Modeling of dispersive transport with inhomogeneous advection coefficient and memory kernel

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Abstract.
Dispersive transport in structures with spatially dependent memory kernel \( \Phi \) and advection coefficient \( V \) is considered. The variations in \( \Phi \) and \( V \) can be related to a nonuniformly distributed electric field or to inhomogeneities in the spatial distribution of localized states. The transient current of the time-of-flight technique is calculated after neglecting the diffusion term. An explicit representation is obtained for a linear decrease in \( V(x) \) over the sample thickness for normal and dispersive transport. The variation in \( \Phi \) and \( V \) leads to additional smearing of non-equilibrium particle package. Dispersive transient current curves can be observed even for normal transport for certain inhomogeneities in the advection term.

1. Introduction
An important method for studying electron transfer in low-conductivity semiconducting materials is the time-of-flight (ToF) experiment. In the ToF method, the photocurrent response is studied after the injection of nonequilibrium charge carriers by a short laser pulse near one of the electrodes. Typically, a strong electric field (> \( 10^5 \) V/cm) close to the dielectric breakdown conditions is applied to the sample in order to eliminate the effects of space charge and reduce the contribution of carrier diffusion to the observed response. The correct interpretation of the ToF measurements in inhomogeneous structures remains relevant. Recently, the ToF method has been used to study the features of charge transport in perovskite solar cells [1] and organic bulk heterojunction cells [2]. For disordered semiconductors, dispersive transport of carriers is usually observed, which is characterized by subdiffusive behavior, power law decay of transient current and nonlinear dependence of the time of flight on the distance between electrodes [3]. Using the ToF method, the author of Ref. [1] measured the drift mobilities of electrons and holes in the perovskite methylammonium lead iodide. It was determined that the dispersive transport mode is typical for both photoinjected charge carriers. It is indicated, that the optimal thickness of the perovskite layer can be determined by calculation and dispersive transport must be taken into account in these calculations.

In present paper, dispersive transport in structures with spatially dependent memory kernel \( \Phi \) and advection coefficient \( V \) is considered. Concentrations of non-equilibrium charge carriers and current density are calculated and analyzed.
2. Equations of dispersive transport

Classic drift-diffusion equations are not applicable to description of dispersive transport in disordered semiconductors [6, 7]. In the dispersive case, the photocurrent decay \( I(t) \) essentially differs from the ‘normal’ step-wise curve corresponding to the Gaussian transport. Universal transient currents are often observed. These currents contain two power law sections: \( I(t) \propto t^{-1+\alpha} \) for \( t < t_T \), and \( I(t) \propto t^{-1-\alpha} \) for \( t > t_T \), where \( \alpha \) is the dispersion parameter [6, 7].

Dispersive transport is observed in various disordered materials. Different physical mechanisms can be responsible for it, such as multiple trapping, hopping, percolation through conducting channels, etc. [7].

The following equation can be considered as a 1D equation of dispersive drift-diffusion controlled by trapping into localized states distributed over energy, or by trapping into localized states distributed in a comb-like structure with a random teeth length \( \lambda \) with power law distribution, \( P\{\lambda > l\} = (l/l_0)^{-\beta} \) [9]:

\[
\frac{\partial}{\partial t} \int_0^t p(x, \tau) \Phi(t-\tau) d\tau + \frac{\partial}{\partial x} \left[ V(x)p(x, t) \right] - C \frac{\partial^2}{\partial x^2} p(x, t) = G(x)\Phi(t). \quad (1)
\]

Here, \( p(x, t) \) is concentration of non-equilibrium charge carriers, \( V(x) \) and \( C \) are advection and diffusion coefficients, \( G(x) \) is a generation function, \( \Phi(t) \) is the integral kernel reflecting the presence of memory caused by trapping into localized states distributed over energy, or by diffusion in dead-ends of a percolation cluster, etc.

(i) In the Continuous Time Random Walk model [6], the Laplace image of this kernel can be expressed via the distribution \( \Psi(t) \) and corresponding density \( \psi(t) \) of localization times, \( \Phi(s) = \tilde{\Psi}(s)/\tilde{\psi}(s) \).

(ii) In the case of different types of localized states, characterized by various waiting times and homogeneously distributed over the sample,

\[
\Psi(t) = \sum_j w_j \Psi_j(t), \quad \psi(t) = \sum_j w_j \psi_j(t), \quad \Phi(s) = \sum_j w_j \tilde{\Psi}_j(s) / \sum_j w_j \psi_j(s).
\]

Here, \( w_j \) are weight coefficients in the mixed distribution.

