Percolation concepts in solid state ionics

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Abstract

Structural disorder is an inherent property of solid materials, which can support a macroscopic ionic current. Many transport phenomena in these solid ionic conductors appear to be related to concepts from percolation theory. We demonstrate this for three classes of materials, namely (i) dispersed ionic conductors, which show conductance properties that can be related to random electrical networks, (ii) ion-doped network glasses, whose concentration-dependent diffusion properties are accessible by critical path analysis, and (iii) polymer ionic conductors. For the latter we discuss Monte Carlo simulations which indicate the applicability of dynamic bond percolation theory. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Among the best-known physical realizations of the model of classical percolative transport is electrical conduction in random insulator–conductor composites [1,2] or in non-homogeneous ultrathin metallic films [3]. Many experiments on such systems have revealed even the detailed critical properties associated with the percolation threshold, as predicted by lattice or continuum percolation theories [4–7]. Moreover, percolation concepts have proved very useful in more general studies of transport phenomena in disordered media, including the description of transport at the atomic level.

This review is concerned with percolation concepts for ionic transport in disordered solids, a field which is of great practical importance from the electrochemical point of view. In addition, the large variety of solid ion-conducting materials enables us to perform fundamental studies of microscopic diffusion processes in many different random structures. Section 2 summarizes the work on dispersed ionic conductors, whose conductance and dielectric properties can be mapped onto electrical impedance networks

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[8,9]. In Section 3 we turn to some aspects of percolative transport in glasses, while Section 4 describes Monte Carlo studies of polymer electrolytes and discusses a possible relationship with the concept of dynamic bond percolation [10–12]. A brief summary is contained in Section 5.

2. Dispersed ionic conductors

Heterogeneous mixtures of two different ionic conductors or of an ion-conducting and an insulating component have been prepared experimentally in very different combinations [13]. Particular interest has focused on such mixtures after the discovery that insulating fine particles, with sizes of the order of 1 μm, dispersed in a conductive medium (e.g. Al_2O_3 in LiI) can lead to a conductivity enhancement [14]. This effect has been found to arise from the formation of a defective, highly conducting layer following the boundaries between the conducting and the insulating phase [15,16]. Effectively, the system thus contains three phases. Theoretical studies therefore have focused on suitable three-component impedance network models [8,9,17]. Fig. 1 shows a two-dimensional illustration of such composites and a corresponding discretized model. In its simplest version this model is constructed by randomly selecting a fraction p of elementary squares on a square lattice, which represent the insulating phase (C), while the remaining squares are the conducting phase (B). The distribution of both phases leads to a correlated bond percolation model with three types of bonds and associated bond conductances $\hat{\sigma}_k$; $k = A, B, C$; as defined in Fig. 1b. For example, bonds in the boundary between phases B and C correspond to the highly conducting component (A). The analogous construction for three dimensions is obvious. Finite frequency effects are readily included, when we allow bond conductances to be complex [18]. For simplicity, we may assume the ideal behaviour $\hat{\sigma}_k = \sigma_k - i\omega C_k$ including constant zero-frequency conductances σ_k and capacitance elements C_k, but more general forms
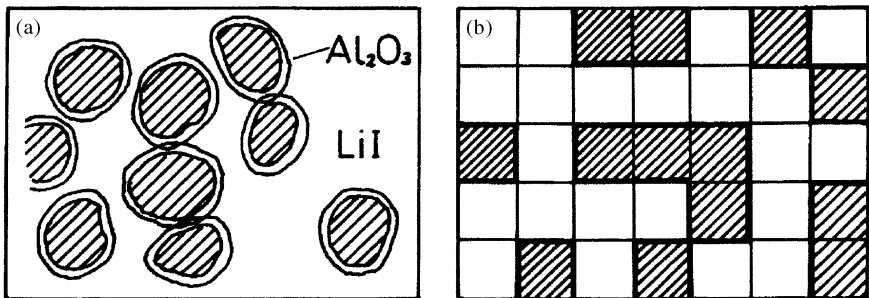

Fig. 1. (a) Two-dimensional illustration of dispersed ionic conductors showing an enhanced conductivity within a narrow interfacial region. (b) Three-component bond percolation model, defined by the random mixture of an ionic conductor (unshaded) and an insulator (shaded). Bonds within the conducting and insulating region have conductances $\hat{\sigma}_B$ and $\hat{\sigma}_C$, respectively, while interfacial bonds have a conductance $\hat{\sigma}_A$.

can be chosen, when necessary. Clearly, the experimental situation described above requires that $\sigma_A/\sigma_B = \tau \gg 1$; $\sigma_C = 0$.

