Charge Transport in Energetically and Spatially Disordered Molecular Solids

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Abstract

Prerequisite to the rational development of organic electronic materials with prescribed electronic and optoelectronic properties is an understanding of the fundamental charge transport mechanisms upon which they rely. The field dependent mobility of disordered molecular solids has recently been shown to depend critically on the degree and morphological character of energetic disorder in the system. In particular, it is now recognized that a key ingredient necessary for understanding the field dependent mobility observed in such systems are spatial correlations that relate the strength of random potential energy fluctuations in the medium to their spatial extent. We review here microphysical mechanisms that can give rise to such fluctuations and study the field dependences that can be expected from them.

Introduction

Recent efforts by a number of workers [1-8] have increased our understanding of nearly universal features of photoinjected charge transport in many molecularly doped polymers [9,10], low weight molecular glasses [11,12], and certain polyconjugated polymers [13,14]. It is now generally appreciated that the Poole-Frenkel (PF) field dependence [9-13]

$$\mu \propto \exp\left(\gamma\sqrt{E}\right) \tag{1}$$

of the drift mobility μ on electric field E that occurs in these materials results from the correlated nature of the random potential energy landscape experienced by a photoinjected carrier migrating through the disordered medium. In polar materials, e.g., energetic fluctuations arise [2] from the random distribution of dopant or host molecules possessing permanent electric dipoles. A carrier's interaction with the latter has been shown to provide a significant contribution to the carriers potential energy $U(r)$. More importantly, the potential energy autocorrelation function [2-4]

$$C(r) = \langle U(0)U(r)\rangle \sim \sigma^2 a/r \tag{2}$$

in such a medium decays very slowly with intersite separation r. Here, $\sigma = \langle U^2\rangle^{1/2}$ is the RMS width of the

dipolar energetic density of states (DOS), and a is a minimal charge-dipole separation. In a previous work [4], an analytical result

$$\mu = \mu_0 \exp\left[-\hat{\sigma}^2 + 2\hat{\sigma}\sqrt{eaE/kT}\right] \tag{3}$$

formally equivalent to Eq. 1 was derived for carriers diffusing along one spatial dimension through a medium with 3D correlations as in Eq. 2. In this expression, $\hat{\sigma} = \sigma/kT$ is the energetic width of the DOS relative to the thermal energy. This same behavior also occurs in 3D simulations [5]. Moreover, recent studies suggest that this mechanism for producing PF behavior is stable under less correlated sources of disorder than those that arise from dipoles [6,7]. A numerical characterization of the results from extensive 3D numerical simulations on correlated disorder models (CDM's) that take into account the spatial correlations associated with dipolar media have led to the following recently proposed empirical relation

$$\mu = \mu_0 \exp\left[-\left(\frac{3\hat{\sigma}}{5}\right)^2 + C_0\left(\hat{\sigma}^{3/2} - \Gamma\right)\sqrt{\frac{eaE}{\sigma}}\right] \tag{4}$$

describing nondispersive transport in correlated media, with simulation-determined parameters $C_0 = 0.78$, and $\Gamma = 1.97$. As pointed out in [1], the parameter μ_0 in Eq. 4 may have additional temperature dependence due to other less correlated sources of energetic disorder or polaron effects.

The empirical relation in Eq. 4 was established in Ref. 1 on the basis of simulations performed on regular ordered lattices possessing energetic disorder of the type that arises in dipolar media. Experience with the much-utilized Gaussian Disorder Model (GDM) of Bässler, Borsenberger, and coworkers [11], which differs from the CDM of recent study in that it does not include these energetic correlations, leads to the general theoretical expectation that the parameter Γ may in fact characterize the degree of geometrical disorder and thus should depend upon transport site concentration and morphological factors such as the size and shape of dopant and host molecules. As of yet, however, the specific dependence of the geometrical disorder parameter Γ on the mobility has not been extensively studied. In this paper we wish to present a preliminary,
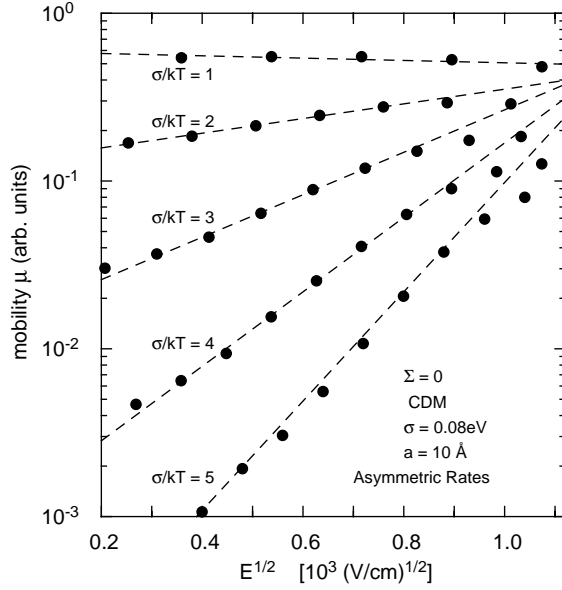
Figure 1: *Field dependent mobility for correlated disorder model with no spatial disorder.*

