The validity of (2) for large t (or y) is already implied by the linearized BE. Our results strongly support the conclusion that (2) holds for all n, d, and $y \geq 0$.

Note that the approach to equilibrium for the distribution function itself, $f(v, t)$, is not monotonic since for some values of v, $\partial f / \partial v$ changes sign at a certain point in time. Yet the H function is monotonic in all the derivatives that we calculated. The solution, (3), starts off very far from equilibrium with no particles of zero velocity.

This is the first solution of the true BE that has been shown to satisfy (2) to such high order of differentiation. We present our results in the hope that they will stimulate further work that will yield a rigorous proof of (2) for the solution that we have considered.

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[1]H. P. McKean, Arch. Ration. Mech. Anal. 21, 343 (1966).
[2]S. Harris, J. Math. Phys. 8, 2407 (1967).
[3]S. Harris, J. Chem. Phys. 48, 3723 (1968).
[4]S. Harris, J. Chem. Phys. 48, 4012 (1968).
[5]S. Harris, Phys. Lett. 11, 687 (1969).
[6]S. Harris, J. Phys. A 9, L153 (1976).
[7]S. Simons, J. Phys. A 2, 12 (1969).
[8]S. Simons, Phys. Lett. 33A, 154 (1970).
[9]D. B. Shear, J. Chem. Phys. 48, 4144 (1968).
[10]D. L. S. McElwain and H. O. Pritchard, J. Am. Chem. Soc. 91, 7693 (1969).
[11]S. I. Yao, J. Chem. Phys. 54, 1237 (1971).
[12]S. Rouse and S. Simons, J. Phys. A 9, L155 (1976).
[13]S. Rouse and S. Simons, J. Phys. A 11, 423 (1978).
[14]S. Simons, J. Phys. A 5, 1537 (1972).
[15]W. Maass, J. Phys. A 3, 331 (1970).
[16]S. Simons, J. Phys. A 4, 11 (1971).
[17]S. Simons, J. Phys. A 4, L58 (1971).
[18]S. Simons, J. Phys. A 9, 413 (1976).
[19]A. V. Bobylev, Dokl. Akad. Nauk SSSR 225, 1296 (1975) [Sov. Phys. Dokl. 20, 820 (1976)].
[20]M. Krook and T. T. Wu, Phys. Rev. Lett. 36, 1107 (1976).
[21]R. M. Ziff, Phys. Rev. A 23, 916 (1981).
[22]H. Cornille and A. Gervois, J. Stat. Phys. 23, 167 (1980).
[23]M. Ernst, Phys. Lett. 69A, 390 (1979).
[24]J. Tjon and T. T. Wu, Phys. Rev. A 19, 883 (1979).
[25]M. Abramowitz and I. Stegun, *Handbook of Mathematical Formulas* (U. S. Government Printing Office, Washington, D. C., 1965), Eq. 13.2.6.
[26]Ref. 25, Eqs. 5.1.4, 5.1.12, 5.1.22, 6.5.3, 6.5.4, 6.5.29, and 6.5.31.

Effective-Medium Approximation for Diffusion on a Random Lattice

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A self-consistent effective-medium approximation is presented for the problem of diffusion and ac conductivity on a lattice characterized by random values of transfer rates between pairs of nearest-neighbor sites. The approximation is applied to a percolation model in which only a fraction of the bonds are assigned a finite transfer rate. The results reflect the existence of a percolation threshold in the system, and are consistent with the properties of clusters of bonds in the critical region.

