

## Charge Carrier Energy Disorder in Polar Amorphous Organic Thin Films

Conor Madigan and Vladimir Bulović\*

*Lab of Organic Optics and Electronics, Department of Electrical Engineering and Computer Science,  
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*

(Received 21 July 2006; published 20 November 2006)

We report Monte Carlo calculations of the charge carrier energy level disorder in polar amorphous organic solids arising from electrostatic interactions between polarizable molecular charge distributions. In contrast with previous reports in which the discrete molecular polarizabilities are modeled as a dielectric continuum having dielectric constant  $\epsilon$ , our calculations take account of the molecular-scale polarization inhomogeneity. We find that the previously reported  $1/\epsilon$  scaling rule underestimates the charge carrier energy level disorder by more than a factor of 2 for typical values of  $\epsilon$ . Such an underestimation strongly impacts the analysis of charge carrier transport in polar amorphous organic thin films, due to the strong dependence of the charge carrier mobility on the energy disorder.

DOI: [10.1103/PhysRevLett.97.216402](https://doi.org/10.1103/PhysRevLett.97.216402)

PACS numbers: 71.23.-k, 34.20.Gj, 71.20.Ps

Recent growth in organic electronics, driven by the development of a wide variety of devices including light emitting devices [1,2], solar cells [3], photodetectors [3], and thin film transistors [4], has highlighted charge transport in amorphous organic solids as a subject of not only fundamental but also immediate technological importance. It is now well understood that physical disorder in amorphous organic solids generates disorder in charge carrier state energies, and the distribution of these energies, also known as the density of states (DOS), plays a central role in controlling charge transport in such materials [5–7]. As a result, the calculation of this DOS has received considerable attention in the literature.

In previously reported DOS calculations for polar organic solids [8–10], the energy disorder arises from interactions between the charge carrier and the randomly oriented static molecular dipoles associated with each molecule in the vicinity of the charge carrier. The interaction is further subject to dielectric screening which reduces the interaction energies by a factor of  $1/\epsilon$ , where  $\epsilon$  is the dielectric constant of the material. Implicit in this approach is the assumption that one can replace the individual molecular polarizabilities with a continuous dielectric medium, an approach referred to generally as a dielectric continuum model (DCM). Although such an assumption significantly simplifies the computational complexity, in this Letter we show that it also significantly underestimates the charge carrier energy disorder for typical  $\epsilon$ . In our calculation of the charge carrier DOS we model the charge distribution of each molecule as explicitly polarizable, thereby eliminating the need to assume a continuous dielectric medium. We analyze the impact of molecular polarization on the energy disorder (as represented by the standard deviation of the DOS,  $\sigma$ ) and find that it does *not* scale as  $1/\epsilon$ .

In obtaining the DOS, we perform calculations of the total electrostatic interaction energy,  $E^{\text{int}}$ , of a particular molecular system before and after introducing a charge

carrier on one molecule in the system. The energy required to form this charged molecular state within the system is then given by the sum of the change in the total electrostatic interaction energy,  $\Delta E^{\text{int}}$ , and the change in the internal electronic energy,  $\Delta E_0$ , of the charged molecule. Assuming the molecules in the system are all of the same type,  $\Delta E_0$  is a constant for every molecule, and the shape of the DOS is entirely determined by the distribution of  $\Delta E^{\text{int}}$  values. To calculate  $\Delta E^{\text{int}}$ , we employ conventional methods to model the polar molecular charge distributions: each molecule is described by a point charge and dipole moment, and to simulate molecular polarization, the total dipole moment includes an induced dipole moment of  $\alpha \vec{F}$  where  $\alpha$  is the molecular polarizability (assumed for simplicity to be isotropic) and  $\vec{F}$  is the local field at the site of the molecule [11].

