Current injection from a metal to a disordered hopping system. I. Monte Carlo simulation

U. Wolf, V. I. Arkhipov,* and H. Bässler
Institut für Physikalische Chemie, Makromolekulare Chemie und Kernchemie und Zentrum für Materialwissenschaften, Philipps Universität, Hans-Meerwein-Strasse, D-35032 Marburg, Germany
(Received 24 July 1998)

Emission-limited charge-carrier injection in the dark from a metal into a random organic dielectric has been studied via Monte Carlo simulations. The dielectric has been modelled in terms of a regular lattice of point sites featuring a Gaussian distribution of energies to represent disorder. The essential input parameters are the zero-field energy barrier for injection (Δ), the variance (σ) of the distribution of the hopping states, electric field, and temperature. By varying the jump distance the unimportance of long-range tunneling transitions has been established. Therefore, Fowler-Nordheim type $j(F)$ charcteristics at high fields have to be considered accidental. The dependence of the injection yield resembles that of Richardson-Schottky (RS) thermionic emission. Quantitative differences are noted, however, concerning the RS coefficient and the temperature dependence. The latter tends to saturate at low temperatures, which is a signature of hopping among sites distributed in energy. [S0163-1829(99)08411-8]

I. INTRODUCTION

A distinguishing feature of organic solids is that they are composed of molecular entities held together by van der Waals forces while intramolecular coupling is strong. It implies that electronic interactions among the molecules is weak and, concomitantly, the mean-free path of charge carriers is of the order of the intermolecular spacing. In amorphous systems, e.g., glasses, polymers, or molecularly doped polymers, charge-carrier transport is incoherent and all transport sites are localized because the disorder potential exceeds the bandwidth of crystalline counterpart structures. In chemical terms, charge transport is a redox process involving adjacent molecules or segments of a polymer. From previous work it is known that a model based upon the random walk in a hopping manifold whose site energies are distributed in energy featuring a Gaussian density of states (DOS) can explain a wide range of the observations such as the temperature and electric-field dependence of the mobility as well as temporal aspects. Most of the conceptual framework has been developed in terms of Monte Carlo[1] simulations because the Gaussian type DOS is difficult to treat analytically.[2]

It is straightforward to conjecture that a hopping concept should also be employed for treating charge-carrier injection from a metallic electrode into a random organic solid, e.g., a light-emitting diode.[3] However, the existence of the long-range Coulombic potential renders an analytic treatment even more difficult. In an attempt in order to simplify the problem, Abkowitz *et al.*[4] set up a model based on thermally assisted tunneling that takes proper account of the hopping character of carrier motion inside the dielectric but ignores both the Coulombic potential and the energetic randomness of the system. A more sophisticated version of this injection concept has been established by Gartstein and Conwell[5] employing Monte Carlo-simulation techniques. Their model takes full account of both the energetic disorder of the system and the Coulombic potential without considering the initial injection from the Fermi level, though. This procedure cannot yield the temperature dependence of the entire injection process because the initial and energetically most costly injection event is disregarded.

Recently Arkhipov *et al.*[6] presented an analytic theory for injection into an organic-hopping system. Recognizing that the problem of hopping in the presence of a Coulombic potential cannot be rigorously solved without making simplifying assumptions they included the primary injection step from the Fermi level of the metal to the first layer of the dielectric explicitly while treating the subsequent diffusive random walk in terms of an Onsager-like process.[7]

In view of the importance of developing an appropriate conceptual framework of injection limited current flow in light-emitting diodes we set up an extensive Monte Carlo-simulation study for hopping injection into a random organic dielectric. It is intended to delineate the phenomenology of charge transport across an energy barrier. In subsequent papers we shall check the validity of the simplifications concerning analytic theory (Sec. II), and compare with experiment (Sec. III).

II. SIMULATION

In the simulations the real-world sample is described as a cubic lattice of $170\times170\times20$ hopping sites. The energies of these sites are chosen randomly from a Gaussian-shaped density of states function (DOS) of variable width σ. Under an applied external field F the center of the DOS is lowered by $-eFx$, where x is the distance from the injection contact. Under the influence of its own image charge the mean energy of a charge carrier located within the DOS is given as

$$U(x) = -\frac{e^2}{16\pi\varepsilon_0\varepsilon x} - eFx \tag{1}$$

if we set the center of the intrinsic DOS as zero.

