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Unified Description of Charge-Carrier Mobilities in Disordered Semiconducting Polymers

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From a numerical solution of the master equation for hopping transport in a disordered energy landscape with a Gaussian density of states, we determine the dependence of the charge-carrier mobility on temperature, carrier density, and electric field. Experimental current-voltage characteristics in devices based on semiconducting polymers are excellently reproduced with this unified description of the mobility. At room temperature it is mainly the dependence on carrier density that plays an important role, whereas at low temperatures and high fields the electric field dependence becomes important. Omission in the past of the carrier-density dependence has led to an underestimation of the hopping distance and the width of the density of states in these polymers.

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Introduction.—The use of conjugated semiconducting polymers in light-emitting diodes (PLEDs) [1] and field-effect transistors (FETs) [2] has triggered intensive research into the optoelectronic and electrical transport properties of these materials [3,4]. Understanding their charge-carrier transport is of crucial importance to design and synthesize better materials and further improve device performances. One of the most important parameters determining performance is the mobility μ of the charge carriers. In particular, the dependence of μ on temperature T and electric field E has been extensively addressed in literature [5–8]. Charge transport in disordered polymers is regarded as a hopping process between localized sites, which are thought to consist of conjugated polymer chain segments. The variations in the on-site energies due to disorder are usually assumed to be Gaussian. Very recent direct measurements of the energy distribution in an electrochemically gated polymer transistor, indeed, showed a nearly Gaussian shape [9]. Monte Carlo simulations of hopping transport were performed by Bäessler *et al.* for the case of a Gaussian disorder model (GDM), showing a non-Arrhenius temperature dependence $\mu \propto \exp(-c\hat{\sigma}^2)$, with $c \approx 0.44$, $\hat{\sigma} \equiv \sigma/k_B T$, and σ the width of the Gaussian, while a Poole-Frenkel $\mu \propto \exp[\gamma\sqrt{E}]$ behavior was found, in a limited field range, for the dependence on the electric field [5,6]. However, as pointed out by Gartstein and Conwell [10], a spatially correlated potential for the charge carriers is needed to explain the Poole-Frenkel behavior in a wide region of field strengths. Several suggestions were put forward as a cause for this correlation, such as charge-dipole interactions [11,12] or thermal fluctuations in molecular geometries [13].

Recently, it was realized that the importance of another parameter had been overlooked: the charge-carrier density p [14,15]. Experiments on hole-only diodes and FETs,

with the same polymer as active material, showed that μ can differ up to 3 orders of magnitude between the diode and the FET [15]. It was demonstrated that the only way to explain this huge difference is by taking a strong dependence of the mobility on p into account. More recent experiments suggested that at room temperature it is sufficient to take only the p dependence of μ into account, but that at low temperatures it is still necessary to assume an E dependence [16]. Experimentally, it is hard to separate the influences of E and p on μ , since under a higher electric field more carriers will be injected. In Ref. [16] the p dependence of μ was taken equal to an empirical form, consisting of an algebraic contribution $p^{T_0/T-1}$, derived by Vissenberg and Matters for the high-density regime [17], plus a density-independent contribution, determined from the current-voltage characteristics of hole-only diodes at low voltages. The failure of this empirical form to reproduce the experimental current-voltage characteristics at low temperatures and high voltages was attributed to an unknown dependence of μ on E . The purpose of this Letter is to establish a unified theoretical description of the full T , p , and E dependence of μ , and to critically compare the results with experiments.

Theory.—We determine the mobility μ unambiguously from a numerical solution of the master equation representing hopping of charge carriers on a lattice of sites:

$$\sum_{j \neq i} [W_{ij} p_i (1 - p_j) - W_{ji} p_j (1 - p_i)] = 0. \quad (1)$$

Here p_i is the probability that site i is occupied by a charge and W_{ij} is the transition rate for hopping from site i to j . The factors $1 - p_i$ account, in a mean-field approximation, for the fact that only one carrier can occupy a site, due to the high Coulomb penalty for the presence of two or more carriers. We consider hopping as a thermally assisted tun-

neling process and assume coupling to a system of acoustic phonons, which, in line with earlier work, leads to transition rates of the form [18]

$$W_{ij} = \begin{cases} \nu_0 \exp[-2\alpha R_{ij} - \beta(\varepsilon_j - \varepsilon_i)], & \varepsilon_j \geq \varepsilon_i, \\ \nu_0 \exp[-2\alpha R_{ij}], & \varepsilon_j < \varepsilon_i, \end{cases} \quad (2)$$

where $\beta \equiv 1/k_B T$, ν_0 is an intrinsic rate, $R_{ij} \equiv |\mathbf{R}_j - \mathbf{R}_i|$ is the distance between sites i and j , α is the inverse localization length of the localized wave functions under consideration, and ε_i is the on-site energy of site i . The energy differences in Eq. (2) are supposed to contain a contribution $-eER_{ijx}$ due to an electric field E in the x direction (e is the charge of the carriers). In the absence of an electric field the occupational probabilities are given by the Fermi-Dirac distribution.

