

Charge carrier injection into insulating media: Single-particle versus mean-field approach

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Self-consistent, mean-field description of charge injection into a dielectric medium is modified to account for discreteness of charge carriers. The improved scheme includes both the Schottky barrier lowering due to the individual image charge and the barrier change due to the field penetration into the injecting electrode that ensures validity of the model at both high and low injection rates including the barrier-dominated and the space-charge-dominated regimes. Comparison of the theory to experiment on a unipolar indium tin oxide-poly(phenylene vinylene)-Au device is presented.

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I. INTRODUCTION

Injection of charge carriers from a conductor to an insulating medium has a crucial impact on the functioning of a wide range of electronic devices, such as light-emitting diodes, field-effect transistors, capacitors, etc., using inorganic or organic semiconductors, wide-gap insulators, and ferroelectrics. Nevertheless, the description of this process still remains controversial. By the simulation of inorganic and organic semiconductor devices, the fixed values of charge-carrier densities at the boundary with the insulating region are often used as boundary conditions.^{1–6} For charge transport in bulk dielectrics, the electric field at the injecting interface is often taken equal to zero assuming space-charge limitation of the current.^{7–10} Given finite values of the electric field at the interface are supposed in numerous papers simulating injection as Fowler-Nordheim (FN) tunneling through the surface energetic barrier^{11–15} or Richardson-Schottky (RS) thermionic emission over this barrier.^{13,16–25} However, the problem is that the field and the carrier density at the interface are, in fact, unknown.

Moreover, the injection treatment in the spirit of the FN or the RS approach applies, strictly speaking, only to the case of a single-particle penetration since the presence of other particles immediately changes the electrostatic potential profile used in these models. This makes the application of the mentioned models questionable, particularly at high injection levels. A consequence of the single-particle approach is that the characteristics of a dielectric medium are virtually absent in the results. Expressions for the FN and RS injection currents look as if it is injected into vacuum (except for the dielectric permittivity) and do not depend either on density of states available or on the charge-carrier mobility in the dielectric medium that contradicts experiment.²⁶ This deficiency of the RS model was properly noticed in Refs. 1 and 27 where the drift-diffusion equation for charge carriers in the insulating medium was combined with RS injection to introduce the carrier mobility and the density of states in the injection current, however, the question remains whether a boundary condition derived from a single-particle model may be coupled with many-particle equations. In view of disordered insulators, sophisticated extensions of the RS approach describing injection as random hopping of a charge carrier in the same potential profile with account of possible injection into the tail states below the barrier were developed^{18,19,21,28–30} which, however, do not fix the general

deficiency of the model of injection which remains a single-particle one.

For a proper description of the charge-carrier injection, a self-consistent determination of the field and the carrier density at the conductor-insulator interface is necessary which would contain both limits of weak (single-particle) and strong (many-particle) injections including the space-charge limit. Recently, a self-consistent continuous description of injection in terms of carrier densities and mean fields was advanced^{31,32} based on the matching of the electric displacement and the electrochemical potential at the interface. This one-dimensional (1D) treatment implies averaging of all variables over the plane perpendicular to the injection current density which pertains to relatively high carrier densities. The model exhibits a plausible crossover from the barrier-dominated behavior at low voltages to the space-charge-dominated behavior at high voltages and also a field-induced reduction of the injection barrier. Nevertheless, at medium voltages, this reduction is much less than the reduction of the Schottky barrier due to the single-particle image potential of three-dimensional (3D) nature³³ which seems to have been confirmed in experiments.^{13,16,17} Apparently, there are restrictions on application of the mean-field description of the charge injection at low carrier densities.

The importance of proper account of the discrete, single-particle nature of the interaction between an injected carrier and the injecting electrode was emphasized in Refs. 34–36 where a sophisticated numerical treatment of the one-dimensional hopping transport in organic semiconductors was developed including the contribution of the modified single-particle image-charge potential. However, for the boundary conditions in this model, the tunneling from an electrode was employed assuming numerous atomistic parameters of the involved media instead of the density of states available and the carrier mobility.

The most advanced approach to charge injection including the Schottky barrier lowering and the space-charge effect was recently developed in Ref. 37 where 3D hopping of charge carriers over the sites of a cubic lattice with randomly distributed energy levels was considered as well as a sophisticated 1D continuous model. The site occupancies and the electric field were calculated self-consistently by solving the three-dimensional master equation and the Poisson equation in consequent iterations with account of the field-dependent injection barriers. On the other hand, the contribution of the individual image potential into injection was accounted in-

consistently which lead to an overestimation of the image effect as will be shown below.

The primary aims of this paper are to establish the requirements, which allow for the mean-field treatment of charge injection, and to extend the boundary conditions for the continuous description^{31,32,38} in such a way that the effect of discreteness of charge carriers is considered. We first look for a simple criterion separating the regions of system parameters (voltage and injection barrier) where either the single-particle (SP) or the many-particle, mean-field (MF) concepts are valid. Then we formulate self-consistent boundary conditions which account for the discrete character of the particle interaction with the electrode and provide the cross-over from low to high injection regime including the case of space-charge domination. Finally, the results are compared to an experiment.

II. COMPARING A SINGLE-PARTICLE AND A MEAN-FIELD CONCEPT

Adequacy of the MF description of the charge-carrier injection or, alternatively, of the SP picture is determined mostly by the relation between two respective characteristic lengths. In the first approach, this length is given by an average, three-dimensional distance between the injected charge carriers defined as $r_s = p_s^{-1/3}$, where p_s is the density of these carriers. It is assumed here that the distribution of the particles is homogeneous at least over the distance of few r_s in all space directions. In the second approach, the relevant length is the distance x_m from the plane surface of an electrode to the position of the potential maximum of the Schottky energetic barrier.³³

We verify now the validity of the SP approach from the point of view of the MF approximation and vice versa. If the density of injected carriers p_s predicted in the continuous consideration is so high that $r_s \ll x_m$, then the presence of many particles between the surface of the electrode and the maximum of the single-particle potential makes the SP approach inappropriate; *nota bene* that MF model density p_s is used in this estimation because in the consistent SP calculations, the density of injected carriers makes no sense. If, on the other hand, $x_m \ll r_s$, then the interaction of a single injected charge carrier with its image is much stronger than with the other distant injected carriers which makes the MF approximation inappropriate. At first sight, the criterion $x_m \approx r_s$ must roughly separate the regions of relevance of the discrete SP and the continuous MF concepts.³⁹ In fact, comparison of the SP image force exerted upon an injected carrier to random forces due to other charge carriers needs more sophisticated analysis and involves additionally other characteristic lengths. To perform this analysis, we first delineate below the SP and the MF approaches and then study their marginal validity. To make this delineation quantitative, we consider in the following exemplarily injection of holes from an indium tin oxide (ITO) electrode into an organic semiconductor.

A. Boundary conditions in the mean-field approach

Here, the treatment in terms of continuous carrier densities and fields is assumed. In the linearized Thomas-Fermi

approximation,⁴⁰ the electric field in the electrode, occupying the space at $x < 0$, reads³¹

$$F_c(x) = \left[F_c(0) - \frac{j}{\sigma_c} \right] \exp\left(\frac{x}{l_{TF}}\right) + \frac{j}{\sigma_c}, \quad x < 0, \quad (1)$$

where j is the position-independent steady-state current density, σ_c the conductivity of the electrode, and

$$l_{TF} = \sqrt{\frac{2\epsilon_0\epsilon_c\kappa_\infty}{3e^2p_\infty}} \quad (2)$$

is the Thomas-Fermi screening length. Here, e is the positive elementary charge, ϵ_0 the dielectric permittivity of vacuum, ϵ_c the static relative permittivity of the electrode, and p_∞ and κ_∞ are, respectively, the equilibrium values of the carrier density and of the chemical potential in the electrode far away from the interface.⁴¹

The electrochemical potential in the electrode equals³¹

$$\kappa_c(x) = E_b + \kappa_\infty + e l_{TF} \left[F_c(x) - \frac{j}{\sigma_c} \right] + e \phi_c(x), \quad x < 0, \quad (3)$$

where E_b terms the position of the conduction-band bottom and $\phi_c(x)$ the electrostatic potential in the electrode.

The electric field in the organic semiconductor, $F_s(x)$, obeys equation^{13,33}

$$\frac{kT}{e} F_s''(x) - F_s(x) F_s'(x) = - \frac{j}{\mu_s \epsilon_0 \epsilon_s}, \quad x > 0, \quad (4)$$

where μ_s denotes the hole mobility in the organic semiconductor, ϵ_s its static relative permittivity, k the Boltzmann constant, and T the absolute temperature. Nonlinear equation (4) is usually solved numerically¹³ but can also be solved analytically^{32,38} which offers a certain advantage as can be seen below. The solution reads as

$$F_s(x) = - \frac{2kT}{e l_{TF}} \frac{\text{Ai}' \left[\iota^{1/3} \left(\frac{x}{l_{TF}} + C_1 \right) \right] + C_2 \text{Bi}' \left[\iota^{1/3} \left(\frac{x}{l_{TF}} + C_1 \right) \right]}{\text{Ai} \left[\iota^{1/3} \left(\frac{x}{l_{TF}} + C_1 \right) \right] + C_2 \text{Bi} \left[\iota^{1/3} \left(\frac{x}{l_{TF}} + C_1 \right) \right]}, \quad (5)$$

where Ai and Bi denote the Airy functions⁴² and $\iota = je^2 l_{TF}^3 / [2\mu_s \epsilon_0 \epsilon_s (kT)^2]$. For the semi-infinite geometry considered in this section, the constant C_2 should be chosen equal to zero since the charge-carrier density vanishes asymptotically³² while the constant C_1 must be determined from the boundary condition at the interface.

Assuming Boltzmann statistics for charge carriers in the organic semiconductor, we proceed, similar to Sze for inorganic semiconductors,³³ with the electrochemical potential

$$\kappa_s(x) = E_b + \kappa_\infty + \Delta + kT \ln \left[\frac{p_s(x)}{N} \right] + e \phi_s(x), \quad x > 0, \quad (6)$$

where the zero-field barrier Δ is here given by the difference between $E_b + \kappa_\infty$ and the highest occupied molecular orbital

(HOMO) in the organic medium, N is the number of states for holes at the HOMO level, $p_s(x)$ the density of holes, and $\phi_s(x)$ the electrostatic potential in the organic medium. In fact, in disordered (organic) semiconductors, the injection barrier becomes an ill-defined quantity because such systems do not exhibit sharp band edges. The barrier is then often defined as a difference between the Fermi level in the injecting electrode and the center of the density of states (DOS) distribution at the HOMO level which is typically of the Gauss type.^{6,18,19,21,28,30,37} Using in the following the narrow-band approximation, we assume a negligible width of the mentioned Gauss DOS $\sigma \ll \Delta$. We note, on the other hand, that the following results apply for wide-band nondegenerate semiconductors and insulators as well in which case $2(2\pi mkT/h^2)^{3/2}$, with m the effective mass of carriers and h the Planck constant, should be taken for the effective number of states.^{33,38}

To obtain the boundary condition at the interface at $x=0$, we assume that:

(1) Electrostatic potential is continuous, $\phi_c(-0)=\phi_s(+0)$, which means absence of a dipole layer at the interface.