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There is a rapidly growing interest in the problem of classical diffusion in random systems.[1-3] It is relevant to a number of physical processes in disordered media such as dispersive hopping transport in amorphous semiconductors[1,2,4] and the migrations of localized electronic excitations among guest molecules in a host.[5,6] The main current theoretical approach to these phenomena is based on the continuous-time random-walk theory.[1,2,4,7] Alternative methods were recently used to study the problem of one-dimensional systems where some aspects of it can be treated more rigorously.[3,8,9]

In this communication a new self-consistent effective-medium approximation (EMA) is proposed for the related problem of diffusion on a lattice characterized by random values of transfer rate $W_{n'n} = W_{nn'}$ between pairs of nearest-

neighbor sites. These values are assigned to the lattice bonds according to a given probability distribution function $\pi(W)$ in a random manner. The approach presented here is closely related to the effective-medium theory (EMT) for the macroscopic conductivity and dielectric properties of random inhomogeneous media,[10] and to the coherent-potential approximation (CPA) for the electronic properties of alloys.[11,12]

For a given realization of the random lattice the diffusion process is described by the following master equation for $P_n(t)$, the probability to be at site n at time t. Given that the diffusing quantity is at $n=0$ at time $t=0$,

$$\frac{\partial P_n(t)}{\partial t}=\sum_{n'}[W_{nn'}P_{n'}(t)-W_{n'n}P_n(t)] \tag{1}$$

with the boundary conditions $P_n(t=0)=\delta_{n,0}$, and with n' the nearest neighbors of n.

Consider the Laplace transform of Eq. (1),

$$\sum_{n'}[W_{nn'}P_{n'}(\omega)-W_{n'n}\tilde{P}_{n'}(\omega)] = \omega\tilde{P}_n(\omega)+\delta_{n,0}P_n(0). \tag{2}$$

Here

$$\tilde{P}_n(\omega)=\int e^{-\omega t}P_n(t)\,dt. \tag{3}$$

Equation (2) can be recast as the following matrix equation,

$$A(\omega)\hat{P}(\omega)=S, \tag{4}$$

where, using bra-ket notation,

$$\hat{P}(\omega)\equiv\sum\tilde{P}_n(\omega)|n\rangle, \tag{5a}$$

$$S=\sum_n\delta_{n,0}|n\rangle, \tag{5b}$$

and

$$A(\omega)\equiv\sum_{kl}|k\rangle[(\omega+\sum_i W_{ik})\delta_{kl}-W_{kl}]\langle l|, \tag{6}$$

where the summation is over all pairs of nearest-neighbor sites.

All the information concerning the diffusion process can be derived from $\{\langle\tilde{P}_n(\omega)\rangle\}$, where the angular brackets denote an average over the ensemble of random lattices. For example, the mean-square displacement of the diffusing quantity from the origin at time t is given by

$$\langle\vec{R}^2(t)\rangle=\mathcal{L}^{-1}[\sum_n\langle\tilde{P}_n(\omega)\rangle\vec{R}_n^{\,2}], \tag{7}$$

where R_n is the location of site n and $\mathcal{L}^{-1}$ denotes inverse Laplace transform. Accordingly what is needed is an approximation to $\langle A(\omega)^{-1}\rangle$.

$A(\omega)$ can be represented as a sum of a homogeneous term and a term which contains the random fluctuations:

$$A(\omega)=A_M(\omega)+\delta A(\omega), \tag{8}$$

where

$$A_M(\omega)=\sum_{kl}|k\rangle[(\omega+zW_M)\delta_{kl}-W_M\Delta_{kl}]\langle l| \tag{9a}$$

$$\delta A(\omega)=\sum_{kl}2(W_{kl}-W_M)\hat{Q}_{kl}, \tag{9b}$$

$$\hat{Q}_{kl}=\tfrac{1}{2}(|k\rangle-|l\rangle)(\langle k|-\langle l|), \tag{9c}$$

and

$$\Delta_{kl}=\begin{cases}1 & \text{if } k,l \text{ are nearest neighbors,}\\ 0 & \text{otherwise.}\end{cases} \tag{9d}$$