A remarkable feature of this model is the existence of two threshold concentrations. At $p = p'_c$, interface percolation (i.e. percolation of C-bonds) sets in, whereas at $p = p''_c = 1 - p'_c$ (normally not accessible by experiment) the system undergoes a conductor–insulator transition. In two dimensions ($d=2$) we have $p'_c = 0.41$, while in $d=3$, $p'_c = 0.097$, corresponding to the threshold for second-neighbour ($d=2$) and third-neighbour ($d=3$) site percolation on a d-dimensional cubic lattice, respectively. At zero frequency, the total, averaged conductance Σ can be obtained from Monte Carlo simulation. Good agreement with experiments is obtained, which show a broad maximum in Σ as a function of p in the range between the two thresholds [19]. Generally, the conductances σ_A and σ_B will display different activation energies, which means that the parameter τ can be controlled via the temperature. This in principle offers the possibility to detect critical transport behaviour associated with interface percolation [17]. In the vicinity of p'_c it seems interesting in addition to study critical AC-effects [18,20]. For example, at p'_c the effective capacitance $C_{eff} = \lim_{\omega \to \infty} \mathrm{Im}\Sigma(\omega)/\omega$ should scale with τ as $C_{eff} \sim \tau^{1-u}$. The exponent $u = \mu/(\mu+s)$ is given in terms of the critical exponents μ and s, describing the near-threshold behaviour of the averaged conductivity in a two-component conductor–insulator or conductor–superconductor mixture, respectively. In $d = 3$, we have μ and $s \simeq 0.7$. AC-properties in the whole range of p-values have been calculated by renormalisation group techniques [18].

Several extensions of this model are conceivable. In the case of DC-transport ($\omega=0$), the variation of the total conductivity with the size of dispersed particles has been calculated and successfully compared with experiments [21]. Subsequent work also emphasised critical aspects of continuum percolation in dispersed ionic conductors [22].

3. Counterion effects in glasses

Network glasses with SiO_2 – or B_2O_3 – building units can show high ionic conductivities after doping with appropriate network modifiers (e.g. alkali oxides) [23]. Cation diffusion in these glassy ionic conductors is accompanied by several remarkable phenomena, like conductivity dispersion, including a nearly constant dielectric loss at high frequencies [24,25], or a sensitive dependence of the DC-conductivity on the ion concentration. In addition, transport properties of glasses containing two species of migrating alkali ions generally depend on their mixing ratio in a highly non-linear way [26–28]. Percolation ideas for explaining these "mixed-alkali effects", which can also occur in certain crystalline ionic conductors, are presented in the contributions by Ingram and by Maass and Meyer to this volume.

For single-alkali glasses at low doping level one expects that the migrating alkali ions get temporarily trapped by the immobile counterions (e.g. oxygen ions) which are introduced into the glassy network through the doping process. This counterion model has proved very useful in explaining frequency-dependent conductivities as well

as DC-transport properties as a function of ion concentration c. For details the reader is referred to the original work, which is largely based on Monte Carlo simulation of charged particle diffusion in the presence of both Coulombic traps and interparticle interactions [29,30].

For brevity, let us focus our discussion on the diffusion constant $D(c)$, which determines the DC-conductivity. Experimentally, $D(c)$ is known to increase drastically with c, but to level off for strongly doped samples [23]. This behaviour mainly results from a decrease in the associated activation energy $E_0(c)$ with c. Qualitatively, such trends with c can be understood by simple percolation arguments. Within a single-particle picture, an ion will diffuse along the most favourable paths within the energy landscape determined by the counterions. Critical path arguments for random walks in a disordered energy landscape have been employed earlier in the context of electron transport in amorphous semi-conductors [31] and also for superionic glasses [32,33]. Here, in order to estimate the dominant activation energy $E_0(c)$, one first determines the saddle point energy $E(r)$ midway between two Coulombic trapping centres at a distance $2r$ [34]. Introducing r_s as a measure of the density of Coulombic traps by $(4\pi r_s^3)^{-1} \propto c$, we can estimate $E_0(c) \simeq E(r_0)$. Here $r_0 = 0.69 r_s$ is the critical radius for percolation in a system of randomly placed (overlapping) spheres. For the diffusion constant $D(c)$ one thus obtains $D(c) = \text{const.} r_0^2 \exp(-E(r_0)/k_B T)$. Because of important many-body effects contained in the counterion model, this expression cannot be expected to reproduce the simulations for $D(c)$ in a quantitative manner. Nevertheless, as shown in Fig. 2 [35], it accounts for the experimentally observed increase of $D(c)$ for small c and, setting $E_0(c^*) = k_B T$, it yields a reasonable estimate of the characteristic concentration c^*, beyond which the strongly doped regime with nearly constant activation energy is reached.