(2) Electric displacement is continuous, $\epsilon_c F_c(-0)=\epsilon_s F_s(+0)$, which implies absence of a surface charge at the interface.

(3) Electrochemical potential is continuous through the system, which provides matching at the interface, $\kappa_c(-0)=\kappa_s(+0)$.

Note that requirements 1 and 2 account for the image charges of all injected carriers in the mean-field approximation. Conditions 1–3 together deliver the boundary condition at the interface^{31,32}

$$\frac{p_s(0)}{N} = \exp \left[-\frac{\Delta}{kT} + \frac{e l_{TF}}{kT} \left(\frac{\epsilon_s}{\epsilon_c} F_s(0) - \frac{j}{\sigma_c} \right) \right], \quad (7)$$

which connects the values of the field and the carrier density in the organic semiconductor at the interface. Due to presence of the current, this boundary condition describes, in principle, a nonequilibrium state of the contact but in fact the contribution of the current in Eq. (7) can be neglected here because it is very small in all practical cases concerning organic semiconductors.^{31,32} That is why it will be omitted in the following modifications of formula (7). We note also that condition (7) does not define explicitly the values of the field and the carrier density at the interface; these quantities can only be found by satisfying Eq. (7) together with Eq. (5).

Since Boltzmann statistics is assumed to calculate the chemical potential in the organic medium, the argument of the exponential function in formula (7) must be negative which imposes a restriction on the field value $F_s(0) < F_{lim} = \epsilon_c \Delta / (\epsilon_s e l_{TF})$. The form of Eq. (7) implies an effective barrier for hole injection

$$\Delta_{eff} = \Delta - e F_s(0) l_{TF} \epsilon_s / \epsilon_c = \Delta - e F_c(0) l_{TF}, \quad (8)$$

which states a barrier modification due to the electric field at the interface. The barrier correction in Eq. (8) is linear in field and may be positive or negative depending on the sign of the local field at the interface. The physical reason for this

barrier modification is a contribution of the work done by the mean electric field on electrons in the electrode.

B. Schottky barrier and image potential in the single-particle approach

In the classical description of a Schottky barrier,^{13,28,33} the barrier for the emission of a single particle through a plane interface is formed by the superposition of the zero-field barrier Δ , the potential of attraction to the image charge of the opposite sign at the electrode, and the contribution of the mean electric field in the organic semiconductor $F_s(x)$,

$$U(x) = \Delta - \frac{e^2}{16\pi\epsilon_0\epsilon_s x} - e F_s(0)x, \quad x > 0, \quad (9)$$

where x denotes the distance from the ITO-organic interface and $F_s(0)$ the value of the electric field at the interface. The electric field $F_s(x)$ is assumed positive and virtually constant within the distance $\approx x_m$ from the interface, since for the negative field the potential exhibits no maximum and does not allow particle escape from the potential well. The maximum of the potential barrier, Eq. (9), is located at a position

$$x_m = \sqrt{\frac{e}{16\pi\epsilon_0\epsilon_s F_s(0)}} \quad (10)$$

and amounts to $U(x_m) = \Delta - e \delta\phi_{Sch}$, with

$$\delta\phi_{Sch} = 2 F_s(0) x_m = \sqrt{\frac{e F_s(0)}{4\pi\epsilon_0\epsilon_s}}, \quad (11)$$

where the latter provides the so-called Schottky-barrier lowering.³³ This barrier modification is proportional to the square root of the field and always reduces the barrier in contrast to the barrier correction in Eq. (8) which is linear in the field and may have different signs. The physical reason for the Schottky-barrier lowering is also different: in contrast to the contribution of the mean electric field at the side of the electrode as described by Eq. (8), Eq. (11) results from the energy profile modification in the dielectric medium due to the individual image-charge effect.

Equation (9) implies ideal screening of the electrostatic field by the metal surface at $x=0$. ITO is, however, a highly doped semiconductor which does not provide ideal screening of the field. Taking into account the dielectric permittivity of the electrode ϵ_c and the characteristic length of the field penetration into the electrode l_{TF} , the energy of the injected charge carrier is substantially modified.⁴³ While at large distances from the interface $x \gg a = (\epsilon_s / \epsilon_c) l_{TF}$ the energy approaches asymptotically Eq. (9), at small distances $x \ll a$, the Coulomb term $\sim e^2(\epsilon_s - \epsilon_c) / [(\epsilon_s + \epsilon_c) 16\pi\epsilon_0\epsilon_s x]$ prevails, which can even change sign from attraction to repulsion depending on the magnitudes of respective permittivities. At such small distances, a consistent quantum-mechanical treatment of injection becomes necessary which, in turn, essentially modifies the energy profile in the close vicinity of the interface.^{44,45} For our consideration, the important maximum of the potential (9) would fall into the region $x_m \sim a$ for a voltage of about $eL / 16\pi\epsilon_0\epsilon_s a^2$, with L the device thickness. For typical parameters of both involved media given in

TABLE I. Typical material parameters for the injecting electrode and an organic semiconductor (Refs. 15, 40, and 46–48). The parameters are deduced assuming $T=300$ K.

ITO						Organic semiconductor			
l_{TF} (Å)	p_{∞} (cm ⁻³)	ϵ_c	μ_c (cm ² /(V s))	κ_{∞} (eV)	E_A (eV)	N (cm ⁻³)	ϵ_s	μ_s (cm ² /(V s))	E_{HOMO} (eV)
8.6	10^{20}	9.3	30	0.225	4.7	10^{21}	3	10^{-4}	5.0

Table I and $L \simeq 100$ nm, this voltage amounts to 200 V which is far too large for organic materials. Therefore, in the following, the classical approximation for the image potential, Eq. (9), will be used keeping in mind possible modifications of this interaction when other electrode and dielectric materials are involved.

C. Microscopic comparison of the single-particle image force and stochastic forces

To establish on what terms the SP approach transforms to the MF one, we first generalize formula (9). In classical statistical mechanics, the microscopic density of injected particles is defined as⁴⁹

$$p(\mathbf{r}, t) = \sum_i \delta[\mathbf{r} - \mathbf{r}_i(t)], \quad (12)$$

where $\delta(\mathbf{r})$ is the three-dimensional Dirac delta function and vectors $\mathbf{r}_i(t)$ indicate random positions of all injected particles and their images. The energy of an injected particle is then given by

$$U_M(\mathbf{r}, t) = U_0(\mathbf{r}) - \frac{e^2}{16\pi\epsilon_0\epsilon_s x} + \int d\mathbf{r}' p(\mathbf{r}', t) \frac{e^2 \text{sgn}(x')}{4\pi\epsilon_0\epsilon_s |\mathbf{r} - \mathbf{r}'|} \quad (13)$$

and the x component of the microscopic force exerted upon this particle reads

$$f_M^x(\mathbf{r}, t) = -\frac{\partial U_0}{\partial x} - \frac{e^2}{16\pi\epsilon_0\epsilon_s x^2} - \frac{\partial}{\partial x} \int d\mathbf{r}' p(\mathbf{r}', t) \frac{e^2 \text{sgn}(x')}{4\pi\epsilon_0\epsilon_s |\mathbf{r} - \mathbf{r}'|}, \quad (14)$$

where the first term in both Eqs. (13) and (14) presents the contribution of an external field, the second term is due to the individual image charge, and the third one accounts for the other injected particles. The signum function $\text{sgn}(x')$ in the last term accounts for opposite sign of the image charges. To judge whether the SP approach is relevant, the impact of the deterministic individual image effect should be compared to the impact of the other particles. Due to the stochastic nature of the interaction of the individual particles leading to the energy and force fluctuations, the comparison must be performed in two ways: the mean value or, alternatively, the variance of the third term in Eq. (13) or (14) should be compared to the second term. As long as the mean value and the variance of the stochastic term is much less than the individual image-charge contribution, the SP approach prevails.

1. Mean-force criterion

By configurational averaging of Eq. (14) over all possible charge-carrier positions, the mean, macroscopic density of particles becomes a continuous function of the only variable x : $\langle p(\mathbf{r}, t) \rangle = p_s(x)$. After integration over the space variables y' and z' , the mean force results in the form

$$\langle f_M^x(\mathbf{r}, t) \rangle = -\frac{\partial U_0}{\partial x} - \frac{e^2}{16\pi\epsilon_0\epsilon_s x^2} + \frac{e^2}{2\epsilon_0\epsilon_s} \int_{-\infty}^{+\infty} dx' p_s(|x'|) \text{sgn}(x') \text{sgn}(x - x'), \quad (15)$$

where the second and the third terms should be compared at $x = x_m$. Keeping in mind the hopping transport over the random atomic or molecular sites typical of disordered (organic) semiconductors, we assume here that the characteristic length in the space dependence of $p_s(x)$ is much larger than the nearest-neighbor distance between the sites occupied by the charge carriers, $r_0 \simeq 0.1 - 1$ nm.

Equations (13)–(15) make sense if the density of injected particles decreases at distances much smaller than the device thickness, L , otherwise the electrostatic potential has to be modified to account for the other electrode as it is done in the Appendix. Nevertheless, even overestimation of the integral in Eq. (15) for the very low constant concentration $p_s(x) \sim r_s^{-3}$ at $-L < x < L$, with $r_s \gg L$, results, by comparison of the second and the third terms, in assessment $x_m \simeq \sqrt{r_s^3/8\pi L} \gg L$. Since such x_m cannot be realized, it means that the third term in Eq. (15) remains always much less than the second one, so that the SP contribution dominates in the limit $r_s \gg L$. This formal statement is in agreement with the obvious fact that, for $r_s > L$, the description in terms of the continuous charge density is not valid.

