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Trapping-to-percolation transition in the hopping diffusion of substitutionally disordered solids with a binary energy distribution

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We consider charge carriers that undergo nearest-neighbor hopping among the sites of a binary random lattice, each site of which is associated with one of two possible energies E_1 or E_2. A general and recently observed feature of this problem not predicted by previous treatments of disordered hopping models is a crossover between trap-limited conduction and percolation. We introduce new energy-projected equations of motion whose solutions reveal the deep conductivity minimum associated with this phenomenon, and compare the results predicted to numerical simulations.

A deep minimum as a function of composition has been reported recently in the high-temperature electrical conductivity of a number of substitutionally mixed conducting ceramics.[1] The conductivity of the La(Cr,Mn)O_3 series typifies the behavior observed. The end member, $LaCrO_3$, exhibits a thermally activated conductivity associted with small-polaron hopping among the nearly cubic array of Cr cation sites. The conductivity of the other end member, $LaMnO_3$, has a significantly greater small polaron conductivity than $LaCrO_3$. The substitutional inclusions of small amounts of Mn into $LaCrO_3$, however, cause the electrical conductivity to *drop* orders of magnitude below that of *either* end member of the series.[1] This drop leads to a deep conductivity minimum as a function of increasing Mn content, followed by a smooth rise of up to 6 orders of magnitude.

This conductivity minimum observed in $LaCr_{1-x}Mn_xO_3$ has been qualitatively explained[1] by associating a lower small-polaron site energy ($\Delta\varepsilon \sim 0.7$–$1.0$ eV) at those sites in which Mn substitutes for Cr. Thus, a small concentration of lower-energy Mn sites act as traps for carriers diffusing among higher-energy Cr sites. In this limit, carriers spend long periods of time trapped, making occasional but relatively short-lived excursions among the higher-energy Cr sites. Conduction is said to be trap limited, and the mobility is significantly less than that of pure $LaCrO_3$. At higher Mn concentrations a percolating conduction path of neighboring lower-energy Mn sites will form. Carriers do not then need to get out of the lower-energy manifold in order to participate in conduction, which will then occur primarily by hops among connected lower-energy states. Conduction increases with concentration as in normal percolation. Both of these limits have been studied previously using appropriate nearest-neighbor hopping models and are well understood.[2–7] For example, the *random-trapping model* describes diffusion on a lattice containing wells of random depth, with the hopping rate out of a given site depending only on the depth of the well from which the particle hops.[2,3] The diffusion constant for this model can be calculated exactly.[4] For a binary lattice it correctly describes trap-limited diffusion of the type seen at low Mn levels in La(Cr,Mn)O_3. By contrast, the *random-hopping model* describes transport on a lattice with energetically equivalent sites separated from one another by barriers of random height.[2,3] The random-hopping model is perhaps best known for its ability to treat percolating systems containing a varying concentration of finite and infinite (or blocking) barriers.[5,7]

The behavior reported in La(Cr,Mn)O_3 and other mixed ceramics demonstrates that real disordered systems display aspects associated with both trapping and percolation, and points out the need for a more general theory that can quantitatively treat the crossover behavior associated with the conductivity minimum. Indeed, while the two models mentioned above are adequate in their respective limits, for a binary lattice they both predict a strictly *monotonic* dependence of the conductivity on the concentration of the substituents.[3] Here we discuss an approach for describing transport on the binary random lattice, advantages of which include the fact that when applied to the random-trapping model it predicts the exact diffusion constant in the lowest order of approximation. In addition, it successfully predicts the conductivity minimum associated with a trapping-to-percolation crossover in the more general binary-lattice problem.

Our approach is motivated by previous treatments,[4–8] which take as their goal the identification of a translationally invariant effective-medium lattice (topologically equivalent to the original) which reproduces the configuration-averaged transport coefficients of the actual disordered system. When applied to systems having sites of different energy, approaches of this type suffer a major drawback: all sites in the lattice become equivalent after averaging and the effective-medium jump rate between nearest-neighbors becomes artificially symmetric with respect to forward and backward jumps. This symmetry (which is artificially imposed by the averaging process) must be broken if detailed information about the contributions to diffusion from different energy states is to be understood. We demonstrate how this average symmetry may be broken through the use of a projected average that takes into account the energy of the states involved in each transition.

The starting point is the hopping transport equation

$$\frac{dP_n}{dt} = \sum_s \left(W_{n,n+s} P_{n+s} - W_{n+s,n} P_n \right) , \tag{1}$$

appropriate to a binary solid, in which $P_n(t)$ is the probability of finding the carrier at the site associated with lattice vector n at time t, and $W_{n+s,n}$ denotes the hopping

rate from site n to $n+s$. The sum runs over lattice vectors $\{s\}$ connecting nearest neighbors.