Adjacent to the dielectric at $x=0$ there is assumed to be a metallic contact with Fermi energy E_F. The simulation starts with the injection of a set of independent charge carriers

from the Fermi level into the hopping sites. The conventional Miller-Abrahams expression has been used for the rate of hopping of a carrier from an energy level ε_i to a site with an energy of ε_j at the distance R_{ij}, including the jump from the Fermi level into an acceptor site in the dielectric,

$$\nu_{ij} = \nu_0 \exp(-2\gamma R_{ij}) \mathrm{Bol}(\varepsilon_i, \varepsilon_j) \tag{2}$$

with

$$\mathrm{Bol}(\varepsilon_i, \varepsilon_j) = \begin{cases} \exp\left(-\dfrac{\varepsilon_j - \varepsilon_i}{kT}\right): & \varepsilon_i < \varepsilon_j \\ 1: & \varepsilon_i \geqslant \varepsilon_j . \end{cases} \tag{3}$$

Because a flat metallic interface forms an equipotential plane the first injection event occurs perpendicular to the interface and the hopping distance becomes equal to multiples of the lattice spacing (a_0). Under this premise, hopping rates to all sites within the first two layers of the lattice are calculated and one of them is chosen randomly according to its probability

$$P_{ij} = \frac{\nu_{ij}}{\sum_{j \neq i} \nu_{ij}}. \tag{4}$$

The actual computing algorithm for this step is, however, much more complicated. Internally the pair of injection layers for each electron is chosen randomly from within the simulation lattice. The real-world x position of each charge carrier is set relative to the first of these layers. All charge carriers will start in the first two layers of the ''real world'' but may use all 20 layers of the ''simulation world'' as starting layer leading to 578 000 possible virtual starting points for each charge carrier. This way we reduce the possibility of multiple occupation of single sites.

In order not to waste computing time by executing a large number of unnecessary activated jumps from the Fermi level to a target site a normalization routine has been introduced. The hopping rates for the injection process reflect the activation of the charge carriers within the tail of the Fermi distribution as well as tunneling between the resulting energy level to the sites within the dielectric. The competing process of relaxation from the excited states within the metal to its Fermi level is not taken into account in the simulaton itself. Instead the charge carriers are injected into the dielectric at unit probability,

$$\sum_{j \neq i} P_{ij} = \frac{\sum_{j \neq i} \nu_{ij}}{\sum_{j \neq i} \nu_{ij}} = 1 \tag{5}$$

and the resulting injection currents are normalized by multiplying by a constant factor

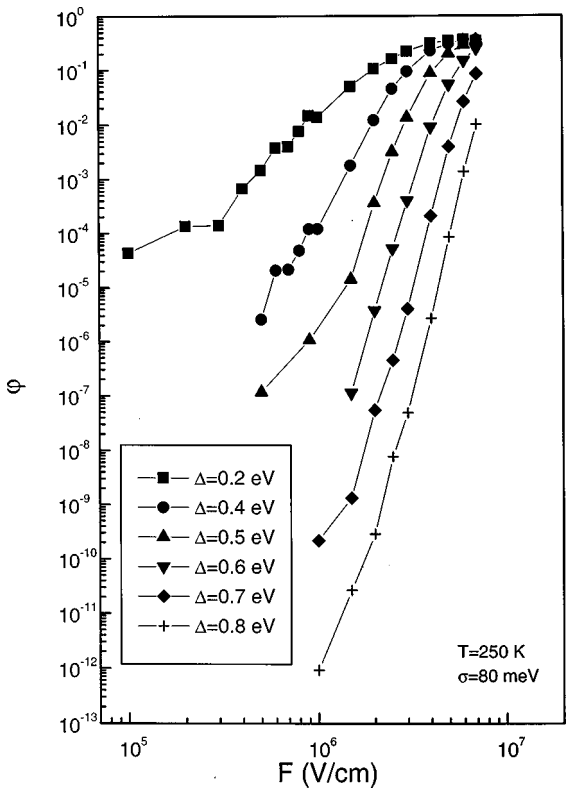

FIG. 1. Field dependence of the injection efficiency parametric in the energy barrier Δ.

$$f = \frac{\sum_{j \neq i} \nu_{ij}}{\nu_0 + \sum_{j \neq i} \nu_{ij}} = \frac{\sum_{j \neq i} \exp(-2\gamma R_{ij}) \mathrm{Bol}(\varepsilon_i, \varepsilon_j)}{1 + \sum_{j \neq i} \exp(-2\gamma R_{ij}) \mathrm{Bol}(\varepsilon_i, \varepsilon_j)}$$

$$\approx \sum_{j \neq i} \exp(-2\gamma R_{ij}) \mathrm{Bol}(\varepsilon_i, \varepsilon_j) \tag{6}$$

assuming the rate of the competing process being ν_0.

After this hop of the charge carrier, the procedure is continued except that R_{ij} no longer can be assumed to be constant. Subsequently, hopping rates according to Eq. (2) are calculated for all sites within an $5 \times 5 \times 5$ lattice around the occupied site. If the electrode happens to be within this range it is treated as one site of energy E_F. Again, a hop is chosen, selected from among all possible hops and the charge carrier may either recombine with the electrode or be transported within the DOS. The procedure will be repeated until all charge carriers have recombined or have reached the ninth layer of the hopping lattice and are considered as dissociated.