For higher concentrations with $r_s \ll L$, we may apply to the evaluation of the integral in Eq. (15) the equilibrium solution of Eq. (4) which is known to prevail in a wide range of applied fields^{31,32}

$$p_s(x) = p_s(0)/(1 + x/\lambda\sqrt{2})^2, \quad (16)$$

with the Debye length $\lambda = \sqrt{\epsilon_0\epsilon_s kT/e^2 p_s(0)}$. By comparing the second and the third terms in Eq. (15), the criterion results

$$x_m = \frac{l_T}{2} + \sqrt{\left(\frac{l_T}{2}\right)^2 + r_s \sqrt{\frac{r_s l_T}{16\pi}}}, \quad (17)$$

where one more characteristic length $l_T = e^2/32\pi\epsilon_0\epsilon_s kT = r_s^3/32\pi\lambda^2$ of the order of the Coulomb capture radius⁵⁰

appears. For typical parameters of organic semiconductors at room temperature,^{31,32} l_T is about 2 nm. In the range of concentrations $L^{-3} \ll p_s(0) \ll l_T^{-3}$, it follows from Eq. (17) in a good approximation that

$$x_m \simeq r_s \left(\frac{l_T}{16\pi r_s} \right)^{1/4} \simeq (0.2 - 0.4) r_s. \quad (18)$$

This means that, for x_m smaller than that given by Eq. (18), the SP term in the force, Eq. (15), dominates while in the opposite case the SP contribution may be considered as embedded in the MF term.

For higher concentrations $p_s(0) \gg l_T^{-3}$, the equilibrium density (16) does not apply anymore. By increasing external field, the injected charge density is known to transform from the diffusion induced equilibrium distribution (16) to virtually constant distribution over the device³¹ which transforms by further field increasing to the distribution $p_s(x) \sim 1/\sqrt{x}$ typical of space-charge limiting currents.⁷ Assuming that at $r_s \lesssim l_T$ the concentration $p_s(x) \sim l_T^{-3}$ remains constant all over the device and $x_m \ll L$, one obtains, by equating the second and the third terms in Eq. (15), the criterion $x_m \simeq r_s \sqrt{r_s/16\pi L} \simeq 10^{-1} l_T$. According to Eq. (10), this can only be realized for very high fields where the classical SP approximation will be violated because of quantum effects discussed in Sec. II B. Thus, in the region of realistic electric fields, the SP contribution remains much lower than the MF one so that the MF approximation prevails for $r_s \lesssim l_T$.

For even higher densities, when r_s becomes much less than l_T , the MF approximation of Sec. II A is expected to fail because of violation of the criterion of applicability of Boltzmann statistics, $F_s(0) < F_{lim}$. On the other hand, the classical SP approximation might also be violated in this region because of the mentioned quantum effects. In any case, this all happens at rather high voltages as will be seen in the following.

2. Energy fluctuation criterion

Considering the variation of the microscopic energy (13), we will need a second central moment of the microscopic carrier density which can be written in the form⁴⁹

$$\langle \delta p(\mathbf{r}', t) \delta p(\mathbf{r}'', t) \rangle = p_s(x) \delta(\mathbf{r}' - \mathbf{r}'') + p_s^2(x) g_2(\mathbf{r}' - \mathbf{r}''), \quad (19)$$

with $\delta p(\mathbf{r}, t) = p(\mathbf{r}, t) - p_s(x)$ and $g_2(\mathbf{r})$ the correlation function. In terms of hopping over the molecular sites, this form assumes that $p_s(x)$ changes on the scale much larger than both the distance between the nearest-neighbor sites, r_0 , and the characteristic length of the correlations contained in the function $g_2(\mathbf{r})$. In Refs. 37 and 51, an assumption of the short-range correlations of the charge-carrier positions was adopted which only excludes the double occupation of sites. This implies that $g_2(\mathbf{r}) = -1$ when $|\mathbf{r}| < r_0$ and $g_2(\mathbf{r}) = 0$ otherwise as in the model of hard spheres.⁴⁹ Such space correlations are compatible with the hypothesis of the uncorrelated Gauss disorder of the energy levels at different sites in a random hopping system considered in Refs. 21, 37, and 51. The validity of the short-range space correlations of the particle positions can be verified by comparison to the screened Coulomb correlations given by the function⁴⁹

$$g_2(\mathbf{r}) = \exp \left[-\frac{8l_T}{r} \exp \left(-\frac{r}{\lambda} \right) \right] - 1, \quad (20)$$

which is also appropriate for the charged plasma of injected particles of the same sign. This formula defines indeed short-range correlations for medium and high charge densities when $r_s \leq 10$ nm since in this case $\lambda \leq 2$ nm. However, for lower particle concentrations with $r_s \simeq L/2 \simeq 50$ nm, the correlation length becomes about $\lambda \simeq 20$ nm. Other possible correlations in organic systems and their effect on the results presented here will be discussed later in the concluding section.

The variation of the energy (13) is due to the stochastic term only and can be estimated as

$$\langle [U_M(\mathbf{r}, t) - \langle U_M(\mathbf{r}, t) \rangle]^2 \rangle \simeq \left(\frac{e^2}{4\pi\epsilon_0\epsilon_s} \right)^2 \int d\mathbf{r}' \frac{p_s(|x'|)}{(\mathbf{r} - \mathbf{r}')^2} [1 + p_s(|x'|)v_0] \simeq \left(\frac{e^2}{4\pi\epsilon_0\epsilon_s} \right)^2 2\pi \int_{-L}^L dx' p_s(|x'|) \ln \left| \frac{L_\perp}{x - x'} \right|, \quad (21)$$

where the correlation volume $v_0 \sim \lambda^3$ and the integration over the variables y' and z' was restricted by the transverse size of the device, L_\perp , which is typically about few nm. The contribution of correlations is about $(\lambda/r_s)^3$ and remains much less than unity for all particle densities considered, therefore it does not affect the final estimation in Eq. (21).

For very low concentrations with $r_s \gg L$, assuming constant $p_s(x) \simeq r_s^{-3}$ all over the device, one finds energy variation of the order of

$$\langle [U_M(\mathbf{r}, t) - \langle U_M(\mathbf{r}, t) \rangle]^2 \rangle \simeq \left(\frac{e^2}{4\pi\epsilon_0\epsilon_s} \right)^2 \frac{4\pi L}{r_s^3} \ln \left(\frac{L_\perp}{L} \right), \quad (22)$$

which cannot match the second term of Eq. (13) squared at any reasonable value of $x_m < L$. This means domination of SP contribution for these concentrations in accordance with the mean-force analysis in the previous section.

For intermediate concentrations such that $l_T \ll r_s \ll L$, the equilibrium particle density may be used. Substituting

Eq. (16) into Eq. (21) and comparing the result to the second term of Eq. (13) squared, one comes to the criterion

$$x_m \approx r_s \left(\frac{l_T}{16\pi r_s} \right)^{1/4} \frac{1}{\sqrt{\ln(L_\perp/\lambda)}} \approx (0.05 - 0.1)r_s, \quad (23)$$

with the coefficient for r_s by factor 0.25 less than that in the mean-force criterion (18). When x_m is less than the value given by the criterion (23), the SP contribution dominates the injection process, in the opposite case, the SP term becomes negligible, comparing to the stochastic contribution to the energy so that the MF mechanism of injection prevails.

For high particle concentrations with $r_s \leq l_T$, assuming again constant $p_s(x) \approx l_T^{-3}$, the energy variation of the form (22) obtains. In the considered parameter range, it dominates strongly over the SP term for all reasonable values of x_m so that the MF contribution prevails in accordance with the mean-force analysis in the previous section.

Summarizing analysis using both the mean-force and energy fluctuation criteria, it is apparent that the SP approach to the injection is in any case relevant for low concentrations of injected particles $p_s \leq L^{-3}$ while the MF approach is valid for high concentrations $p_s \geq l_T^{-3}$ whereas individual contributions of single particles and their images are lost in the collective mean field. In the intermediate range $L^{-3} \leq p_s \leq l_T^{-3}$, the two mentioned criteria bring about somewhat different estimations of the crossover from the SP to the MF domination regime, Eqs. (18) and (23), that can be roughly compromised by the criterion

$$x_m \approx 0.2r_s, \quad (24)$$

which will be used in the following analysis. The above specified microscopic conditions imply restrictions on the macroscopic variables and system parameters which define description of injection in terms of the SP or the MF approach when x_m is smaller or larger than the value given by Eq. (24), respectively. The corresponding macroscopic conditions for fields and voltages are revealed in the next section.

D. Macroscopic criterion for the validity of the mean-field and the single-particle concepts

Let us consider the intermediate range of concentrations of injected charge carriers, $L^{-3} \leq p_s(0) \leq l_T^{-3}$. Substituting expressions for $r_s = p_s(0)^{-1/3}$, Eq. (7), and for x_m , Eq. (10), into the criterion (24), we arrive at a transcendent equation for the field $F_s(0)$,

$$\sqrt{\frac{e}{16\pi\epsilon_0\epsilon_s F_s(0)}} = 0.2N^{-1/3} \exp \left[\frac{\Delta}{3kT} - \frac{eF_s(0)l_{TF}\epsilon_s}{3kT\epsilon_c} \right]. \quad (25)$$

A graphical solution of the above equation for typical parameters of ITO and organic semiconductors at room temperature (see Table I) is shown in Fig. 1 which exhibits two points of intersections. The dependence of the two corresponding field magnitudes on the barrier height Δ is shown in Fig. 2. The MF approximation is expected to be valid in the range of interface fields smaller than F_{min} or larger than

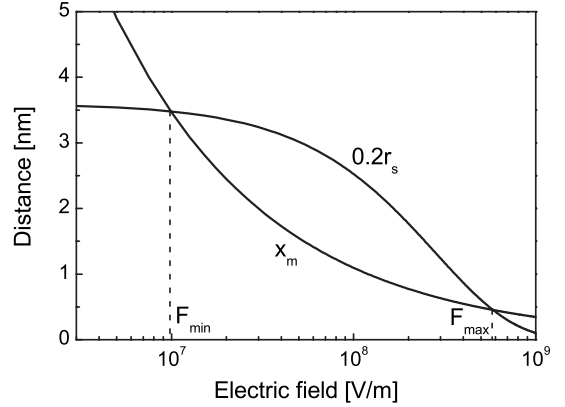


FIG. 1. Position of the potential maximum of the Schottky barrier, x_m , and 0.2 of the mean distance between injected charge carriers in the MF approach, r_s , as functions of the electric field at the interface for $\Delta=0.225$ eV and $T=300$ K.

F_{max} , where $0.2r_s < x_m$, with the SP approximation prevailing between these lines as indicated in Fig. 2 with account of the assumed restrictions $l_T < r_s < L$.

The area of high carrier densities $p_s(0) \geq l_T^{-3}$ is indicated by the line F_T where the condition $r_s = l_T$ is fulfilled. Above this line determined by temperature, the density of injected particles is so high that individual image forces are strongly overwhelmed by the mean field. Note also the line F_{lim} indicating the border at which the Boltzmann statistics used in the MF consideration is violated.