4. Polymer ionic conductors

Chain polymers carrying an electro-negative atom (oxygen or nitrogen) in their repeat unit, can act as solvents for certain salts, as a consequence of the attractive interaction between chains and cations. Well-known examples are Li-salts dissolved in polyethylene-oxide (PEO). At temperatures sufficiently above their glass transition temperature these polymer-salt solutions show significant DC-mobilities. Materials of this type are known as polymer electrolytes [36,37] and are used, for example, in battery applications.

Thermodynamical studies, optical measurements and diffusion studies have revealed a subtle interplay between ionic and polymer network degrees of freedom [36–40]. Deeper insight into this problem emerged from Monte Carlo simulations of a microscopic diffusion model designed for PEO-based electrolytes [39–42]. It consists of interacting lattice chains and two species of point particles, which represent anions and cations. The latter can bind specific beads (oxygen beads) in the chains. Details of this model are described elsewhere [42]. Its main features are:
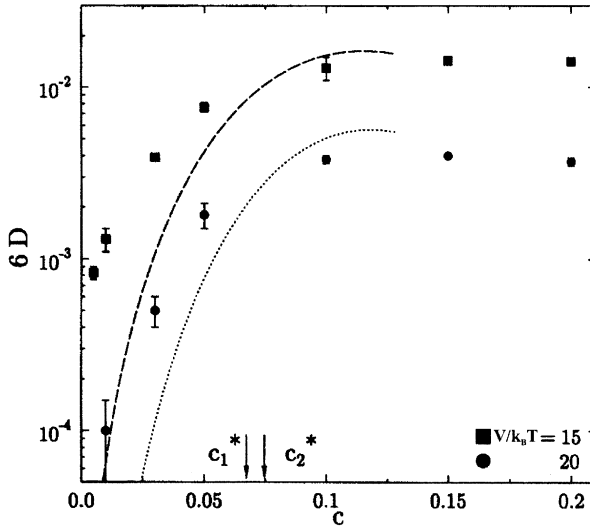
Fig. 2. Diffusion constant $D(c)$ versus ion-concentration in the counterion model for two different temperatures, $V/k_B T = 15$ and 20, where V is a typical Coulomb energy. Data points are from simulation. Dashed and dotted line result from critical path analysis. A constant prefactor in the analytic expression for $D(c)$ (see text) has beeen chosen such that the curves agree with the simulations at the respective concentrations c_1^* and c_2^*, which characterize the cross-over to the strongly doped regime.

(i) The centre-of-mass diffusion constants $D^{(P)}(T,c)$ of the polymer chains nicely follow the Vogel–Fulcher–Tammann (VTF) law, as shown in Fig. 3. VTF-temperatures $T_0(c)$ increase nearly linearly with the concentration c of sites occupied by ions, see the inset in Fig. 3. This trend is consistent with the experimentally known increase in the glass transition temperature upon adding salt [43,44].

(ii) Cation diffusion constants $D^+(T,c)$ as a function of temperature T are proportional to $[D^{(P)}(T,c)]^{n_+(c)}$ over at least three decades in $D^{(P)}$. The exponent $n_+(c)$ decreases with c, again see Fig. 3. Qualitatively, we expect that chain diffusion constants reflect the behaviour of the viscosity of the system. The proportionality mentioned before therefore is reminiscent of Walden's rule [45,46], which relates electrical conductivities of ionic solutions to their viscosity. The appearance of a fractional power in the relation between D^+ and $D^{(P)}$ appears interesting in connection with recent measurements of the conductivity–viscosity relationship in ionic melts [47].

(iii) Anion diffusion constants as a function of both T and c approximatively scale as $D^-(T,c) \simeq f(D^{(P)}(T,c))$, where $f(x) \simeq x^{0.2}$ for the majority of simulation data for D^-.