For a system of  $N$  molecules, with the index  $A$  denoting the “active” molecule having the extra charge,  $E^{\text{int}}$  is given by

$$E^{\text{int}} = -Q_A \sum_{i \neq A}^N \frac{\vec{p}_i \cdot \hat{r}_{iA}}{r_{iA}^2} - \sum_i^N \sum_{j>i}^N \vec{p}_i \cdot \frac{3(\vec{p}_j \cdot \hat{r}_{ij})\hat{r}_{ij} - \vec{p}_j}{r_{ij}^3} + \frac{1}{2} \sum_i^N \alpha_i F_i^2, \quad (1)$$

where  $Q_i$ ,  $\vec{F}_i$ ,  $\alpha_i$ ,  $\vec{p}_i$ , and  $\vec{r}_i$  are, respectively, the charge, local field, polarizability, total dipole moment, and position of the  $i$ th molecule,  $\vec{r}_{ij} \equiv \vec{r}_i - \vec{r}_j$ , and  $\hat{r}_{ij}$  denotes the unit vector parallel to  $\vec{r}_{ij}$ . The  $\vec{p}_i$  are obtained by summing the static dipole moment and the induced dipole moment of each molecule:

$$\vec{p}_i = \vec{\mu}_i + \alpha_i \vec{F}_i. \quad (2)$$

The  $\vec{F}_i$  are obtained by summing the contribution to the local field at each molecule from each of the surrounding molecules:

$$\vec{F}_i = \sum_{j \neq i}^N \left[ \frac{Q_j \hat{r}_{ij}}{r_{ij}^2} + \frac{3(\vec{p}_j \cdot \hat{r}_{ij}) \hat{r}_{ij} - \vec{p}_j}{r_{ij}^3} \right]. \quad (3)$$

The expressions governing the  $\vec{p}_i$  and  $\vec{F}_i$  form a system of  $2N$  coupled linear equations in  $2N$  unknowns. The value of  $\Delta E^{\text{int}}$  is then given by  $E_f^{\text{int}} - E_i^{\text{int}}$ , where  $E_f^{\text{int}}$  and  $E_i^{\text{int}}$  are the total interaction energies in the charged final and neutral initial states, respectively.

Note that in the limit of  $\alpha \rightarrow 0$ , our model becomes equivalent to previously reported charge carrier DOS calculations [8,10], so long as we scale the resulting  $E^{\text{int}}$  values by  $1/\epsilon$ . In this approach, referred to here as the uniform DCM (UDCM), the charge distributions are entirely static, and the  $\vec{F}_i$  are trivially obtained by replacing the  $\vec{p}_j$  with  $\vec{\mu}_j$ . Furthermore, since the interactions between the uncharged molecules remain unchanged by the presence of the charged state, they can be dropped from the calculation of  $\Delta E^{\text{int}}$ , so that

$$\Delta E^{\text{int}} = -\frac{1}{\epsilon} Q_A \sum_{i \neq A}^N \frac{\vec{\mu}_i \cdot \hat{r}_{iA}}{r_{iA}^2}. \quad (4)$$

The DOS obtained under the UDCM was first reported by Dieckmann *et al.* [8]. Using Monte Carlo calculations on a cubic lattice of  $50 \times 50 \times 50$  sites subject to periodic boundary conditions, the authors demonstrated that when every site contains a randomly oriented static dipole of magnitude  $\mu$ , the DOS,  $g(E)$ , is Gaussian, i.e.,  $g(E) \propto \exp[-E^2/2\sigma^2]$ , where  $\sigma$  is the standard deviation of the distribution. Young [10] subsequently reported an analytic calculation in which the Gaussian form of the DOS was confirmed, with  $\sigma$  given by

$$\sigma[\text{eV}] = \frac{1}{\epsilon} \frac{7.07}{(D_{\text{site}}[\text{\AA}])^2} \mu[D], \quad (5)$$

where the nonstandard units of this expression are denoted within the brackets [12].

We performed Monte Carlo (MC) calculations in which  $\alpha = 0$  (i.e.,  $\epsilon = 1$ ), using cubic lattices of  $L \times L \times L$  sites with lattice constant  $D_{\text{site}}$  in which each site has a randomly oriented static dipole moment of magnitude  $\mu$ . Periodic boundary conditions are employed to simulate an infinite lattice, and only interactions between sites separated by a distance less than or equal to  $R_{\text{int}}$  are included in the calculation, with the restriction that  $R_{\text{int}} < LD_{\text{site}}/2$  to avoid double counting of interactions between the same pair of sites. We have investigated the impact of  $L$  and  $R_{\text{int}}$  on the calculation, and find that the results are insensitive to further increases in  $L$  and  $R_{\text{int}}$  for  $L \geq 40$  and  $R_{\text{int}} \geq 19.9D_{\text{site}}$ . Values of  $L = 40$  and  $R_{\text{int}} = 19.9D_{\text{site}}$  yield the expected Gaussian DOS with  $\sigma$  equal to the value predicted by Young [10].