The preceding analysis in this section implied treatment in terms of the continuous particle density and mean field. For the low carrier densities $p_s(0) \leq L^{-3}$, these quantities make no sense. The line F_L indicates the border where the condition $r_s = L$ is fulfilled. Below this line determined by the de-

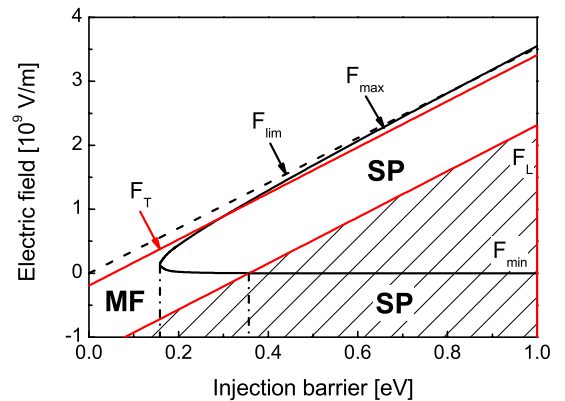


FIG. 2. (Color online) Two field solutions of the equation $x_m = 0.2r_s$ are shown with solid lines which delineate the areas where the MF and the SP concepts are valid. Dashed line F_{lim} restricts from above the field values calculated under the assumption of Boltzmann statistics. At solid lines F_T and F_L , the equations $r_s = l_T$ and $r_s = L$ are, respectively, satisfied. Thereby the area above F_T is described by the MF approximation. In the hatched area below F_L , the continuous description of the transport and injection fails. To the left of the dash-dotted line at $\Delta=0.16$ eV, the inequality $0.2r_s < x_m$ holds always. The other dash-dotted line at $\Delta=0.38$ eV marks the intersection of the lines F_{min} and F_L .

vice thickness, the injected particles are so sparse that the continuous description fails but the SP approach applies. This hatched area in Fig. 2 overlaps with the abovementioned SP area but has another physical meaning. Here, the Richardson-Schottky formula³³ for the SP thermionic emission should apply or more sophisticated concepts adapted to the hopping conductivity typical of organic systems^{18,19,28–30} be implemented. In the upper SP region above the lines F_{min} and F_L , the continuous description still works but the injection is dominated by the SP mechanism.

To the left of the characteristic value of the injection barrier of $\Delta \approx 0.16$ eV, where the lines F_{min} and F_{max} merge, the MF approach is valid for all fields between the values F_L and F_{lim} . To the right of the characteristic value of the barrier of $\Delta \approx 0.38$ eV, at which the lines F_{min} and F_L intersect, the SP approach is valid for all fields up to the value of F_T . In the region of barrier values $0.16 \text{ eV} < \Delta < 0.38 \text{ eV}$, the chart becomes nontrivial. Namely, by increasing the electric field from the very low values, first the only SP approach is applicable, then MF approach becomes applicable too and describes injection, later the reentrant SP regime prevails due to domination of individual image forces, and by further field increasing, the reentrant MF regime is realized at high carrier concentrations when reaching the lower one of the fields F_T or F_{max} . The drift-diffusion equation (4) applies thereby for the description of charge transport inside the organic semiconductor in the whole region $F_L < F_s < F_{lim}$.

Note that all the characteristic field lines presented in the chart on Fig. 2 result from estimations such as the criterion (24) and, hence, are not sharp boundaries but rather indicate the location of transition regions between the SP and MF domains. From the derivation of the criteria (18), (23), and (24), it is clear that the uncertainty of the numerical factor in Eq. (25) may cause only a weak logarithmic change in the characteristic fields. The consequent uncertainty of the positions of the above field lines characterizes the width of the transition regions which appears to be much less on the logarithmic scale than the SP and MF regions themselves.

Now, using the obtained threshold values of the fields in Fig. 2, we have to establish the range of voltages and barrier heights where the relevant field strengths can be achieved. Note that changing the injection barrier Δ for a fixed electrode means considering organic materials with different positions of the HOMO level.

Combining the solution (5) with the boundary condition (7), one finds that the field at the interface is negative in equilibrium ($j=0$) or when the applied voltage is small.^{5,31,32} The reason for this is that the field has to compensate the positive diffusion current caused by the huge difference in charge-carrier concentrations between the different sides of the interface. When a positive bias is applied, the field changes its sign at some point inside the dielectric usually called a “virtual electrode.”⁵ In the parameter range where the electric field is negative at the interface, the Schottky barrier concept does not apply because a single charge carrier cannot escape from the potential well. In this case, however, the collective injection can occur which thus could be described within the MF approach. The boundary of this parameter region is delineated by the condition that the field at the interface equals zero or, in other words, that the virtual

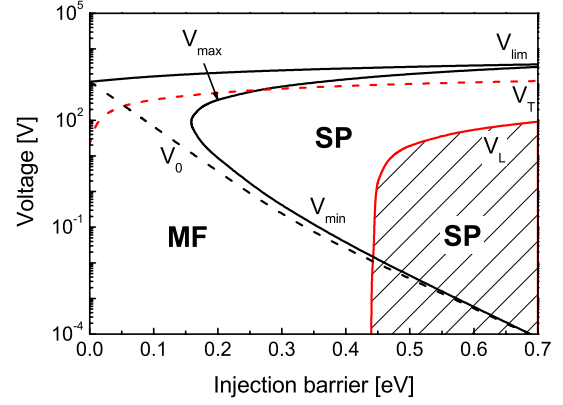


FIG. 3. (Color online) Two solid lines, V_{min} and V_{max} , outline areas of validity of the SP and the MF approaches. Increasing dashed line V_T further bounds the SP region from above. Line V_{lim} bounds from above the region where the Boltzmann statistics applies. Decreasing dashed line V_0 shows the voltage at which the field at the interface vanishes. Line V_L delineates the boundary of the hatched area where the mean-field treatment loses any sense.

electrode coincides with the physical interface. For a given value of the barrier, the current magnitude at which this occurs may be found exactly using the solution (5) and reads as

$$j_0 = e\mu_s N \sqrt{\frac{kTN}{2\epsilon_0\epsilon_s}} |z_0|^{-3/2} \exp\left(-\frac{3\Delta}{2kT}\right), \quad (26)$$

where $z_0 \approx -1.02$ is the first zero of the Airy function $\text{Ai}'(z)$ (Ref. 42). The current-voltage (I - V) relation for a single ITO-organic interface is³²

$$V = l_{TF} \left[\frac{\epsilon_s}{\epsilon_c} F_s(0) - \frac{j}{\sigma_c} \right] + 2 \frac{kT}{e} \ln \left[1 - \frac{eL}{2kT} F_{s0}(0) \right] - l_{TF} \frac{\epsilon_s}{\epsilon_c} F_{s0}(0) - \frac{2kT}{e} \ln \left| \frac{\text{Ai}[l^{1/3}(L/l_{TF} + C_1)]}{\text{Ai}[l^{1/3}C_1]} \right|, \quad (27)$$

where the constant $F_{s0}(0)$ has to be determined from the boundary condition (7) at the interface in the equilibrium case $j=0$ while the constants $F_s(0)$ and C_1 have to be determined satisfying Eq. (7) with the solution (5). Using the current value j_0 and the current-voltage relation (27), a magnitude of the voltage $V_0(\Delta)$ may be obtained which defines the line $F_s(0)=0$ on the V - Δ plane (see Fig. 3).

Using the characteristic field values of the Fig. 2, also the voltages V_{min} , V_{max} , V_{lim} , V_T , and V_L which separate the MF and SP regions can be found by adjusting the current until the respective field values F_{min} , F_{max} , F_{lim} , F_T , and F_L are achieved at the interface as is presented in Fig. 3. The above calculations using continuous particle densities are applicable as long as the inequality $r_s < L$ roughly holds that is above the line V_L below which only SP consideration makes sense. The line V_T crosses the line V_{max} so that the SP-dominated region is bound from above by the voltage $\min\{V_{max}, V_T\}$. Above this voltage, the MF approach is valid until the voltage V_{lim} is achieved at which it fails together with the Boltzmann statistics.

Though it looks counterintuitive, the continuous MF description of injection may be valid for low voltages while the discrete SP description, expected to work at low injection rates, applies also for rather high voltages. The reason can be seen in the very small escape distances x_m at high voltages for which $x_m \ll r_s$, if the injection barrier Δ is not low, so that the individual image force on the charge-carrier dynamics dominates. At low voltages and low barriers, however, the density of injected particles is diffusion driven and therefore relatively high which reduces the interparticle distance r_s to values small compared to the distance for the individual particle escape x_m and entails domination of the mean field.

III. MODIFIED MEAN-FIELD BOUNDARY CONDITIONS FOR A SINGLE INTERFACE

The deficiency of the MF approach to the description of the injection within the SP parameter range in Fig. 3 below the lines $\min\{V_{max}, V_T\}$ and above the lines $\max\{V_{min}, V_L\}$ is the missed contribution from the individual image forces of each single charge carrier. This strong but short-range deviation from the mean field near the interface may be accounted for as a dipole layer of a characteristic width x_m as long as the latter distance is much less than r_s , which is true in the mentioned region. Indeed, this layer contributes to the shift in energy of each injected charge carrier through the work performed by the individual image force, which results in the shift in the electrostatic potential at the interface given by $\delta\phi_{Sch}$, Eq. (11). Accounting for that in the mentioned SP region, the boundary condition (requirement 1 of continuity of the electrostatic potential in the Sec. II A) has to be replaced by the condition

$$\phi_s(+0) - \phi_c(-0) = \delta\phi_{Sch}. \quad (28)$$

Applying this boundary condition at $x=0$, the dipole layer is formally considered as an infinitesimal sheet so that the drift-diffusion equation (4) applies for $x>0$.

Taking this into account, the modified boundary condition reads

$$\frac{p_s(0)}{N} = \exp \left[-\frac{\Delta}{kT} + \frac{eF_s(0)l_{TF}}{kT} \frac{\epsilon_s}{\epsilon_c} + \left(1 - \frac{b}{0.2r_s} \right) \frac{1}{kT} \sqrt{\frac{e^3 F_s(0)}{4\pi\epsilon_0\epsilon_s}} \right] \quad (29)$$

in the SP region restricted by the inequality $\max\{V_{min}, V_L\} \leq V \leq \min\{V_{max}, V_T\}$ with $b = \max\{x_m, 0.2l_{TF}\}$. An interpolation factor $(1 - b/0.2r_s)$ introduced in the last term provides smooth switching of the dipole layer contribution at the boundary of the SP region which ensures that the position of this boundary is defined consistently when evaluated from inside and outside of this region. Indeed, crossing the line V_{min} or V_{max} from the SP region to the MF region, the length x_m exceeds $0.2r_s$ and can no more be considered as the dipole layer thickness. In this case, the image force averaged over all injected carriers and their images is accounted for in the mean-field value $F_s(0)$. The same occurs also at the line V_T according to analysis in Sec. II C. Thus, the last term in the

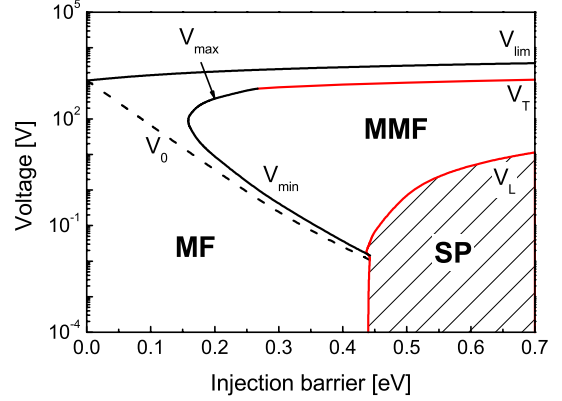


FIG. 4. (Color online) Solid voltage lines V_{min} , V_{max} , V_T , and, partly, V_L outline the MMF area where the MF concept with the boundary condition (29) applies in contrast to the MF area where the boundary condition (7) holds above and below the line V_0 . Latter line shows the voltage at which the field at the interface vanishes. The MF approach fails completely only in the hatched SP region under the line V_L . Line V_{lim} bounds from above the region where the Boltzmann statistics applies.

brackets in Eq. (29) following from the potential difference (28) has to vanish at the boundary of SP region which is provided by the above-introduced interpolation factor.

