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Transport and Percolation in Disordered Systems—A Self-Consistent Time-Local Approach

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A new self-consistent equation for the transport of excitations in disordered systems, which forms the basis for a new class of time-domain coherent potential approximations, is developed. As an example, we calculate the probability of remaining in the original site $G_0(t)$ as well as the second moment of the distribution of excitations $\langle r^2(t)\rangle$ for a random mixture of donors which satisfy a master equation with short-range transition rates. A percolation-type transition is observed and its characteristics are analyzed both above and below the transition point.

KEY WORDS: Density resummation; self-consistent equations; percolation.

Transport properties of disordered systems such as electron transfer, exciton migration, etc. are of considerable current interest both experimentally and theoretically.[1-8] Master equations with random transition rates are widely used in these studies.[2] Lattice models involving site or bond disorder are known to exhibit a percolation-type transition whereby the long-time behavior of the system undergoes a phase transition from a "localized" to an "extended" type, as the degree of disorder is varied.[9-12] A new type of reduced equations of motion which are time local was introduced recently toward the theoretical treatment of transport in disordered systems.[13] In this approach, we postulate that the ensemble-averaged quantities (e.g., survival probability in a trapping problem) obey an equation of the type

$$\frac{d\langle P\rangle}{dt} = -K(t)\langle P(t)\rangle \tag{1a}$$

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This form is different from the more conventional memory-type equation

$$\frac{d\langle P\rangle}{dt} = -\int_0^t d\tau\, \tilde{K}(t-\tau)\langle P(\tau)\rangle \tag{1b}$$

Equations of the form (1a) were found recently extremely useful in the studies of systems with fractal geometry.[14-18] In this paper we develop a self-consistent equation (SCE) for the transport in disordered systems based on the time-local formalism. Our SCE provides a new kind of effective medium approximation which allows a systematic calculation of the time-dependent kernels $K(t)$. We apply it to a simple continuum master equation model with short-range transition rates. A percolation-type transition is found and the long-time (and dc conductivity) properties of the system are analyzed.

We consider a system of N particles distributed randomly in a volume V. At time $t=0$, one particle located at the origin is excited. The excitation can hop among the particles according to the master equation

$$\frac{d}{dt}P_i = \sum_{j=1}^{N} W_{ij}(P_j - P_i) \tag{2}$$

P_i is the probability of finding the excitation on the ith particle. $W_{ij} \equiv W(r_{ij})$ depends only on the distance r_{ij} between the ith and the jth particles. We shall be interested in calculating $\langle P(r,t)\rangle$, i.e., the probability of finding the excitation at point r at time t, averaged over all possible configurations of the random system. In particular we consider the probability of the excitation to remain on the initially excited particle $G_0(t) \equiv \langle P(r=0,t)\rangle$, and the second moment of the distribution of excitations:

$$\langle r^2(t)\rangle \equiv \int dr\, r^2 \langle P(r,t)\rangle \tag{3a}$$

The latter quantity is related, in frequency space, to the diffusion coefficient $D(\varepsilon)$ by the relation

$$\langle r^2(\varepsilon)\rangle \equiv \int_0^\infty d\tau\, \exp(-\varepsilon\tau)\langle r^2(\tau)\rangle = \frac{2d}{\varepsilon^2} D(\varepsilon) \tag{3b}$$

where d denotes the number of dimensions of the system. Of special interest is the long-time behavior of these quantities and its dependence on the form of the transfer rate $W(r)$.

