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DRIFT-DIFFUSION TRANSPORT IN A RANDOMLY INHOMOGENEOUS ONE-DIMENSIONAL MEDIUM

STEFANO TURZI*

Abstract. Organic semiconductors are intrinsic randomly inhomogeneous materials where charge transport occurs by hopping of the carriers between localized sites having a distribution of energy levels. However, the average carrier density seems to be accurately described by a simple drift-diffusion equation. We investigate the reasons for the effectiveness of the drift-diffusion model in a random material and show that the key assumption for its validity is that the correlation lengths of the randomly perturbed coefficients are much smaller than any other characteristic length of the problem. As a by product, we find how the effective drift and diffusion coefficients depend on the randomness.

Key words.

AMS subject classifications. 34E10, 82C70, 82C31, 82D30 60H10

1. Introduction. Modeling of electronic transport in thin-film solar cells or organic semiconductor devices is mostly based on the drift-diffusion model, which has been the classical method to simulate the transport in silica electronic device since decades [16, 28, 23]. However, in contrast to electronic conduction in metals, charge transport in soft condensed matter and organic polymers mostly takes place via an incoherent diffusion process. In disordered organic materials the deviation from a periodic crystalline structure makes the concept of band-transport inapplicable. Instead, charges are spatially localized and charge transport occurs by transitions between localized states, a process termed as hopping [29, 18]. Furthermore, the hopping sites are not characterized by a unique energy level, but rather by a distribution of possible energy levels and the transition can occur, with different probabilities, between any two of these levels. This makes the transport in organic semiconductors an intrinsically random phenomenon, where the important physical properties are not related to the transport of a single carrier, but are measures of the average properties of the carriers.

The most prominent theoretical method that tends to mimic the microscopic transport mechanisms is based on the master equation of the hopping mechanism with random transition rates [22, 30], suitably extended to include Pauli exclusion principle [11, 12]. In the continuous case and for single-carrier systems, this is an evolution equation for the probability $p(x, t)$ that a carrier is in position x at time t

$$(1.1) \quad \frac{\partial p(x, t)}{\partial t} = \int_0^L [W(x|x')(1 - p(x, t))p(x', t) - W(x'|x)(1 - p(x', t))p(x, t)] dx',$$

where L is the device length and $W(x|x')$ is the transition rate for hopping from site x' to site x . A popular expression for the transition rate $W(x|x')$ is given by the Miller-Abrahams formula [19, 22, 29] which rapidly decays to zero with distance and depends on the energy difference $\Delta E = E(x) - E(x')$. In a randomly inhomogeneous medium, such as an organic semiconductor, ΔE (at fixed $|x - x'|$) is a random variable and site energies are usually drawn randomly from a Gaussian distribution [22, 18]. Indeed, charge transport occurs by transitions between localized sites that are distributed

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according to the polymer chains. Such long chains are highly disordered and this creates a non-homogeneous distribution of energy levels that can host charge and enable a carrier to move across a device.

Monte Carlo or kinetic Monte Carlo simulations are often used to solve the master equation in its stationary regime [26, 23]. However, these methods are still computationally intensive and most often for real device simulations the drift-diffusion model is employed. Usually drift-diffusion type equations are used on the whole device scale by both physicists [6, 1, 10, 5, 17, 33, 8] and mathematicians [4, 7, 24], whereas on a microscopic scale, particularly around interfaces, stochastic models are preferred [32, 21].

If we assume that the master equation approach is the most effective from a microscopic point of view, the derivation of a macroscopic drift-diffusion model can be justified in several ways. For example, a possible approach is to use a discrete master equation to describe the motion of a particle in a quasi-periodic one dimensional landscape, where at each instant of time there is a non-vanishing probability that the particle jumps to a neighboring energy well. In a continuous limit, for a very large number of lattice sites, it is possible to show [25] that the particle number density satisfies a drift-diffusion equation.

Another popular approach is to use a Kramer-Moyal expansion [31, 9] of the continuous master equation (1.1), in the limit of low carrier density, to derive the corresponding Fokker-Planck equation, which is a drift-diffusion equation for the carrier density. This last method is particularly suited to the analysis of random media and we will follow this approach in the present paper.

For a given realization of the random medium the Kramer-Moyal expansion yields the drift and diffusion coefficients as first and second jump moments

$$(1.2) \quad m_1(x) = \int_0^L (x' - x)W(x'|x)dx',$$

$$(1.3) \quad m_2(x) = \frac{1}{2} \int_0^L (x' - x)^2W(x'|x)dx',$$

and, due to the randomness of the transition rate $W(x'|x)$, $m_1(x)$ and $m_2(x)$ should be considered as random functions.

Since we are interested in the average properties of the carriers, to what extent the average carrier density still obeys a deterministic drift-diffusion equation? In other words, since a large body of experimental and numerical analysis relies on the classical drift-diffusion equation, what is the mathematical justification of its general effectiveness, even in the presence of a random medium? Finally, what are the effective drift and diffusion coefficients and how do they depend on randomness? These are the key questions that we try to address in the paper.

