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## Charge-Dipole Model for the Universal Field Dependence of Mobilities in Molecularly Doped Polymers

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Using the general result that the mobility  $\mu$  of charge carriers driven in a spatially correlated random potential by an electric field  $E$  can be expressed in terms of the Laplace transform of a particular correlation function related to the random potential, we demonstrate that the exponential dependence of  $\mu$  on  $\sqrt{E}$  universally observed in molecularly doped polymers arises naturally from the interaction of charge carriers with randomly distributed permanent dipoles. [S0031-9007(96)00689-8]

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High-field time-of-flight experiments have been used for over two decades to characterize carrier mobilities in photoexcited molecularly doped polymers and amorphous molecular glasses [1–3]. Numerous measurements over a large range of fields  $E$  and temperatures  $T$  have established that, in many materials, the carrier mobility  $\mu$  exhibits a universal Poole-Frenkel behavior [4]

$$\mu = \mu_0 \exp\left[-\frac{\Theta}{kT}\right] \exp[\gamma\sqrt{E}], \quad (1)$$

where  $\mu_0$  is a temperature independent prefactor and  $k$  is Boltzmann's constant. In a particular form of this phenomenological expression proposed by Gill [5], the activation energy  $\Theta$  is temperature independent, and the Poole-Frenkel factor is written  $\gamma = B(\beta - \beta_0)$ , where  $\beta = 1/kT$ , and  $B$  and  $\beta_0 = 1/kT_0$  are constants. In a second form, motivated by extensive numerical simulations on the Gaussian disorder model (GDM) of Bäessler and co-workers [2],  $\Theta/kT = (2\sigma/3kT)^2$ , and  $\gamma = C(\beta^2\sigma^2 - \Sigma^2)$ , where  $\sigma$  is the width of the energetic disorder, and  $C$  and  $\Sigma$  are constants. Many recent theoretical attempts to explain this observed proportionality between  $\ln\mu$  and  $\sqrt{E}$  have focused on the role played by spatial and energetic disorder [2,6–8]. The GDM, for example, describes transport as a biased random walk among dopant molecules with Gaussian-distributed random site energies [2]. Of the various mechanisms proposed as the source of this disorder, it has been shown that the interaction of charge carriers with permanent dipoles (located on either dopant or host molecules) can give rise to a Gaussian-like density of states of the type assumed in the GDM [9,10]. Considerable data establishing a relationship between carrier mobilities and group dipole moments of molecular constituents support this view of charge-dipole interactions as the source of energetic disorder in these systems [9,11–15].

Unfortunately, although the standard GDM satisfactorily explains many features of experiment, such as the time-of-flight transients, it displays a field dependence similar to (1) only in a relatively narrow range and only at large fields ( $E > 10^5$  V/cm). Indeed, a general feature of

Monte Carlo simulations [2,6] and other numerical work [8] on this problem is a significant regime at low fields in which the field dependence is much weaker than that described by (1). In experiments, by contrast, the linear dependence of  $\ln\mu$  on  $\sqrt{E}$  often [16] persists down to the lowest fields probed ( $8 \times 10^3$  V/cm).

In this Letter we develop an analytical theory for the field dependence based upon an idea introduced recently by Gartstein and Conwell [17]. We show, using a relation for the drift velocity that is exact for motion in one dimension, how the mobility for charge carriers moving in a spatially correlated random potential can be expressed in terms of the Laplace transform of a particular correlation function related to the random energy field in which the carriers move. Using this relationship we then demonstrate that an exponential dependence of the mobility on  $\sqrt{E}$  at low fields arises naturally from fluctuations in site energies that arise from the interaction of charge carriers with fixed permanent dipoles. As such, our calculation represents the first analytical theory of transport in disordered systems to explain in a simple way the ubiquitous behavior observed in this class of materials.

As pointed out by a number of workers [15,17], the charge-dipole interactions often identified as the source of energetic disorder are of sufficient range to lead to significant positive correlations among the energies of neighboring hopping sites. Gartstein and Conwell [17] showed that finite-range correlations imposed upon the standard GDM can push the regime over which the field dependence is described by (1) to lower fields, in better agreement with experiment. Physically, a strong field dependence should occur [17] when the potential drop  $F = eE\ell$  across a relevant length of the system is comparable to  $kT$ . With uncorrelated energies the only length scale in the problem is the mean interdopant spacing  $\ell = \rho$ . Correlations introduce a new length scale, namely, the correlation length associated with the energetic disorder, thereby decreasing the critical field.