We solve Eq. (1) by an iteration procedure similar to that suggested by Yu *et al.* [13]. For simplicity we take a regular cubic lattice with lattice constant a . For the inverse localization length we take $\alpha = 10/a$, a typical value for the relevant polymers [15] (we checked that varying α predominantly changes the prefactor of the mobility). Our method allows for variable-range hopping [19], but for the parameter range studied here it was sufficient to consider hopping to a maximum distance of $\sqrt{3}a$. We apply periodic boundary conditions and the site energies without electric field are drawn randomly from a Gaussian distribution of width σ . From the solution of Eq. (1) the mobility μ is obtained as $\mu = \sum_{i,j} W_{ij} p_i (1 - p_j) R_{ijx} / pEV$, with $p = \langle p_i \rangle / a^3$ and V the system volume. The sizes of the lattices are taken large enough such that finite size effects are negligible (sizes up to 150^3 for the lowest temperatures). Averages over a number of different disorder configurations are taken until an accuracy better than 10% is obtained for μ .

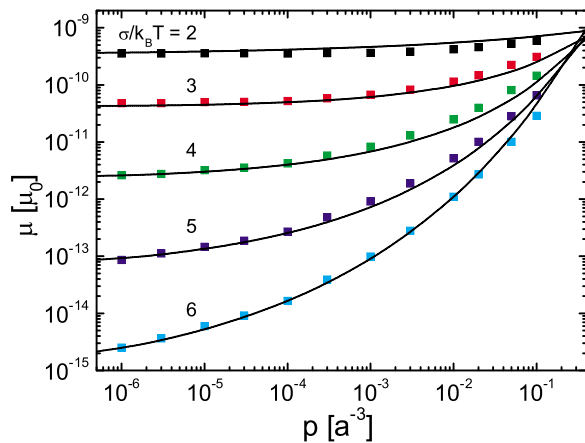


FIG. 1 (color online). Carrier-density dependence of the mobility at various temperatures for a vanishing electric field, in units of μ_0 [see Eq. (3c)]. Symbols: numerical results. Lines: fits using the parametrization scheme given in Eq. (3).

Results.—In Fig. 1 we display the p dependence of μ for different temperatures. This dependence shows a striking similarity to the p dependence found by Tanase *et al.* [15,16]. The numerical data of Fig. 1 can be rather well described by the following parametrization scheme [20]:

$$\mu(T, p) = \mu_0(T) \exp[\frac{1}{2}(\hat{\sigma}^2 - \hat{\sigma})(2pa^3)^\delta], \quad (3a)$$

$$\mu_0(T) = \mu_0 c_1 \exp[-c_2 \hat{\sigma}^2], \quad (3b)$$

$$\delta \equiv 2 \frac{\ln(\hat{\sigma}^2 - \hat{\sigma}) - \ln(\ln 4)}{\hat{\sigma}^2}, \quad \mu_0 \equiv \frac{a^2 \nu_0 e}{\sigma}, \quad (3c)$$

with $c_1 = 1.8 \times 10^{-9}$ and $c_2 = 0.42$. This parametrization is, in particular, satisfactory for not too high densities. Because of particle-hole symmetry $\mu(T, p) = \mu(T, a^{-3} - p)$, so the parametrization obviously fails at densities approaching $a^{-3}/2$. In the limit of vanishing densities, we recover the $\mu \propto \exp(-c\hat{\sigma}^2)$ temperature dependence found by Bässler *et al.* [5,6].