The configuration average of this equation appears in previous treatments, with specific limiting forms assumed for the hopping rates. In the random-trapping model jump rates are independent of the site to which a jump occurs, so that $W_{n+s,n}=W_n$. In the random-hopping model rates are symmetric with respect to forward and backward jumps, so that $W_{n,n+s}=W_{n+s,n}$. We make no such simplifications, but focus specifically on the binary random lattice containing sites of energy E_1, which occur at random with probability x_1, and sites of energy E_2, which occur with probability $x_2=1-x_1$. Thus, the hopping rates that appear in the set of equations (1) are drawn from a set containing just four possibilities $\{W_{12},W_{21},W_{11},W_{22}\}$, in which (using α and β to distinguish energy labels) the microscopic rate $W_{\beta\alpha}$ describes hops to sites of energy E_β from neighboring sites of energy E_α. It is assumed that the microscopic hopping rates between sites of different energy obey the detailed balance relation $W_{12}/W_{21}=\exp[-\beta(E_1-E_2)]$ necessary to ensure thermal equilibration to a unique equilibrium state. We note that these assumptions are broad enough to include, in appropriate limits, binary versions of the random-trapping model and the random-hopping model.

The actual configuration of hopping rates, and thus the probabilities which appear in (1) depend upon the exact configuration of the lattice. It is possible and convenient to specify a given configuration by means of a complete set $\{\zeta_n^\alpha\}$ of indicator variables defined so that

$$\zeta_n^\alpha \equiv \begin{cases} 1 \text{ if site } n \text{ is of type } \alpha \ , \\ 0 \text{ otherwise} \ . \end{cases} \tag{2}$$

These variables can also be used to define a projection $P_n^\alpha(t)\equiv P_n(t)\zeta_n^\alpha$ of the probability $P_n(t)$ onto those configurations having an atom of type α at site n. (Alternatively, the quantity P_n^α is the joint probability that the carrier is at site n and that site n is of type α.) Through straightforward manipulations, we obtain an exact rewriting of the equations of motion. After performing a Laplace transform over time we find (for $\alpha=1,2$) that

$$z\tilde{P}_n^\alpha(z)-P_n^\alpha(0)=\sum_{s,\beta} W_{n,n+s}^{\alpha\beta}\tilde{P}_{n+s}^\beta(z)-W_{n+s,n}^{\beta\alpha}\tilde{P}_n^\alpha(z) \ , \tag{3}$$

in which $\tilde{P}_n^\alpha(z)$ is the Laplace transform of $P_n^\alpha(t)$, and $W_{n,n+s}^{\alpha\beta}\equiv W_{\alpha\beta}\zeta_n^\alpha$. It is to be emphasized that in obtaining these projected equations, which formally resemble the equations for a system with two-states per unit cell, no approximations have been made. Thus, although we have essentially doubled the number of variables in the problem by giving the site probabilities an energy index, it is to be remembered that in any particular configuration exactly one-half of the projected probabilities are identically equal to zero. This apparent redundancy, however, has the desirable feature that when the solutions to these equations are averaged (over the entire ensemble of random configurations) a structure is obtained which retains the distinction between the two different kinds of site.

Let us denote by $p_n^\alpha(z)\equiv\langle\tilde{P}_n^\alpha(z)\rangle$ the average of the actual projected probability, where the angular brackets denote an average over all configurations of site energies, weighted by the probability with which they occur. Specifically, if $A=A[\{\zeta_n^\alpha\}]$ is any quantity whose value depends upon the specific configuration, its weighted average over configurations is

$$\langle A\rangle=\sum_{\{\zeta_n^\alpha\}} A[\{\zeta_n^\alpha\}]w[\{\zeta_n^\alpha\}] \tag{4}$$

in which, with sites of type α occurring with probability x_α, the appropriate weighting function can be written

$$w[\{\zeta_n^\alpha\}]=\prod_{n,a} x_\alpha^{\zeta_n^\alpha}=\exp\left[\sum_{\alpha,n}\zeta_n^\alpha \ln x_\alpha\right] . \tag{5}$$

This definition leads to the obvious result $\langle\zeta_n^\alpha\rangle=x_\alpha$.