An interesting, but difficult, related problem is how to express the macroscopic transport coefficients in terms of the microscopic parameters describing random inhomogeneities in the material. However, we do not try to address this question in the present paper. Indeed, the Miller-Abrahams formula is not the only possible choice, other choices of transition rates or energy level distributions are possible, which are compatible with a macroscopic drift-diffusion transport [30]. Therefore, the answers to our previous questions must be largely independent on the particular form of the transition rate or density of states.

Hence, we assume from the beginning that m_1 and m_2 are random process, with some given properties, and look for an equation that governs the evolution of the mean

carrier density. We limit our analysis to the one-dimensional case. We are aware that this may be a limitation as some essential physics may depend on the spatial dimension of the system. However, this is a valid assumption in many cases because it has been shown that the carriers flow mainly along filamentary structures in the presence of high electric fields and material inhomogeneity [34, 15, 30]. Such filamentary structures in the current distribution are believed to be caused by percolation effects [30].

Finally, it is worth noticing that the application of our results is not limited to organic semiconductors, but may be generally useful to describe the average features of carrier transport in any medium with spatial and energetic disorder.

The paper is organized as follows. In §2 we introduce the mathematical aspects of the problem and perform a perturbation analysis for small random perturbations. A complicated integro-differential equation is obtained for the average carrier density $q(x)$. In §3 we show that a small-correlation-length approximation is sufficient to reduce the equation for $q(x)$ to a simple drift-diffusion equation, with effective coefficients which depend on the random perturbation. A numerical comparison is reported in §4, and the conclusions follow in §5. Some mathematical details are reported in Appendix.

2. Mathematical formulation. The Kramer-Moyal expansion of Eq.(1.1) leads, in the stationary case, to the following one-dimensional stationary Fokker-Planck equation (which is a conservation law for the probability flux)

$$(2.1) \quad \frac{\partial(m_1(x)p(x))}{\partial x} - \frac{\partial^2(m_2(x)p(x))}{\partial x^2} = 0,$$

where x is the space variable and p is the carrier number density. The coefficients $m_1(x)$ and $m_2(x)$ are random processes, i.e., a collection of random variables defined on a common probability space. If we denote with Ω the sample space, i.e, the space of possible outcomes of a random experiment, m_i are actually functions of two variables, $x \in [0, L]$ and $\omega \in \Omega$, where L is the length of the domain. Hence, for any fixed $x \in [0, L]$ it is possible to assign a probability to events such as $\{a < m_1(x) < b\}$, which measures the probability that a random sample of the device has drift-coefficient within (a, b) for all x . Naturally, the same holds for m_2 . When we observe a single outcome of the random process for all x that is formed by taking a single possible value of each random variable of the stochastic process we speak of a particular realization (or sample path) of the process. In particular, numerical simulations are performed by generating many realizations and then taking the sample average of the solutions. The analysis of random functions can be approached in different ways, but for our purposes that based on mean square convergence suffices [27, 3]. In an abstract setting, we can think of m_i as $C^k[0, L]$ -valued random variables ($k \geq 2$), that is, any random experiment generates two C^k -functions of the position, $m_1(x)$ and $m_2(x)$, that are a realization of the drift and diffusion coefficients in that particular sample.

In the following, we will omit the dependence on ω and it will be implicitly assumed that $m_1(x)$ and $m_2(x)$ are random variables at x . As a consequence, also the solution p is a random process $p(x)$ and we are interested in the equation that governs its expectation value $\langle p(x) \rangle$. Angle brackets denote ensemble averaging with respect to probability measure. For ease of notation, we denote with $q(x)$ this expectation value: $q(x) := \langle p(x) \rangle$.

It is interesting to observe that our final results will not depend crucially on the boundary conditions. In other words, we will derive an approximate equation for the

mean process that is valid regardless of the chosen boundary conditions, provided that it is possible to find a Green function for the problem. For concreteness, we will develop the theory using Dirichlet boundary conditions [6, 18].

The questions we would like to address are: (1) What is the equation that governs the mean $q(x) = \langle p(x) \rangle$ when m_1 and m_2 in (2.1) are affected by slight random perturbations? (2) Under what circumstances the expectation value $q(x)$ still obeys a drift-diffusion equation, commonly employed in the analysis of organic devices? (3) In such a case, how are the drift and diffusion coefficients affected by the statistical properties of the random processes?

2.1. Perturbative analysis. In order to find an approximate equation for q , we employ a regular perturbation method originally developed to study the wave propagation in random media [13]. A more comprehensive description of this method can be found in [14, 27, 3].