A^{-1} can now be expressed as a t-matrix expansion[12,13]:

$$A^{-1}=A_M^{-1}+A_M^{-1}TA_M^{-1}, \tag{10}$$

where

$$T[A_M^{-1}]=\sum_{kl}t_{kl}+\sum_{\substack{kl\neq mn\\ kl,mn\neq pq}}t_{kl}A_M^{-1}t_{mn}+\sum t_{kl}A_M^{-1}t_{mn}A_M^{-1}t_{pq}, \tag{11}$$

and the t matrix for the bond kl is

$$t_{kl}=\hat{Q}_{kl}\frac{W_M-W_{kl}}{1-\frac{1}{2}(\langle k|-\langle l|)A_M^{-1}(|k\rangle-|l\rangle)(W_M-W_{kl})}. \tag{12}$$

The effective-medium approximation is obtained by setting

$$T=\sum_{kl}t_{kl} \tag{13}$$

and solving the following equation for $W_M(\omega)$ (Ref. 14):

$$\langle t_{kl}\rangle\equiv\langle t\rangle=\int t(w',W_M(\omega))\pi(w')\,dw'=0. \tag{14}$$

As discussed below this equation leads to the vanishing of $\langle T(W_M(\omega))\rangle$ through the third order in t

so that

$$\langle A^{-1}\rangle = A_M^{-1}(W_M(\omega)) + O(t^4). \tag{15}$$

Equation (15) implies that the ensemble averages $\langle \tilde{P}_n(\omega)\rangle$ obey the following equation[15]:

$$\sum_{n'} W_M(\omega)[\langle \tilde{P}_{n'}(\omega)\rangle - \langle \tilde{P}_n(\omega)\rangle] = \omega \langle \tilde{P}_n(\omega)\rangle. \tag{16}$$

Using Eq. (12) one is led to the following equation for $W_M(\omega)$:

$$\left\langle \frac{W_M(\omega) - W'}{W'[1-\epsilon G_0(\epsilon)] + [\frac{1}{2}z - 1 + \epsilon G_0(\epsilon)] W_M(\omega)} \right\rangle = 0, \tag{17}$$

where $G_0(\epsilon) \equiv \langle 0 | A_M^{-1}(W_M(\omega)) | 0\rangle$ is the diagonal element of the lattice Green function at $\epsilon = \omega / W_M(\omega)$,[16] and z is the coordination number of the lattice. For a cubic lattice in d dimensions $G_0(\epsilon)$ is given by

$$G_0(\epsilon) = \int_0^\infty \exp[-(\tfrac{1}{2}z + \epsilon)x][I_0(x)]^d \, dx,$$

where $I_0(x)$ is the modified Bessel function of order 0.

The mean-square displacement $\langle R^2(t)\rangle$ and the frequency-dependent conductivity $\sigma(\omega)$ for the hopping transport on the lattice are related to $W_M(\omega)$ by the following relations[2]:

$$\begin{aligned} &\langle R^2(t)\rangle = \mathcal{L}^{-1}[(z/\omega^2) W_M(\omega)], \\ &\sigma(\omega) = \tfrac{1}{2} z \, W_M(i\omega). \end{aligned} \tag{18}$$

The approximation presented here has the following features as a version of CPA or EMT: (a) The condition $\langle t\rangle = 0$ leads to the vanishing of the averages of the next two terms in the expansion of T given by Eq. (11). This result is due to the absence of correlation between values of W' assigned to different bonds, together with the restrictions on the summations in Eq. (11). The first nonvanishing term in $\langle T\rangle_{\mathrm{EMA}}$ is thus $O(t^4)$. (b) Since this scheme is based on expansion in t matrices (rather than expansion in δA) it is not perturbative and thus not limited to weak disorder. (c) The corrections to the effective-medium approximation can be estimated by studying the nonvanishing terms in T_{EMA}.[17] The approximation is also amenable to systematic improvement by going beyond the single-bond approximation implied by Eq. (13) and solving $T = 0$ up to a higher order in t than t^3.[17]

For $\omega = 0$, Eq. (17) reduces to an equation equivalent to the EMT for the dc conductivity, and it yields a result for the diffusion coefficient, $D = \frac{1}{2} z W_M(0)$. The limits of validity of the EMT for the disordered resistor network have been studied by comparison with numerical results.[13,18] It was found to be a good approximation even for rather broad distributions of local transfer rates $\pi(W')$.