The fundamental difference between anion and cation diffusion [48] is not surprising because anion–polymer interactions in the model of Ref. [42] are always repulsive. The anions thus find themselves in an environment where pathways open up and rearrange according to the chain motion, which in this way facilitates anion diffusion. This picture bears the essential idea of the dynamic bond percolation (DBP) model, proposed long
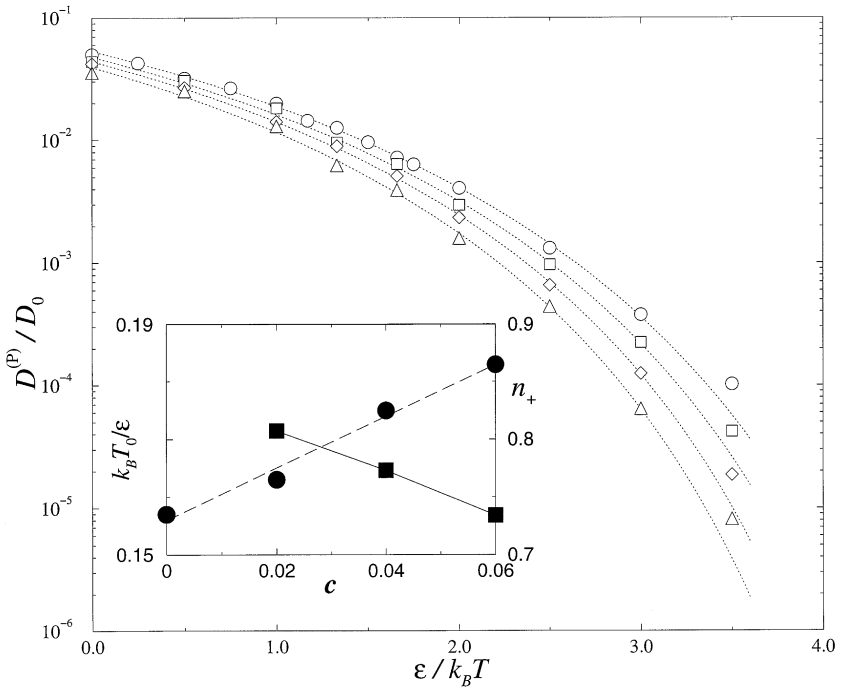
Fig. 3. Simulated diffusion constants of polymer chains, $D^{(P)}$, normalized by the bare diffusion constant D_0 of point particles, as a function of temperature for different ion concentrations, $c = 0$ ($\bigcirc$); 0.02 ($\square$); 0.04 ($\diamond$); 0.06 ($\triangle$), demonstrating VTF-behaviour. The inset shows VTF-temperatures $T_0(c)$ ($\bullet$) and exponents $n_+(c)$ ($\blacksquare$) characterizing a power-law relation $D^+ \propto [D^{(P)}]^{n_+}$.

ago, in connection with a qualitative description of diffusion data and viscosities in polymer electrolytes [10,49]. Basically, in the DBP one is considering the random walk of a single particle in a bond percolation model, with a total fraction p of broken bonds, but bonds independently fluctuate at a rate λ between two states, where they are conducting or broken, respectively. An important outcome of this model is the fact that its frequency-dependent diffusivity $D(-i\omega, p, \lambda)$, irrespective of the exact form of the diffusivity of the frozen lattice, $D^{(f)}(-i\omega, p) = D(-i\omega, p, 0)$, can be obtained by analytic continuation [50],

$$D(-i\omega, p, \lambda) = D^{(f)}(-i\omega + \lambda, p) . \tag{1}$$

In fact, the simulation results for D^- in our complete polymer electrolyte model, see (iii), imply that only one time scale characterizing the polymer network dynamics is relevant with respect to D^-, in agreement with the DBP-concept for anion diffusion.