We assume that the material parameter $m_i(x)$ ($i = 1, 2$) is the sum of a deterministic term and a small random perturbation $A_i(x)$, which, in general, depends on the space variable x

$$(2.2) \quad m_1(x) = \bar{m}_1(x) + \varepsilon A_1(x),$$

$$(2.3) \quad m_2(x) = D + \varepsilon A_2(x),$$

where ε is a non-dimensional smallness parameter. We assume that $\bar{m}_1(x)$ may vary spatially in x , while we take a constant diffusion coefficient D to simplify the mathematical derivation. In a typical physical context, the drift term $\bar{m}_1(x)$ would be the gradient of a potential and we would write $\bar{m}_1(x) = -\frac{\partial \psi}{\partial x}$. The random processes A_1 and A_2 have vanishing mean and represent stochastic perturbation about the deterministic mean: $\langle A_1(x) \rangle = 0$, $\langle A_2(x) \rangle = 0$. We look for a solution to (2.1) in the form of an asymptotic expansion

$$(2.4) \quad p(x) = p_0(x) + \varepsilon p_1(x) + \varepsilon^2 p_2(x) + O(\varepsilon^3),$$

where the zeroth-order term is deterministic. The leading-order (deterministic) problem reads

$$(2.5) \quad (\bar{m}_1(x) p_0)' - D p_0'' = 0,$$

where, for shortness, we have used the primed notation instead of $\frac{\partial}{\partial x}$. It is possible to write the general solution of (2.5)

$$(2.6) \quad p_0(x) = e^{-\psi(x)/D} \left(K_1 + K_2 \int_0^x e^{\psi(s)/D} ds \right),$$

where $\bar{m}_1(x) = -\psi'(x)$ and K_1, K_2 are two integration constants. However, we will not need to use the explicit solution (2.6) in the rest of the paper to derive an equation for $q(x)$.

A number of carriers are created instantaneously in the material at or very near one electrode in the presence of an applied electric field which drives these carriers toward a second electrode where they are removed from the material. In a physical system at equilibrium one expects to have the same carrier density at the electrodes. However, from a mathematical standpoint, we can allow for more general boundary conditions and take Dirichlet conditions at the boundary $p(0) = \zeta_0$ and $p(L) = \zeta_1$. This choice simplifies the mathematical presentation, but it is not essential for our

analysis. What really counts is the existence of a Green function that allows us to find unique solutions to inhomogeneous higher-order problems.

Since the boundary conditions are deterministic, they only enter the zeroth-order problem. Therefore, higher-order problems have vanishing boundary conditions. To this end, it is convenient to define two Banach spaces of continuous functions

$$(2.7) \quad X = \{u \in C^2[0, L] : u(0) = u(L) = 0\},$$

$$(2.8) \quad Y = \{u \in C^0[0, L] : u(0) = u(L) = 0\},$$

where $C^k[0, L]$ is the space of k -times continuously differentiable functions in $[0, L]$, and we write $L(X, Y)$ for the space of linear maps $X \rightarrow Y$. Next, we define the linear operator $T_0 \in L(X, Y)$ and the $L(X, Y)$ -valued random variable T_1 as ($u \in X$)

$$(2.9) \quad T_0 u = (\bar{m}_1(x) u)' - D u'',$$

$$(2.10) \quad T_1 u = (A_1(x) u)' - (A_2(x) u)'.$$

Thus, the substitution of (2.2), (2.3) and (2.4) into (2.1) yields the equations to order $O(\varepsilon)$ and $O(\varepsilon^2)$, and these can be simply written as

$$(2.11) \quad T_0 p_1 = -T_1 p_0,$$

$$(2.12) \quad T_0 p_2 = -T_1 p_1,$$

where we use the boundary conditions $p_1(0) = p_1(L) = 0$ and $p_2(0) = p_2(L) = 0$, with probability one.

It is important to observe that T_0 is an invertible operator and we denote with $T_0^{-1} \in L(Y, X)$ its inverse. In other words, there is a unique solution to the problem

$$(2.13) \quad \begin{cases} (\bar{m}_1(x) u)' - D u'' = f \\ u(0) = u(L) = 0 \end{cases}$$

for any continuous function f . This solution can be constructed using standard Green's function methods

$$(2.14) \quad u(x) = T_0^{-1} f = \int_0^L G(x, s) f(s) ds.$$

where $G(x, s)$ is the Green's function. Its explicit expression depends on the function $m_1(x)$. For instance, when the drift coefficient is constant $\bar{m}_1(x) = \bar{m}_1$, the Green function is

$$(2.15) \quad G(x, s) = \begin{cases} \frac{e^{-\bar{m}_1 s/D}}{\bar{m}_1 (e^{\bar{m}_1 L/D} - 1)} (e^{\bar{m}_1 s/D} - 1) (e^{\bar{m}_1 L/D} - e^{\bar{m}_1 x/D}) & \text{if } s < x, \\ \frac{e^{-\bar{m}_1 s/D}}{\bar{m}_1 (e^{\bar{m}_1 L/D} - 1)} (e^{\bar{m}_1 x/D} - 1) (e^{\bar{m}_1 L/D} - e^{\bar{m}_1 s/D}) & \text{if } s > x. \end{cases}$$

We can now use (2.11) and (2.12) to find p_1 and p_2 , so that the asymptotic approximation of the carrier density reads

$$(2.16) \quad p(x) = p_0 - \varepsilon T_0^{-1} T_1 p_0 + \varepsilon^2 T_0^{-1} T_1 T_0^{-1} T_1 p_0 + O(\varepsilon^3).$$