To analytically pursue this idea we consider a carrier migrating across a sample of width  $L = N\rho$  in the

presence of an electric field  $E$ . We assume this motion can be described by a biased random walk through nearest-neighbor rates among dopant molecules having random but correlated Gaussian energies  $u_n$  of zero mean and width  $\sigma > kT$ . Focusing only on those molecules along which the particle drifts, we write

$$\frac{dP_n}{dt} = - (W_{n-1,n} + W_{n+1,n})P_n + W_{n,n-1}P_{n-1} + W_{n,n+1}P_{n+1}, \quad (2)$$

for the probability  $P_n(t)$  of finding the particle at the  $n$ th site along this path. For simplicity we assume a symmetric detailed balance relation  $W_{n\pm 1,n} = \nu_0 \exp[-\frac{1}{2}\beta(u_{n\pm 1} - u_n \mp F)]$ , where  $F = eE\rho$  is the energy change induced between two sites by the field [18]. The steady-state drift velocity can be written exactly using a general solution due to Derrida [19], which for the hopping rates assumed above takes the form

$$v = \frac{\nu_0 \rho e^{\beta F/2} (1 - e^{-\beta NF})}{\frac{1}{N} \sum_{m=0}^{N-1} e^{-m\beta F} \sum_{n=1}^N e^{-\beta u_n} e^{\beta u_{n+m}} e^{\beta \delta_{n+m}}}, \quad (3)$$

where  $2\delta_n = u_{n+1} - u_n$ . The exponential  $e^{-\beta NF}$  in the numerator is negligible, since  $\beta NF$  is the ratio of the potential drop across the sample to the mean thermal energy. In the limit that the site-energy difference is small compared to  $kT$  (as occurs when the energies of neighboring sites are strongly correlated) we ignore factors involving  $\delta_{n+m}$ , so that

$$v = \frac{\nu_0 \rho e^{\beta F/2}}{\sum_{m=0}^{N-1} e^{-m\beta F} \langle e^{-\beta u_n} e^{\beta u_{n+m}} \rangle}, \quad (4)$$

where we have identified the sum

$$\langle e^{-\beta u_n} e^{\beta u_{n+m}} \rangle = \frac{1}{N} \sum_{n=1}^N e^{-\beta u_n} e^{\beta u_{n+m}} \quad (5)$$

over the macroscopic crystal ( $N \rightarrow \infty$ ) with the ensemble average of the associated exponentials. For  $\beta F < 1$ , we can approximate  $e^{\beta F/2}$  by unity, the remaining sum in the denominator can be replaced by an integral, and the field dependent mobility

$$\mu = v/E = \frac{\mu_0}{\epsilon \int_0^\infty dy e^{-\epsilon y} \langle e^{-\beta U(0)} e^{\beta U(y)} \rangle} \quad (6)$$

involves the Laplace transform of the correlation function (5), in which  $U(y)$  represents the zero-field energy of a site at  $y$ , the Laplace variable  $\epsilon = \beta eE$  represents the applied field, and  $\mu_0 = \beta \nu_0 e \rho^2$ . For  $\delta_n$ ,  $F < kT$ , Eq. (6) is independent of the particular way in which the detailed balance condition for the hopping rates is implemented. We note in passing that (6) has considerable generality and applicability and can be derived from the Fokker-

Planck equation [20] for a particle diffusing in a continuous random potential  $U(y)$ .

We now address the correlation function  $\langle e^{-\beta U(0)} \times e^{\beta U(y)} \rangle = \langle e^{\beta \Delta_y} \rangle$  appearing in (6), where  $\Delta_y = U(y) - U(0)$  represents the spatially fluctuating energy difference between two sites separated by a displacement  $y$ . This quantity will display a characteristic  $y$  dependence that depends upon the correlations. Making the same Gaussian approximation which forms the basis for the GDM [2], we take the energy difference  $\Delta_y$  to have zero mean, and the required correlation function to have the form

$$\langle e^{\beta \Delta_y} \rangle = e^{\frac{1}{2}\beta^2 \langle \Delta_y^2 \rangle} \quad (7)$$

