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Frequency-dependent response and dynamic disorder

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This paper discusses selected aspects of the application of dynamic percolation models to ionic transport in mixed-ion superionic conductors. The discussion is based on an AB lattice gas model with hard-core repulsions and a ratio τ, $0 \leq \tau \leq \infty$, between the transition rates of particles A and B. The frequency-dependent conductivity for a tracer particle is calculated within an effective-medium theory. The motion of the background B-particles is regarded as providing a fluctuating disordered environment for the tracer particles A. A crossover frequency separating high-frequency and low-frequency response is found which scales with τ as $\omega_c \sim \tau^{-1/2}$. The results for the dc limit are compared with simulations and are found to be in very good agreement.

An important class of theoretical models for the study of hopping transport in superionic solids are lattice gases [1,2]. In the simplest form of this model two species of particles, A and B, occupy the sites of a regular lattice and interact with each other via a hard-core repulsive potential. The particles perform random walks between vacant lattice sites. Their interaction prevents double occupancy of lattice sites. The transition rates may be different for the two types of particles. In more realistic, models the particles may also interact with each other via more extended potentials. The experimental system which has motivated the present investigation of such models is Na^+/Ba^{++}-β''-alumina. In these systems, charge transport occurs via hopping of Na^+ and Ba^{++} ions. The ionic motion is two-dimensional, being confined to the mirror planes. The underlying regular lattice of equilibrium positions is the two-dimensional honeycomb lattice. The activation energy for Na^+ is roughly 0.35 eV while that for Ba^{++} is around 0.58 eV [3]. At sufficiently low temperatures, the transition rates for the Ba^{++} will be so small that they can be considered frozen on the timescale of the experiment. In this case, the Na^+ will experience a disordered network of conduction paths. At higher temperatures, the network of available sites will become time dependent.

My objective here is to discuss some results of recent calculations of the frequency dependent conductivity, $\sigma(\omega)$, for simple lattice gas models of such systems [4–7]. Emphasis is placed on the concept of dynamic disorder and on correlation effects. The calculation of $\sigma(\omega)$ for hopping transport is based on the well-known fluctuation–dissipation theorem for localized quantities [8] which relates $\sigma(\omega)$ to the generalized frequency-dependent diffusion coefficient, $D(\omega)$, of a random walk.

Despite much analytical work and simulations, a theory for the frequency-dependent conductivity over the full range of transition rates and concentrations of the two species has remained difficult because an exact calculation involves the solution of a many-particle master equation. For reviews, the reader is referred to refs. [1] and [9]. Most theoretical work concentrates on two special cases: one is the case of frozen B-particles randomly occupying the lattice sites, the other is the case of tracer diffusion where both species of particles are equally fast. Simulations on the other hand have considered mainly the dc limit. The basic idea for improving previous approaches was first introduced in ref. [4]. It consists in viewing the tracer diffusion problem as diffusion in a dynamically-disordered environment.

Given the transition rates w_A, w_B of the two particles and the concentration p of B-particles, the problem is to calculate the frequency-dependent diffusion coefficient for a single A-particle moving in a time-dependent background of B-particles. The concentration p and the dimensionless ratio $\tau = w_A/w_B$ are the physical parameters of the model. The concentration of vacancies is $1-p$. For $\tau = \infty$ the A-particle moves in a frozen disordered background of B-particles. For $\tau = 0$, one has a slow A-particle in a fast background, and the case $\tau = 1$ will be referred to as tracer diffusion. If $\tau = \infty$ and if the B-particles randomly occupy the lattice sites, there will exist a percolation threshold p_c above which the A-particle cannot find a connected path of vacancies through the system, and thus $\sigma(\omega = 0) = 0$ for $p > p_c$. If τ is large but finite and $p > p_c$, the A-particle will eventually pass through the network, and one expects a finite dc conductivity determined by τ according to $\sigma(0) \sim 1/\tau$. In this case, there will also exist a crossover frequency, ω_c, above which the A-particle will essentially see a frozen arrangement of B-particles. Above ω_c, the conductivity is expected to be strongly affected by the dynamics of the B-particles. This crossover frequency can again be related to the parameter τ by the following qualitative argument.