However, we are not interested in the single realization of the process, but rather to the expectation value $q(x)$. Specifically, we wish to find an equation for $q(x) := \langle p(x) \rangle$,

albeit approximate. To this end, we take the average of (2.16) and use the fact that $\langle T_1 \rangle = 0$ (by assumption $\langle A_i(x) \rangle = 0$), to get

$$(2.17) \quad q(x) = \left(I + \varepsilon^2 T_0^{-1} \langle T_1 T_0^{-1} T_1 \rangle \right) p_0 + O(\varepsilon^3),$$

where I is the identity operator. This equation can be inverted to give

$$(2.18) \quad p_0 = \left(I - \varepsilon^2 T_0^{-1} \langle T_1 T_0^{-1} T_1 \rangle \right) q(x) + O(\varepsilon^3).$$

We now apply T_0 to both sides of this equation and truncate the resulting expression to order $O(\varepsilon^2)$ to get the equation for $q(x)$

$$(2.19) \quad T_0 q(x) - \varepsilon^2 \langle T_1 T_0^{-1} T_1 \rangle q(x) = 0,$$

where we have used equations (2.5) and (2.9). Therefore, the associated problem for the mean process is finally found to be

$$(2.20) \quad \begin{cases} (\bar{m}_1(x) q)' - D q'' - \varepsilon^2 \langle T_1(x) T_0^{-1} T_1(x) \rangle q = 0, \\ q(0) = \zeta_0, \quad q(L) = \zeta_1. \end{cases}$$

In order to get a better insight into this equation, we need to find out how the $O(\varepsilon^2)$ -term depends on the random coefficients

$$(2.21) \quad T_1 q = (A_1(x) q)_{,x} - (A_2(x) q)_{,xx}$$

$$(2.22) \quad T_0^{-1} T_1 q = \int_0^L G(x, s) [(A_1(s) q(s))_{,s} - (A_2(s) q(s))_{,ss}] ds$$

$$(2.23) \quad \begin{aligned} T_1 T_0^{-1} T_1 q &= \frac{\partial}{\partial x} \int_0^L A_1(x) G(x, s) [(A_1(s) q(s))_{,s} - (A_2(s) q(s))_{,ss}] ds \\ &- \frac{\partial^2}{\partial x^2} \int_0^L A_2(x) G(x, s) [(A_1(s) q(s))_{,s} - (A_2(s) q(s))_{,ss}] ds, \end{aligned}$$

where a comma denotes differentiation. We now introduce the correlation functions

$$(2.24) \quad \Gamma_{ij}(x, s) = \langle A_i(x) A_j(s) \rangle, \quad i, j = 1, 2$$

and take the expectation value

$$(2.25) \quad \begin{aligned} \langle T_1 T_0^{-1} T_1 \rangle q &= \frac{\partial}{\partial x} \int_0^L G(x, s) [(\Gamma_{11}(x, s) q(s))_{,s} - (\Gamma_{12}(x, s) q(s))_{,ss}] ds \\ &- \frac{\partial^2}{\partial x^2} \int_0^L G(x, s) [(\Gamma_{21}(x, s) q(s))_{,s} - (\Gamma_{22}(x, s) q(s))_{,ss}] ds, \end{aligned}$$

where we have used the property (see Soong [27], p.98)

$$(2.26) \quad \langle A^{(n)}(t) B^{(m)}(s) \rangle = \frac{\partial^{n+m}}{\partial t^n \partial s^m} \Gamma_{AB}(t, s),$$

for any mean square differentiable random processes A, B . Therefore, Eq.(2.20) turns out to be the following integro-differential equation

$$(2.27) \quad \begin{aligned} &(\bar{m}_1(x) q)_{,x} - D q_{,xx} - \varepsilon^2 \frac{\partial}{\partial x} \int_0^L G(x, s) [(\Gamma_{11}(x, s) q(s))_{,s} - (\Gamma_{12}(x, s) q(s))_{,ss}] ds \\ &+ \varepsilon^2 \frac{\partial^2}{\partial x^2} \int_0^L G(x, s) [(\Gamma_{21}(x, s) q(s))_{,s} - (\Gamma_{22}(x, s) q(s))_{,ss}] ds = 0. \end{aligned}$$

It is apparent from this equation that the correlation functions of A_1 and A_2 are the key statistical properties that determines the main difference between the deterministic solution $p_0(x)$ and $q(x)$. Thus, we do not need to know every detail of the random processes A_1 and A_2 , it is sufficient to know their correlation functions.

3. Small-correlation-length approximation. The final equation (2.27) shows that $q(x)$ is not in general governed by a simple drift-diffusion transport. Hence, what is the origin of the general effectiveness of the drift-diffusion equation, even in the context of randomly inhomogeneous media?

We now want to explore what possible approximation reduces (2.27) to a drift-diffusion equation. There are essentially two characteristic lengths in the problem: one is the domain length (i.e., the device length) L and the other is the diffusion-to-drift ratio $L_D = D/\max(\bar{m}_1)$ which becomes small in the small-diffusion limit.