Now, Fig. 3 has to be reconsidered on the basis of the modified boundary condition (29). It is obvious that the lines V_0 , V_{min} , V_{max} , and V_T do not change their positions since, at these lines, the boundary condition (7) still holds (see Fig. 4). The equation $r_s = L$, however, is affected by the modified density of injected particles in Eq. (29). This is followed by the revised value of the field F_L producing the new borderline V_L . The MF approach applies now also in the SP region above the line V_L , however, with account of the dipole layer in Eq. (29), therefore it will be called from now on a modified mean-field (MMF) region. The genuine SP domain where the SP concept only applies shrinks now to the region below the V_L line.

Finally, the generalized boundary conditions (7) and (29) apply on the whole $V-\Delta$ plane below the V_{lim} and above the V_L lines and can be used together with standard continuous equations for the field and charge densities while the RS or FN single-particle concepts are expected to hold below the line V_L . To make these results comparable to experiment, we address below two examples of practically relevant two-electrode devices.

IV. MODIFIED MEAN-FIELD APPROACH FOR TWO-ELECTRODE DEVICES

In the case of the organic layer sandwiched between two electrodes, located at the positions $x = \pm L/2$, multiple images of an injected hole will contribute to the potential in the SP approach. Consequently, the second term in Eq. (9) has to be replaced by the energy of charge interaction with both electrodes derived in the Appendix. We have to account now for possible injection of charge carriers from both electrodes. If the mean field F_s becomes positive at the left interface at

$x = -L/2$ or negative at the right interface $x = L/2$ (which never occurs at the same time³¹), the SP Schottky mechanism of injection may become relevant at the respective electrodes. In the spirit of our modification of the boundary condition at the single interface $x = 0$ in Eqs. (28) and (29), the boundary conditions at $x = \pm L/2$ should be modified by the potential discontinuities $\delta\phi_{Sch}^\pm$ if the distance from the potential maximum to the respective electrode $L/2 - |x_m| < 0.2r_s^\pm$, with $r_s^\pm = [p_s(\pm L/2)]^{-1/3}$ being the mean distance between injected particles near the electrodes at $\pm L/2$. In this case, the mean field may be assumed constant within the distances r_s^\pm from the respective electrodes and the following approximations used for the energy profile near the electrodes:

$$U_\pm(x) \cong \Delta^\pm - eF_s(\pm L/2)(x \mp L/2) + \frac{e^2}{16\pi\epsilon_0\epsilon_s L} \left[\psi\left(\frac{1}{2} + \frac{x}{L}\right) + \psi\left(\frac{1}{2} - \frac{x}{L}\right) + 2\gamma \right], \quad (30)$$

where Δ^\pm denote the injection barriers at $x = \pm L/2$, γ is Euler's constant, and $\psi(x)$ is the digamma function.⁴² The expression in square brackets reproduces the behavior of the Coulomb potential in Eq. (9) when approaching one of the electrodes at $x = \pm L/2$ but is symmetric and has a maximum at $x = 0$. Note that the criterion (24) derived using the energy (9) for a single interface accounts, in fact, for the second electrode and can therefore be applied to the two-electrode devices.

According to the approximations (30), the position of the maximum is defined by one of the equations

$$\psi'\left(\frac{1}{2} + \frac{x_m}{L}\right) - \psi'\left(\frac{1}{2} - \frac{x_m}{L}\right) = \frac{16\pi\epsilon_0\epsilon_s L^2}{e} F_s(\pm L/2), \quad (31)$$

taking the upper sign, if $F_s(L/2) < 0$, or the lower sign, if $F_s(-L/2) > 0$. The respective potential discontinuities are given then by the formula

$$e\delta\phi_{Sch}^\pm = \Delta^\pm - U_\pm(x_m), \quad (32)$$

which determines them as functions of the field at the respective interfaces.

The boundary conditions 1–3 of Sec. II A modified with the potential discontinuities (28) and (32) at both interfaces result in the conditions

$$\frac{p_s(\pm L/2)}{N} = \exp \left[-\frac{\Delta^\pm}{kT} \mp \frac{eF_s(\pm L/2)l_{TF}^\pm}{kT} \frac{\epsilon_s}{\epsilon_c^\pm} + \left(1 - \frac{b^\pm}{0.2r_s^\pm} \right) \frac{e\delta\phi_{Sch}^\pm}{kT} \right], \quad (33)$$

where quantities identified with superscript \pm denote here and below the parameters of the two electrodes contacted at $x = \pm L/2$. Note that the last term in the exponent appears only inside the MMF area on the V - Δ plane whose boundaries are determined self-consistently by the criterion $L/2 - |x_m| = 0.2r_s^\pm$ using formula (33) itself. The cases of symmetric and asymmetric devices are considered separately below.

A. Modified validity chart and current-voltage characteristics of a unipolar symmetric organic device

We examine first the case of a symmetric unipolar device consisting of two ITO electrodes and an organic layer in between providing p -type conductivity. At zero bias, the diffusion-mediated electric field is directed outwards at both electrodes, i.e., is negative at $x = -L/2$ and positive at $x = L/2$. In this case, the Schottky-type contribution in formula (33) vanishes and the MF boundary conditions of the type of Eq. (7) apply at both interfaces as long as the barrier is not too large which is in agreement with the chart for the single ITO-organic interface (Fig. 4). Note, further, that for a positive bias, a positive field always prevails at the right, collecting electrode so that the Schottky-type barrier lowering does not arise here at all and this electrode remains in the MF regime as long as the continuous approach is valid.

On the other hand, when the bias is high enough, the field at the left, injecting electrode becomes positive and may exceed the characteristic field F_{min} in which case the modified boundary condition (33) includes the Schottky lowering term. Since $\delta\phi_{Sch}^-$ is not known as explicit function of the field $F_s(-L/2)$, Eq. (33) should be solved together with Eqs. (30)–(32). Then the mean interparticle distance r_s^- can be evaluated and the equation $L/2 - |x_m| = 0.2r_s^-$ solved with respect to the field $F_s(-L/2)$, resulting in the positions of the lines F_{min} and F_{max} on the F - Δ plane for the injecting electrode. Additionally, the characteristic field F_{lim} can also be found equating the exponent in Eq. (33) to zero and the field F_T can be determined from the equation $r_s^- = l_T$. Determination of the line F_L , where the continuous approach fails, is a bit less straightforward. When the charge carriers are so sparse in the device that the mean distance between them equals the distance between the electrodes, their concentration is defined by injection from both electrodes. Therefore, the mean particle density \bar{p}_s and the corresponding mean distance $\bar{r}_s = \bar{p}_s^{-1/3}$ should be used for the definition of F_L from equation $\bar{r}_s = L$. Integrating the Gauss equation over the device thickness, one finds that

$$\bar{p}_s = \frac{\epsilon_0\epsilon_s}{eL} [F_s(L/2) - F_s(-L/2)]. \quad (34)$$

Thus the procedure of F_L determination is as follows. Below the line F_{min} , the MF boundary conditions, Eq. (7), are satisfied at both electrodes with Eq. (5) and the current is increased until equation $\bar{r}_s = L$ is fulfilled. Above the line F_{min} , the boundary condition (33) should be satisfied at the left electrode and the MF boundary condition (7) at the right electrode while the current is adjusted until the requirement $\bar{r}_s = L$ is fulfilled. The mentioned lines delineate together the MMF region on the field-barrier plane similar to Fig. 2. This chart, however, plays only an auxiliary role and will not be presented here.

Having determined F_{min} , F_{max} , F_{lim} , F_L , and F_T as functions of Δ^- , one can calculate, using the solution (5), the respective voltages V_0 , V_{min} , V_{max} , V_{lim} , V_L , and V_T which delineate the MMF region. To this end, the current is varied as parameter until the respective field magnitude is achieved at $x = -L/2$; the voltage then follows by direct integration of

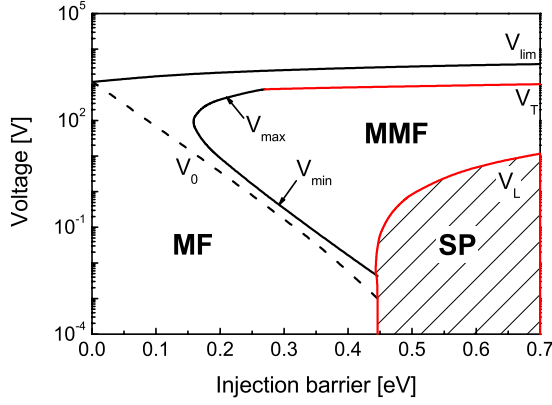


FIG. 5. (Color online) Solid lines V_{min} , V_{max} , V_T , and, partly, V_L outline the MMF area for a symmetric ITO-organic-ITO device where the SP contribution to the MF approach must be accounted for. Dashed line indicates the voltages V_0 at which the field at the left interface vanishes. Line V_{lim} bounds from above the area where the Boltzmann statistics applies and line V_L the hatched area where the continuous description fails completely.

the field over the device thickness.^{31,52} Thereby the free constants C_1 and C_2 in Eq. (5) are obtained by satisfying the conditions (33) and (7) at $x = -L/2$ and $x = L/2$, respectively. This method, however, appears to be numerically unstable because of fast oscillations of the Airy functions providing multiple solutions for the constants. Alternatively, Eq. (4) can be directly numerically integrated using the same boundary conditions which proves to be a robust procedure. The resulting chart on the $V-\Delta^-$ plane is depicted in Fig. 5.