We have derived a new type of self-consistent equation (SCE) for $G_0(t)$ using the time-local reduced equation of motion.[13] The input to the SCE is a "naive" expansion of $G_0(t)$ in the density of particles $\rho = N/V$,

$$G_0(\rho, t) = 1 + \sum_{n=1}^{\infty} \rho^n B^{(n)}(t) \tag{4}$$

and each $B^{(n)}$ may be obtained by solving a problem with $n+1$ particles. When using a cumulant expansion G_0 assumes the form

$$G_0(\rho, t) = \exp\left[-\int_0^t d\tau (t-\tau) F_1(\rho, \tau)\right] \tag{5}$$

where F_1 may be expanded in density, i.e.,

$$F_1(\rho, t) = \sum_{n=1}^{\infty} \rho^n F_1^{(n)}(t) \tag{6}$$

The coefficients $F_1^{(n)}(t)$ are straightforwardly obtained by expanding (5) in powers of density and comparing with (4). We are now in the position to derive a resummed expression by F_1 [Eq. (5)] which will hold for high densities. This is done by making the following ansatz:

$$F(\rho, G_0(\rho, \varepsilon)) \equiv F_1\left(\rho, \frac{1}{\varepsilon}\right) \tag{7}$$

where

$$F_1\left(\rho, \frac{1}{\varepsilon}\right) \equiv \int_0^{\infty} e^{-\varepsilon t} F_1(\rho, t)\, dt \tag{8}$$

and

$$G_0(\varepsilon) = \int_0^{\infty} e^{-\varepsilon t} G_0(t)\, dt \tag{9}$$

This ansatz is analogous to that made by GAF[6] using the more conventional memory-type equations. We feel that the time-local approach is to be preferred in this case since in the Forster problem, e.g., when we have one donor $+ N$ traps, F is rigorously first order in density, whereas the corresponding memory kernel is infinite order in density. A detailed discussion of this point was given recently.[13] A comparison of this type of density resummations (for the memory-type equations) with the mean field

CPA[5,7] was also made.[19] In order to get an expression of F we make use of the density expansion F and of G_0, i.e.,

$$F(\rho, G_0) = \sum_{n=1}^{\infty} \rho^n F^{(n)}(G_0(\rho, \varepsilon)) \tag{10a}$$

and

$$G_0(\rho, \varepsilon) = \frac{1}{\varepsilon} + \sum_{n=1}^{\infty} \rho^n B^{(n)}(\varepsilon) \tag{10b}$$

Upon expansion of $F^{(n)}$ in powers of $(G_0 - 1/\varepsilon)$ and making use of the known coefficients $B^{(n)}$ we obtain a systematic density expansion of $F(\rho, G_0)$. To first order in density we then get

$$G_0(t) = \exp\left[\frac{\rho}{2\pi}\int_{-\infty}^{\infty} d\varepsilon \frac{\exp(i\varepsilon t)}{\varepsilon^3}\int d\mathbf{r}\frac{W(r)}{1 + 2W(r)\, G_0(i\varepsilon)}\right] \tag{11}$$

Equation (11) is our final SCE which should be solved for G_0.

A resummed expression for the second moment is obtained by using a similar procedure. This time, the input is the naive expansion of the entire Green's function $G(r, t) = \langle P(r, t)\rangle$. It is convenient to work with the transformed Green's function

$$G(k, \varepsilon) = \int_0^{\infty} e^{-\varepsilon t}\, dt \int dr\, e^{ik\cdot r}\, G(r, t) \tag{12}$$

for which the naive expansion is known,[4] i.e.,

$$G(k, \varepsilon) = 1 + \sum_{n=1}^{\infty} \rho^n b^{(n)}(k, \varepsilon) \tag{13}$$

When using the cumulant expansion, Eq. (13) assumes the form

$$G(k, t) = \exp\left[\frac{\rho}{2\pi}\int_{-\infty}^{\infty} \frac{d\varepsilon}{\varepsilon^2} k^2 D_1\left(k, \rho, \frac{1}{i\varepsilon}\right) \exp(i\varepsilon t)\right] \tag{14}$$

In analogy with Eq. (7) we now define a new kernel $D(k, \rho, G_0(\rho, \varepsilon))$ such that

$$D(k, \rho, G_0(\rho, \varepsilon)) \equiv D_1(k, \rho, 1/\varepsilon) \tag{15}$$

so that the second moment [Eq. (2)] is given by

$$\langle r^2(\varepsilon)\rangle = \frac{2d}{\varepsilon^2} D(0, G_0(\varepsilon)) \tag{16}$$