An interesting example for which one can obtain some analytical results from Eq. (17) is the case of a disordered lattice with the following distribution,

$$\pi(W') = p\,\delta(W' - W_0) + (1-p)\,\delta(W'), \tag{19}$$

i.e., the case where a fraction $(1-p)$ of the bonds are characterized by a zero transfer rate. Using the asymptotic expression for $G_0(\epsilon)$ for $\epsilon \ll 1$ for a simple cubic lattice in Eq. (17) one obtains the following results for $W_M(\omega)$:

$$W_M(p,\omega) = \begin{cases} \frac{3}{2} W_0(p - p_c)\left(1 + \dfrac{2}{9}\dfrac{a\omega}{W_0(p-p_c)^2}\right), & p > p_c, \\ \dfrac{a\omega}{3\epsilon}\left(1 - \dfrac{1}{18}\dfrac{a\omega}{W_0(p-p_c)^2}\right), & p < p_c, \end{cases} \tag{20}$$

in the small ω limit, $\omega \ll W_0(p-p_c)^2$. Here $p_c = \frac{1}{3}$ and $a = G_0(0)$.

An analysis of the long-time diffusive behavior based on Eq. (20) leads to the following results: (a) In the limit of large t,

$$\begin{aligned} &\langle R^2(t)\rangle = Dt, \quad D \propto W_0(p - p_c) \ \text{ for } p > p_c, \\ &\lim_{t\to\infty} \langle R^2(t)\rangle \propto a/(p_c - p) \ \text{ for } p < p_c. \end{aligned} \tag{21}$$

(b) For both $p > p_c$ and $p \ll p_c$ the above asymptotic behavior is obtained for $t \gg \tau$ where τ diverges as $p \to p_c$:

$$\tau \sim W_0^{-1}(p - p_c)^{-2}. \tag{22}$$

These results reflect in a qualitative manner the properties of the clusters of bonds of one type on a lattice with a percolation threshold at $p = p_c$. Below p_c the mean-square cluster size is finite and diverges as $p \to p_c$. This is consistent with the divergence of $\langle R^2(\infty)\rangle$ and of τ as $p \to p_c$. Above p_c the infinite cluster can be viewed as a sparse lattice of nodes connected by tortuous one-dimensional channels where the distance between nodes is of the order of the correlation length $\xi \sim (p - p_c)^{-\nu}$. This picture, proposed by de Gennes,[19] suggests that the time of approach to

normal diffusion, τ, will diverge as $p \to p_c$.

At the percolation threshold $p = p_c$

$$W_M(\omega) = (a\omega/W_0)^{1/2}. \tag{23}$$

At long times one obtains anomalous diffusive behavior of the type

$$\langle R^2(t)\rangle \propto (W_0 t)^{1/2}. \tag{24}$$

The expressions for $W_M(\omega)$ in Eqs. (20) and (23) can be recast in the following scaling form:

$$W_M(p-p_c, \omega) = W_0(p-p_c)^{t_c} f(y), \qquad y = a\omega W_0^{-1} |p-p_c|^{-\gamma}. \tag{25}$$

A similar scaling form near p for an analogous problem has been suggested by Stephen.[20]

Equation (25) leads to the following general time-dependent diffusive behavior near the percolation threshold:

$$\langle R^2(t)\rangle = Dt, \quad D \propto W_0(p-p_c)^{t_c}, \quad p > p_c, \quad t \gg \tau;$$
$$\lim_{t\to\infty} \langle R^2(t)\rangle \propto a|p-p_c|^{-(\gamma - t_c)}, \tag{26}$$
$$\tau \sim W_0^{-1}|p-p_c|^{-\gamma}, \quad p < p_c, \quad t \gg \tau;$$