Apparently, this chart is very similar to that of the single interface depicted in Fig. 4 except the voltage region below 0.1 V where the V_0 and V_{min} curves go down a bit steeper. This means, on the one hand, that the injecting interface dominates the behavior of a symmetric device. On the other hand, this similarity shows that accounting for the collecting electrode in the energy profile of a single particle, Eq. (30), does not add much to the simpler formula for a single interface, Eq. (9).

I - V characteristics for different injecting barrier values are plotted in Fig. 6 for a symmetric device, employing typical parameters of ITO and organic semiconductors (see Table I). The essential contribution of the SP Schottky barrier lowering in the wide region of voltages is evident.

B. Modified validity chart and current-voltage characteristics of a unipolar asymmetric organic device

Asymmetric devices are considerably different from symmetric ones due to the presence of the built-in potential, V_{bi} , which is defined by the difference between the work functions of the two electrodes, $eV_{bi} = E_A^+ - E_A^- = E_b^+ + \kappa_z^+ - E_b^- - \kappa_z^-$. At equilibrium, due to equalization of the electrochemical potential in the entire system, an internal electric field emerges. For that reason, the electric field at one of the electrodes may change its sign providing favorable conditions for the SP injection scenario already at zero bias. To account for this effect, the field-barrier charts should

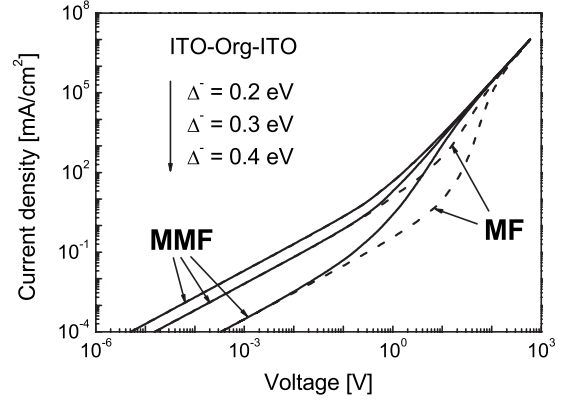


FIG. 6. I - V characteristics for symmetric organic devices with and without account of charge-carrier discreteness are shown by solid and dashed lines, respectively. The barrier magnitude is changed from the upper to the lower curve as is shown in the plot. For the barrier values below 0.2 eV and smaller, the solid and the dashed lines cannot be distinguished.

be considered separately for both electrodes by solving equations $L/2 - |x_m| = 0.2r_s^\pm$ which result in corresponding characteristic fields for both electrodes. Consequently, Eq. (4) should be solved implementing the boundary conditions (33) self-consistently at $x = \pm L/2$. Thereby potential discontinuities $\delta\phi_{Sch}^\pm$ from Eq. (32) should be applied in Eq. (33) as long as $\max\{|F_{min}^\pm(\Delta^\pm)|, |F_L^\pm(\Delta^\pm)|\} < |F_s(\pm L/2)| < \min\{|F_{max}^\pm(\Delta^\pm)|, |F_{lim}^\pm(\Delta^\pm)|, |F_T^\pm(\Delta^\pm)|\}$. Note that the fields F_L^\pm are defined simultaneously from the mean value of the carrier density using Eq. (34) as for the symmetric device. As soon as the characteristic fields are known, the corresponding characteristic voltages may be evaluated as was described in the preceding section. The line V_L is obviously common for the $V-\Delta^\pm$ charts of the left and right electrodes.

Application of the self-consistent boundary conditions (33) may look a bit cumbersome but it is substantially simplified by the fact that the sole maximum of the energy (30), x_m , occurs at each moment only near one of the two electrodes. Thus, if the external bias has the same sign as the built-in potential, then the SP contribution may arise at the injecting electrode only. If the external bias has the sign opposite to that of the built-in potential, the SP contribution may arise first in equilibrium at the collecting electrode due to the internal electric field while the injecting electrode is described in the MF approach. By the increasing external field, the collecting electrode goes over to the MF regime too and by further field increasing, the injecting electrode goes over to the SP regime where the discontinuity $\delta\phi_{Sch}$ applies.

To investigate possible effects induced by the presence of the built-in potential, the case of an asymmetric unipolar device consisted of the organic layer sandwiched between ITO and Al electrodes is considered. For the ITO electrode at $x = -L/2$ and Al electrode at $x = L/2$, the built-in potential equals -0.4 V (see the electrode parameters in Table II). The $V-\Delta^-$ chart for this system is presented in Fig. 7 where the behavior of the right electrode is also comprised.

Changing the injection barrier Δ^- for fixed electrodes means considering organic materials with different positions

TABLE II. Parameter values for collecting electrodes (see Ref. 40).

	l_{TF}^+ (Å)	p_{∞}^+ (cm ⁻³)	μ_c^+ (cm ² /(V s))	κ_{∞}^+ (eV)	E_A^+ (eV)
Al	0.5	1.81×10^{23}	13.05	11.7	4.3
Au	0.6	5.9×10^{22}	44	5.53	4.3

of the HOMO level. This implies, in turn, the change of the injection barrier at the other electrode, Δ^+ , to the same extent. This allows one to show the area where the SP injection mechanism is relevant at the right electrode on the same $V - \Delta^-$ chart.

The V_0 curve for the asymmetric case, where the field vanishes at the left, injecting interface, nearly coincides with that of the symmetric case (cf. Fig. 5) for barrier values below $\Delta^- = 0.22$ eV. Above the value of 0.35 eV, it coincides virtually with the lower boundary of the MMF region given by the V_{\min} curve because F_{\min} value becomes equal to zero. When $\Delta^- > 0.25$ eV, the V_0 curve differs substantially from the corresponding line for the symmetric device and saturates at about the value of $-V_{bi}$. The V_{lim} curve which delineates the upper boundary of the chart almost coincides for the symmetric and asymmetric cases. Thus, the presence of the built-in potential reveals itself in the extension of the low-voltage area, where the Schottky correction can be neglected at the injecting electrode, up to approximately $-V_{bi}$. On the other hand, this correction should be included at the collecting electrode at almost all voltages below $-V_{bi}$ as is indicated by the lower dashed line.

I - V characteristics for different injecting barrier values are plotted in Fig. 8 for the asymmetric device, employing typical parameters of ITO and organic semiconductors.³² As in the symmetric case, the Schottky lowering of the barrier en-

hances the current by orders of the magnitude for high voltages compared to the pure MF description.³² This results in the disappearing of the second exponential increase in the case of asymmetric devices and, generally, in an earlier transition to the space-charge-limited regime in both symmetric and asymmetric cases. Note that account for the charge-carrier discreteness does not change the I - V curves below $-V_{bi}$ in Fig. 8.

V. COMPARISON TO EXPERIMENT

To evaluate the presented model, the results for an asymmetric device are compared to experimental data obtained on a unipolar device consisting of a single poly[*p*-(2-methoxy-5-(3,7-dimethyloctyloxy)phenylene-vinylene)] (OC₁C₁₀-PPV) layer of thickness $L = 100$ nm sandwiched between ITO and Au electrodes. The characteristic energy of the HOMO level of the employed OC₁C₁₀-PPV is 5 eV and the hole mobility μ_s is reported between 5×10^{-7} and 3×10^{-5} cm²/(V s) or even larger.⁵³⁻⁵⁶ Note that for an organic semiconductor, the mobility is typically scattered by orders of the magnitude.⁵⁷ It is known also that the work function of ITO is sensitive to the cleaning procedure and thus it may vary from 4.7 to 5 eV (up to the energy of the HOMO level). Additionally, a dipole layer may possibly emerge at the metal-organic interface, typical for these systems.^{58,59} Therefore, we consider the injection barriers Δ^- and Δ^+ as independent fitting parameters.

In Fig. 9, the measured I - V characteristic of the ITO/OC₁C₁₀-PPV/Au structure is shown as well as the I - V

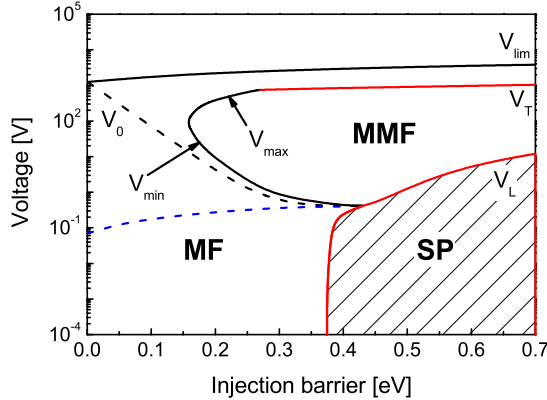


FIG. 7. (Color online) Solid lines V_{\min} , V_{\max} , V_T , and, partly, V_L outline the MMF area for an asymmetric ITO-organic-Al device where the SP contribution to the MF approach must be accounted for at the left, injecting electrode. Upper dashed line indicates the voltages V_0 at which the field at the left interface vanishes. Lower dashed line delimits the low-voltage region, where the SP contribution to the MF approach must be accounted for at the right, collecting Al electrode. In the hatched SP region bound by the line V_L , the description of the device with the continuous carrier density fails completely. The Boltzmann statistics is valid below the line V_{lim} .

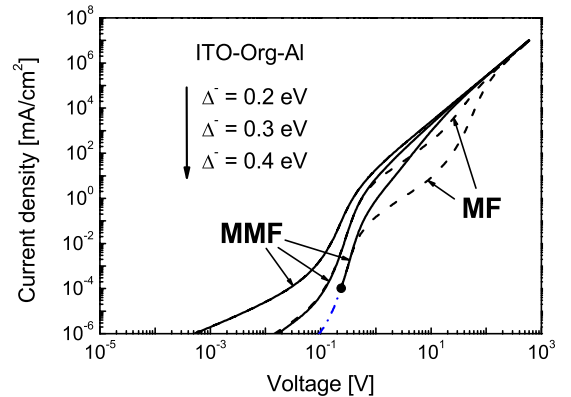


FIG. 8. (Color online) I - V characteristics for asymmetric organic devices with and without account of charge-carrier discreteness are shown by solid and dashed lines, respectively. The barrier magnitude is changed from the upper to the lower curve as is indicated in the plot. Solid circle on the characteristic for $\Delta^- = 0.4$ eV marks where it enters to the low-voltage region (dash-dotted line) where the mean-field approach is no more valid.