Throughout the paper specific effects of the interface between the electrode and the organic medium, such as the inadvertent or intentional formation of interfaces, have not been considered. They will be dealt with in a forthcoming paper.

III. RESULTS

Figure 1 shows the efficiency of charge-carrier injection as a function of the electric-field parametric in the average zero-field energy barrier (Δ) on a double logarithmic scale.

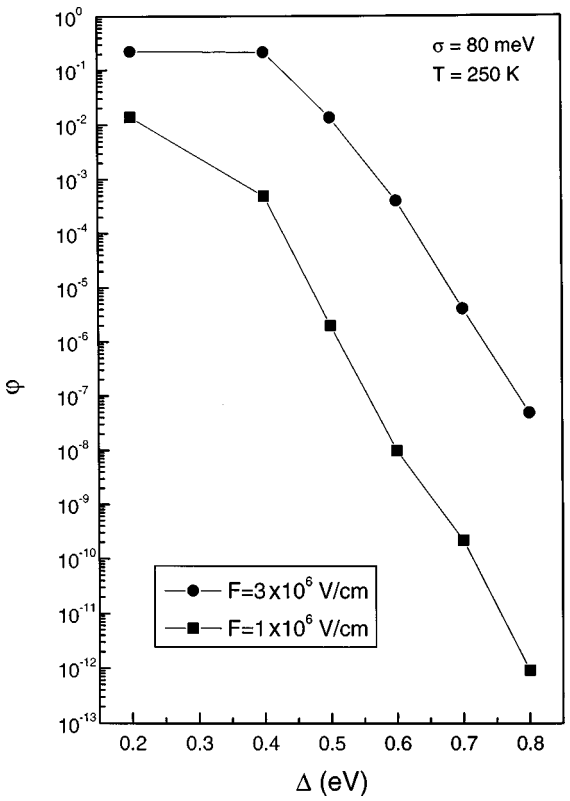

FIG. 2. Dependence of the injection efficiency on the energy barrier for variable electric field.

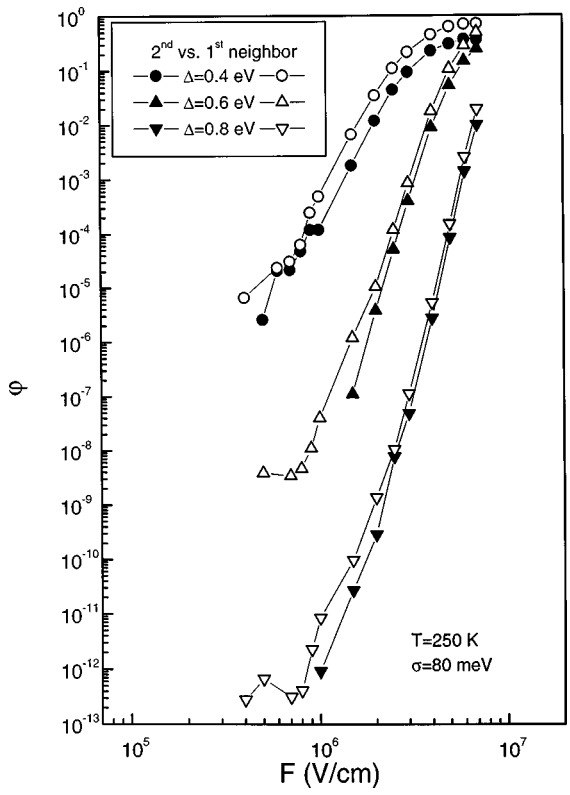

FIG. 3. Comparison of the injection efficiency between simulation under the assumption of nearest-neighbor jumps and nearest and next nearest-neighbor jumps, respectively.

Increasing the barrier causes the slope $\partial \ln \varphi / \partial \ln F$ to increase accordingly while the efficiency decreases. The dependence of the efficiency on the injection barrier is plotted in Fig. 2 for fields of 1×10^6 and 3×10^6 V/cm. At large barriers the yield decreases exponentially with Δ. Depending on the electric field $\lg\varphi$ tends to saturate as Δ goes below a critical value.

One of the advantages of Monte Carlo simulation is that one can change the system parameters seperately at will in order to assess their influence on the system irrespective of experimental constraints. As an example we studied the influence on the injection yield taking into account either jumps from the Fermi level of the metal into the adjacent layer of the dielectric or jumps into the nearest and next nearest-neighbor plane. The purpose was to delineate the importance of long-distance jumps. It is quite remarkable that the injection efficiency tends to be slightly smaller for injection into the first and second layers of the dielectric as compared to the first layer (Fig. 3). The difference is hardly beyond the statistical limit but becomes bigger as Δ gets smaller.