As in the unprojected case, the averaging process will lead to a translationally invariant set of integrodifferential equations for the averaged (but now projected) probabilities. We therefore define a set of four *effective-medium* hopping rates $\{\omega_{\alpha\beta}(z)$: $\alpha,\beta=1,2\}$ connecting nearest neighbors of respective types on the (site-doubled) effective-medium lattice. As in treatments which do not incorporate energy projection,[7] these rates are assumed to govern the evolution of the configuration-averaged probabilities $p_n^\alpha(z)$ through a translationally invariant equation of the same form as that which they replace, i.e.,

$$zp_n^\alpha(z)-P_n^\alpha(0)=\sum_{s,\beta}\omega_{\alpha\beta}(z)p_{n+s}^\beta(z)-\omega_{\beta\alpha}(z)p_n^\alpha(z) \ , \tag{6}$$

in which $P_n^\alpha(0)$ represents the averaged initial condition. Equation (6) is equivalent to a time-nonlocal integrodifferential equation and, apart from the approximate restriction to nearest-neighbor memory kernels, is an exact consequence of the linearity of the original nonaveraged master equation.[8]

The problem reduces at this point to (1) the determination of the four effective-medium hopping rates $\omega_{\beta\alpha}(z)$, and (2) the calculation of the diffusion constant as a function of these effective-medium rates. The first step is, of course, the hard part of the problem. It is, in the unprojected theories, the point to which a variety of approximation schemes are usually addressed. In what follows we demonstrate that better (sometimes exact) results can be obtained using lower-order approximations on these projected equations than would be obtained without projection.

The second step enumerated above, namely the calculation of the diffusion constant as a function of the effective-medium rates, can be done exactly. We therefore address this step first. To this end we introduce a Fourier representation of the probabilities with

$$p_k^\alpha(z)\equiv\sum_n e^{-\mathbf{k}\cdot\mathbf{n}}p_n^\alpha(z) \ , \tag{7}$$

defining the Fourier transform of $p_n^\alpha(z)$ at wave vector $k=(k_1,\ldots,k_d)$. The Fourier transform of Eq. (6) is

$$zp_k^\alpha(z)-P_k^\alpha(0)=\sum_{\beta=1}^{2}\Gamma_k^{\alpha\beta}(z)p_k^\beta(z) \tag{8}$$

with $\Gamma_k^{\alpha\beta}(z)\equiv\sum_s e^{i\mathbf{k}\cdot\mathbf{s}}\omega_{\alpha\beta}(z)-\delta_{\alpha\beta}\sum_{s,\gamma}\omega_{\gamma\beta}(z)$. The solution to (8) can be written

$$p_k^\alpha(z)=\sum_{\beta=1}^{2} g_k^{\alpha\beta}(z)P_k^\beta(0) \tag{9}$$

in which the 2×2 Green's function matrix $g_k(z)=(z-\Gamma_k)^{-1}$ can be calculated exactly,

$$g_k(z)=\frac{1}{\Delta_k(z)}\begin{bmatrix}(z-\Gamma_k^{22}) & \Gamma_k^{12}\\ \Gamma_k^{21} & (z-\Gamma_k^{11})\end{bmatrix} \tag{10}$$

with $\Delta_k(z)=(z-\Gamma_k^{22})(z-\Gamma_k^{11})-\Gamma_k^{21}\Gamma_k^{12}$.

The diffusion constant D characterizes the asymptotic growth of the mean-square displacement of a transport particle as a function of time and is, through Einstein's relation, proportional to the conductivity. This quantity is readily obtained from the solution given in (9) and (10). A standard Tauberian theorem, along with (7), implies that

$$2dD\equiv\lim_{t\to\infty}\frac{d}{dt}\langle n^2(t)\rangle=\lim_{z\to0}\sum_{n,\beta}z^2n^2p_n^\beta(z)$$
$$=-\lim_{\substack{k\to0\\z\to0}}\sum_{\beta=1}^{2}z^2\nabla_k^2p_k^\beta(z)\ . \tag{11}$$

Applying to (9) and (10) the derivatives and limits indicated by (11), we obtain after some manipulation the essential result

$$D\equiv\sum_{\alpha,\beta=1}^{2}\rho_\alpha\omega_{\beta\alpha}(0)\ , \tag{12}$$

in which the quantities ρ_α represent the infinite-time (equilibrium) limit of the total occupation probabilities for sites of each type in the projected effective-medium lattice, i.e.,

$$\rho_\alpha=\lim_{t\to\infty}\sum_n\langle P_n^\alpha(t)\rangle=\lim_{\substack{k\to0\\z\to0}}zp_k^\alpha(z)\ . \tag{13}$$

A straightforward calculation using (9) and (10) allows these quantities to be evaluated explicitly, i.e.,

$$\rho_1=\frac{\omega_{12}(0)}{\omega_{12}(0)+\omega_{21}(0)}\ ,\quad \rho_2=\frac{\omega_{21}(0)}{\omega_{12}(0)+\omega_{21}(0)}\ . \tag{14}$$

Thus, the hopping rates $\omega_{\beta\alpha}$ appearing in the energy-projected effective-medium equations uniquely determine the asymptotic transport properties from Eqs. (12) and (14). The projection technique sketched above, therefore, provides a basis for a theory that retains the energetic topology of the original problem.

