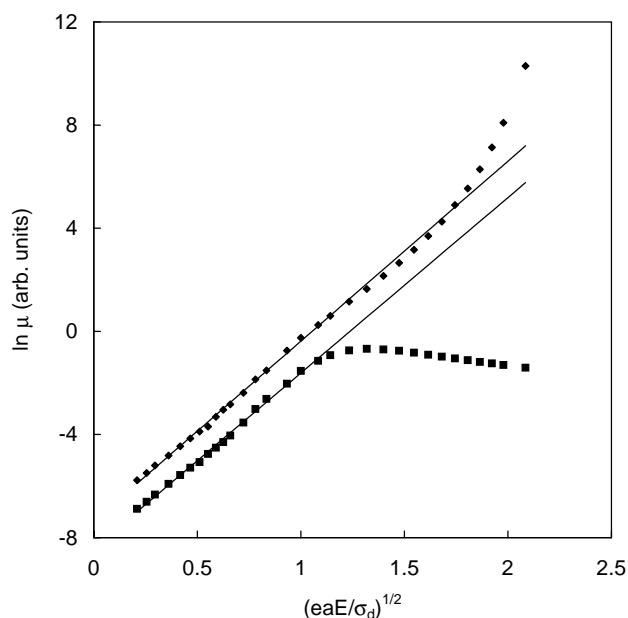


FIG. 3. Field dependent mobility for the CDM for $\hat{\sigma}_d = 5.1$ and two different types of hopping rate: Miller-Abrahams (squares) and symmetric (diamonds).

$$\mu = \mu_0 \exp[-A_1 \hat{\sigma}^n + A_2 (\hat{\sigma}^m - A_3) \sqrt{eaE/\sigma}], \quad (8)$$

with constants n, m, A_1, A_2, A_3 to be determined. In the standard GDM, $n = m = 2$, and in the 1D treatment, $n = 2, m = 3/2$. The coefficient A_1 was determined from the temperature dependence of μ at zero field, and A_2 and A_3 from the temperature dependence of the slope of $\ln \mu$ versus \sqrt{E} in the PF region. To find the exponents n and m , a linear fit was made of the PF region for simulation data generated using $L = 10^4$ lattice planes, and the fit parameters used with (8) to calculate a correlation coefficient R for different values of n and m . Maximization of R^2 gives the most probable values $n \approx 1.8$ and $m \approx 1.55$. These are close enough to those in the 1D analysis (4) that we may reasonably take $n = 2$ and $m = 1.5$ (small differences in n and m may arise from non-Gaussian deviations of the site energy distribution). For these values of n and m we then find $A_1 = 0.35 \approx (3/5)^2$, $A_2 = 0.78$, and $A_3 = 1.97$, leading to our proposed Eq. (5). The main difference with the 1D model is the nonzero value of A_3 , i.e., Γ .

To demonstrate use of (5), we present here a limited comparison with experiment, focusing on the organic glass NPPDA [10]. This particular material was chosen because of its high dipole moment of 3.02 D, relatively nondispersive charge transport [10], and the close resemblance between a material with 100% concentration of transport sites and our current studies of spatially ordered dipolar lattices. Using Eq. (5) to analyze data on NPPDA digitized from Ref. [10], we find from the temperature dependence of the PF factor the value $\sigma_d = 0.095$ eV, in reasonable agreement with the value

$\sigma_d = 0.084$ eV found using Eq. (7). As we have mentioned previously, this slope should depend only on the dipole component of disorder. These values are obtained assuming $a = 9.2$ Å, calculated using a reasonable mass density $\rho = 1.1$ g/cm³. On the other hand, the extrapolated zero field mobility for the same data, assuming only dipolar disorder, gives using (5) a different width, $\sigma_d = 0.109$ eV. The increase over our previous value is clearly a measure of the other sources of energetic disorder (e.g., Van der Waals [10,11]) present in the system, sources that affect the zero-field mobility but not the PF factor. Assuming only a Van der Waals contribution, we expect, based upon the GDM, that the prefactor μ_0 in Eq. (5) is proportional to $\exp[-(2\hat{\sigma}_{vdw}/3)^2]$. Using this gives $\sigma_{vdw} = 0.04$ eV.

The only significant difference between simulation and experimental data for NPPDA is the difference in Γ ; the experimental value is 4.55 rather than the proposed $\Gamma = 2$. The coefficient Γ is analogous to the positional disorder parameter Σ^2 of the GDM [14]. NPPDA glass is a material with randomly located molecules, while our present calculations on the CDM have included no explicit positional disorder in the transport sites. It is therefore reasonable that Γ for the glass would be greater than for a regular lattice. The small difference between calculated and experimental values of σ_d may also be associated with this neglect of positional disorder, since σ_d is greater for randomly distributed dipoles than for a regular lattice of the same density. Investigations into the effects of explicit positional disorder on the CDM will be reported elsewhere.

In summary, we have (i) presented a comparison of the transport properties of the (older) GDM and a (new) CDM expected to more closely describe transport in disordered organic polar materials; (ii) shown that Poole-Frenkel field dependence of μ is a universal feature of the CDM, independent of the kind of hopping rate, unlike in the case of the GDM; and (iii) proposed, on the basis of numerical and analytical studies, an explicit operational prescription (5) for the analysis of mobility measurements. We hope that the present analysis will encourage further experimental studies designed to critically examine Eq. (5) through the systematic variation of polarity of the transport medium.

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