The temperature dependence of the injection efficiency at selected electric fields approaches an Arrhenius law at high temperatures but levels gradually at lower temperatures. Data are shown for $\Delta=0.4$ eV and a width $\sigma=150$ meV of the DOS (Fig. 4) and for $\Delta=0.6$ eV and $\sigma=80$ meV (Fig. 5). The influence of the width of the DOS on the injection yield depends on both the injection barrier and temperature. While the yield hardly changes for $\Delta=0.4$ eV upon increasing σ from 80 to 150 meV (Fig. 6) at $T=300$ K a big effect is

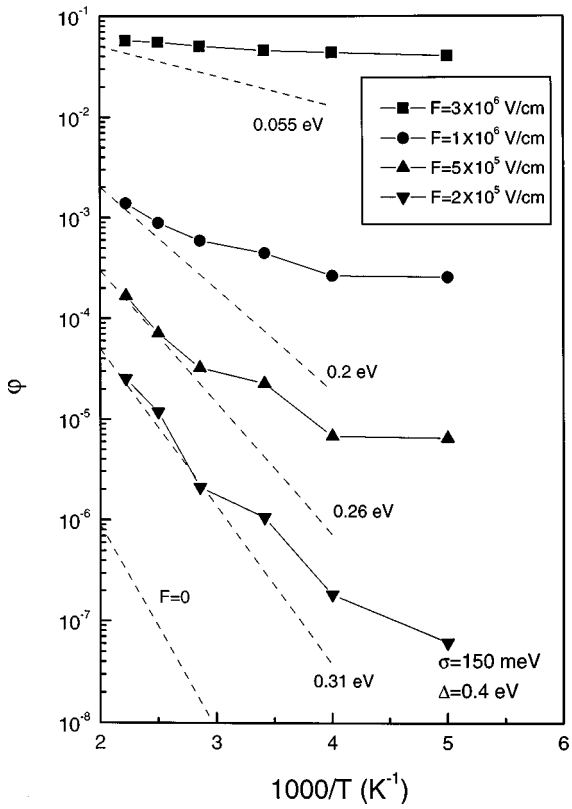

FIG. 4. Temperature dependence of the injection efficiency of a disordered hopping system characterized by a Gaussian DOS with $\sigma=150$ meV ($\Delta=0.4$ eV).

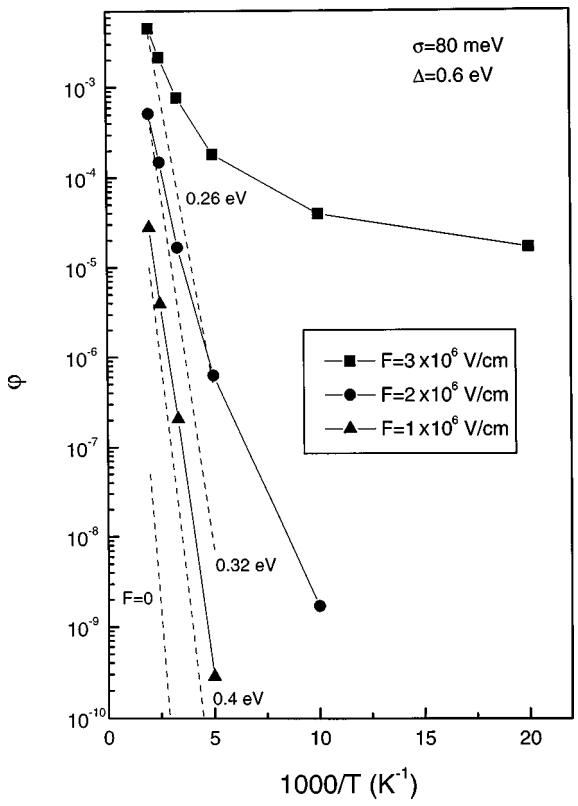

FIG. 5. Temperature dependence of the injection efficiency of a disordered hopping system characterized by a Gaussian DOS with $\sigma = 80$ meV ($\Delta = 0.6$ eV).

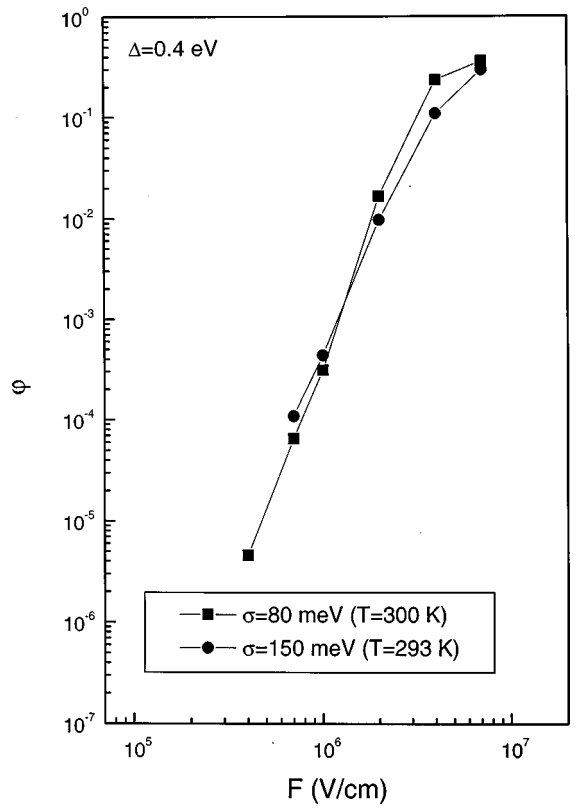

FIG. 6. Field dependence of the injection efficiency for hopping systems and different width of the distribution of hopping states.