We now turn to the more difficult problem of evaluating the effective medium rates $\omega_{\beta\alpha}$. Treatments which do not employ energy projection often proceed by defining a reference system about which to expand, and performing perturbation theory on the Green's function, treating the deviation of the actual system as a perturbation. This leads to various decoupling schemes,[3] which vary in complexity from the simple virtual crystal approximation (VCA) to the self-consistent coherent potential approximation (CPA). In the VCA the effective-medium hopping rates are approximated by the configuration-averaged values of the rates that actually occur in the disordered system. The resulting description is often qualitatively inaccurate. In the CPA, the effective-medium itself is formally chosen as the reference system, the effect of fluctuations about the effective medium being required to vanish upon averaging.

With the energy-projected equations we find, in contrast to unprojected theories, that excellent results can be obtained using the simplest approximation (i.e., the VCA). Consider for example, the binary random-trapping model in which the hopping rate depends only upon the depth of the well from which the particle hops.[4] This is a particular limit of the general case to which the projection approach applies in which there are only two distinct rates in the problem: $W_{11}=W_{21}=W_1$ describing hops out of sites with energy E_1, and $W_{22}=W_{12}=W_2$ describing hops out of sites of energy E_2. Within the VCA we let the effective-medium rates $\omega_{\beta\alpha}$ appearing in (6) be approximated by the averages of the rates appearing in the unaveraged Eq. (3). For the binary random-trapping model this entails setting $\omega_{\alpha\beta}(0)\equiv\langle W_{n,n+s}^{\alpha\beta}\rangle=W_\beta\langle\xi_n^\alpha\rangle=x_\alpha W_\beta$. This approximation, with (12) and (14), yields upon simplification a result

$$D=\left[\frac{x_1}{W_1}+\frac{x_2}{W_2}\right]^{-1}=\left\langle\frac{1}{W_\alpha}\right\rangle^{-1} \tag{15}$$

which has been shown to be the exact diffusion constant for this simplified model system.[4] In this form it is easy to see that the diffusion constant vanishes in the random-trapping model for any finite concentration of infinitely deep wells (i.e., traps for which the exit rate W_β vanishes). Application of the VCA to the *unprojected* equations, by contrast, leads to very poor results that fail, e.g., to predict this vanishing of the diffusion constant in the deep trap limit.

The random-trapping model, being a limiting form of the more general binary lattice problem treated here, does not lead to a percolation transition. To see the combined effects of trapping and percolation, and in particular to study the kind of trapping-to-percolation crossover observed in the ceramic oxides we need a more appropriate model for the microscopic hopping rates which connect real sites of different types in the solid. To illustrate the essential features of this crossover we consider a model system in which the energy E_2 of the deeper energy states leads (through detailed balance) to a greatly reduced hopping rate for jumps out of lower-energy sites into higher-energy sites. We assume, however, that the hopping rate between two neighboring deeper energy sites is comparable to that associated with hops between adjacent sites of higher energy E_1 (a choice which is motivated by the behavior observed in the ceramic oxides where conduction actually occurs more rapidly through connected clusters of the lower-energy polaron states of $LaMnO_3$ than through the higher-energy states associated with $LaCrO_3$). Hops from higher-energy sites into lower-energy sites are assumed to occur at the same rate as between adjacent sites of higher energy. Thus a model system of interest is one in which $W_{22}\sim W_{11}\sim W_{21}\gg W_{12}$. The effective medium rates $\omega_{\alpha\beta}$ for this system we approximate as follows. Effective medium rates connecting sites of different energy are approximated by the averages of the rates appearing in (3):

$$\omega_{\alpha\beta}(0)\equiv\langle W_{n+s,n}^{\alpha\beta}\rangle=W_{\alpha\beta}\langle\xi_n^\alpha\rangle=x_\alpha W_{\alpha\beta}\quad(\alpha\neq\beta)\ , \tag{16}$$

which is just the VCA for these rates. While not unique, this choice ensures that the equilibrium populations predicted for sites of each energy by the projected effective