We assume that the correlation functions are rapidly decaying functions of the position and we posit the following approximate smooth behavior for Γ_{ij}

$$(3.1) \quad \Gamma_{ij}(x, s) \approx R_{ij} e^{-(x-s)^2/(2\ell_{ij}^2)},$$

where R_{ij} is a covariance and the correlation length, ℓ_{ij} , between the random variables A_i and A_j is assumed to be much smaller than L and L_D ($\ell_{ij} \ll \max(L, L_D)$). For simplicity, we assume that R_{ij} and ℓ_{ij} are constants (do not depend on x). When $\ell_{ij} \ll \max(L, L_D)$, the main contribution of the exponential to the integrals is concentrated around $x = s$ so that we can make use of the Laplace method [2, 20] to find the asymptotic approximation of the integrals of the type

$$(3.2) \quad \int_0^L h(s) \underbrace{R e^{-(x-s)^2/(2\ell^2)}}_{\Gamma(x,s)} ds \sim R\sqrt{2\pi} \ell h(x),$$

where $0 < x < L$ and $h(x)$ is an arbitrary continuous non-vanishing function. It is worth noticing that the integrals are best approximated the smaller ℓ is and when x is sufficiently away from the boundary. Furthermore, we observe that

$$(3.3) \quad \frac{\partial \Gamma(x, s)}{\partial s} = -\frac{R}{\ell^2} (s-x) e^{-(x-s)^2/(2\ell^2)}$$

$$(3.4) \quad \frac{\partial^2 \Gamma(x, s)}{\partial s^2} = \left(\frac{R}{\ell^4} (x-s)^2 - \frac{R}{\ell^2} \right) e^{-(x-s)^2/(2\ell^2)}.$$

Hence, Laplace method cannot be directly applied to integrals containing $\partial \Gamma(x, s)/\partial s$ or $\partial^2 \Gamma(x, s)/\partial s^2$, since the corresponding function $h(s)$ in (3.2) vanishes at $s = x$, exactly the maximum point of the exponential function. However, it is shown in Appendix A that the leading-order asymptotic approximations of such integrals, in terms of the smallness parameter $\eta = \ell^2/L^2 \ll 1$, are

$$(3.5) \quad \int_0^L h(s) \frac{\partial \Gamma(x, s)}{\partial s} ds \sim -R\sqrt{\frac{\pi}{2}} \ell (h'_+(x) + h'_-(x))$$

$$(3.6) \quad \int_0^L h(s) \frac{\partial^2 \Gamma(x, s)}{\partial s^2} ds \sim R(h'_+(x) - h'_-(x)),$$

where we have used (3.3), (3.4) and (A.10). Therefore, it is important to observe that, in the limit of small ℓ , the dominant contribution to the integrals comes only from expressions of the form (3.6). In agreement with the notation employed in

the Appendix, the derivative $h'_-(x)$ ($h'_+(x)$) is the left-derivative (respectively, right-derivative) of $h(s)$ at $s = x$. In particular, h is of the form $h(s) = G(x, s)q(s)$ so that (3.6) reads

$$(3.7) \quad \int_0^L G(x, s)q(s) \frac{\partial^2 \Gamma(x, s)}{\partial s^2} ds \sim R(G_{+,s}(x, s) - G_{-,s}(x, s)) \Big|_{s=x} q(x),$$

while (3.2) and (3.5) are higher order. In order to simplify the difference $(G_{+,s}(x, s) - G_{-,s}(x, s)) \Big|_{s=x}$ we can use the Green function (2.15), written for constant \bar{m}_1

$$(3.8) \quad (G_{+,s}(x, s) - G_{-,s}(x, s)) \Big|_{s=x} = -\frac{1}{D} e^{\bar{m}_1(x-s)/D} \Big|_{s=x} = -\frac{1}{D}.$$

It should be noted, however, that the identity (3.8) is not specific to (2.15). It is only a consequence of the fact that $G(x, s)$ is a fundamental solution of (2.13). Therefore (3.8) holds for any Green function, with possibly space-dependent drift coefficients, $\bar{m}_1(x)$, or different boundary conditions.

Hence, we have the simple asymptotic approximation

$$(3.9) \quad \int_0^L G(x, s)q(s) \frac{\partial^2 \Gamma(x, s)}{\partial s^2} ds \sim -\frac{R}{D} q(x),$$

while the integrals containing the correlation function or its first derivative are of higher order $O(\eta)$. As a result, to leading order, we can consider only the integrals that contain a second-order derivative of the correlation functions.

We can now simplify the integrals in (2.27). For example, to leading order $O(1)$, we find

$$(3.10) \quad \int_0^L G(x, s) (\Gamma_{12}(x, s) q(s))_{,ss} ds = \int_0^L G(x, s) (\Gamma_{12}(x, s)_{,ss} q(s) + 2\Gamma_{12}(x, s)_{,s} q'(s) + \Gamma_{12}(x, s) q''(s)) ds \sim -\frac{R_{12}}{D} q(x),$$

and similarly for the other integrals. Therefore, we obtain the following approximation for the $O(\varepsilon^2)$ -term

$$(3.11) \quad \langle T_1 T_0^{-1} T_1 \rangle q \sim \frac{R_{12}}{D} q'(x) - \frac{R_{22}}{D} q''(x).$$