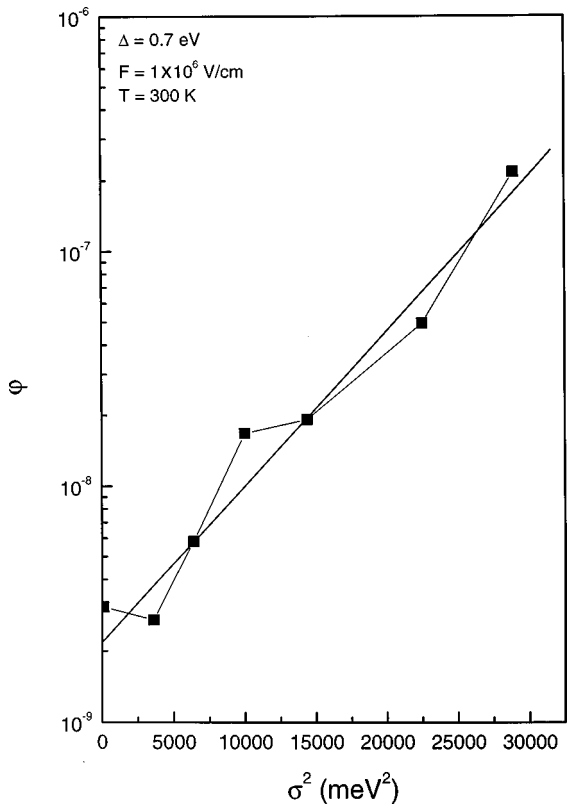

FIG. 7. The injection efficiency as a function of σ^2 for $\Delta = 0.7$ eV. The ordinate intercept is set by the Boltzmann factor for $\Delta = 0.7$ eV taking into account of field lowering.

noted for $\Delta = 0.7$ eV and fixed field (10^6 V/cm) and temperature (300 K) (Fig. 7).

IV. DISCUSSION

It has become common practice to analyze injection limited currents in light-emitting diodes dominated by majority carriers at high electric fields in terms of tunneling. Often lg$j$ vs F^{-1} plots feature an asymptotic straight-line behavior.[8–10] If one evaluates the slope $\partial \ln \varphi / \partial F^{-1}$ on premise of Fowler-Nordheim theory, often ignoring the preexponental factor F^2 and assuming an effective mass equal to the free-electron mass, one arrives at values for the injection barrier that correlate reasonably with those expected on the basis of oxidation/reduction potentials and Fermi levels of the electrodes. However, at lower fields, typically $\lesssim 10^6$ V/cm, the current decreases with decreasing electric field less strongly than theory predicts and begins to show a temperature dependence suggestive of thermionic emission taking over. The present simulation data (Fig. 8) indicate, though, that the notion of tunneling is not warranted because next nearest jumps turn out to be unimportant as evidenced by Fig. 3. This is a plausible result. Consider an electric field of 3×10^6 V/cm and a dielectric constant of $\varepsilon = 3.5$. In that case the maximum of the image potential is located at 0.6 nm, comparable to the assumed intersite distance. Even at such high fields a carrier had to overcome at least two intersite distances from the interface in order to be carried away by the collecting electric field. If the injection process were to proceed from the Fermi energy of the metal via tunneling the

