Crossover from percolation to diffusion

D. N. Tsigankov and A. L. Efros
Department of Physics, University of Utah, Salt Lake City, Utah 84112
(Received 1 May 2000; revised manuscript received 26 October 2000; published 27 February 2001)

A problem of the crossover from percolation to diffusion transport is considered. A general scaling theory is proposed. It introduces phenomenologically four critical exponents which are connected by two equations. One exponent is completely new. It describes the increase of the diffusion below percolation threshold. As an example, an exact solution of one-dimensional lattice problem is given. In this case the new exponent $q=2$.

DOI: 10.1103/PhysRevB.63.132301 PACS number(s): 64.60.Ak, 72.60.+g, 72.20.−i

Percolation theory is often used to describe transport properties of disordered systems with a large disorder. The typical problems of this type are, for example, the conduction of random mixture of conducting and nonconducting elements and hopping conduction.[1] Above the percolation threshold the transport in such systems may be described in terms of electrical conductivity and diffusion coefficient, that are connected by the Einstein relation.[2] It is important, however, that such a description is valid at a distances much larger than the correlation length of the percolaton theory. This length tends to infinity at the percolation threshold and it is large near the threshold. One can consider this length as a typical size of the percolation network.[1] At smaller distances diffusion equation is not applicable and the process is not Markovian.

For calculation of the large-scale diffusion coefficient one should use the percolation theory which is very far from any Boltzmann-type transport approach. Say, both the electrical conductivity and the diffusion coefficient of the conductive and nonconductive mixture behave like $(p-p_c)^t$, where p is a fraction of conductive elements, p_c is a percolation threshold value, and t is a critical exponent. Both of them are zero at $p<p_c$.

Thus, there is an important difference between a regular diffusion, which is a Markovian process at all lengths,starting with the characteristic length of the order of a diffusion hop, and the large-scale diffusion resulting from the percolation-type process. For brevity we call these two processes diffusion and percolation, respectively.

The regular percolation theory assumes that the random elements do not change their positions with time so that the percolation paths do not change their spatial locations. The low-temperature electron transport is one of examples where this assumption is not valid. Due to the electron-electron interaction the random potential persistently and substantially changes with time,[3,4] which may affect conductivity near the metal-insulator transition. Such problems appear outside solid state physics as well. The class of this problem is known as *dynamical percolation*. They have been studied theoretically using effective medium approximation (See, e.g., Ref. 5, and references therein). One-dimensional problems of this type have been considered for some models without any approximations,[6] but far from the percolation transition $p_c=1$.

We concentrate here on the case when the diffusion through a conducting medium is drastically faster than the fluctuations of the positions of the conducting and nonconducting elements. In this case the transition from diffusion to percolation mechanism has all features of the phase transition and it can be characterized by critical exponents. In this paper we introduce a set of these exponents and establish relation between them. For illustration we present an exact solution of one dimensional lattice problem.

Thus, we consider here a random mixture of the conducting and nonconducting elements which can change their spatial configuration but very slowly. In this situation the resulting diffusion (or conductivity) of the particles *is nonzero at any small fraction p of the conducting elements*. The mechanism of this diffusion is as follows. A particle can diffuse only in the conducting medium. To move from one conducting element to the other it is waiting until another conducting element comes to the element where it resides. At this moment of time a particle is able to do a next move. This is a regular diffusion which is characterized by some slow waiting time τ_s. The diffusion inside the conducting medium is characterized by much faster time τ_f. When the fraction of conducting elements p becomes close to the percolation threshold p_c, but it is still less than p_c, the resulting diffusion increases as $1/(p_c-p)^q$, where q is a novel critical exponent. This happens because the conducting clusters become large. But since they are disconnected the particle still should wait before jumping from one of them to the other. Finally, above the percolation threshold, when $p-p_c$ becomes larger than the width of some critical region described below, the diffusion is described by a regular percolation law $D\sim(p-p_c)^t$ and slow motion of the conducting elements is not important. In our terminology this is a crossover from regular diffusion to percolation with increasing p. The diffusion coefficient D has a critical behavior in a small interval near p_c. To describe this physics one can use the same scaling arguments as for the problem of the frozen mixture of elements with large and small conductivity.[7,8] Note that the new problem is not equivalent to the old one, so that the exponent q might be different. The scaling hypothesis is valid in the proximity of the percolation threshold so that $|X|/p_c\ll 1$, where $X=p-p_c$. In this region the scaling hypothesis can be written in the form

$$d=h^s\psi\left(\frac{X}{h^m}\right). \tag{1}$$

Here $d=D/D_f$, $h=D_s/D_f$, where D is the resulting diffusion coefficient at a given value of p, $D_f=a^2/2\tau_f$ is the diffusion coefficient in the conducting medium, a is a characteristic length which depends on the model, $D_s=a^2/2\tau_s$, and $\psi(Z)$ is some analytical function at all real values of its argument, $-\infty<Z<\infty$. We assume that $h\ll 1$ and that $\psi(0)=1$.