Let the dynamics of the B-particles be such that its effect can be modelled as independently fluctuating bonds. The lattice bonds between nearest-neighbour sites are classified at each instant as conducting or open if they connect two vacant sites. Otherwise they will be classified as being blocked. Each bond is assumed to fluctuate independently between these two possibilities, blocked or open, with a relaxation time, τ. The bond system is assumed to be in a stationary state in which the probability for each bond to be blocked is p, while the probability of an open bond is $1-p$. The A-particle is started at time $t = 0$. The number of bonds remaining in the same state as at $t = 0$ decreases exponentially with time. As long as the A-particle does not jump across a bond that has changed its state since $t = 0$, it explores the configuration of $t = 0$ as if it were frozen. This defines the crossover time as the time after which the walker first encounters a bond that has switched at least once since $t = 0$. Consider n steps of the A-particle. The average length of the time interval during which all of the n crossed bonds remain in their original state is τ/n. The crossover occurs when this average time equals the number of steps, i.e. $n \cdot 1 \sim \tau/n$, where it is assumed that $1/\omega_A$ defines the units of time. Therefore one expects $t_c \sim \tau^{1/2}$ for the crossover time and $\omega_c \sim \tau^{-1/2}$ for the crossover frequency.

The problem can be approached more quantitatively using an effective-medium approach. The idea is to apply the analytic continuation rule of dynamic percolation theory [10] which was originally derived for an artificial background dynamics. If $D(\omega)$ is the generalized frequency-dependent diffusion coefficient of the A-particle in the dynamically disordered system, then the rule states that $D(u) = D_0(u + 1/\tau)$, where $u = i\omega$ is the spectral variable corresponding to Laplace transformation with respect to time and D_0 is the generalized frequency-dependent diffusion coefficient for the frozen system (i.e. for $\tau = \infty$). The same analytic continuation rule was found to apply within effective-medium theory to the model of independently fluctuating bonds discussed above [11]. The analytic continuation rule allows the calculation of D for the problem with dynamic disorder from the calculation of the same quantity for frozen disorder.

Figure 1 shows the result for $\mathrm{Re}\, D(\omega) \sim \mathrm{Re}\, \sigma(\omega)$, where D_0 was obtained from the single-bond effective-medium approximation for bond percolation [8]. One finds a crossover from $\sigma(\omega) \sim 1/\tau$ for $\omega < \omega_c$ to the behaviour of the frozen problem at high frequencies. The crossover frequency is seen to scale with $\omega_c \sim \tau^{-1/2}$. These results confirm the simple scaling argument above. Formulating the problem in the language of continuous time random walks shows however that the low-frequency behaviour can be different if correlations between A- and B-particles give rise to a sequential mechanism for the release fo the A-particle from a finite cluster of vacant sites [5].

The EMA calculation based on the analytic continuation rule given above an also be checked against simulation results. Such results are available for the honeycomb lattice from ref. [12] where the dc conductivity was measured as a function of