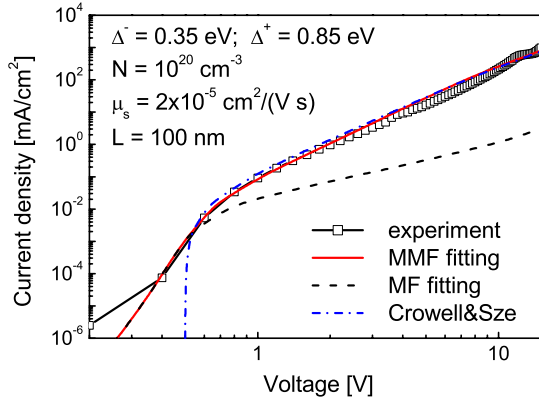


FIG. 9. (Color online) Measured I - V characteristic of ITO/OC₁C₁₀-PPV/Au structure (squared curve) and its approximations within different theoretical models. The best-fitting parameters in the MMF approach are indicated in the plot.

dependencies calculated for different model approximations. One can see that the advanced MMF approach gives a good approximation for the measured I - V curve in the wide range of applied voltages with the best-fitting parameters indicated in the figure. At the same time, the dashed curve for the MF approach with the same fitting parameters underestimates the current by orders of the magnitude at high voltages. Note that the widely used Crowell and Sze model^{27,54} (the dash-dotted curve) fails to describe the I - V characteristic at voltages below $-V_{bi}$.

Notice, however, that the best fit was found for slightly higher magnitudes of the injection barriers than the largest values reported in the literature: $\Delta_{max}^- = 0.3$ eV and $\Delta_{max}^+ = 0.7$ eV (the work function of Au is 4.3 eV, see Table II). This deviation of the barrier values may originate from the uncertain position of the HOMO level in OC₁C₁₀-PPV depending on details of the material production as well as from the abovementioned possible dipole layers at the electrode/OC₁C₁₀-PPV interfaces. Also, the *exact* shape of the I - V curve cannot be fully approximated because of the fact that the proposed model still misses some important features of insulators, in particular of organic semiconductors. Those are the realistic DOS shapes including energetically distributed trap states^{7,53} and the field- and concentration-dependent carrier mobilities^{54,60} characteristic of organic semiconductors. Remarkable deviation of the theory from the experiment below the current densities of 10^{-4} mA/cm² may have origin in some other physical mechanisms as, for example, leakage effect or impurity doping. Nonetheless, a sufficiently good matching of experiment and MMF model is found over 2 orders of magnitude in the applied voltage and 7 orders of magnitude in the current density.

VI. DISCUSSION AND CONCLUSIONS

In this work, we have advanced boundary conditions for a continuous description of charge injection and transport in dielectrics in terms of mean electric field and charge density accounting for discreteness of charge carriers. The latter becomes important for a wide range of values of injection bar-

riers and voltages applied where individual image force dominates the injection process. Regions of parameters, where charge-carrier discreteness plays a decisive role, are approximately delineated in the V - Δ charts for symmetric and asymmetric conductor-insulator-conductor devices using an organic semiconductor as example for an insulator sandwiched between two electrodes. Implementing generalized boundary conditions allows for the description of charge transport in such systems in both low injection and high injection regimes including space-charge-limited transport. The advanced theory applies to a wide class of devices where injection of charge carriers into dielectrics takes place, particularly to organic light-emitting diodes, thin-film ferroelectric capacitors, etc. Though in this work only the problems of simple plain geometry were treated, the developed approach is not intrinsically one-dimensional and can be applied as well to complicated two- and three-dimensional configurations of conductor-insulator interfaces as, for example, those of organic field-effect transistors, however, with duly adapted boundary conditions (33).

The presented description of injection applies directly to inorganic crystal insulators and wide-gap nondegenerate semiconductors as well as to the very narrow-band insulators and semiconductors as was indicated in Sec. II A. When applying this theory to the wide-gap organic semiconductors, one should take into account specific features of these media. Being disordered semiconductors with typically hopping conductivity, organic systems differ from inorganic crystals mostly in two respects concerning the injection process, namely, they (1) possess as a rule a relatively wide (Gauss) DOS distribution without sharp band edges^{6,18,19,21,28,30,37,51} and (2) possibly exhibit long-range correlations of the random energy levels.^{61,62}

Considering point (1), the absence of a sharp band edge makes the injection barrier an ill-defined parameter. If the barrier Δ is defined as a difference between the Fermi level in the injecting electrode and the center of the density of states distribution at the HOMO level as it was done in Refs. 18, 19, 21, and 28, the injection into the “gap” states below the barrier is thereby implied because of numerous states available at least to the depth of $\Delta - \sigma$, where σ is the width of the Gauss DOS. Nevertheless, a nontrivial fact is the possible injection into the tail states well below the barrier^{18,19,21,28} (to the depth of about $\Delta - \sigma^2/kT$) which results in the field-dependent mobility of carriers²¹ or in the allegedly possible space-charge regime²⁸ for high injection barriers. The problem of the concept of injection into the deep tail states is that the injection is considered as a single-particle process ignoring the fact that these states may be occupied. Particularly problematic becomes, therefore, a combination of the SP injection with the drift-diffusion equation²⁸ at high injection levels because, in the space-charge regime, the density of injected charge is especially high near the injecting electrode. On the other hand, the concept of injection into the tail states may be well applicable at low injection levels, particularly, in the genuine SP region of the V - Δ chart of Fig. 7. In our simulation of the experiment in Fig. 9, we have assumed a narrow-band approximation for the HOMO level ignoring the finite width of the DOS and, thus, the disorder effect on injection. This might explain the

deviation of the theoretical characteristic from the experimental one at low voltages. In fact, to ignore the role of disorder on injection, the inequality $\sigma \ll kT$ should be satisfied which is not typically the case for organic semiconductors. Proper integration of the finite DOS width in our self-consistent concept is currently in progress.

A rather elaborated many-particle description of charge injection and transport in organic semiconductors with uncorrelated Gauss disorder was developed recently in Ref. 37 where boundary conditions similar to our MMF ones were used to account for the image-charge effect. Two models were presented and compared in this paper: a discrete model of 3D hopping over the sites of a cubic lattice and a continuous 1D description in the spirit of the drift-diffusion concept, which exhibit good agreement with each other. However, in both models, the individual image effect was substantially overestimated. In the 3D approach, the individual image contribution was accounted for at all internal sites of the lattice in addition to the mean field derived from the charge averaged over the planes parallel to electrodes. As was discussed above in Secs. II and III, the individual image effect reveals itself as strong deviation from the mean field only in the vicinity of the electrodes due to its short-range nature. In fact, close to the electrode surface, the individual image force may dominate over the mean field. In contrast to this, far from the electrode, a charge carrier “observes” not only its own image but all the other injected particles with their images which together constitute the mean field. In the latter case, there is no reason to single out the carrier’s own image which would mean duplication of the image account. This problem was discussed in detail in Refs. 34–36 where such duplication was explicitly excluded. In the continuous 1D model of Ref. 37, the line V_0 was chosen as a boundary between the MF and MMF regions, where the barrier lowering due to the image effect is included. This line is close to our lower boundary of the MMF region V_{min} on the V – Δ charts in Figs. 4, 5, and 7 for a certain range of barrier values. This approach, however, also overestimates the image effect for low barriers and misses the fact that, below some threshold barrier value of about 0.2 eV, the MF approach is always valid independently of the field direction at the electrode.

The property (2) of organic semiconductors which may be relevant to statistical grounds of our concept of injection, namely, the correlated disorder of the energy levels at different sites, is not so well established and is still disputed in the literature. The idea of the correlated disorder was suggested in Refs. 61 and 62 to explain the field dependence of mobility $\ln \mu \sim \sqrt{F}$ in a wide region of field values. We note, first, that this single-particle concept is based on the arbitrary hypothesis of independently and randomly oriented dipoles at each lattice site.⁶² Second, such field dependence of the mobility was also explained within another single-particle model considering the injection in the deep tail states of the uncorrelated Gauss disordered energy levels.²¹ Many-particle models assuming uncorrelated disorder combined with concentration dependence of the mobility^{37,51} can provide good agreement with experiments too. Pasveer *et al.* concluded that there is no necessity to account for correlated disorder at least around room temperature.⁵¹ Hence, possible correla-

tions in charge positions due to the correlated disorder are not regarded in our study.

Considering the Schottky-barrier lowering, we have to note the general problem of this concept caused by the too large distances between the electrode and the potential barrier maximum at low voltages. In fact, this value is restricted for different physical reasons depending on the material type. In crystalline dielectrics, this concept, implying usually ballistic overcoming the potential barrier by a charge carrier,³³ makes sense as long as the mentioned distance does not exceed the mean-free path which may be large enough. On the other hand, in organic semiconductors characterized by hopping conductivity, the ballistic description fails because of typical hopping distance of 0.1–1 nm. In this case, more sophisticated descriptions of injection such as multiple random hopping of a single charge carrier in the SP potential may be relevant.^{18,19} Applicability of the latter model seems to be restricted to the SP region in the charts of Figs. 4, 5, and 7 where the effect of the other carriers is reduced. After all, we would like to stress that, in the formulation of the thermodynamic boundary conditions 1–3 of Sec. II A together with Eq. (28), the ballistic mechanism of charge injection was not assumed.

Finally, we considered in this paper the corrections to the self-consistent mean-field description of injection due to the effect of discreteness of charge carriers. It is apparent, however, that below the line V_L , where continuous description is no more valid, the pure SP approach will also be distorted because of the long-range interaction with the other injected charge carriers at the distance L or larger. This is a sort of MF corrections to the SP picture which is yet to be elaborated.

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APPENDIX: ENERGY OF A POINT CHARGE BETWEEN TWO PLANE ELECTRODES

When a point charge q is located in the dielectric medium with relative permittivity ϵ_s between two plane electrodes taking positions at $x = \pm L/2$, the Coulomb potential used in formula (9) for the single interface does not satisfy anymore the boundary conditions for the electrostatic potential at the electrodes: $\varphi(x = \pm L/2) = 0$ (no voltage applied). To satisfy these boundary conditions, the method of images may be used⁶³ which results, in the case of two electrodes,⁶⁴ in the potential expression

$$\varphi(x, y, z) = \frac{q}{4\pi\epsilon_0\epsilon_s} \sum_n \frac{(-1)^n}{\sqrt{(x-x_n)^2 + y^2 + z^2}}, \quad (\text{A1})$$

where $(x_0, 0, 0)$ is the position of the point charge and $x_n = x_0(-1)^n + nL$, with $n = \pm 1, \pm 2, \dots$ are the x coordinates of its images.