but systematic study of the effects of geometrical disorder on transport in energetically correlated random media. To this end we provide in the next section a description of our basic model and computational approach, along with the major results of the investigation. The last section contains a discussion.

Model and Computational Approach

We consider a simple extension of the CDM of Ref. 1 which is intended to include effects of geometrical disorder in a way parallel to that implemented in the GDM of Bässler and coworkers [11]. Specifically, we consider a model in which transport occurs among the sites of a simple cubic lattice. On each site of this lattice we place a randomly oriented electric dipole of fixed magnitude $p = |\vec{p}_m|$. The energy of a carrier when at lattice site m then develops due its interaction with the dipoles on all such sites except the one on which it resides, i.e.,

$$u_m = -\sum_{n \neq m} \frac{e\vec{p}_n \cdot (\vec{r}_n - \vec{r}_m)}{4\pi\varepsilon \, |\vec{r}_n - \vec{r}_m|^3}, \qquad (5)$$

where e is the electronic charge and ε the dielectric permittivity of the medium. This assignment generates a Gaussian-like DOS with the right kind of spatial correlation, and

having an approximate width

$$\sigma = \sqrt{\langle u_m^2 \rangle} = 2.35 \frac{ep}{\varepsilon a_0^2} \qquad (6)$$

The hopping rate between two sites on the lattice we take to have the following "Miller-Abrahams" form

$$W_{n,m} = \nu_0 \exp\left[-\frac{\Gamma_{nm} R_{nm}}{a} - \frac{\Delta_{nm} + |\Delta_{nm}|}{2kT} \right], \quad (7)$$

where $\Delta_{nm} = u_n - u_m - eEr\cos\theta$ is the energy difference between the two sites, altered in the presence of an electric field, R_{nm} is the intersite separation, and $\Gamma_{nm} = \Gamma_n + \Gamma_m$, which represents the geometrical disorder, is taken to be the sum of dimensionless independent random variables assigned to each site from a Gaussian distribution of width Σ. The question we are interested in studying is how the field dependence of the mobility depends upon the strength Σ of the geometrical disorder, in the presence of the type of correlations that have been shown to give rise to the Poole-Frenkel behavior.

To compute the mobility, we have performed numerical calculations to solve the steady-state equations of motion

$$\frac{d\rho_n}{dt} = 0 = \sum_m \left(W_{n,m}\rho_m - W_{m,n}\rho_n \right) \qquad (8)$$

for a periodically-repeated cubic sample containing $N = 50^3$ sites using a simple relaxation method. From the steady-state occupation probabilities ρ_n the drift mobility

$$\mu = \frac{1}{E} \sum_{n,m} W_{m,n} R_{m,n} \rho_n \qquad (9)$$

is then straightforward to compute.