In Fig. 2 we display the E dependence of μ for different temperatures at a low and a high density, typical for LEDs and FETs, respectively. We find that the E dependence can be approximately modeled by a *density-independent* prefactor $f(T, E)$:

$$\mu(T, p, E) \approx \mu(T, p) f(T, E). \quad (4)$$

The prefactor can be rather well parametrized by

$$f(T, E) = \exp\left\{0.44(\hat{\sigma}^{3/2} - 2.2) \left[\sqrt{1 + 0.8 \left(\frac{Eea}{\sigma} \right)^2} - 1 \right] \right\}. \quad (5)$$

This parametrization is optimized for the low-density region, but it is also rather accurate in the high-density region (see inset of Fig. 2). The parametrization Eq. (5) correctly yields an E^2 dependence at low fields, which should hold because of field-reversal symmetry $E \rightarrow -E$, and de-

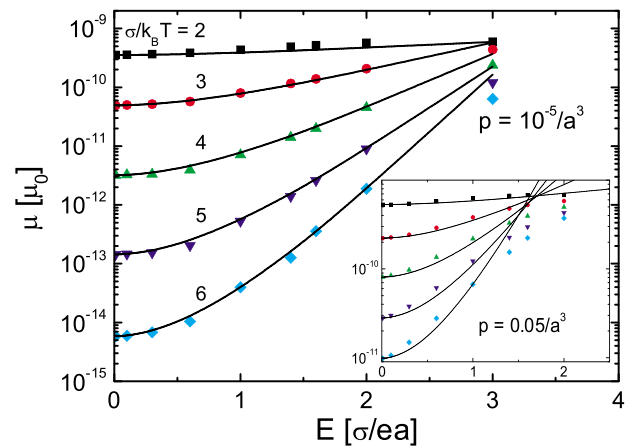


FIG. 2 (color online). Field dependence of the mobility at various temperatures, for a typical density in LEDs (main panel) and FETs (inset). Symbols: numerical results. Lines: Eqs. (3)–(5).

scribes the approximately linear field dependence of $\ln(\mu/\mu_0)$ found when a critical field strength of about σ/ea is passed. At very high fields, where μ saturates and eventually decreases as a function of E , the parametrization breaks down. Although a field range could be given in which an approximate dependence $\mu \propto \exp[\gamma\sqrt{E}]$ holds, the parametrization Eq. (5) is a more useful one.

Roichman and Tessler [14] determined a p and E dependence of μ for the GDM with a very simple model in which local fluctuations of the electrochemical potential are neglected. We checked that in this model the mobilities are overestimated by several orders of magnitude at low temperatures, making this model very unrealistic.

Application to hole-only devices.—Using the above results, we now proceed to calculate the current-voltage characteristics of a polymer layer of thickness L , sandwiched between two electrodes. The carrier density at the injecting electrode is assumed to be so high that complications related to injection need not be considered. The relation between the space-charge limited current (SCLC) density J and voltage V then follows from the solution of the equations

$$\begin{aligned} J &= p(x)e\mu(T, p(x), E(x))E(x), \\ \frac{dE}{dx} &= \frac{e}{\epsilon_0\epsilon_r}p(x), \\ V &= \int_0^L E(x)dx, \end{aligned} \quad (6)$$

where x is the distance from the injecting electrode, ϵ_0 is the vacuum permeability, and ϵ_r is the relative dielectric constant of the polymer. We take $\epsilon_r = 3$, a typical value for the relevant polymers. From calculations for a constant mobility including diffusion we conclude that diffusion effects, causing a significant increase of the current only at low voltages and a change of the density and field only close to the electrodes, can be neglected. Experimental $J-V$ measurements were done on hole-only devices of poly[4'-(3,7-dimethyloctyloxy)-1,1'-biphenylene-2,5-vinylene] (NRS-PPV), with layer thickness $L = 560$ nm, and poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene) (OC₁C₁₀-PPV), with $L = 275$ nm, as well as with an indium tin oxide bottom electrode as anode and an evaporated gold contact as top electrode. The results are displayed in Fig. 3. We also display in Fig. 3 the solution of Eq. (6) with the T -, p -, and E -dependent mobility from the parametrization given above. The parameters μ_0 , σ , and a are determined in such a way that an optimal overall fit is obtained.