involving the variance  $\langle \Delta_y^2 \rangle$ . Note that, as  $y \rightarrow 0$ , the quantity  $\Delta_y^2$  vanishes, and  $\langle e^{\beta \Delta_y} \rangle \rightarrow 1$ . Moreover, for large  $y$ , the quantities  $U(0)$  and  $U(y)$  become independent, and  $\langle \Delta_y^2 \rangle \rightarrow 2\sigma^2$ , where  $\sigma^2$  is the variance of  $U$ . The correlation function (7) is, therefore, bounded by the relation  $1 \leq \langle e^{\beta \Delta_y} \rangle \leq e^{\beta^2 \sigma^2}$ . This bound can be used to determine limiting forms for the mobility predicted by (6). For example, using Tauberian theorems for the Laplace transform we find a low field mobility,  $\lim_{\epsilon \rightarrow 0} \mu = \mu_0 e^{-\beta^2 \sigma^2}$ , which is exponentially suppressed by the energetic disorder. On the other hand, because (6) has been derived under the assumption of low electric fields, its high-field limit,  $\lim_{\epsilon \rightarrow \infty} \mu = \mu_0$ , displays the behavior of a system with no disorder, rather than that appropriate to (2). These bounds are useful, however, in that they determine the maximum variation of  $\mu$  with  $E$  which can be attributed to correlated Gaussian disorder. The large changes observed experimentally in the mobility, e.g., suggests considerable energetic disorder,  $\beta^2 \sigma^2 \gg 1$ .

To determine the actual field dependence we now perform an explicit calculation of  $\langle \Delta_y^2 \rangle$ . To this end we consider the potential energy

$$U(\vec{r}_0) = - \sum_m \vec{p}_m \cdot \vec{E}_{\vec{r}_0}(\vec{r}_m) = - \int d^3 r \vec{p}(\vec{r}) \cdot \vec{E}_{\vec{r}_0}(\vec{r}) \quad (8)$$

of a charge  $e$  located at a point  $\vec{r}_0$  in a medium containing a distribution of randomly oriented but identical point dipoles  $\vec{p}_m$ . In this expression,

$$\vec{E}_{\vec{r}_0}(\vec{r}) = \frac{e}{4\pi\epsilon} \frac{\vec{r} - \vec{r}_0}{|\vec{r} - \vec{r}_0|^3} \quad (9)$$

is the field at  $\vec{r}$  due to the charge at  $\vec{r}_0$ , and  $\vec{p}(\vec{r}) = \sum_m \vec{p}_m \delta(\vec{r} - \vec{r}_m)$  is a fluctuating polarization density. We exclude the interaction energy of the charge with the molecule on which it is sitting, which will be the same for all similar dopant molecules, by excluding from the region of integration a volume of some radius  $a$  comparable to the size of a molecule. Equivalently, we can view the field in (9) as arising from a uniformly charged sphere of radius  $a$ , inside of which the field vanishes. The energy difference

$\Delta_y = U(\vec{y}) - U(0)$  between two points separated by an arbitrary displacement  $\vec{y}$  then becomes

$$\Delta_y = \int d^3r \vec{p}(\vec{r}) \cdot \vec{E}(\vec{r}), \quad (10)$$

where  $\vec{E}(\vec{r}) = \vec{E}_0(\vec{r}) - E_y(\vec{r})$  can be interpreted as the field due to a positive sphere of radius  $a$  located at the origin and a negative sphere located at  $\vec{y}$ . This interpretation is useful for evaluating  $\langle \Delta_y^2 \rangle$ , which may now be written as the double integral,

$$\langle \Delta_y^2 \rangle = \int d^3r \int d^3r' \vec{E}(\vec{r}) \cdot \langle \vec{p}(\vec{r}) \vec{p}(\vec{r}') \rangle \cdot E(\vec{r}'). \quad (11)$$

Evaluation of the average in (11) over the random orientations and positions of the independently distributed dipoles is straightforward, and yields  $\langle \vec{p}(\vec{r}) \vec{p}(\vec{r}') \rangle = \frac{1}{3} p^2 n_0 \delta(\vec{r} - \vec{r}') \mathbf{1}$ , where  $p = |\vec{p}_m|$ ,  $n_0$  is the average dipole density, and  $\mathbf{1}$  represents the unit tensor of second rank. With this result, (11) can be expressed in the form

$$\langle \Delta_y^2 \rangle = \frac{2p^2 n_0}{3\epsilon} \int d^3r \frac{1}{2} \epsilon |\vec{E}(\vec{r})|^2. \quad (12)$$