Results and Discussion

In the calculations presented in Figs. 1-5 we have adjusted the parameters of the dipole field to generate a DOS with a width $\sigma = 80$ meV, with different curves (data sets) in each figure corresponding to different temperatures as described by the dimensionless parameter $\hat{\sigma} = \sigma/kT$. In Fig. 1 the field dependent mobility is presented for an ordered system having no spatial disorder; filled circles indicate numerical calculations as described earlier and dashed lines represent linear fits to each data set. The curves in this figure display the robust Poole-Frenkel mobility observed earlier for the correlated disorder model characterized by Eq. 4 with a value $\Gamma \approx 1.97$ (which corresponds to a vanishing Poole-Frenkel slope at a temperature for which $\sigma/kT \approx \Gamma^{2/3} \approx 1.6$). In Figs. 2-5, similar data is presented for systems with spatial disorder parameters taking the values $\Sigma = 1, 2, 3$, and 4.
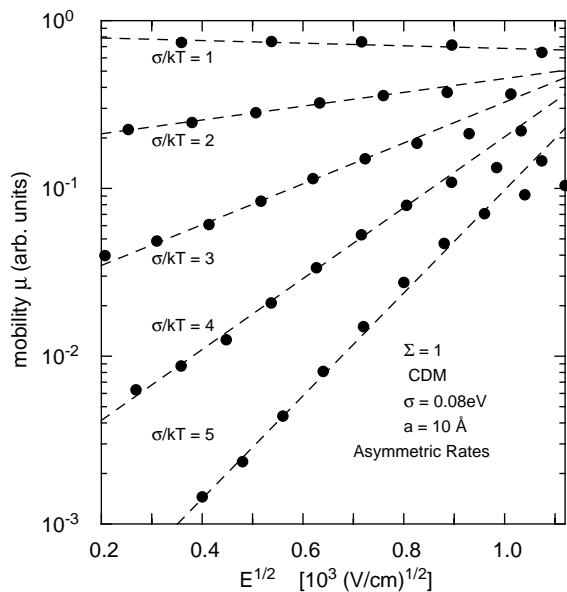
Figure 2: Field dependent mobility for correlated disorder model with spatial disorder parameter $\Sigma = 1$.
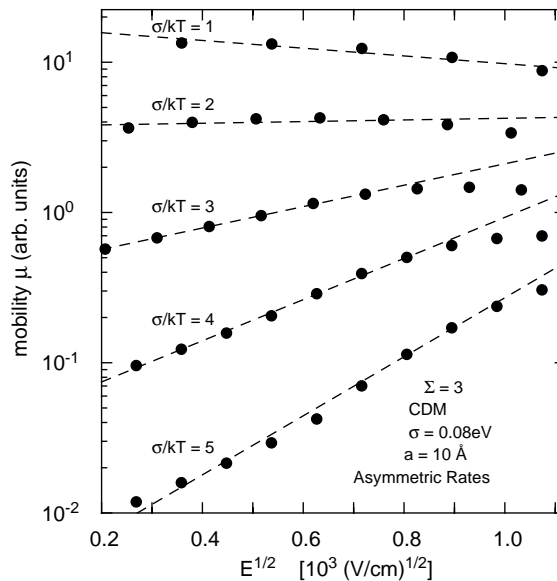

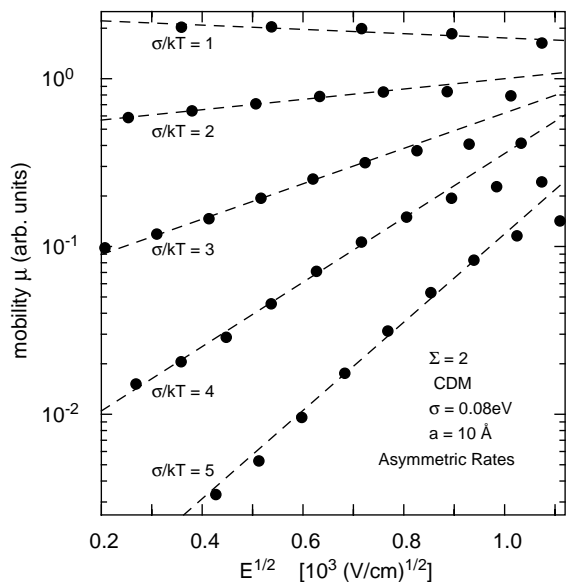*Figure 4*: Field dependent mobility for correlated disorder model with spatial disorder parameter $\Sigma = 3$.

Figure 3: Field dependent mobility for correlated disorder model with spatial disorder parameter $\Sigma = 2$.
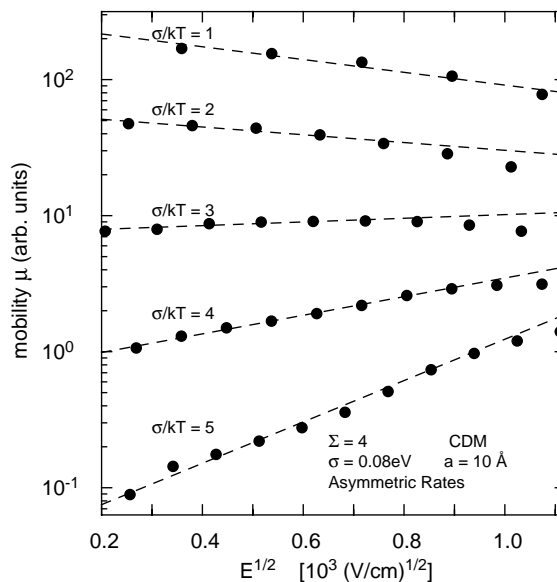