A clear observation is that the agreement between experiment and theory is excellent. For the NRS-PPV device the E dependence at lower temperatures and high voltages is clearly important in explaining the measurements,

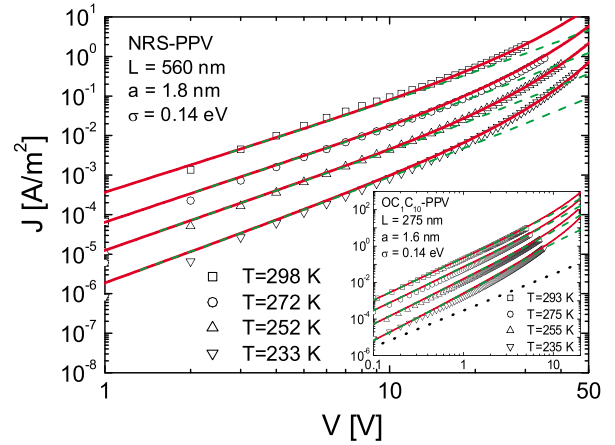


FIG. 3 (color online). Experimental (symbols) and theoretical (lines) current-density vs voltage results for polymer layers of NRS-PPV (main panel) and OC₁C₁₀-PPV (inset). Full line: solution of SCLC Eq. (6) with the T -, p -, and E -dependent mobility from the present work. Dashed line: SCLC result without E dependence. Dotted line: SCLC result without p or E dependence (shown only in the inset, for $T = 235$ K). The values used for μ_0 are 72 and 6400 m²/V s, respectively.

whereas under these conditions the E dependence for the OC₁C₁₀-PPV device is on the edge of becoming important. In the inset of Fig. 3 the dotted line gives the current density in the absence of the p and E dependence of μ , as expressed by the Mott-Gurney law $J = \frac{9}{8}\epsilon_0\epsilon_r\mu V^2/L^3$ [21], for $T = 235$ K. The huge effect of the density dependence of μ is clearly visible. We checked that the calculated carrier-density and electric field distribution in the device are very different for the three different situations (no p or E dependence, only p dependence, and p and E dependence of the mobility). Hence, for a correct description of the charge-carrier injection, transport, and recombination in PLEDs, the effects of both p and E need to be accounted for. The strong density dependence and the weaker field dependence, as compared to previous studies, also has important consequences for the interpretation of time-of-flight measurements [22].

The fits lead to values of σ for the two polymers that are essentially the same (0.14 ± 0.01 eV) and to values for the lattice constants that are slightly different (1.8 ± 0.1 nm and 1.6 ± 0.1 nm). An important result is that the values for σ and a found by us are markedly larger than reported in previous work [8], where the deviation from the Mott-Gurney law was attributed to an E dependence of the mobility. In the case of OC₁C₁₀-PPV, values of $\sigma = 0.112$ eV and $a = 1.2$ nm were reported as optimal fitting parameters [8] (these values are also typical for the present samples). The lower value of σ can be mainly attributed to the omission of the p dependence, whereas the lower value of a can be mainly attributed to the overestimation of the E dependence.

Discussion and conclusions.—The excellent fits we obtain with experimental current-voltage data of two semi-conducting polymers strongly suggest that the underlying dependencies of the mobility on temperature, carrier density, and electric field in these materials are correctly described by this Letter, at least in the regime of carrier densities considered here. Because in the present work the site energies are uncorrelated, an important conclusion is that, for the materials investigated here, our analysis does not indicate that there is a need to assume a certain spatial energy correlation, as suggested before [10–13]. Another important conclusion is that a satisfactory description can be given with a Gaussian site energy distribution. Hence, a simple *uncorrelated Gaussian disorder model* can be used. Considering the excellent agreement with experiment, there is no indication for a need to go beyond the simple starting point Eq. (2) for the transition rates, by considering multiphonon hop processes [23]. We confirm recent claims that the carrier-density dependence of the mobility in PLEDs is more important than the field dependence, but show that a field dependence is still required to describe current-voltage characteristics at low temperatures and high fields. These conclusions have consequences for the internal field distribution and density of charge carriers of both signs in devices like LEDs and FETs, which should be different than assumed thus far. Moreover, markedly larger values of the width of the Gaussian energy distribution and the typical hopping distance are found than obtained before.

We should, however, point at the drastic approximation made in replacing the hopping problem in a polymer by an isotropic hopping model on a regular lattice. The fitted values of 1.6–1.8 nm for the lattice constants are considerably smaller than the typical length of 6–7 nm of a conjugated segment of derivatives of PPV (about 10 repeat units) and considerably larger than the typical distance of 0.3–0.4 nm between neighboring polymer chains. Also, intrachain and interchain hopping processes are expected to have very different characteristics. Therefore, our model parameters should be considered as the effective result of an average of intrachain and interchain hopping. This complicates an identification with microscopic parameters of the polymer. Finally, we mention that the description presented here should also be applicable to small-molecule based materials, for which such an identification should be easier to make.

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