The integral in (12) is the energy required to set up the field  $\vec{E}(\vec{r}) = \vec{E}_{\vec{r}_0}(\vec{r}) - E_{\vec{y}}(\vec{r})$  of two oppositely charged spheres separated by a distance  $y$ . Provided the two spheres do not overlap,

$$\langle \Delta_y^2 \rangle = \frac{2p^2 n_0}{3\epsilon} \left( \frac{e^2}{4\pi\epsilon a} - \frac{e^2}{4\pi\epsilon y} \right) = 2\sigma^2 \left( 1 - \frac{a}{y} \right), \quad (13)$$

where  $\sigma = (e^2 p^2 n_0 / 12\pi\epsilon^2 a)^{1/2}$ . Thus, for  $y > 2a$ , the correlation function (7) takes the form

$$\langle e^{\beta\Delta_y} \rangle = \exp \left[ \beta^2 \sigma^2 \left( 1 - \frac{a}{y} \right) \right]. \quad (14)$$

We now substitute (14) into (6), evaluate the integral [21], and obtain the mobility

$$\mu = \frac{\mu_0 e^{-\beta^2 \sigma^2}}{2\beta\sigma(\beta e E a)^{1/2} K_1[2\beta\sigma(\beta e E a)^{1/2}]}, \quad (15)$$

where  $K_1(z)$  is the first-order modified Bessel function of the third kind. In writing (15) we have neglected a correction term which accounts for the domain  $y < 2a$  in which the function (14) should be set equal to zero (to avoid contributions from overlapping molecules). For the large values of disorder required, i.e.,  $\beta^2 \sigma^2 \gg 1$ , the correlation function (14) drops exponentially to zero in this region, making the correction negligible, independent of  $E$ . Finally, we note that in the limit of sufficiently large disorder,  $2\beta\sigma(\beta e E a)^{1/2} > 1$ , the Bessel function in (15) is well represented by its asymptotic expansion

[21]  $K_1(z) \sim \sqrt{\pi/2z} \exp(-z)$ , leaving a mobility

$$\mu = \mu_0(E) \exp(-\beta^2 \sigma^2) \exp(2\beta\sigma\sqrt{\beta e E a}), \quad (16)$$

which displays the field dependence commonly observed in molecularly doped polymers. In this expression,  $\mu_0(E) = \mu_0(\pi\beta\sigma\sqrt{\beta e E a})^{1/2}$  is a prefactor which is algebraic in the field and is, therefore, slowly varying relative to the exponential factors. The field independent factor  $\exp(-\beta^2 \sigma^2)$  supports the quadratic temperature dependence associated with the GDM, but omits the factor  $2/3$  that appears in that model.

Equations (15) and (16) are exact asymptotic results for transport in one dimension for low fields ( $\beta e E a < 1$ ) and large disorder and constitute the main formal results of the present Letter. Observation of such a regime requires, according to this result, enough energetic disorder so that  $2\beta\sigma > (\beta e E a)^{-1/2}$ . At higher fields, the mobility will depend more critically on the actual form of the microscopic hopping rate, and on the way in which detailed balance is implemented [18]. Our derivation emphasizes the fact that site-energy correlations associated with charge-dipole interactions in three dimensions are algebraic [15], and thus do not have a well-defined correlation length of the type numerically investigated by Gartstein and Conwell [17]. It is this algebraic structure that is responsible for the observed (algebraic) universal field dependence of the mobility. Similarly, one can show that a correlation function which decays with distance as  $y^{-p}$  leads to an exponential dependence of the mobility on  $E^\nu$  with  $\nu = p/(p+1)$ . Calculations show, e.g., that an induced charge-dipole interaction ( $\sim 1/r^4$ ) should lead to an exponential dependence of  $\mu$  on  $E^{5/6}$ . There are good reasons to believe that (16) will remain valid in higher dimensions. In the absence of energetic disorder, the percolating transport path followed by a carrier will be determined largely by spatial fluctuations. When smoothly varying energetic disorder is superimposed upon this structure, this low dimensional path need not change. A carrier will then traverse all barriers on this predetermined path, a tendency which is reflected in the structure of our result (6).

The functional form (16) is in obvious agreement regarding the field dependence of the mobility. We now ask whether reasonable choices for the parameters of the charge-dipole model lead to empirical coefficients in agreement with those measured experimentally. To check for quantitative agreement, we have fit our full expression (15) to the field dependent mobility of 50% DEH-doped polycarbonate [16], which exhibits Poole-Frenkel behavior over a wide range of field from  $8 \times 10^3$  V/cm to  $2 \times 10^6$  V/cm. Over this range the mobility increases at room temperature by 3 orders of magnitude. To obtain this variation, it follows from the high- and low-field limits already established that the quantity  $\exp(\beta^2 \sigma^2)$  must be at least of order  $10^3$ , and therefore the width  $\sigma$  of the energetic disorder must be at least  $\sigma = kT\sqrt{3 \ln 10} = 70$  meV.