(iii) For the multiple trapping into localized states, the memory kernel is related to the density of localized states (DoS) [8],

\[
\Phi(t) \equiv \Phi_{MT}(t) = \delta(t) + \int_0^\infty \omega \exp \left\{ -\omega t \frac{N_f}{N_l} e^{-\varepsilon/\varepsilon_0} \right\} \rho(\varepsilon) d\varepsilon. \quad (2)
\]

Here \( \rho(\varepsilon) \) is DoS, \( \omega_\varepsilon \) is the trapping rate independent of energy. For the exponential density of localized states \( \rho(\varepsilon) \propto e^{-\varepsilon/\omega_\varepsilon} \) in case of weak dependence \( \omega_\varepsilon \) on \( \varepsilon \) \( (\omega_\varepsilon \approx \omega_0) \) the kernel is a power law function

\[
\Phi_{MT}(t) = \delta(t) + \frac{\omega_0 (c_\alpha t)^{-\alpha}}{\Gamma(1-\alpha)} \quad \text{with} \quad c_\alpha = \frac{\omega_0 N_f}{N_l} \left( \frac{\sin \pi \alpha}{\pi \alpha} \right)^{1/\alpha}, \quad \alpha = \frac{kT}{\varepsilon_0}. \quad (3)
\]

The Laplace transformation \( s \ll \omega_0 N_f/N_l \) of this kernel has the form

\[
\tilde{\Phi}_{MT}(s) \sim 1 + \frac{\omega_0}{c_\alpha s^{1-\alpha}}. \quad (4)
\]

(iv) In the case of transfer controlled by trapping into localized states distributed in a comb-like structure with a random teeth length \( \lambda \) with power law distribution, \( P\{\lambda > l\} = (l/l_0)^{-\beta} \) [9]:

\[
\tilde{\Phi}(s) = \left[ \frac{s \tilde{\Psi}(s)}{\tilde{\psi}(s)} \right]^\gamma, \quad \gamma = \frac{1}{2} + \frac{\beta}{2}.
\]

From this list, we can see that equation (1) describes dispersive drift-diffusion controlled by various mechanisms. Mechanism defines memory kernel \( \Phi(t) \) and diffusion-advection coefficients. Under certain conditions, fractional Fokker-Planck equation with different fractional-order derivatives can be obtained [4, 10, 11, 12].
3. Dispersive advection in a multilayer sample

Further, we consider a simplified situation neglecting the diffusion term. In the time-of-flight experiment, a strong field close to the breakdown conditions is applied. Note that even under these conditions, the diffusion term can play a significant role, but for simplicity we neglect it. To study transport in non-homogeneous sample, we divide it into many layers, each of which is characterized by a constant advection coefficient. Equation of dispersive advection in \( k \)-th layer is written in the form

\[
s\tilde{\Phi}_k(s)\tilde{p}_k(x, s) + V_k \frac{\partial}{\partial x} \tilde{p}_k(x, s) = \tilde{\Phi}_k(s) \tilde{G}_k(x, s), \quad d_{k-1} < x < d_k.
\]

Generation term in the right-hand side is related to the injection from the left boundary

\[
\tilde{G}_k(x, s) = \tilde{j}_{k-1}(d_{k-1}, s) \delta(x - d_{k-1}).
\]

For the first layer, carriers are injected by short laser pulse

\[
\tilde{G}_1(x) = N\delta(x).
\]

Under such conditions, the solution for nonequilibrium charge concentrations has the form

\[
\tilde{p}_k(x, s) = \tilde{j}_{k-1}(d_{k-1}, s) \frac{\tilde{\Phi}_k(s)}{V_k} \exp\left(-\frac{s\tilde{\Phi}_k(s)}{V_k}(x - d_{k-1})\right).
\]

Corresponding conduction current density is as follows

\[
\tilde{j}_k(d_k, s) = \frac{V_k}{\tilde{\Phi}_k(s)} \tilde{p}_k(d_k, s) = \tilde{j}_{k-1}(d_{k-1}, s) \exp\left(-\frac{s\tilde{\Phi}_k(s)}{V_k}a_k\right).
\]

Performing a cyclic substitution, we arrive at

\[
\tilde{j}_k(d_k, s) = N \exp\left(-s \sum_{i=1}^{k} \tilde{\Phi}_i(s) a_i\right).
\]