Dropping the ε^2 (or absorbing it in the definition of the R_{ij}), the equation for the average density $q(x) = \langle p(x) \rangle$ is finally found to be

$$(3.12) \quad \frac{\partial}{\partial x} \left[\bar{m}_1(x) \left(1 - \frac{R_{12}}{\bar{m}_1(x)D} \right) q(x) \right] - D \left(1 - \frac{R_{22}}{D^2} \right) \frac{\partial^2 q(x)}{\partial x^2} = 0.$$

This equation is in the form of a drift-diffusion equation with effective coefficients

$$(3.13) \quad m_1^{\text{eff}}(x) = \bar{m}_1(x) \left(1 - \frac{R_{12}}{\bar{m}_1(x)D} \right),$$

$$(3.14) \quad D^{\text{eff}} = D \left(1 - \frac{R_{22}}{D^2} \right).$$

This shows that, under broad assumptions, the average density still follows an approximate drift-diffusion equation with effective drift and diffusion coefficients that depend on the amplitude of the correlation functions. Of course, higher order corrections are possible and these are more or less important depending on the value of the smallness parameters, ε and η .

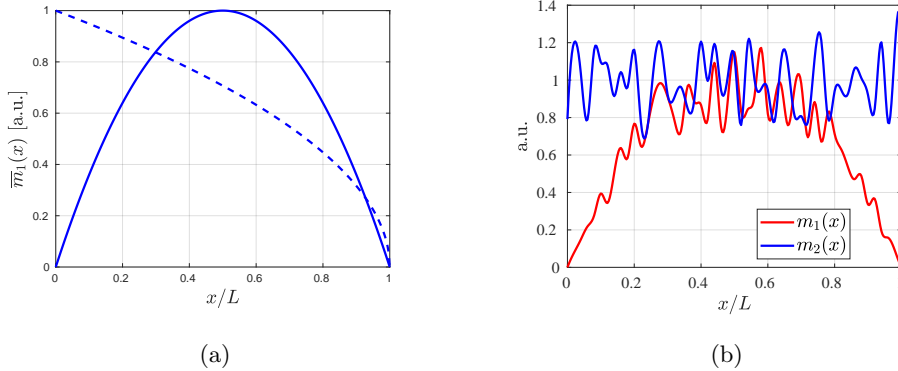


Fig. 1: (a) Unperturbed drift profiles as given in Eqs. (4.2) and (4.3). (b) Typical drift and diffusion coefficients after a uniform perturbation, as described in (4.1), with amplitudes $c_1 = 0.5$, $c_2 = 0.5$. There are 50 evenly-spaced perturbation nodes in $[0, L]$ and the functions $m_1(x)$, $m_2(x)$ are then calculated using a spline interpolation over these nodes. The unperturbed drift and diffusion coefficients are those reported in (4.2).

4. Numerical simulations. We believe that the greatest merit of our analysis lies in giving a theoretical basis to the use of drift-diffusion model to study the average distribution of carriers, under reasonable assumptions. However, in order to check the accuracy of our approximation, in this section we compare the numerical solution of (3.12) with the averaged density profile obtained from the sampling of many spatially dependent problems of the type (2.1). To this end, we perturb $\bar{m}_1(x)$ and D , in 50 evenly-spaced nodes, x_k , with a uniform probability density. More precisely, we generate a perturbation of node values of the form

$$(4.1) \quad m_1(x_k) = \bar{m}_1(x_k)(1 + c_1\xi_k), \quad m_2(x_k) = D(1 + c_2\xi_k),$$

where c_1 and c_2 are two constants that set the amplitude of the perturbation and ξ_k ($k = 1, 2, \dots, 50$) are sample points extracted from a uniform distribution $U[-1/2, 1/2]$. In particular, we consider the following drift profiles (see Fig.1(a))

$$(4.2) \quad \bar{m}_1(x) = 1 - 4 \left(\frac{x}{L} - \frac{1}{2} \right)^2, \quad D = L \bar{m}_1(L/2),$$

$$(4.3) \quad \bar{m}_1(x) = \sqrt{1 - x/L}, \quad D = L \bar{m}_1(0),$$

where (4.3) mimics the electric field in a Au/MEH-PPV/Au device [6].

The randomly perturbed functions $m_1(x)$ and $m_2(x)$ are then obtained by interpolating the random values with a cubic spline to generate a Monte Carlo (MC) sample. A typical profile is drawn in Fig. 1(b). In the examples below, the unit of length is fixed by choosing $L = 1$. Finally, the corresponding Fokker-Plank equation is solved using a simple finite difference scheme with $N = 300$ nodes, for each of the generated $m_1(x)$ and $m_2(x)$. We compare the average carrier density with the solution of (3.12), where the effective coefficients are obtained by fitting the average