and at $p = p_c$,

$$\langle R^2(t)\rangle \propto (W_0 t)^{(\gamma - t_c)/\gamma}. \tag{27}$$

The EMA value for the percolation conductivity exponent is $t_c = 1$ while $\gamma_{\mathrm{EMA}} = 2$. The numerical values for t_c are ~1.6 in $d = 3$ and 1.1–1.3 in $d = 2$.[13,18] A scaling law $\gamma = t_c + 2\nu - \beta$, where β is the percolation probability exponent, has been proposed.[20] Accordingly $\gamma \cong 2.8$ in $d = 3$. Thus the EMA results follow the correct scaling behavior but yield incorrect values for the exponents. One can expect the EMA to be more accurate away from the critical region or for random systems with distributions $\pi(W')$ which do not lead to critical behavior.

Work is presently in progress to obtain results for various distributions $\pi(W')$. Numerical studies intended to assess the range of validity of the effective-medium approximation in various cases will also be carried out.

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[1]H. Scher and M. Lax, Phys. Rev. B 7, 4491, 4502 (1973).

[2]E. W. Montroll and B. J. West, in *Fluctuation Phenomena*, edited by E. W. Montroll and J. L. Lebowitz (North-Holland, Amsterdam, 1979), and references therein.

[3]S. Alexander, J. Bernasconi, W. R. Schneider, and R. Orbach, Rev. Mod. Phys. 53, 175 (1981), and references therein.

[4]H. Scher and E. W. Montroll, Phys. Rev. B 12, 2455 (1975).

[5]S. W. Haan and R. Zwanzig, J. Chem. Phys. 68, 1877 (1977).

[6]J. Klafter and R. Silbey, J. Chem. Phys. 72, 843 (1980).

[7]E. W. Montroll and G. H. Weiss, J. Math. Phys. 6, 167 (1965).

[8]J. Bernasconi, S. Alexander, and R. Orbach, Phys. Rev. Lett. 41, 185 (1978).

[9]T. Odagaki and M. Lax, Phys. Rev. Lett. 45, 847 (1980).

[10]R. Landauer, Phys. Rev. 94, 1386 (1954).

[11]K. M. Watson, Phys. Rev. 103, 489 (1956), and 105, 1388 (1957); R. J. Elliot, J. A. Krumhansl, and P. L. Leath, Rev. Mod. Phys. 46, 465 (1974).

[12]A coherent-medium approximation for stochastic transport was recently obtained by an alternative approach and applied to the study of frequency-dependent hopping conductivity [T. Odagaki and M. Lax, Phys. Rev. B 24, 5284 (1981)]. Their work came to my attention after the present work was completed.

[13]S. Kirkpatrick, Rev. Mod. Phys. 45, 574 (1973).

[14]It is sufficient to assume $\langle t_{kl}^n\rangle = \langle t_{kl}\rangle^n$ for all n, a somewhat weaker condition than Eq. (13), in order that $\langle t_{kl}\rangle = 0$ will entail $\langle T(W_M(\omega))\rangle = 0$.

[15]The time-dependent averages $\{\langle P_n(t)\rangle\}$ will now be the solutions of a generalized master equation:

$$\frac{\partial \langle P_n(t)\rangle}{\partial t} = \sum_{n'} \int W_M(t-t')[\langle P_{n'}(t')\rangle - \langle P_n(t')\rangle]\,dt'.$$

This result agrees with the observation made by J. Klafter and R. Silbey, Phys. Rev. Lett. 64, 55 (1980).

[16]G. F. Koster and J. L. Slater, Phys. Rev. 96, 1208 (1954).

[17]I. Webman, M. H. Cohen, and F. Yonezawa, unpublished.

[18]I. Webman, J. Jortner, and M. H. Cohen, Phys. Rev. B 11, 2885 (1975).

[19]P. G. de Gennes, J. Phys. (Paris), Lett. 37, L1 (1976).

[20]M. J. Stephen, Phys. Rev. B 17, 4444 (1978).