To perform calculations with nonzero  $\alpha$  we employ what we refer to as the matrix decomposition (MD) method to solve for the fields and dipoles. In this procedure, we

rewrite the problem in the form of a matrix equation:

$$\mathbf{M}_3 \mathbf{F} = \mathbf{M}_1 \mathbf{Q} + \mathbf{M}_2 \boldsymbol{\mu}, \quad (6)$$

where

$$\mathbf{Q} \equiv \begin{bmatrix} Q_1 \\ Q_1 \\ Q_1 \\ \vdots \\ Q_N \\ Q_N \\ Q_N \end{bmatrix}, \quad \boldsymbol{\mu} \equiv \begin{bmatrix} \mu_{1,x} \\ \mu_{1,y} \\ \mu_{1,z} \\ \vdots \\ \mu_{N,x} \\ \mu_{N,y} \\ \mu_{N,z} \end{bmatrix}, \quad \mathbf{F} \equiv \begin{bmatrix} F_{1,x} \\ F_{1,y} \\ F_{1,z} \\ \vdots \\ F_{N,x} \\ F_{N,y} \\ F_{N,z} \end{bmatrix},$$

using the notation that  $\vec{F}_i = F_{i,x}\hat{x} + F_{i,y}\hat{y} + F_{i,z}\hat{z}$  and similarly  $\vec{\mu}_i = \mu_{i,x}\hat{x} + \mu_{i,y}\hat{y} + \mu_{i,z}\hat{z}$ . These matrices are obtained from Eqs. (2) and (3). To illustrate, the explicit form of  $\mathbf{M}_2$  is reproduced here:

$$\mathbf{M}_2 = \frac{\hat{r}_{ij}}{r_{ij}^3} \cdot \begin{bmatrix} \mathbf{m}_2^{1,1} & \cdots & \mathbf{m}_2^{1,N} \\ \vdots & \ddots & \vdots \\ \mathbf{m}_2^{N,1} & & \mathbf{m}_2^{N,N} \end{bmatrix},$$

where the  $\mathbf{m}_2^{i,j}$  represent  $3 \times 3$  matrices given by the null matrix if  $i = j$ , and

$$\mathbf{m}_2^{i,j} = \begin{bmatrix} \hat{x}(3\hat{r}_{ij} \cdot \hat{x} - 1) & \hat{x}(3\hat{r}_{ij} \cdot \hat{y}) & \hat{x}(3\hat{r}_{ij} \cdot \hat{z}) \\ \hat{y}(3\hat{r}_{ij} \cdot \hat{x}) & \hat{y}(3\hat{r}_{ij} \cdot \hat{y} - 1) & \hat{y}(3\hat{r}_{ij} \cdot \hat{z}) \\ \hat{z}(3\hat{r}_{ij} \cdot \hat{x}) & \hat{z}(3\hat{r}_{ij} \cdot \hat{y}) & \hat{z}(3\hat{r}_{ij} \cdot \hat{z} - 1) \end{bmatrix}$$

if  $i \neq j$ . Finally, we solve for  $\mathbf{F}$  by performing an in-place ‘‘lower-upper’’ triangular decomposition of  $\mathbf{M}_3$ , and applying this decomposition to the particular  $\mathbf{M}_1 \mathbf{Q} + \mathbf{M}_2 \boldsymbol{\mu}$  by sequential forward and backward substitution.

We find that only DOS calculations with relatively small  $L$  are practical due to time and memory constraints, and we employ  $L = 14$  and  $R_{\text{int}} = 6.9D_{\text{site}}$  in the following. Since these  $L$  and  $R_{\text{int}}$  are smaller than the optimal values suggested by our DOS calculations for static charge distributions, we investigated the error incurred by using such a small lattice. For static charge distributions, these parameters yield a Gaussian DOS with  $\sigma$  that is 8% smaller than the theoretical value [given by Eq. (5)]; thus the smaller lattice slightly underestimates the total disorder arising from the static dipoles in the system. In this Letter, however, our objective is to evaluate the *relative* impact of polarization on the disorder; thus we correct for this systematic underestimation of  $\sigma$  by normalizing the  $\sigma$  obtained with  $\alpha > 0$  to the  $\sigma$  obtained with  $\alpha = 0$  for the same  $L$  and  $R_{\text{int}}$ .