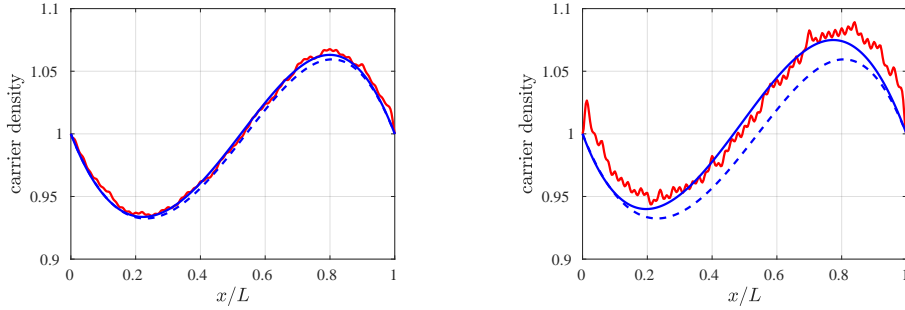


Fig. 2: Carrier density profile (red solid line), calculated as the average of 2000 Monte Carlo samples, with $c_1 = c_2 = 0.25$ (left) and with $c_1 = c_2 = 0.5$ (right). The values at the boundary are $p(0) = 1$, and $p(L) = 1$. A fitting of the average density yields $R_{12}/L \approx 0.27$ and $R_{22}/D \approx 0.013$ (left); $R_{12}/D \approx 1.2$ and $R_{22}/D \approx 0.047$ (right). The corresponding solutions of (3.12) are shown as blue solid lines. For comparison, dashed blue lines depict the solution of the zeroth-order problem, with $m_1(x) = \bar{m}_1(x)$ and $m_2(x) = D$, as given in Eq.(4.2).

MC solution, and the corrections of the unperturbed coefficients, namely R_{12}/D and R_{22}/D , are then calculated.

Fig. 2 reports the density profiles for 2000 Monte Carlo samples and, respectively, $c_1 = c_2 = 0.25$ (left) and $c_1 = c_2 = 0.5$ (right). The drift and diffusion coefficients are those as in (4.2). The numerical solution of (3.12) is shown as a blue solid line, and the corresponding corrections to the coefficients are reported in the caption. As discussed in the text, Laplace approximation is not particularly accurate close to the boundary, and this is visible from Fig.2(b).

An analogous analysis is shown in Fig.3, where the drift profile is now given as in (4.3). A more refined simulation, with 20000 MC samples (instead of 2000 as in Fig.3), is reported in Fig.4.

5. Conclusions. Organic semiconductors are randomly inhomogeneous media: different carriers may undertake very different paths to go across an organic device. Only average properties of the carriers are measured and even if the evolution of one particle could be accurately described, the same evolution would not apply, in general, to a different particle. Transport cannot be described adequately by carriers moving freely in conduction and valence bands, but rather by stochastic hopping between energy levels on different molecules.

However, on a macroscopic level, i.e., on a scale much larger than the molecular structure, transport is commonly described using a simple drift-diffusion model for the average density of the carriers. We have shown that it is possible to provide a mathematical justification for the effectiveness of the drift-diffusion model, that has a natural physical interpretation.

The main approximation is that the random drift and diffusion coefficients, obtained for instance as jump moments of the corresponding master equation, have exponentially decaying correlation functions. This means that the random perturbation at one site is nearly independent of the random perturbation of the neighboring

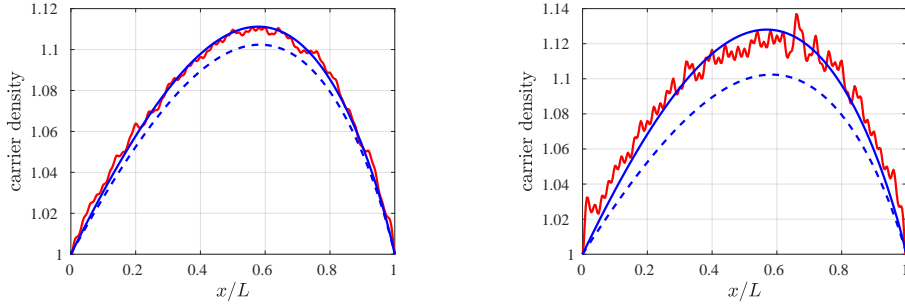


Fig. 3: Carrier density profile (red solid line), calculated as the average of 2000 Monte Carlo samples, with $c_1 = c_2 = 0.25$ (left) and with $c_1 = c_2 = 0.5$ (right). The values at the boundary are $p(0) = 1$, and $p(L) = 1$. A fitting of the average density yields $R_{12}/D \approx 0.16$ and $R_{22}/D \approx 0.072$ (left); $R_{12}/D \approx 0.42$ and $R_{22}/D \approx 0.18$ (right). The corresponding solutions of (3.12) are shown as blue solid lines. For comparison, dashed blue lines depict the solution of the zeroth-order problem, with $m_1(x) = \bar{m}_1(x)$ and $m_2(x) = D$, as given in Eq.(4.3).

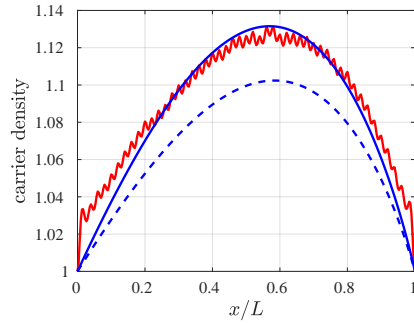


Fig. 4: As in Fig.3, but with 20000 Monte Carlo samples and $c_1 = c_2 = 0.5$. The numerical fitting yields $R_{12}/D \approx 0.41$ and $R_{22}/D \approx 0.20$.

sites.

