Journal of Computational Physics 293 (2015) 409–426

Contents lists available at ScienceDirect

Journal of Computational Physics

www.elsevier.com/locate/jcp

Dispersive transport of charge carriers in disordered nanostructured materials

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ARTICLE INFO

Article history:
Received 1 May 2014
Received in revised form 7 January 2015
Accepted 14 January 2015
Available online 19 January 2015

Keywords:
Dispersive transport
Disordered semiconductor
Fractional calculus
Multiple trapping
Hopping
Percolation
Comb model
Anomalous diffusion

ABSTRACT

Dispersive transport of charge carriers in disordered nanostructured semiconductors is described in terms of integral diffusion equations nonlocal in time. Transient photocurrent kinetics is analyzed for different situations. Relation to the fractional differential approach is demonstrated. Using this relation provides specifications in interpretation of the time-of-flight data. Joint influence of morphology and energy distribution of localized states is described in frames of the trap-limited advection–diffusion on a comb structure modeling a percolation cluster.

1. Introduction

As is known, transport phenomena in disordered solids can essentially differ from the classic theory developed for ordered say crystalline structures [34,39,84,89]. These phenomena covered by term *anomalous* or *generalized transport* are not compatible with the local equilibrium hypothesis. The non-Fickian properties of the diffusion are observed in amorphous hydrogenated silicon [28,39], amorphous selenium [48,51], amorphous chalcogenides [35,64], organic semiconductors, polymers [14,78], porous solids [8,9,31], nanostructured materials [22], polycrystalline films [55], liquid crystals [18], etc. Investigation of such processes represents one of the main trends in contemporary non-equilibrium statistical mechanics [36] for modern applications of disordered materials and mesoscopic systems [29,57,60,61,75].

Solving transport problem here, we deal with two interacting substances: particles (charge carriers) and medium (disordered solid matrix). Two or more coupled local equations describe this complicated system, but elimination of one of them (for instance, the medium equation) transforms remaining one (in this case, the moving particle equation) into an equation nonlocal with respect to spatial or/and time variables. The mathematical basement of this phenomenon is uncovered by the statistical mechanics. Let us cast an eye on this conclusion.

According to statistical mechanics, evolution of a closed Hamiltonian dynamical system composed of two interacting subsystems A and B is described by the Liouville equation

$$\frac{d\rho_{A+B}(t)}{dt} = (\mathsf{L}_A + \mathsf{L}_B + \mathsf{L}_{AB})\rho_{A+B}(t),$$

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http://dx.doi.org/10.1016/j.jcp.2015.01.022
0021-9991/

where $\rho(t)$ is the statistical operator and L is the correspondent Liouvillian.

Under the condition that initially subsystems A and B are uncorrelated, the Zwanzig–Mori projection method allows to eliminate one of two statistical operators and reduce the local (differential) equation for a closed mechanical system into the nonlocal (integro-differential) Lindblad equation [37] for an open system being the subsystem of the closed Hamiltonian system

$$\frac{d\rho_S(t)}{dt} = \mathsf{L}_S\rho_S(t) + \int_{t_0}^{t} G_S(t-\tau)\rho_S(\tau)d\tau, \tag{1}$$

where S stands for A or B, and G_S is the corresponding memory kernel (operator).

However, the Lindblad equation is rather abstract and doesn't supply us by handy representation for the influence function G_S. Nevertheless, it gives a basis for understanding a general idea of anomalous diffusion. Indeed, in quasiclassic approximation, the statistical operator $\rho_S(t)$ turns into spatial density $\rho(x,t)$ and the memory integral in (1) becomes a double integral (subscripts are omitted for short)

$$\frac{d\rho(x,t)}{dt} = \mathsf{L}\rho(x,t) + \int_{t_0}^{t} d\tau \int_{\mathrm{R}^n} d\xi\, G(x-\xi, t-\tau)\rho(\xi,\tau). \tag{2}$$

Practically, until we get a detailed information on inner structure of the sample, the most reasonable way to solution of the problem ran through constructing phenomenological models. In connection with this problem, it is very instructive to recall a Heisenberg article [27]. One of outstanding physicists-theorists of XX century defined a phenomenological theory as such a formulation of laws observed in physical phenomena, which does not attempt to completely reduce them to general fundamental "first principles", through which they could be understood. The phenomenological theories played always a value-significant role in the development of physics. Referring to semi-empirical laws in meteorology, valency rules, interrelations between radii of atoms and ions, binding energies and excitation energies in chemistry, main interrelations in turbulent hydrodynamics, the Drude dispersive theory, phenomenological thermodynamics and Ptolemaic system in antique astronomy, Heisenberg wrote: "For technical and other applications, they were often more important than the apprehension of relations, and from a purely pragmatic point of view phenomenological theories can make the knowledge of the nature laws to a large extent even redundant."[1]

Taking into account the stick-slip nature of charge carriers motion in disordered semiconductors, one can neglect (in first but really natural approximation) correlations between random waiting times and jump lengths:

$$\frac{d\rho(x,t)}{dt} = \mathsf{L}\rho(x,t) + \int_{t_0}^{t} d\tau \int_{\mathrm{R}^n} d\xi\, p(x-\xi)q(t-\tau)\rho(\xi,\tau). \tag{3}$$

Operator relates to the particles motion: it is a negative scalar in case when they are immobile between jumps. Thus, we arrive at the continuous time random walk (CTRW) model [45] taken by Scher and Montroll [59] as a theoretical foundation of a new approach to kinetics of charge carriers in disordered semiconductors called the dispersive transport (DT). It is worth to note that initially this model was stated without any relationship to statistical mechanics theorems.

Numerous experiments manifest the presence of universal DT properties which weakly depend on the detailed atomic and molecular structure of matter [30,59]. This universality is partly due to power laws governing transport processes in such systems. In turn, the power form of the kernels p and q directly leads to fractional integrals and derivatives (with respect to space- and time-variables, respectively). It is reasonable to believe that kinetic equations describing such transport processes can be presented in similar forms for different materials. Nevertheless, the Sher–Montroll version of DT for disordered systems is expressed in form of integral equations while the standard version for ordinary systems has form of partial differential equation. Embedding fractional derivatives in the theory [11,16,17,40,41,44,46,69,88] removed this unwanted feature and opened opportunities for the development of normal and anomalous kinetics in the framework of unified mathematical formalism. The fractional version of the dispersive transport theory is developed in our book [84].

From a microscopic point of view, the dispersive transport may be explained by involving various mechanisms: multiple trapping of charge carriers into localized states distributed in the mobility gap, hopping conduction assisted by phonons, percolation through conducting states, etc. [7,47,59,76,89]. Experimental data revealing universal behavior of some important characteristics of dispersive transport (e.g. time-behavior of transient photocurrent) indicates predominance of statistical laws over dynamical ones. Interest in non-Gaussian transport theory has recently revived in connection with the observation of anomalous relaxation–diffusion processes in nanoscale systems: nanoporous silicon, glasses doped by quantum dots (QDs), quasi-1D systems, and arrays of colloidal QDs. These systems are very promising for applications in spintronics and quantum computing. They can also be useful for studying the fundamental concepts of physics of disordered solids: localization, nonlinear effects associated with long-range Coulomb correlations, occupancy of traps and the Coulomb blockade.

[1] Not wanting to give an absolute sense of the latter assertion, we would like to emphasize his trust relationship to phenomenological theories.