medium equations is the same as that which will occur in a typical realization of the disordered model system. For the effective medium rates $\omega_{\alpha\alpha}$ connecting sites of the same energy we adopt a slightly different tack. With the rates between sites of different energy turned off, the system reduces to two unconnected percolating sublattices associated with sites of each energy (one increasing in connectivity as the other decreases). The effective medium rates $\omega_{\alpha\alpha}$ must, under these conditions, reproduce the percolative diffusivity associated with each sublattice. If the *effective medium* rates $\omega_{\alpha\alpha}$ for hopping between sites of the *same energy* depend only weakly on the *actual* hopping rates $W_{\alpha\beta}$ coupling the two *different* sublattices, they can be approximated by a form which describes diffusion on a site-percolating lattice. In what follows we use a well-known approximate relation[5]

$$\omega_{\alpha\alpha}(0)=W_{\alpha\alpha}[1-1.52(1-x_\alpha)]\ , \tag{17}$$

which does an excellent job of describing the site-percolation diffusivity above the percolation threshold. In Fig. 1 we show representative logarithmic plots of the diffusion constant D (normalized to the rate $W\equiv W_{22}$) predicted by Eqs. (12), (14), (16), and (17) as a function of the concentration $x\equiv x_2$ of lower-energy sites. In all curves we take $W_{11}=W_{22}=W_{21}$. The three curves shown correspond to systems in which the limiting rates out of the deeper energy states take the values $W_{12}/W=10^{-5}$, 10^{-3}, and 10^{-1}, respectively. For comparison we include numerical calculations of the diffusion constant for the same system. In the numerical calculations, each diffusion constant has been evaluated by performing an effective-medium average over the distribution of conductances obtained from a large ensemble of disordered lattices (500 realizations), each lattice consisting of a periodically repeated cubic region containing $N=5^3$ energetically disordered sites. (Details of the method used, which reproduces with good accuracy the diffusion constant associated with a pure site-percolating lattice, will appear in a future publication.)

The diffusion constant depicted in Fig. 1 displays the features that would be expected: a trap-limited regime at low concentrations of the energetically lower sites; a percolative regime that develops at the point at which the lower-energy sites connect together at the critical point to produce a lower-energy conducting pathway; and a deep minimum in the diffusivity that falls significantly below that of either end member. Note that the critical point of the solid curve (which makes use of Kirkpatrick's approximate expression) occurs at $x\sim 0.34$, whereas the true site percolation critical point occurs at a concentration closer to 0.31, a fact more accurately predicted by the numerical simulation. All curves lie *above* the limiting percolation curve for the lower-energy sites, a result which is intuitively reasonable since conduction among the lower-energy sites can only be helped by the presence of higher-energy sites which are partially accessible. The numerical simulations agree with the effective medium theory rather well except in the immediate vicinity of the critical point and confirm that in spite of the somewhat simplified form we have assumed for the effective medium hopping rates, the correct basic physics has been included in the approximate treatment. While this supports the view that the projection approach provides the correct structure for describing energetically disordered systems, it also points out the need for a more rigorous treatment of the effective medium rates than that which we have used. The simulations, while subject to large fluctuations in the critical region, appear to indicate that the sharpness of the transition predicted by the approximate treatment given here is artificial. This could be an important point in comparing theory to existing conductivity data, in which a softening of the transition has been observed. This softening of the transition has previously been conjectured to arise from greater than nearest-neighbor hopping.[1,9]

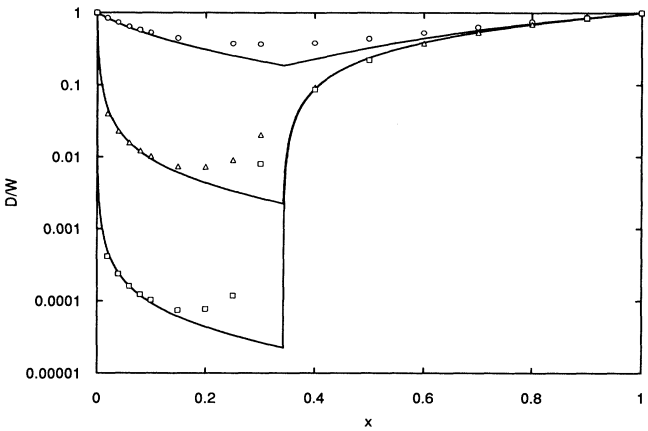

FIG. 1. The solid lines show logarithmic plots of the normalized diffusion constant D vs the fractional concentration x of deeper energy sites for a binary system of the type discussed in the text. Symbols denote the diffusion constant for the same systems obtained from numerical simulations. Detrapping parameters associated with the curves and data shown correspond to the values $W_{12}/W=10^{-5}$ (squares), $W_{12}/W=10^{-3}$ (triangles), and $W_{12}/W=10^{-1}$ (circles).

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