Appendix A. Asymptotic approximation of the integrals. We first recall Watson's lemma [2, 20]

LEMMA A.1. Consider the integral

$$(A.1) \quad I(M) = \int_0^b f(t)e^{-Mt} dt,$$

where $b > 0$, the function $f(t)$ is continuous and has an asymptotic expansion at the

origin

$$(A.2) \quad f(t) \sim t^\alpha \sum_{n=0}^{+\infty} a_n t^{\beta n}, \quad t \rightarrow 0_+,$$

with $\alpha > -1$ and $\beta > 0$. Then, the integral $I(M)$ has an asymptotic approximation for $M \rightarrow +\infty$ given by

$$(A.3) \quad I(M) \sim \sum_{n=0}^{+\infty} \frac{a_n}{M^{\alpha+\beta n+1}} \Gamma(\alpha + \beta n + 1), \quad M \rightarrow +\infty,$$

where Γ is the gamma function.

It is important to remark that only the asymptotic behavior of $f(t)$ at $t = 0$ contributes to the integral $I(M)$. Indeed the exponential function e^{-Mt} in $[0, b]$ has a steep maximum at $t = 0$ and vanishes quickly away from 0, in the limit of large M . Thus, changing the upper limit of integration introduces only exponentially small errors and b can even be replaced with $+\infty$.

Let us now apply this lemma to the evaluation of the integrals of the type

$$(A.4) \quad I(M) = \int_{-a}^b f(t) e^{-Mt^2} dt, \quad a > 0, \quad b > 0,$$

which is the case of our interest after the substitution $t = s - x$. The function $f(t)$ is continuous, but contains the Green function $G(x, s)$ so that, in general, it only has a piecewise definition:

$$(A.5) \quad f(t) = \begin{cases} f_-(t) & t < 0, \\ f_+(t) & t \geq 0. \end{cases}$$

However, we can assume that, separately, $f_\pm(t)$ have asymptotic expansions of the form (A.2)

$$(A.6) \quad f_\pm(t) \sim t^\lambda (a_0^\pm + a_1^\pm t + a_2^\pm t^2 + \dots), \quad t \rightarrow 0_\pm,$$

where we denote with a_n^- and a_n^+ the coefficients of the series of $f_-(t)$ and $f_+(t)$, respectively, and λ is a non-negative integer. We are interested in the case $a_0^- = a_0^+ = a_0 \neq 0$. Of course, the asymptotic assumption (A.6) is not the most general, but it is sufficient to simplify the integrals (3.2)-(3.6).

The integral (A.4) can be split into two integrals

$$(A.7) \quad I(M) = \int_{-a}^0 f_-(t) e^{-Mt^2} dt + \int_0^b f_+(t) e^{-Mt^2} dt.$$

We then change variable $t = -\sqrt{\tau}$ in the first integral and $t = \sqrt{\tau}$ in the second so that (A.7) becomes

$$(A.8) \quad I(M) = \frac{1}{2} \int_0^{a^2} \tau^{-1/2} f_-(-\sqrt{\tau}) e^{-M\tau} d\tau + \frac{1}{2} \int_0^{b^2} \tau^{-1/2} f_+(\sqrt{\tau}) e^{-M\tau} d\tau.$$

Therefore, we can apply Watson's lemma to both integrals.

When $f(0) \neq 0$ (i.e., $\lambda = 0$) we have $\alpha = -1/2$, $\beta = 1/2$, so that to leading order we obtain (3.2). More generally, when $\lambda \geq 0$ (see equation (3.5) and the quadratic term in (3.6)), we have $\alpha = (\lambda - 1)/2$, $\beta = 1/2$, so that we get

$$(A.9) \quad I(M) \sim \sum_{n=0}^{+\infty} \left(\frac{a_n^+ + (-1)^{n+\lambda} a_n^-}{2} \right) \frac{\Gamma((\lambda + n + 1)/2)}{M^{(\lambda+n+1)/2}}, \quad M \rightarrow +\infty.$$

In particular, the approximations for the integrals (3.2), (3.5) and (3.6) are obtained by truncating (A.9) in the following way

$$(A.10) \quad I(M) \sim \begin{cases} a_0 \frac{\Gamma(1/2)}{M^{1/2}} + \frac{1}{2}(a_1^+ - a_1^-) \frac{\Gamma(1)}{M} & \text{if } \lambda = 0, \\ \frac{1}{2}(a_1^+ + a_1^-) \frac{\Gamma(3/2)}{M^{3/2}} & \text{if } \lambda = 1, \\ a_0 \frac{\Gamma(3/2)}{M^{3/2}} + \frac{1}{2}(a_1^+ - a_1^-) \frac{\Gamma(2)}{M^2} & \text{if } \lambda = 2, \end{cases}$$

where we recall that $\Gamma(1/2) = \sqrt{\pi}$, $\Gamma(1) = 1$, $\Gamma(3/2) = \sqrt{\pi}/2$, and $\Gamma(2) = 1$. In order to simplify (3.2)-(3.6) we substitute $M = 1/2\ell^2$.

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