Equation (1) contains two independent critical exponents. The meaning of the exponent s is that $d=h^s$ at $p=p_c$. The exponent m describes the width of the critical region $|p-p_c|=h^m$ between the percolation and diffusion.

All the critical exponents which describe $d(X)$ can be related to s and m. At $X>0$ and $X\gg h^m$ the slow changes of the percolation paths are not important. Thus, we have the diffusion on the percolation cluster. If the system is larger than the correlation radius of the percolation cluster, the diffusion coefficient is related to the conductivity by the Einstein relation. Then one has $d\sim X^t$, where the exponent t is a usual percolation exponent which describes the conductivity above the percolation threshold. To get this result from Eq. (1) one should assume that $m=s/t$. At $X<0$ and $|X|\gg h^m$ we expect that $d\sim h/(|X|)^q$. This gives $s+mq=1$. Finally we get two connections between four exponents s,q,t, and m, namely $q=t(s^{-1}-1)$ and $m=s/t$.

As an example, we consider below an exactly soluble one dimensional site or bond model on a lattice. At the beginning we concentrate on the site model. The sites may be white and black with the fractions p and $1-p$, respectively. The particle may occupy the white sites only and it is able to jump at the nearest site, if this site is white, during the time τ_f. The configuration of the white and black sites slowly changes with time. This change can be introduced by many ways. We consider the simplest one. After each time interval τ_s the configuration of all sites completely changes preserving the same p, while the particle remains at the same site and this site remains white. In this model time τ_s can be called a renewal time. We assume that $\tau_s\gg\tau_f$. Since $p_c=1$ in the one-dimensional case, our solution may only illustrate the increase of the diffusion coefficient $D\sim(1-p)^q$ and the width of the critical region $|X|$, where it deviates from this law and tends to the value $D_f=a^2/2\tau_f$ as $p\to 1$.

Thus, in our model the particle occurs inside the completely different cluster of white sites after each time interval τ_s. Then the time average of squared displacement $\overline{r^2(t)}$ can be written in a form

$$\overline{r^2(t)}=\overline{[r_1(\tau_s)+r_2(\tau_s)+\cdots+r_N(\tau_s)]^2}, \tag{2}$$

where $t=N\tau_s$, $r_i(\tau_s)$ is a displacement of a particle inside the cluster number i.

Since both the numbers of sites in any new cluster and the initial positions of a particle inside this cluster are random, all $r_i(\tau_s)$ are statistically independent. Then

$$\overline{r^2(t)}=\overline{r_1^2(\tau_s)}+\overline{r_2^2(\tau_s)}+\cdots+\overline{r_N^2(\tau_s)}. \tag{3}$$

If we divide the right-hand side of Eq. (3) by N, we get a squared displacement averaged over both the number of sites in clusters and the initial positions of a particle within each cluster. This type of averaging we denote $\langle\ldots\rangle$. Now we introduce the function $\langle\overline{r^2(\tau_s)}\rangle$ by the equation

$$\lim_{N\to\infty}\frac{\overline{r^2(t)}}{N}=\langle\overline{r^2(\tau_s)}\rangle. \tag{4}$$

The diffusion coefficient D can be expressed through this function

$$D=\lim_{t\to\infty}\frac{r^2(t)}{2t}=\frac{\langle\overline{r^2(\tau_s)}\rangle}{2\tau_s}. \tag{5}$$

Our strategy to find $\langle\overline{r^2(\tau_s)}\rangle$ is as follows. We assume first that the clusters of the white sites are not very large so that the particle, which changes position during the time τ_f, crosses these clusters to and fro many times during the time τ_s. In this approximation we find the diffusion coefficient D_1. For the larger clusters we use the continuum approximation, which is valid at $1-p\ll 1$ only, and find D_2. We show that these two approximations have a large region of overlap if

$$\frac{\tau_f}{\tau_s}\ll 1. \tag{6}$$

Matching D_1 and D_2 in the overlap region we find the result which is exact if Eq. (6) is fulfilled.

To calculate D_1 we assume that the particle appears on each white site of a cluster so many times during the time τ_s, that it can be found on each site of the cluster with the same probability.

If the particle is within the cluster of size L, the average quadratic displacement $R^2(L)$ is given by the equation

$$R^2(L)=\frac{a^2}{L^2}\sum_{n=1}^{L}\sum_{k=1}^{L}(n-k)^2=\frac{a^2}{6}(L^2-1), \tag{7}$$

where we have averaged over initial positions of the particle within the cluster. The probability that a particle is within a cluster of L white sites is

$$w_L=(1-p)^2p^{L-1}L. \tag{8}$$

By averaging $R^2(L)$ over all cluster sizes L one gets

$$\langle\overline{r^2(\tau_s)}\rangle=\frac{a^2}{6}(1-p)^2\sum_{L=1}^{\infty}p^{L-1}L(L^2-1)=\frac{a^2p}{(1-p)^2}. \tag{9}$$

Thus,

$$D_1=\frac{\langle\overline{r^2(\tau_s)}\rangle}{2\tau_s}=\frac{D_sp}{(1-p)^2}. \tag{10}$$

Note that Eq. (10) has been obtained by Druger *et al.*[6] and it also can be extracted from the paper by Plyukhin.[9] The Eq. (10) is valid if $\langle\overline{r^2(\tau_s)}\rangle\ll D_f\tau_s$. That means that displacement of a particle during the time τ_s is much less than it would be in the infinite system. This condition is fulfilled if

$$\frac{p}{(1-p)^2} \ll \frac{\tau_s}{\tau_f}. \tag{11}$$

At $p \ll 1$ one gets $D_1 = pD_s$.