A systematic expansion for D may be obtained if we proceed along the same lines which led to the expansion of F. To lowest order in density this yields

$$\langle r^2(t)\rangle = -\rho \int_{-\infty}^{\infty} \frac{d\varepsilon}{2\pi} \frac{\exp(u\varepsilon t)}{\varepsilon^2} \int dr\, r^2 \frac{W(r)}{1+2W(r)\, G_0(i\varepsilon)} \tag{17}$$

Our final procedure is thus to solve Eq. (11) for G_0 and then, upon the substitution of the result in Eq. (17) we get $\langle r^2(t)\rangle$. Note that we do not need the expansion of G [Eq. (13)] in order to get the SCE for G_0. In this respect, our procedure is impler than the analogous deviation of GAF.[6]

We have solved our SCE [Eq. (11)] using the following model for $W(r)$:

$$W(r) = \begin{cases} W_0, & r \leqslant r_0 \\ 0, & r > r_0 \end{cases} \tag{18}$$

This model represents the universality class of short-range transfer rates $W(r)$ with cut-off, and is similar to a lattice percolation model. Hereafter, we shall switch to dimensionless time and frequency units by taking $W_0 = 1$.

For this model Eq. (11) assumes the form

$$G_0(t) = \exp\left[\frac{c}{2\pi} \int_{-\infty}^{\infty} \frac{d\varepsilon}{\varepsilon^2} \exp(i\varepsilon t) \cdot \frac{1}{1+2G_0(i\varepsilon)}\right] \tag{19}$$

Here V_d is the volume of a d-dimensional sphere of radius r_0 and $c \equiv \rho V_d$ is the number of particles in that volume. Also in this case Eq. (6) results in

$$\langle r^2(t)\rangle = -\frac{d}{d+2} r_0^2 \ln G_0(t) \tag{20}$$

Note that this relation holds only for our particular model (18) within the two-body (lowest order in density) approximation. This is not a universal relation and is very different from the simple scaling relation[2,13,20–22]

$$\langle r^2(t)\rangle = r_0^2\, G_0(t)^{-2/d} \tag{21}$$

It is not clear at present which approximation [(20) or (21)] is more realistic. The solution of Eq. (11) for long times may be obtained by postulating the asymptotic form

$$G_0(t) \sim A \exp(-Bt), \qquad r \to \infty \tag{22}$$

Upon substitution of Eq. (22) into (19) and considering the long time limit, we obtain

$$A \exp(-Bt) = \exp\left[\frac{c}{B+2A}\left(-Bt - \frac{2A}{B+2A}\right)\right] \tag{23}$$

Two cases will now be considered, for $B = 0$ Eq. (23) yields

$$A = \exp(-c/2A) \tag{24}$$

which can be solved iteratively, resulting in

$$A = \exp\left(-\frac{c}{2}\chi\right) \tag{25a}$$

$$\chi = \exp\left(\frac{c}{2}\exp\left(\frac{c}{2}\exp\left(\frac{c}{2}\cdots\right)\right)\right) \tag{25b}$$

For $B \neq 0$ Eq. (23) results in

$$B = c - 2A \tag{26a}$$

and

$$A = \exp(-2A/c) \tag{26b}$$

whose iterative solution is

$$A = \exp\left(-\frac{2}{c}\exp\left(-\frac{2}{c}\exp\left(-\frac{2}{c}\cdots\right)\right)\right) \tag{27}$$

Equations (25) and (27) clearly show the existence of a percolution-type critical point at $c^* \equiv 2/e$ for which $A^* = 1/e$ and $B^* = 0$. Below the critical point, $c < c^*$, the appropriate solution is given by Eq. (25) since Eq. (26) gives an unphysical solution whereby B is negative. In this region, A, as given by Eq. (25), varies from $A = 1$ for $c = 0$ to $A = 1/e$ for $c = c^*$, and the long-time solution is "localized." [Both $G_0(t)$ and $\langle r^2(t)\rangle$ tend to a finite nonzero value at long times.] On the other hand for $c > c^*$ the solution is "extended" since by Eqs. (26) and (27) both A and B assume finite, nonnegative values. In Figure 1, we present the solution of Eqs. (24) and (26) for A and B which gives the long-time behavior of $G_0(t)$.