To evaluate the impact of the lattice size on *polarization* effects, we calculated for a range of  $L$  and  $R_{\text{int}}$  the polarization energy associated with introducing a dipole on a single site in a lattice with  $\mu = 0$  and nonzero  $\alpha$ . Since each site in such a lattice is identical to every other (because  $\mu = 0$  and the lattice is cubic), only a single site in a single lattice needs be analyzed, greatly reducing the com-

putation time [13]. We find that for  $L = 14$  and  $R_{\text{int}} = 6.9D_{\text{site}}$ , the polarization energy is within 0.2% of the fully converged energy, which is obtained for  $L = 30$  and  $R_{\text{int}} = 14.9D_{\text{site}}$  [14]. Since the randomly oriented dipoles are the sole source of charge carrier energy disorder in the lattices employed in this study, we conclude that  $L = 14$  and  $R_{\text{int}} = 6.9D_{\text{site}}$  are indeed adequate for analyzing the impact of polarization on the energy disorder.

With this  $L$  and  $R_{\text{int}}$  we performed DOS calculations for a range of  $\alpha$  and  $\mu$  values using the MD method. For each calculation  $D_{\text{site}} = 1$  nm. We use the Clausius-Mossotti equation to relate  $\alpha$  and  $\epsilon$ :

$$\alpha = \frac{\epsilon - 1}{\epsilon + 2} \frac{3}{4\pi} V_m, \quad (7)$$

where  $V_m$  is the molecular volume (here given by  $D_{\text{site}}^3$  in units of  $\text{cm}^3$ ). All of the reported results are averaged over 10 different randomly generated lattices. To reflect the typical range of molecular dipole moments, dielectric constants, and molecular densities encountered in polar amorphous organic materials, we computed the DOS for  $\mu \in \{1, 2, 6\}$  nm,  $D_{\text{site}} \in \{0.5, 1.0, 2.0\}$  nm, and  $\epsilon \in \{1, 2, 3, 4\}$ . In all cases the DOS is Gaussian to within the statistical uncertainty of the calculation. To describe the impact of polarization on the energy disorder we calculate the ratio  $\Phi(\epsilon) \equiv \sigma(\epsilon)/\sigma(\epsilon = 1)$ . This ratio gives the scaling of  $\sigma$  as a function of  $\epsilon$  relative to the  $\epsilon = 1$  value.

For each set of  $\mu$  and  $D_{\text{site}}$ , we find that  $\Phi(\epsilon)$  is the same to within the statistical uncertainty of the calculation, indicating the scaling of  $\sigma$  with  $\epsilon$  is independent of  $\mu$  and  $D_{\text{site}}$  for this range of molecular parameters. For  $\mu = 2$  nm and  $D_{\text{site}} = 1.0$  nm, we performed calculations at additional values of  $\epsilon$  between 1 and 4, and in Fig. 1 is shown the  $\Phi(\epsilon)$  obtained from these data. Also shown in Fig. 1 is the  $1/\epsilon$  line reflecting the prediction of the UDCM. The results of our MC calculations substantially diverge from the UDCM for all  $\epsilon > 1$ , and for typical amorphous organic materials, i.e.,  $\epsilon \approx 3$ , the UDCM underestimates  $\sigma$  by more than a factor of 2. We obtain the following polynomial fit to the data,

$$\Phi(\epsilon) = 1.48 - 0.613\epsilon + 0.155\epsilon^2 - 0.0137\epsilon^3, \quad (8)$$

also shown in Fig. 1.