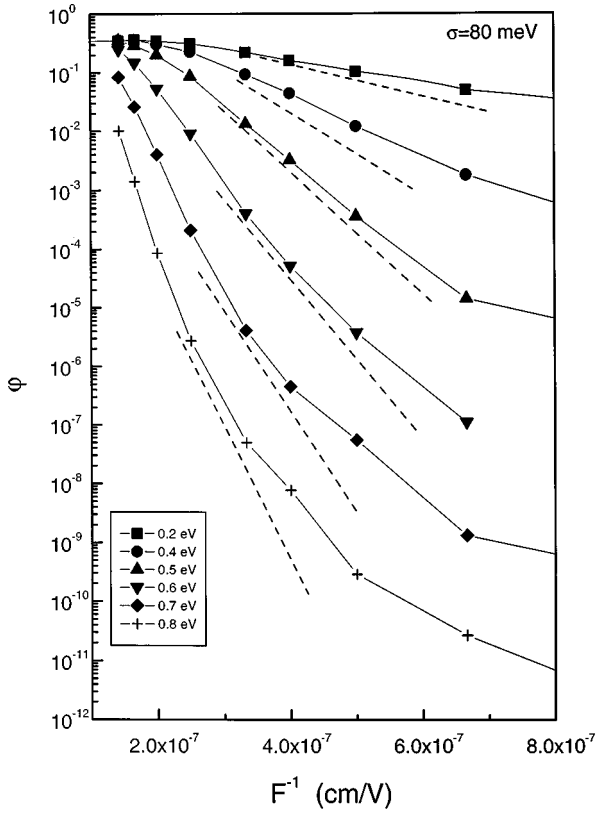

FIG. 8. Fowler-Nordheim plot of the injection efficiency parametric in barrier Δ. The dashed lines indicate the slope as predicted by Fowler-Nordheim theory ignoring the F^2 factor in the prefactor.

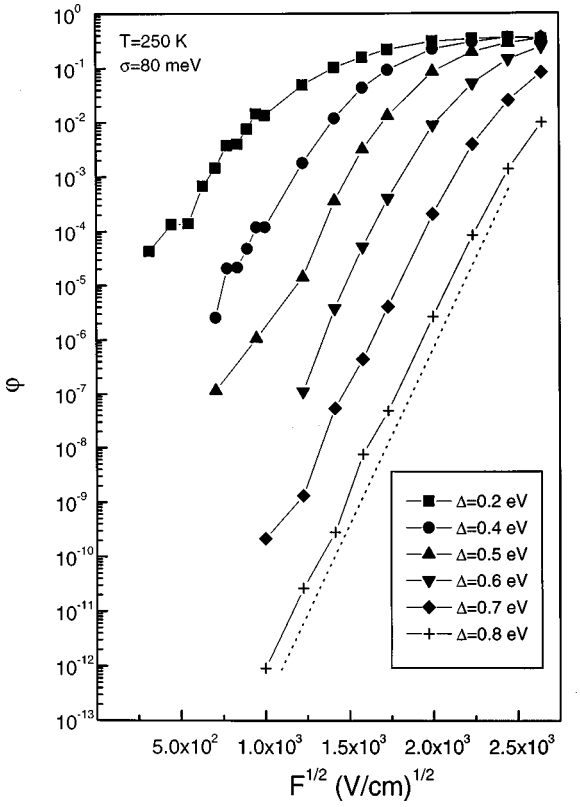

FIG. 9. The injection efficiency plotted as a function of $F^{1/2}$ parametric in barrier Δ. The dashed line indicates the slope $\partial \ln \varphi/\partial F^{1/2}=1.5\times10^{-2}$ $(\mathrm{V/cm})^{-1/2}$.

tunneling distance would be even larger, i.e., be no less than 2 nm, corresponding to an average of 3.5 intersite distances and a barrier of 0.7 eV and a field of 3×10^6 V/cm. Further, the results indicate that at smaller barrier the injection into the second layer of the dielectric is even counterproductive concerning the injection efficiency. Anticipating the result that experimental injection currents agree with simulation and analytic theory, premised upon short-range transitions only, one has, therefore, to conclude that tunneling is not involved in experiment either. It is remarkable, though, that plots of $\lg\varphi$ vs F^{-1} feature similar slopes at a relevant range of fields as predicted by Fowler-Nordheim theory for input barriers Δ (Fig. 8). This demonstrates that the use of that formalism is accidental.

Next, we shall compare the simulation results in terms of the concept of thermionic injection (Richardson-Schottky, RS mechanism). It predicts the injection current to be

$$j_{RS}=AT^2\exp\left[-\frac{\Delta-\left(\frac{e^3}{4\pi\varepsilon\varepsilon_0}\right)^{1/2}F^{1/2}}{kT}\right]. \tag{7}$$

For a dielectric constant of 3.5 the RS coefficient $\beta_{RS}=(e^3/4\pi\varepsilon\varepsilon_0)^{1/2}=0.77\times10^{-2}(\mathrm{cm/V})^{1/2}$ is obtained. Plots of $\lg j_{RS}$ vs $F^{1/2}$ should feature a family of straight lines whose slope is independent of Δ. Due to barrier lowering j_{RS} should saturate above a critical field $F_{sat}^{1/2}=\Delta/(e^3/4\pi\varepsilon\varepsilon_0)^{1/2}$. Similarly, the slope of $\lg j_{RS}$ vs Δ plots should be $(-kT)^{-1}$ and j_{RS} should saturate for $\Delta\leqslant(e^3F/4\pi\varepsilon\varepsilon_0)^{1/2}$.