The force, exerted upon the point charge, results from the interaction with image charges to the left and to the right of its position

$$\begin{aligned} f(x_0) &= \frac{q^2}{4\pi\epsilon_0\epsilon_s L^3} \sum_{n=1}^{\infty} (-1)^n \left[\frac{1}{(x_0 - x_{-n})^2} - \frac{1}{(x_0 - x_n)^2} \right] \\ &= \frac{2q^2 x_0}{\pi\epsilon_0\epsilon_s L^3} \sum_{m=0}^{\infty} \frac{2m+1}{[(2m+1)^2 - (2x_0/L)^2]^2} \\ &= \frac{q^2}{16\pi\epsilon_0\epsilon_s L^2} \left[\psi' \left(\frac{1}{2} + \frac{x_0}{L} \right) - \psi' \left(\frac{1}{2} - \frac{x_0}{L} \right) \right], \quad (\text{A2}) \end{aligned}$$

where a summation formula from Ref. 65 was used and $\psi(x)$ denotes the digamma function.⁴²

The energy of the point-charge interaction with electrodes, U_q , can be obtained by integration of the force (A2) considering the relation $f(x_0) = -U'_q(x_0)$. The integration constant $U_q(0)$ should be chosen so that, in the limit $|x_0 + L/2| \ll L$, the energy $U_q(x_0)$ reduces to the case of a single interface, Eq. (9). Thus, the expression

$$U_q(x_0) = \frac{q^2}{16\pi\epsilon_0\epsilon_s L} \left[\psi \left(\frac{1}{2} + \frac{x_0}{L} \right) + \psi \left(\frac{1}{2} - \frac{x_0}{L} \right) + 2\gamma \right] \quad (\text{A3})$$

results, where $\gamma = 0.5772$ is Euler's constant.⁴²

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- ¹P. R. Emtage and J. J. O'Dwyer, Phys. Rev. Lett. **16**, 356 (1966).
- ²R. C. Hughes and R. J. Sokel, J. Appl. Phys. **52**, 6743 (1981).
- ³M. Hack and M. Shur, J. Appl. Phys. **58**, 997 (1985).
- ⁴J. Shen and J. Yang, J. Appl. Phys. **83**, 7706 (1998).
- ⁵V. Cech, J. Appl. Phys. **88**, 5374 (2000).
- ⁶S. L. M. van Mensfoort and R. Coehoorn, Phys. Rev. B **78**, 085207 (2008).
- ⁷M. A. Lampert and P. Mark, *Current Injection in Solids* (Academic Press, New York, 1970).
- ⁸T. Christen and M. Seeger, J. Electrostat. **65**, 11 (2007).
- ⁹H.-J. Fitting, N. Cornet, M. Touzin, D. Goeuriot, C. Guerret-Piecourt, and D. Treheux, J. Eur. Ceram. Soc. **27**, 3977 (2007).
- ¹⁰F. Neumann, Y. A. Genenko, R. Schmechel, and H. von Seggern, Synth. Met. **150**, 291 (2005).
- ¹¹P. W. M. Blom, M. J. M. de Jong, and J. J. M. Vleggaar, Appl. Phys. Lett. **68**, 3308 (1996).
- ¹²G. G. Malliaras and J. C. Scott, J. Appl. Phys. **83**, 5399 (1998).
- ¹³A. B. Walker, A. Kambili, and S. J. Martin, J. Phys.: Condens. Matter **14**, 9825 (2002).
- ¹⁴S. J. Martin, J. M. Lupton, I. D. W. Samuel, and A. B. Walker, J. Phys.: Condens. Matter **14**, 9925 (2002).
- ¹⁵S. J. Martin, A. B. Walker, A. J. Campbell, and D. D. C. Bradley, J. Appl. Phys. **98**, 063709 (2005).
- ¹⁶P. S. Davids, I. H. Campbell, and D. L. Smith, J. Appl. Phys. **82**, 6319 (1997).
- ¹⁷I. H. Campbell, P. S. Davids, D. L. Smith, N. N. Barashkov, and J. P. Ferraris, Appl. Phys. Lett. **72**, 1863 (1998).
- ¹⁸V. I. Arkhipov, E. V. Emelianova, Y. H. Tak, and H. Bässler, J. Appl. Phys. **84**, 848 (1998).
- ¹⁹V. I. Arkhipov, U. Wolf, and H. Bässler, Phys. Rev. B **59**, 7514 (1999).
- ²⁰G. G. Malliaras and J. C. Scott, J. Appl. Phys. **85**, 7426 (1999).
- ²¹A. L. Burin and M. A. Ratner, J. Chem. Phys. **113**, 3941 (2000).
- ²²N. Tessler, D. J. Pinner, and R. H. Friend, Synth. Met. **111-112**, 269 (2000).
- ²³B. Ruhstaller, S. A. Carter, S. Barth, H. Riel, W. Riess, and J. C. Scott, J. Appl. Phys. **89**, 4575 (2001).
- ²⁴Y. Preezant and N. Tessler, J. Appl. Phys. **93**, 2059 (2003).
- ²⁵A. R. Hosseini, M. H. Wong, Y. Shen, and G. G. Malliaras, J. Appl. Phys. **97**, 023705 (2005).

- ²⁶Y. Shen, M. W. Klein, D. B. Jacobs, J. Campbell Scott, and G. G. Malliaras, Phys. Rev. Lett. **86**, 3867 (2001).
- ²⁷C. R. Crowell and S. M. Sze, Solid-State Electron. **9**, 1035 (1966).
- ²⁸V. I. Arkhipov, H. v. Seggern, and E. V. Emelianova, Appl. Phys. Lett. **83**, 5074 (2003).
- ²⁹J. Reynaert, V. I. Arkhipov, G. Borghs, and P. Heremans, Appl. Phys. Lett. **85**, 603 (2004).
- ³⁰T. van Woudenberg, J. Wildeman, and P. W. M. Blom, Phys. Rev. B **71**, 205216 (2005).
- ³¹F. Neumann, Y. A. Genenko, C. Melzer, and H. von Seggern, J. Appl. Phys. **100**, 084511 (2006).
- ³²F. Neumann, Y. A. Genenko, C. Melzer, S. V. Yampolskii, and H. von Seggern, Phys. Rev. B **75**, 205322 (2007).
- ³³S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1969).
- ³⁴M. N. Bussac, D. Michoud, and L. Zuppiroli, Phys. Rev. Lett. **81**, 1678 (1998).
- ³⁵E. Tutiš, M. N. Bussac, and L. Zuppiroli, Appl. Phys. Lett. **75**, 3880 (1999).
- ³⁶E. Tutiš, M. N. Bussac, B. Masenelli, M. Carrard, and L. Zuppiroli, J. Appl. Phys. **89**, 430 (2001).
- ³⁷J. J. M. van der Holst, M. A. Uijtewaalt, B. Ramachandhran, R. Coehoorn, P. A. Bobbert, G. A. de Wijs, and R. A. de Groot, Phys. Rev. B **79**, 085203 (2009).
- ³⁸V. I. Shashkin and N. V. Vostokov, J. Appl. Phys. **104**, 123708 (2008).
- ³⁹Y. A. Genenko, S. V. Yampolskii, C. Melzer, and H. von Seggern, 9th European Conference on Application of Polar Dielectrics, August 2008, Rome, Italy 2008, p. 156; Integr. Ferroelectr. **106**, 49 (2009).
- ⁴⁰N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Thomson Learning, Florence, 1976).
- ⁴¹Field penetration in the conductor electrode was recently considered in a similar way for the ferroelectric thin-film capacitors [M. Dawber and J. F. Scott, Jpn. J. Appl. Phys. **41**, 6848 (2002)].
- ⁴²*Handbook on Mathematical Functions*, edited by M. Abramowitz and I. Stegun (Dover Publications, New York, 1970).
- ⁴³A. A. Kornyshev, A. I. Rubinstein, and M. A. Vorotyntsev, Phys. Status Solidi B **84**, 125 (1977).

- ⁴⁴A. M. Gabovich, L. G. Il'chenko, and E. A. Pashitskii, *Fiz. Tverd. Tela (Leningrad)* **21**, 1683 (1979) [*Sov. Phys. Solid State* **21**, 965 (1979)].
- ⁴⁵A. I. Voitenko, A. M. Gabovich, and L. G. Il'chenko, *Fiz. Tverd. Tela (Leningrad)* **23**, 1531 (1981) [*Sov. Phys. Solid State* **23**, 896 (1981)].
- ⁴⁶D. Mergel and Z. Qiao, *J. Phys. D* **35**, 794 (2002).
- ⁴⁷D. Mergel and Z. Qiao, *J. Appl. Phys.* **95**, 5608 (2004).
- ⁴⁸H. Fujiwara and M. Kondo, *Phys. Rev. B* **71**, 075109 (2005).
- ⁴⁹Y. L. Klimontovich, *Statistical Physics* (Harwood, Chur, 1986).
- ⁵⁰J. C. Scott and G. G. Malliaras, *Chem. Phys. Lett.* **299**, 115 (1999).
- ⁵¹W. F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P. A. Bobbert, P. W. M. Blom, D. M. de Leeuw, and M. A. J. Michels, *Phys. Rev. Lett.* **94**, 206601 (2005).
- ⁵²S. V. Yampolskii, Yu. A. Genenko, C. Melzer, K. Stegmaier, and H. von Seggern, *J. Appl. Phys.* **104**, 073719 (2008).
- ⁵³P. W. M. Blom and M. J. M. de Jong, *Philips J. Res.* **51**, 479 (1998).
- ⁵⁴P. W. M. Blom and M. C. J. M. Vissenberg, *Mater. Sci. Eng. R.* **27**, 53 (2000).
- ⁵⁵W. Geens, S. E. Shaheen, B. Wessling, C. J. Brabec, J. Poortmans, and N. Serdar Sariciftci, *Org. Electron.* **3**, 105 (2002).
- ⁵⁶F. C. Krebs and M. Jorgensen, *Macromolecules* **36**, 4374 (2003).
- ⁵⁷R. W. I. de Boer, M. Johensen, T. M. Klapwijk, A. F. Morpurgo, J. Niemax, A. K. Tripathi, and J. Pflaum, *J. Appl. Phys.* **95**, 1196 (2004).
- ⁵⁸H. Ishii, K. Sugiyama, E. Ito, and K. Seki, *Adv. Mater. (Weinheim, Ger.)* **11**, 605 (1999).
- ⁵⁹A. Kahn, N. Koch, and W. Gao, *J. Polym. Sci., Part B: Polym. Phys.* **41**, 2529 (2003).
- ⁶⁰D. M. Pai, *J. Chem. Phys.* **52**, 2285 (1970).
- ⁶¹D. H. Dunlap, P. E. Parris, and V. M. Kenkre, *Phys. Rev. Lett.* **77**, 542 (1996).
- ⁶²S. V. Novikov, D. H. Dunlap, V. M. Kenkre, P. E. Parris, and A. V. Vannikov, *Phys. Rev. Lett.* **81**, 4472 (1998).
- ⁶³L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1963).
- ⁶⁴Yu. A. Genenko and A. Snezhko, *J. Appl. Phys.* **92**, 357 (2002).
- ⁶⁵A. P. Prudnikov, Yu. A. Brychkov, and O. I. Marychev, *Integrals and Series* (Gordon and Breach, New York, 1986).