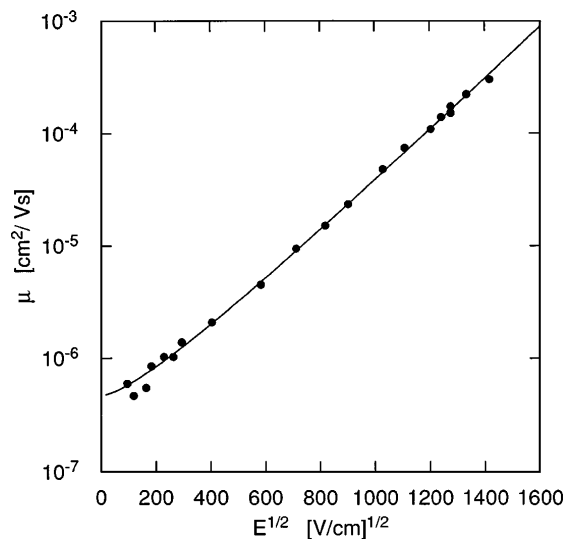


FIG. 1. Solid curve is a fit of Eq. (15) to measured field-dependent mobility  $\mu(E)$  for 50% DEH-doped polycarbonate (solid symbols), taken from Ref. [16]. See text for description and values of fitting parameters.

An excellent fit, shown in Fig. 1, was obtained with  $\mu_0 = 7.2 \times 10^{-3} \text{ cm}^2/\text{Vs}$ ,  $a = 2.1 \text{ \AA}$ , and  $\sigma = 80 \text{ meV}$ .

We can relate these values to the parameters  $\Theta$ ,  $T_0$ , and  $B$  obtained in fits with the Gill form of (1) by expanding the exponents of Eq. (16) about a typical temperature  $T_R$  lying in the range  $T \approx 200\text{--}350 \text{ K}$  probed experimentally. Choosing  $T_R = 300 \text{ K} = 1/k\beta_R$  and expanding in powers of  $\beta - \beta_R$  we find  $\Theta = 2\beta_R\sigma^2 = 0.5 \text{ eV}$ ,  $T_0 = 3T_R = 900 \text{ K}$ , and  $B = 3\sigma\sqrt{\beta_R e a} = 3 \times 10^{-4} (e^2 \text{ V cm})^{1/2}$ . While the inferred compensation temperature  $T_0$  is too large by about a factor of 2, values inferred for  $\Theta$  and  $B$  are close to those measured [16] for DEH, and typical of molecularly doped polymers [3].

A similar analysis can be performed to relate the values obtained in our fit to the parameters  $\sigma_{\text{GDM}}$  and  $C$  which appear in the form of Eq. (1) that arises in the GDM of Bässler and co-workers. Since we have neglected effects due to geometrical or off-diagonal disorder in our derivation of (16), we compare our results with the simplified form of Bässler's expression in which  $\Sigma^2 = 0$ . An analysis using the standard GDM expression with no correlations would lead to an estimate of the energetic disorder  $\sigma_{\text{GDM}} = 3\sigma/2 = 120 \text{ meV}$ . Using this value and performing another Taylor series expansion, this time in powers of  $\beta^2 - \beta_R^2$ , we obtain the estimate  $C = \sqrt{4eakT_R/9\sigma^2} = 2 \times 10^{-4} (\text{cm/Vs})^{1/2}$ . Both of these values are typical of those inferred using the GDM [1].

Finally, it is also straightforward from our expression to extract information about the microscopic dipolar disorder through the variance  $\sigma$ , as given by the expression following (13). Taking  $\sigma = 80 \text{ meV}$ ,  $a = 2.1 \text{ \AA}$ ,  $n_0 = 10^{21} \text{ cm}^{-3}$ , and  $\epsilon = 3\epsilon_0$ , we obtain an estimate  $p = \sqrt{12\pi a/n_0}(\sigma\epsilon/e) = 0.4 e \text{ \AA} = 2 \text{ D}$ , of the dipole moment necessary to generate this level of disorder. This

value is typical of an organic polar molecule and consistent with earlier studies of the charge-dipole model [9].

In summary, we have analytically confirmed the idea that correlations arising from charge-dipole interactions should cause a significant field dependence of the mobility at lower fields, obtaining a mobility in quantitative agreement with what is observed in experiment. Ongoing work includes an investigation of the effects of general correlations on disordered transport, the consequences of higher dimensionality, and dispersive characteristics of time-of-flight transients in the presence of correlated disorder [20].

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