These results demonstrate that the UDCM inadequately approximates the impact of polarization on charge carrier energy disorder. We attribute the shortcomings of the UDCM to two factors. First, as with all DCMs, the premise of the model is to replace the individual polarizable molecules with a continuous polarizable medium, and this leads to an unphysical model of nearest neighbor interactions: under the UDCM a continuous dielectric medium fills the space between such molecules, while in the real system the molecules are separated by vacuum. The importance of this error depends on how much of the total disorder arises

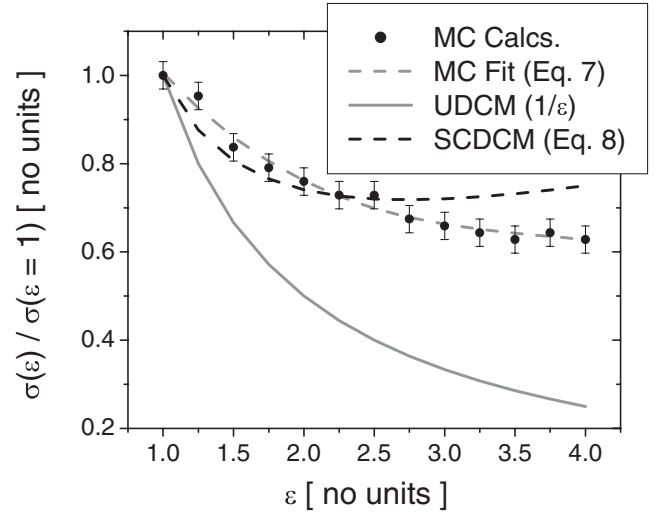


FIG. 1. Evolution of charge carrier energy disorder as a function of dielectric constant  $\epsilon$ , in terms of  $\Phi(\epsilon) = \sigma(\epsilon)/\sigma(\epsilon = 1)$ , where  $\sigma$  is the standard deviation of the charge carrier density of states. The symbols are obtained from Monte Carlo (MC) calculations as described in the text, while the solid gray line represents the UDCM, i.e.,  $1/\epsilon$ , and the dashed gray line represents the polynomial fit of Eq. (8). The dashed black line represents the SCDCM from Eq. (9).

from nearest neighbor interactions. We calculated this fraction for the case of static charge distributions and find that it comprises roughly half of the total disorder, demonstrating that nearest neighbor interactions contribute strongly to the overall energy disorder [15]. Since one would expect little or no dielectric screening of nearest neighbor interactions, the impact of this effect would be to reduce the strength of the  $1/\epsilon$  dielectric screening on  $\sigma$ , which is consistent with our MC results in that  $\Phi(\epsilon)$  is greater than  $1/\epsilon$  for all  $\epsilon > 1$ .

Second, the UDCM neglects the enhancement of the static dipoles due to the polarization of the surrounding medium. When the static dipole of a molecule polarizes a surrounding medium, it induces a reaction field that induces an additional dipole on that molecule. In the simplest model, due to Onsager [16], one places the molecular charge distribution in a spherical cavity surrounded by a continuous dielectric medium; in this case, the reaction field is parallel to the static dipoles, and enhances the strength of the original dipole by a factor  $(\epsilon + 2)(2\epsilon + 1)/9\epsilon$ . It is not simple to apply such a spherical cavity model self-consistently to the calculation of the interaction energies between a charged state and a collection of surrounding dipoles. However, an approximate calculation is possible if one neglects: (1) the internal polarization energy and (2) interactions between dipoles induced by the charged state. In this case, the static molecular dipoles are scaled by  $(\epsilon + 2)(2\epsilon + 1)/9\epsilon$ , and the local field at each dipole due to the charged state is scaled by  $(\epsilon + 2)/3\epsilon$ . The scaling of the local field combines a factor of  $1/\epsilon$  arising

from the polarization of a charge in a spherical cavity [17], with the Lorentz local field correction,  $(\epsilon + 2)/3$ , which gives the local field in a virtual spherical cavity [18]. This approach, here referred to as the spherical cavity DCM (SCDCM), thus yields

$$\Phi_{\text{SCDCM}}(\epsilon) = \frac{(\epsilon + 2)}{3\epsilon} \frac{(\epsilon + 2)(2\epsilon + 1)}{9\epsilon}. \quad (9)$$

This result is plotted in Fig. 1, and the agreement with the MC calculation, while not quantitative, is still significantly better than for the UDCM. We note, however, that in addition to the approximations discussed above, the SCDCM employs the Lorentz local field correction, which is predicated on an assumption of homogeneous fields and the fields here are highly inhomogeneous on the molecular size scale. Thus quantitative accuracy is not expected from this theory. Nevertheless, the SCDCM still serves to illustrate the basic principle that the enhancement of molecular dipole moments in polarizable media will tend to counteract the  $1/\epsilon$  reduction in  $\sigma$  predicted by the UDCM, a finding that is again consistent with our MC results.