Distribution of current in the sample is given by the following density

\[
\tilde{j}_k(x, s) = N \exp\left(-s \sum_{i=1}^{k-1} \tilde{\Phi}_i(s) a_i - s \tilde{\Phi}_k(s) \frac{a_k}{V_k} (x - d_{k-1})\right).
\]

Transient current that is a displacement current can be found by averaging of the conduction current density over the sample thickness,

\[
\tilde{I}(s) = \frac{1}{L} \int_0^L \tilde{j}(x, s) dx = \frac{N}{L} \left\{ \sum_{k=1}^{n} \frac{V_k}{s \tilde{\Phi}_k(s)} \left[ 1 - \exp\left(-s \tilde{\Phi}_k(s) a_k\right)\right] \exp\left(-s \sum_{i=0}^{k-1} \tilde{\Phi}_i(s) a_i\right) \right\}.
\]

These formulae can be generalized to the case of a memory kernel and advection coefficient continuously varying over the sample thickness. For conduction current density, we have

\[
\tilde{j}(x, s) = N \exp\left(-s \int_0^x \frac{\tilde{\Phi}(s; x')}{V(x')} dx'\right).
\]

The Laplace transform of the transient current is determined by formula

\[
\tilde{I}(s) = \frac{N}{L} \int_0^L \exp\left(-s \int_0^x \frac{\tilde{\Phi}(s; x')}{V(x')} dx'\right) dx.
\]
4. Variable advection coefficient

Consider the case of the memory kernel independent of coordinate, i.e. non-homogeneity is implied in the dependence of advection coefficient $V$ on $x$. This dependence can be due to space dependent electric field or due to variations in concentration of localized states. In this case, the Laplace image of transient current is

$$\tilde{I}(s) = \frac{N}{L} \int_0^L \exp \left( -s \tilde{\Phi}(s) \int_0^x \frac{dx'}{V(x')} \right) dx.$$

Consider special case of linear decrease of advection coefficient with $x$, $V(x) = V_0 - kx$. Here, $V_0$ is an advection coefficient near the injection surface, and $k$ is a decrease coefficient. In this case,

$$\tilde{I}(s) = \frac{N}{L} \int_0^L \exp \left( -s \tilde{\Phi}(s) \int_0^x \frac{dx'}{V_0 - kx'} \right) dx = \frac{NV_0}{L} \frac{1 - (1 - kL/V_0)^{1 + \frac{s}{k \Phi(s)}}}{k + s \Phi(s)}.$$ 

![Figure 1. Transient current (5) for different values of $\alpha$.](image)

Assuming fractional exponential distribution of waiting times in localized states, we imply

$$\tilde{\psi}(s) = \frac{\mu}{\mu + s^\alpha}.$$

The Laplace image of the memory kernel in this case is

$$s \tilde{\Phi}(s) = \frac{1 - \tilde{\psi}(s)}{\tilde{\psi}(s)} = \mu^{-1}s^\alpha.$$

Considering the case, when the advection coefficient decreases to zero at the opposite electrode, we obtain

$$\tilde{I}(s) = \frac{N \mu V_0/L}{(\mu V_0/L) + s^\alpha}.$$ 

This transform corresponds to the fractional exponent,

$$I(t) = N \frac{\mu V_0}{L} t^{\alpha - 1} E_{\alpha,\alpha} \left( -\frac{\mu V_0}{L} t^\alpha \right).$$

Transmit current curves given by (5) are shown in Figure 1.
5. Conclusion
Dispersive transport in structures with spatially dependent memory kernel $\Phi$ and advection coefficient $V$ is considered. The variation of $V$ can be related to a nonuniformly distributed electric field or to inhomogeneities in the spatial distribution of localized states. The equation of one-sided dispersive transport and transient current are obtained as a result of dividing the samples into thin layers perpendicular to the electric field. In separate layers, the advection coefficient was considered constant. By solving the boundary problem for each layer and combining the solutions, charge carrier concentrations, conduction current density, and transient current were calculated. The transient current of the time-of-flight technique is calculated after neglecting the diffusion term. An explicit representation is obtained for a linear decrease in $V(x)$ over the sample thickness. The variation in $V$ leads to additional smearing of non-equilibrium particle package. Dispersive transient current curves can be observed even for normal transport for certain inhomogeneities in the advection term.

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