In a preliminary attempt to work out this idea more explicitly, we confine ourselves to $\omega = 0$ and assume $D^{(-)}$ to be identical with the diffusion constant of an underlying, effective DBP-model. This procedure, in fact, is in the spirit of effective medium theories developed for interacting lattice gases with the help of the DBP [51]. In view of
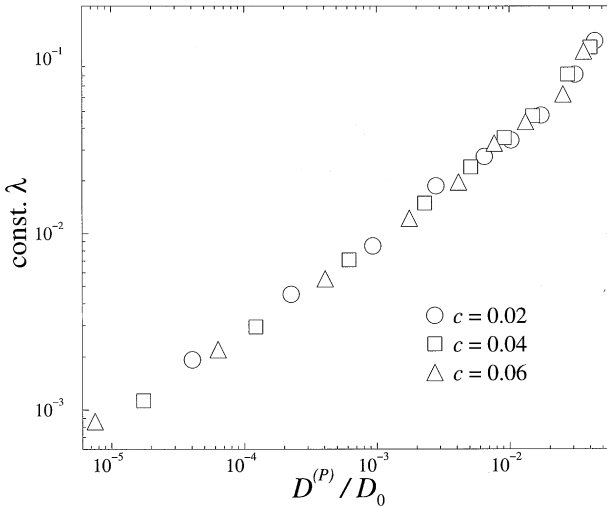
Fig. 4. Relation between the rate λ for bond fluctuations in an effective DBP-model and polymer chain diffusion constants, as obtained from simulation.

Eq. (1) we therefore write

$$D^{-}(T, c) = D^{(f)}(\lambda, p) . \tag{2}$$

Here the parameter p is a purely formal quantity which may not be related directly to the concentrations of polymer beads or ions in our complete model. Nevertheless, we can argue that p should be slightly above the threshold p_c of the associated DBP-model, because the case of a frozen lattice ($\lambda = 0$) should be recovered at the VTF-temperature T_0, and diffusion constants $D^{(-)}$ extrapolated to T_0 (corresponding to $\lambda = 0$ in Eq. (2)) are very small, actually of the order of $D^{-}/D_0 \sim 10^{-4}$.

Moreover, the temperature range considered in the simulations, which is well above T_0, should correspond to the regime of fast bond fluctuations. Standard scaling theory therefore yields $D^{(f)}(\lambda, p) \sim \lambda^{1-k}$, where k is the exponent describing anomalous diffusion in a percolation system at criticality. Its value in three dimensions is $k \sim 0.3$. It follows that $D^{-}(T, c) \sim \lambda^{1-k}$.

This result allows us to relate the relaxation rate λ to $D^{(P)}$, as shown in Fig. 4. Obviously, as $D^{(P)}/D_0$ becomes small (smaller than about 10^{-3}) λ decreases more slowly than $D^{(P)}$. This trend seems reasonable, because segmental motions of the chains may still facilitate anion diffusion while the centre-of-mass motion of chains is almost frozen.

A firm theory of mapping the polymer electrolyte model onto a DBP model might proceed as follows. In a first step one can simulate the anion motion in a frozen polymer environment and thereby extract the function $D^{(f)}(-i\omega)$. Second, following Ref. [51], one may obtain the relaxation rate λ directly from the simulated decay of the local occupational correlation function in the case of moving chains. This second

step requires simulating the complete polymer electrolyte model only for relatively short times. Combination of both steps by using $D^- = D^{(f)}(\lambda)$ should yield the anion diffusion constants. (Note that here the parameter p becomes irrelevant.) It would be interesting to test the validity of such an approach, which would save a large amount of computational effort needed in long-time simulations of the complete polymer electrolyte model.

5. Summary

We demonstrated the utility of percolation concepts for ionic transport in various disordered solids. As a first example, we considered DC-transport and dynamic properties of dispersed ionic conductors, which involve an enhanced interfacial conductivity. This problem can be mapped in a rather direct way onto a correlated three-component electrical network. Two threshold concentrations, p_c' and p_c'', can be identified. Critical properties related to them are analogous to random conductor–superconductor and normal conductor–insulator networks, respectively. Experimentally, the shape of curves, describing the overall conductance versus the concentration p of dispersed particles, shows large variations in the different composites, and certainly depends on the size and shape distributions and on possible correlated spatial arrangements of the insulating particles. It is important to note that such effects can be taken into account in a straightforward manner within suitably generalized network models.

Furthermore, some percolation ideas for transport in weakly doped network glasses were advanced, based on the spirit of critical path analysis. Very recent Monte Carlo studies of diffusion in polymer electrolytes have revived the concept, suggested long ago, of an underlying effective dynamic bond percolation model. This concept, if successful, could greatly simplify the problem of obtaining quantitative information on the dynamics at long times in a coupled ion-polymer system.

Acknowledgements

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