Qualitatively, the series of simulated $\varphi(F)$ data parametric in the injection barrier Δ and plotted on a $\lg\varphi$ vs $F^{1/2}$ scale follows the prediction of the RS model (Fig. 9). The low-field portion approaches a straight line independent of Δ and the yield saturates at high fields at small barrier Δ. There are quantitative differences, though. In the case of a Gaussian distribution of hopping sites of variance $\sigma=80$ meV the related coefficient $\partial\ln\varphi/\partial F^{1/2}$ turns out to be $1.4\ldots1.5\times10^{-2}$ $(\mathrm{cm/V})^{1/2}$ at $T=300$ K compared to $\beta_{RS}=7.7\times10^{-3}$ $(\mathrm{cm/V})^{1/2}$. In addition, the current saturates at somewhat lower field already. If one defines the saturation field by the intersection of the asymptotes, RS theory would predict saturation at fields 1×10^6, 4×10^6, and 1×10^7 V/cm for $\Delta=0.2$, 0.4, and 0.7 eV, respectively, while simulation yields approximately $F_{sat}\simeq1\times10^6$, 2×10^6, and 5×10^6 V/cm (Fig. 10).

It is not surprising that injection into a hopping system resembles Richardson-Schottky type thermionic emission yet fails as far as quantitative agreement is concerned. At larger electric field, say $\simeq3\times10^6$ V/cm, the maximum of the electrostatic potential is close to the first molecular lattice plane. Lowering of the energy barrier must, therefore, be in accordance with RS theory, i.e., $-(e^3F/4\pi\varepsilon\varepsilon_0)^{1/2}$. However, as the potential maximum moves away from the interface as the field decreases, charge carriers injected into the interface layer will commence their random walk within the manifold of the hopping states. On average, this will lead to increasing energetic relaxation towards the tail of the DOS. Therefore, the injection current will decrease faster with decreasing electric field than RS theory predicts, but in agreement with experiment.[10,11]

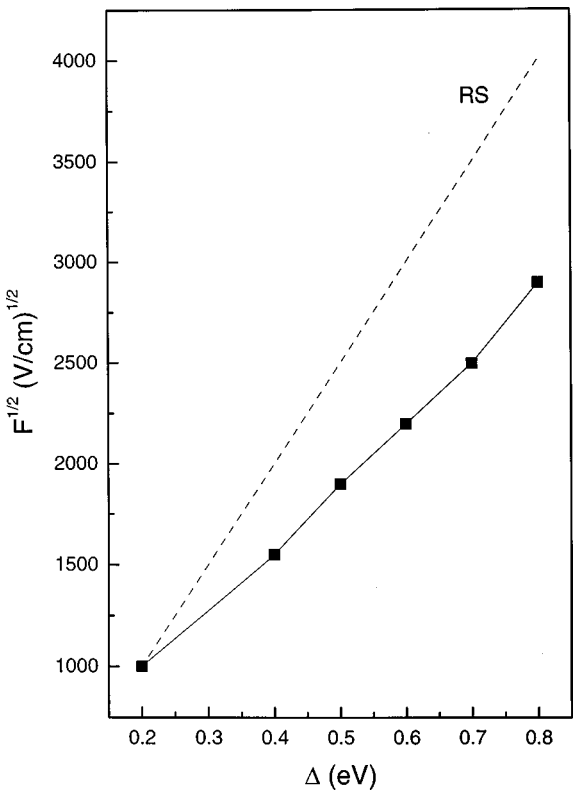

FIG. 10. Dependence of the saturation energies on the energy barrier Δ. The dashed line indicates the predicton of Richardson-Schottky theory. The saturation field has been defined by the intersection of the asymptotes.

On the more fundamental side there is a conceptual difference between classic RS-type thermionic emission and thermally assisted hopping injection. The former implies that every carrier that has got enough thermal energy to pass the potential maximimum will be injected rather than be reflected or scattered inside the potential well next to the interface. Further it is assumed that injection occurs into unbound electron states obeying a parabolic $E(k)$ dependence. In hopping injection, on the other hand, most of the injection events proceed via the first layer of the dielectric in the course of an optimization procedure concerning site energy and density of states. Subsequently, the injected carrier will either return into the electrode or will escape over the potential maximum via a field and temperature assisted diffusion resembling an Onsager process except that the medium is a disordered manifold of point sites rather a homogenous medium. It is also obvious that the prefactor of the injection rate into a two-dimensional sheet of hopping sites must be orders of magnitude less than predicted by classic RS theory, which is AT^2 at $A \simeq 120$ A/cm^{2}K^2.[12]

The temperature dependence of thermally assisted hopping injection is of particular interest. Previous Monte Carlo simulations of geminate pair dissociation in random-hopping systems[13] and experiments[14] on both intrinsic and extrinsic photoconduction reveal a sublinear temperature dependence if plotted on an Arrhenius scale. While at high temperature the dissociation yield approaches the anticipated activation energy it tends to saturate at low temperatures. The reason is that in a Gaussian DOS charge carriers tend to relax towards lower localized states.[2,15] Under stationary conditions an ensemble of carriers settle at an average energy $-\sigma^2/kT$ below the center of the DOS. However, in the actual process, injection occurs far away from equilibrium. Lowering the temperature and increasing the width the DOS will, thus drive the ensemble of injected carriers further away from equilibrium. In other words, the injection process becomes the more efficient as the system deviates from equilibrium. At high temperatures, on the other hand, the effect of disorder vanishes and the rate limiting step approaches that determined by the Boltzmann factor, i.e., $\exp\{-[\Delta-(e^3F/4\pi\varepsilon\varepsilon_0)^{1/2}]/kT\}$.