Figure 5: Field dependent mobility for correlated disorder model with spatial disorder parameter as $\Sigma = 4$.
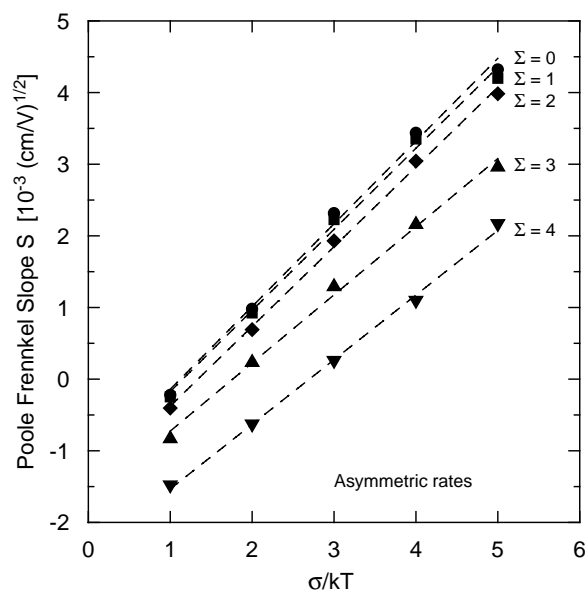
Figure 6: *Poole-Frenkel slope S for correlated disorder model as a function of the energetic width σ/kT.*

As can be seen from the curves in Figs. 2-5, there is very little change in the field dependent mobility for small values of the geometrical disorder parameter ($\Sigma \leq 1$). Significant change is beginning to be observed for $\Sigma \approx 2$, and a noticeable reduction of the slope of each curve relative to those appearing in Fig. 1 appears in Fig. 4 and Fig. 5, corresponding to spatial disorder parameters $\Sigma = 3$ and $\Sigma = 4$.

This behavior is reminiscent of that observed earlier for the GDM of Bässler and coworkers [11]. Important quantitative differences exist, however, between the present set of calculations performed with correlated energetic disorder than and the uncorrelated situation studied within the context of the GDM. In particular, in the GDM it has been empirically observed that the Poole-Frenkel slope $S = \partial \ln (\mu/\mu_0) /\partial \sqrt{E}$ in the high field regime is a quadratic function of the energetic width σ with a coefficient C_0 that is independent of the spatial disorder parameter, i.e., $S = C_0 \left(\hat{\sigma}^2 - \Sigma^2 \right)$. In the correlated disorder model of the present study, however, the Poole-Frenkel slope is empirically found to be a linear function of the dipolar component of the width σ, which is the leading dependence of the slope associated with the empirical relation in Eq. 4. This behavior is demonstrated in Fig. 6, which contains a plot of the Poole-Frenkel slope S associated with the linear fits to the data appearing in Figs.1-5.

The results of these preliminary calculations indicate

that much of the intuition regarding the effects of energetic disorder developed from extensive studies of the Gaussian Disorder Model may be qualitatively applied to characterize the predictions of the Correlated Disorder Model of recent study. A more complete quantitative characterization of the effects of geometric disorder on the mobility of the CDM, including the effects of different types of hopping rates (e.g., Marcus or "small polaron" type rates), and other more realistic models of geometrical disorder will be presented in a future publication. This work is supported by the National Science Foundation. The author is grateful for stimulating discussions and ongoing collaboration with D.H. Dunlap, V.M. Kenkre, and S.V. Novikov.

Biography

Paul Parris is professor of theoretical physics at the University of Missouri, in Rolla Missouri. He received his B.S. degree in Physics from George Mason University in 1980 and a Ph.D. in physics from the University of Rochester in 1984. He is an expert in the field of hopping transport in disordered systems and has worked extensively in recent years on the problem of photoinjected charge transport in disordered organic materials, with applications to xerographic photoreceptors and organic electronic devices.

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