In this Letter we report MC calculations of the charge carrier energy level disorder in polar amorphous organic solids arising from electrostatic interactions between polarizable molecular charge distributions. These calculations, which differ from conventional calculations because the molecular charge distributions are explicitly polarizable, demonstrate the inadequacy of that the conventional UDCM, in which the energy disorder is scaled by a factor  $1/\epsilon$ . We argue that the shortcomings of the UDCM are principally due to improper treatment of nearest neighbor interactions, and neglect of the enhancement of static molecular dipoles in polarizable media. We report an empirical expression for the proper scaling of the energy disorder as a function of  $\epsilon$ . Our calculations show that the UDCM underestimates the disorder by more than a factor of 2 for typical  $\epsilon$ , and since charge carrier mobilities scale exponentially with  $\sigma$  [5–7], such an underestimation has a significant impact on the modeling of charge carrier transport.

The authors thank Ethan Howe for helpful discussions. This work was supported in part by the NSF CAREER Grant, Graduate NDSEG Grant, and the MARCO Focused Research Center on Materials, Structures, and Devices.

\*Electronic address: bulovic@mit.edu

- [1] C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.* **51**, 913 (1987).
- [2] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, *Nature (London)* **395**, 151 (1998).
- [3] P. Peumans, A. Yakimov, and S. R. Forrest, *J. Appl. Phys.* **93**, 3693 (2003).
- [4] C. D. Dimitrikopolous and P. R. L. Malenfant, *Adv. Mater.* **14**, 99 (2002).
- [5] H. Bässler, *Phys. Status Solidi B* **107**, 9 (1981).
- [6] H. Bässler, *Phys. Status Solidi B* **175**, 15 (1993).
- [7] S. V. Novikov, *J. Polym. Sci., B Polym. Phys.* **41**, 2584 (2003).
- [8] A. Dieckmann and H. Bässler, *J. Chem. Phys.* **99**, 8136 (1993).
- [9] S. V. Novikov and A. V. Vannikov, *JETP* **79**, 482 (1994).
- [10] R. Young, *Philos. Mag. B* **72**, 435 (1995).
- [11] In this calculation we assumed Coulomb interactions between charge carriers are negligible, as appropriate for the charge carrier densities typically encountered in organic electronic devices.
- [12] Novikov [9] reports an expression for  $\sigma$  that is a factor of 3 smaller than the value reported by Young [10]. As noted in the text, our calculations are consistent with the Young result.
- [13] In these calculations we employ an alternative to the MD method which we refer to as the “convergent field” (CF) method. This approach produces identical results to the MD method but is more computationally efficient for calculations involving a single point per lattice. For CF calculations, we make an initial guess for the  $\vec{F}_i$  and then iteratively adjust the fields at each site until a self-consistent solution is obtained.
- [14] The convergence in this context denotes the point at which further increases in  $L$  and  $R_{\text{int}}$  have no impact on the results to within the calculation uncertainty, which here is 0.05% of the total energy.
- [15] More precisely, for static charge distributions  $\sigma^2 = \sigma_{\text{near}}^2 + \sigma_{\text{far}}^2$ , where  $\sigma_{\text{near}}$  and  $\sigma_{\text{far}}$  are the standard deviations of the DOS due only to nearest neighbor and non-nearest neighbor interactions, respectively, and we find that  $\sigma_{\text{near}} = k\sigma_{\text{far}}$  where  $k = 0.9 \pm 0.2$ .
- [16] L. Onsager, *J. Am. Chem. Soc.* **58**, 1486 (1936).
- [17] M. Born, *Z. Phys.* **1**, 45 (1920).
- [18] The use of a virtual cavity here reflects the fact that the molecule in the cavity is assumed to be itself polarized by the local field.