In Figs. 4 and 5 the slope of Arrhenius graphs, $\partial \ln \varphi/\partial T^{-1}$, calculated on the premise of the Richardson-Schottky model in absence of disorder have been indicated. Simulation data approach theoretical slopes in the high-temperature limit. An important message of those results is that apparent activation energies if inferred from $\ln j$ vs T^{-1} plots of experimental data, in particular if the temperature regime is restricted, will underestimate the true energy barrier at the interface.

V. CONCLUDING REMARKS

Monte Carlo simulation is a unique way (i) to delineate the behavior of a system on the premise of well-specified input parameters, (ii) to check the validity of the simplifying assumptions that one has to introduce in order to develop an analytic theory, and (iii) to decide which mechanism one has to invoke in order to reproduce an experimental result. Take, for instance, the simulated $j(F)$ characteristics plotted on a double logarithmic scale (Fig. 1). Over a limited field range they feature an almost straight line behavior as if the current was space charge limited (SCL) in the presence of an exponential distribution of traps.[16] In that case a power law behavior is predicted, $j \propto F^{l+1}/L^l$, where L is the sample thickness, $l = T_c/T$, and T_c is the characteristic temperature of the distribution. For a Gaussian distribution of traps the field dependence of a SCL current[17] is even closer to that of an injection limited current. It is obvious, therefore, that the field dependence of the current in a diode is insufficient to distinguish between injection and transport limited conduction. Necessary conditions to conclude on the prevalence of space charge limited conduction[18–20] are the thickness dependence of the current at constant electric field and the independence on the injection barrier at small barrier.

ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft (SFB383) and the Fond der Chemischen Industrie.

*On leave from Laboratorium voor Halfgeleiderfysica, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Heverlee-Leuven, Belgium.

[1] H. Bässler, Phys. Status Solidi B **175**, 15 (1993).

[2] B. Ries, H. Bässler, M. Grünewald, and B. Movaghar, Phys. Rev. B **37**, 5508 (1988).

[3] N. Greenham and R. H. Friend, Solid State Phys. **49**, 1 (1995).

[4] M. A. Abkowitz, H. A. Mizes, and J. S. Facci, Appl. Phys. Lett. **66**, 1288 (1995).

[5] Yu. N. Gartstein and E. M. Conwell, Chem. Phys. **255**, 93 (1996).

[6] V. I. Arkhipov, E. V. Emelianova, Y. H. Tak, and H. Bässler, J. Appl. Phys. **84**, 848 (1998).

[7] D. F. Blossey, Phys. Rev. B **9**, 5183 (1974).

[8] I. D. Parker, J. Appl. Phys. **75**, 1656 (1994).

[9] A. I. Heeger, I. D. Parker, and Y. Yang, Synth. Met. **67**, 23 (1994).

[10] H. Vestweber, J. Pommerehne, R. Sander, R. F. Mahrt, A. Greiner, W. Heitz, and H. Bässler, Synth. Met. **68**, 263 (1995).

[11] O. Schäfer, A. Greiner, J. Pommerehne, W. Guss, H. Vestweber, H. Y. Tak, H. Bässler, C. Schmidt, G. Lüssem, B. Schartel, V. Stümpflen, J. Wendorff, S. Spiegel, C. Möller, and H. W. Spieß, Synth. Met. **82**, 1 (1996).

[12] C. Weißmantel and C. Hamann, *Grundlagen der Festkörperphysik* (VEB Deutscher Verlag der Wissenschaften, Berlin, 1981).

[13] U. Albrecht and H. Bässler, Chem. Phys. Lett. **199**, 207 (1995).

[14] S. Barth, D. Hertel, Y. H. Tak, H. Bässler, and H. H. Hörhold, Chem. Phys. Lett. **274**, 165 (1997).

[15] B. Moveghar, B. Ries, and M. Grünewald, Phys. Rev. B **34**, 5574 (1986).

[16] P. Mark and W. Helfrich, J. Appl. Phys. **33**, 205 (1962).

[17] S. Nespurek and E. A. Silinsh, Phys. Status Solidi A **34**, 747 (1976).

[18] P. W. M. Blom, M. J. M. de Jong, and J. J. M. Vleggar, Appl. Phys. Lett. **68**, 3308 (1996).

[19] A. J. Campbell, D. D. C. Bradley, and D. G. Lidzey, J. Appl. Phys. **82**, 6326 (1997).

[20] E. M. Conwell and M. W. Wu, Appl. Phys. Lett. **70**, 1867 (1997).