

Microscopic model of charge carrier transfer in complex media

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Received 30 September 2004; accepted 13 June 2005

Available online 9 August 2005

Abstract

We present a microscopic model of a charge carrier transfer under an action of a constant electric field in a complex medium. Generalizing previous theoretical approaches, we model the dynamical environment hindering the carrier motion by dynamic percolation, i.e., as a medium comprising particles which move randomly on a simple cubic lattice, constrained by hard-core exclusion, and may spontaneously annihilate and re-appear at some prescribed rates. We determine analytically the density profiles of the “environment” particles, as seen from the stationary moving charge carrier, and calculate its terminal velocity, V_c , as the function of the applied field and other system parameters. We realize that for sufficiently small external fields the force exerted on the carrier by the “environment” particles shows a viscous-like behavior and define an analog of the Stokes formula for such dynamic percolative environments. The corresponding friction coefficient is also derived. We show that the density profile of the environment particles is strongly inhomogeneous: In front of the stationary moving charge carrier the density is higher than the average density, ρ_s , and approaches it as an exponential function of the distance from the carrier. Behind the carrier the local density is lower than ρ_s and the approach towards ρ_s may proceed differently depending on whether the particles number is or is not explicitly conserved. © 2005 Elsevier B.V. All rights reserved.

Keywords: Charge transfer; Dynamic percolation; Friction; Stokes law

1. Introduction

The percolation concept has been a key notion for understanding transport and conduction processes in a wide range of complex disordered media. A few stray examples are ionic conduction in polymeric, amorphous or glassy ceramic electrolytes, diffusion in biological tissues and permeability of disordered membranes [1–4].

Most of physical situations studied so far (see [1–4] and references therein) concern systems in which complex disordered environment can be considered as “frozen”; that is, the random environment in which a given transfer process takes place does not change in time.

This is certainly the case in many instances, but it is not true in general. In fact, there are many experimental systems in which the static percolation picture is not valid since the structure of the host material reorganizes itself on a time scale comparable to that at which the transfer itself occurs. Such a reorganization happens, namely, in certain biomembranes [5], solid protonic conductors [6], oil-continuous microemulsions [7–10] or polymer electrolytes [11–13].

In particular, ionic transport across a biomembrane, such as, e.g., gramicidin-A, proceeds by the motion of ions through molecular channels along which they encounter potential barriers whose heights fluctuate randomly in time. The fluctuations of potential barriers may impede the transport constituting an important controlling factor [5]. In the case of protonic conduction

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by the Grotthuss mechanism [6], site-to-site hopping of charge carriers takes place between neighboring H_2O or NH_3 groups that have a favorable relative orientation. Here, the structural host-reorganization process interacting with the carrier motion occurs due to thermally activated rotation of the H_2O or NH_3 groups. In a similar fashion, within oil-continuous microemulsions, the charge transport proceeds by charge being transferred from one water globule to another, as globules approach each other in their Brownian motion [7–10]. Last but not least, in polymer electrolytes, such as, e.g., polyethylene oxide complexed non-stoichiometrically with the ionic salt NaSCN , the Na^+ ions are largely tetrahedrally coordinated by polyether oxygens, but at the same time that Na^+ ions hop from one fourfold coordination site to another, the oxygens themselves, along with the polymeric backbone, undergo large-amplitude wagging and even diffusive motion [11–13].

Clearly, all these examples involve two characteristic time scales: the typical time τ between two successive hops of the charge carrier and a typical renewal time τ^* of the environment itself; that is, the time at which the host complex medium re-organizes itself sufficiently enough to provide a new set of available pathways for charge carrier transfer. Accordingly, the conventional static percolation picture can be strictly valid when only the characteristic time τ^* gets infinitely large. Only in this case one may expect an anomalous large-scale dynamics. On contrary, when τ^* is finite, *dynamic percolation* picture has to be applied. In this situation, one encounters quite a different behavior when compared to the random environments with quenched disorder. As a result, one expects an Ohmic-type or Stokes-type linear velocity–force relation for the carrier’s terminal velocities as a function of the applied field, in contrast to the threshold behavior and anomalous dynamics predicted by the conventional static percolation theory.

The prefactor in the linear velocity–force relation may depend, however, in a non-trivial way on the system’s parameters and this dependence constitutes the main challenge for the theoretical analysis here. On the other hand, we note that in the above mentioned examples of the dynamic percolative environments quite different physical processes are responsible for the time evolution of the host medium. Consequently, one expects that the prefactor in the Stokes-type velocity–force relation should also be dependent on the precise mechanism which underlies the temporal re-organization of the environment.

Theoretical modeling of charge carrier transfer in dynamic percolative environments has followed basically two different lines of thought. Early models of dynamic percolation [14,15] described the random environment within the framework of a standard bond-percolation model allowing the strength of each bond to fluctuate in time between zero and some finite value. In this ap-

proach, the dynamics of the host medium [14,15] was accounted for by a series of instantaneous renewal events. These events were assumed to occur at random times, chosen from a renewal time distribution. In the renewal process the positions of all unblocked bonds are being reassigned, such that after each renewal event a carrier sees a newly defined network. This approach is thus characterized by a *global dynamical disorder* without global conservation laws and correlations, since the entire set of random hopping rates is renewed independently of the previous history. Another model characterized by a *local dynamical disorder* has been proposed in [16] and [17], and subsequently generalized to the non-Markovian case in [18]. The difference of this model in regard to the previous one is that here the hopping rates at different sites fluctuate *independently* of each other. That is, states of individual bonds, rather than that of the whole lattice change in the renewal events. To describe the dynamical behavior in the *local dynamical disorder* case, a dynamical mean-field theory has been proposed [16,17], based on the effective medium approximation introduced for the analysis of random walks on lattices with static disorder [19]. Subsequently, this model has been generalized to include the possibility of multistate transformations of the *dynamically* random complex medium [20]. More recently, several exactly solvable one-dimensional models with *global* and *local* dynamical disorder have been discussed [21].

The second approach to the problem emerged within the context of ionic conductivity in superionic solids. Here, the dynamical percolative environment has been considered as a multicomponent mixture of mobile species in which one or several neutral components block the carrier component [22]. In particular, such a situation can be observed in a superionic conductor β'' -alumina, doped with two different ionic species (e.g., Na^+ and Ba^{2+}), where small Na^+ ions are rather mobile, while the larger Ba^{2+} ions move essentially slower and temporarily block the Na^+ ions. Contrary to the previous line of thought, the dynamics of such a percolative environment has essential correlations, generated by hard-core exclusion interactions between the species involved. Moreover, a salient feature of these situations is that here the total number of the particles involved is conserved, i.e., dynamics of the environment is globally constrained by a certain “conservation law”. The impact of this property on charge carrier transfer will become clearer as we proceed.

Further on, in [22] the frequency-dependent ionic conductivity of the light species has been analyzed combining a continuous time random walk approach for the dynamical problem with an effective medium approximation describing the frozen environment of slow species. Next, as an explanation of the sharp increase of electrical conductivity transition in water-in-oil

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