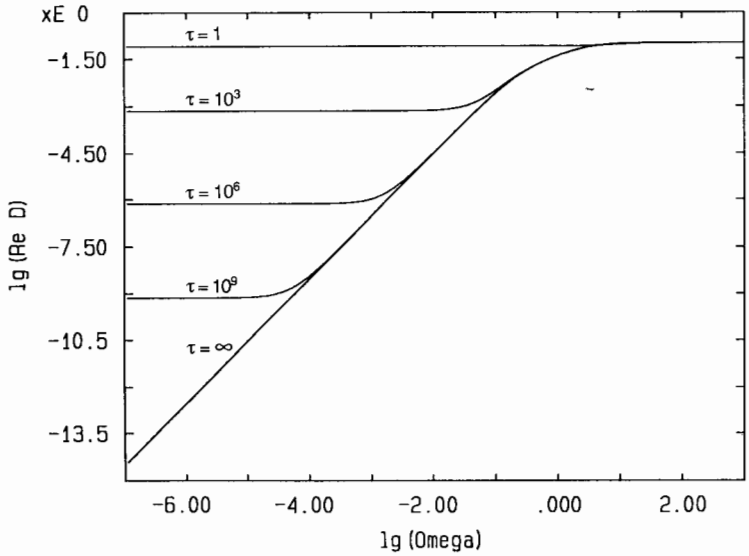

Fig. 1. Real part of the generalized diffusion coefficient Re $D(\omega)$ as a function of frequency, ω, in a logarithmic plot for several values of τ. The result shown is representative for blocker concentrations p above and bounded away from the conductivity threshold. $\sigma(0, \tau = \infty) = 0$.

B-particle concentration. More precisely, in fig. 2 the correlation factor $f = D(0)/D(\infty)$ has been plotted as a function of p. The crosses are the simulation results for $\tau = 1$ from ref. [12]. Although the theoretical curves contain no adjustable fit parameters, they are found to agree very

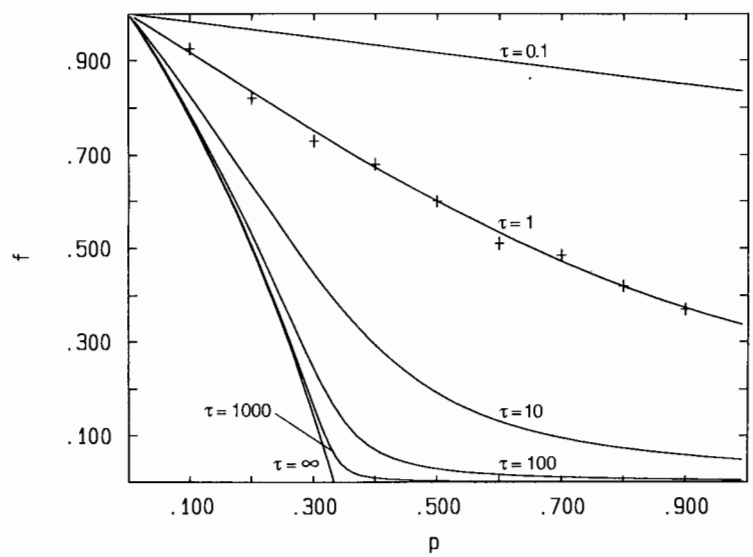

Fig. 2. Correlation factor f versus concentration p for several values of τ for the hexagonal lattice. The crosses are simulation results from ref. [12] for the case $\tau = 1$. There are no adjustable fit parameters.

well with the simulations. Similar simulations [13,14] for an fcc lattice gave equally good agreement [4].

Finally, I would like to comment on the effect of correlations. Correlations can arise from Coulomb interactions, correlated hops of groups of particles or lattice relaxation effects. In general these will change the transition rate of the A-particle to the previously occupied site as compared with the rate for transitions to all other neighbouring sites. This leads immediately to a generalization of Fürth's model for correlated random walks [15–17] to disordered systems [6,7]. This gives rise to several interesting effects [6], two of which are mentioned here. For certain values of the correlation strength, the real part of $\sigma(\omega)$ can show a maximum as a function of frequency. For other values of the correlation strength crossover behaviour can give rise to approximate 'power laws' $\mathrm{Re}\ \sigma(\omega) \sim \omega^{\alpha}$ with $\alpha \simeq 0.5$ over much more than a decade in frequency.

Conclusions

Summarizing, this paper has discussed recent work on hopping transport in dynamically disordered systems. For details the reader is referred to refs. [4] and [6]. It was shown that tracer diffusion in lattice gases can profitably be viewed as a dynamic disorder problem (see also ref. [18] for the same idea in a different context). In particular, such an approach gives very good agreement between the results of Monte Carlo simulations and an analytic effective-medium treatment.

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