We have further solved our SCE [Eq. (11)] iteratively in order to get the entire time dependence of $G_0(t)$. The iteration is done by taking a zero-

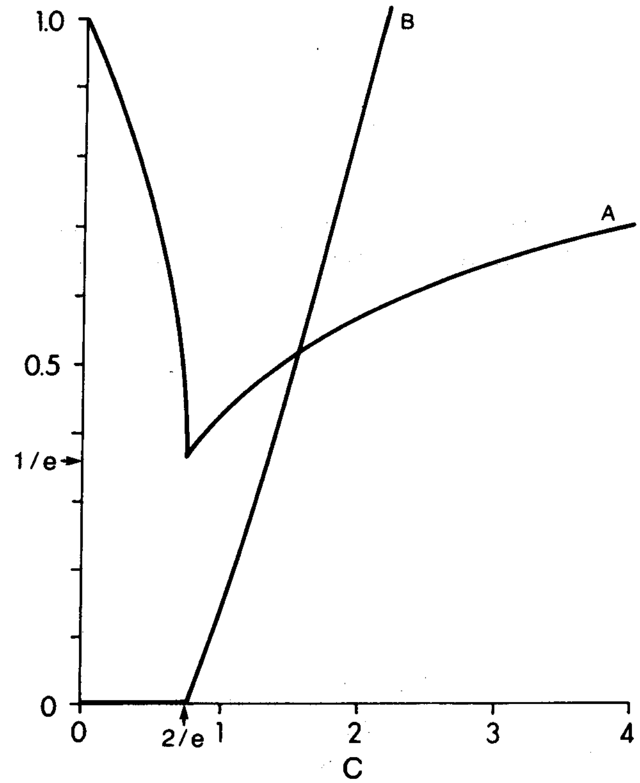

Fig. 1. Solutions of Eq. (23) above and below the critical point $c^* = 2/e$. A and B are related to the asymptotic form $G_0(t) \sim A \exp(-Bt)$ as $t \to \infty$ [Eq. (22)]. For $c < c^*$, $B = 0$ and $G_0(\infty)$ is finite or "localized," whereas for $c > c^*$, $G_0(t)$ decays exponentially and the solution is "extended."

order approximation for $G_0(t)$, and substituting it in the right-hand side of Eq. (11). The resulting $G_0(t)$ is subsequently substituted back into Eq. (11) and the procedure is repeated until it converges.

For $c < c^*$ we have used $G_0(t) = A$ as the zeroth iteration where A is given in Fig. 1. The first iteration then becomes

$$G_0(t) = \exp\left\{-\frac{c}{2A}[1 - \exp(-2At)]\right\} \tag{28}$$

which is found to be a reasonable approximation for $G_0(t)$ for $c < c^*$. For $c > c^*$ we have used $G_0(t) = A \exp[-(c - 2A)t]$ as a zeroth iteration where

A is given in Fig. 1. The first iteration, which is again found to be a reasonable approximation for $G_0(t)$, is

$$G_0(t) = \exp\left\{-(c-2A)t - \frac{2A}{c}\left[1-\exp(-2ct)\right]\right\} \tag{29}$$

The converged solutions of our SCE both above and below the transition are shown in Fig. 2. In conclusion we shall summarize the general characteristics of our solutions:

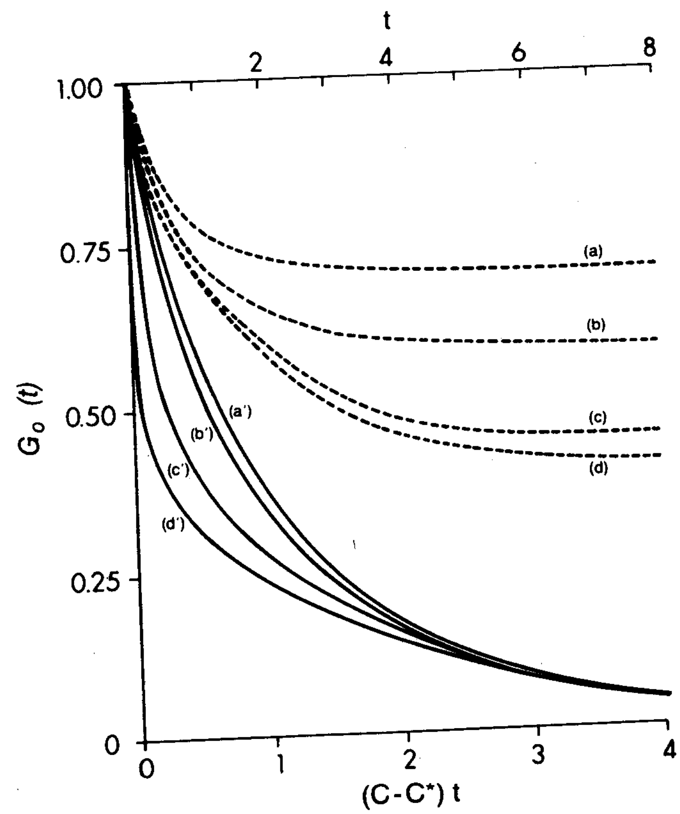

Fig. 2. The converged solutions of the SCE [Eq. (19)] $W_0 = 1$. The dashed curves correspond to $c < c^*$ and the time axis is shown on the top of the figure. The various curves correspond to different values of $c^* - c$: (a) 0.24, (b) 0.1, (c) 0.01, (d) 0.0001. The solid curves are for $c > c^*$. The time axis shown on the bottom of the figure is scaled by $(c - c^*)$. The values of $c - c^*$ are (a′) 2.26, (b′) 1, (c′) 0.1, (d′) 0.01.

(a) The long-time ($t \to \infty$) behavior of $G_0(t)$ is

$$G_0(t) \sim \begin{cases} A & c < c^* \\ A \exp[-(c-2A)t], & c > c^* \end{cases} \tag{30}$$

where A is a function of c is shown in Fig. 1.

(b) The long-time behavior of the second moment is

$$\langle r^2(t) \rangle \sim \begin{cases} -\dfrac{d}{d+2} r_0^2 \ln A, & c < c^* \\ \dfrac{d}{d+2} r_0^2 (c-2A)t, & c > c^* \end{cases} \tag{31}$$

(c) The low-frequency limit of the diffusion coefficient close to the critical point is

$$D(\varepsilon) \sim \begin{cases} \dfrac{\varepsilon r_0^2}{2(d+2)}, & c < c^* \\ \dfrac{1}{4(d+2)} (c-c^*) r_0^2, & c > c^* \end{cases} \tag{32}$$

(d) The critical exponents of A and B near the critical point are

$$(A - A^*) \sim \begin{cases} \left(\dfrac{c^* - c}{e}\right)^{1/2}, & c < c^* \\ (c-c^*)/4, & c > c^* \end{cases} \tag{33}$$

$$B \sim (c - c^*)/2 \qquad c > c^* \tag{34}$$

The exponent 1 for B is characteristic of mean field theories.[10,11]

(e) The small and large concentration limits of A and B are

$$A \sim \begin{cases} 1 - c/2, & c \to 0 \\ 1 - 2/c, & c \to \infty \end{cases} \tag{35}$$

$$B \sim \begin{cases} 0, & c \to 0 \\ c - 2, & c \to \infty \end{cases} \tag{36}$$

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