To calculate D_2 we use the continuous approximation which is valid when the sizes of white clusters $L \gg 1$. This is true if $1-p \ll 1$. In this approximation one should use the diffusion equation for the probability density $u(x,t)$.

$$\frac{\partial u(x,t)}{\partial t} = D_f \frac{\partial^2 u(x,t)}{\partial x^2} \tag{12}$$

assuming zero current at the beginning and at the end of the cluster $(x=0,L)$

$$\left.\frac{\partial u(x,t)}{\partial x}\right|_{x=0,L} = 0. \tag{13}$$

The initial condition is

$$u(x,t)|_{t=0} = \delta(x-x_0), \tag{14}$$

where x_0 is a random point within the interval $(0,L)$.

The solution has a form

$$u(x,t) = \frac{1}{L} + \sum_{n=1}^{\infty} \cos\left(\frac{\pi n x_0}{L}\right)\cos\left(\frac{\pi n x}{L}\right)\exp\left(-\frac{\pi^2 n^2}{L^2} D_f t\right). \tag{15}$$

The mean-square displacement with respect to the initial position x_0 is

$$\begin{aligned}\overline{r_L^2(x_0,t)} &= \int_0^L (x-x_0)^2 u(x,t)\,dx \\ &= \frac{L^2}{3} - (L-x_0)x_0 + 4L^2 \sum_{n=1}^{\infty} \frac{\cos\left(\frac{\pi n x_0}{L}\right)}{(\pi n)^2} \\ &\quad \times \left[\frac{x_0}{L} + (-1)^n\left(1-\frac{x_0}{L}\right)\right]\exp\left(-\frac{\pi^2 n^2}{L^2} D_f t\right).\end{aligned} \tag{16}$$

By averaging over the initial positions x_0 on the cluster, we get the time dependence of the mean-square displacement of the particle on the cluster of the size L.

$$\begin{aligned}\overline{r_L^2(t)} &= \frac{1}{L}\int_0^L \overline{r^2(x_0,t)}\,dx_0 \\ &= \frac{L^2}{6} - L^2 \sum_{n=0}^{\infty} \frac{1}{\left[\frac{\pi}{2}(2n+1)\right]^4}\exp\left[-\frac{\pi^2(2n+1)^2}{L^2} D_f t\right] \\ &= \frac{16}{\pi^4} L^2 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^4}\left[1-\exp\left(-\frac{\pi^2 n^2}{L^2} D_f t\right)\right].\end{aligned} \tag{17}$$

One can see from Eq. (17) that for relatively small times, $t \ll L^2/D_f$, the displacement $\overline{r_L^2(t)}$ grows as $2D_f t$, just as for the normal diffusion, while at large times the value $\overline{r_L^2(t)}$ tends to the asymptotic value $L^2/6$ indicating that the particle crosses the cluster many times.

To find the diffusion coefficient D_2 one has to average $\overline{r_L^2(\tau_s)}$ over all clusters with the distribution function given by Eq. (8). In the region $(1-p) \ll 1$ one can substitute summation over the cluster sizes by integration to get

$$\begin{aligned}\langle\overline{r^2(\tau_s)}\rangle &= \frac{(1-p)^2}{a^2}\int_0^{\infty} \overline{r_L^2(\tau_s)} L \exp\left(\frac{L}{a}\ln p\right) dL \\ &= \frac{a^2}{(1-p)^2} - \frac{16}{\pi^4 a^2}(1-p)^2 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^4} \\ &\quad \times \int_0^{\infty} L^3 \exp\left(\frac{L}{a}\ln p - \frac{\pi^2 n^2 a^2}{2L^2}\frac{\tau_s}{\tau_f}\right) dL.\end{aligned} \tag{18}$$

The diffusion coefficient D_2 can be represented in a form

$$\begin{aligned}D_2 &= \frac{\langle\overline{r^2(\tau_s)}\rangle}{2\tau_s} \\ &= \frac{16 D_s}{\pi^4 a^4}(1-p)^2 \sum_{n=0}^{\infty} \frac{1}{(2n+1)^4}\int_0^{\infty} L^3 \exp\left(\frac{L}{a}\ln p\right) \\ &\quad \times \left[1-\exp\left(-\frac{\pi^2 n^2 a^2}{2L^2}\frac{\tau_s}{\tau_f}\right)\right] dL\end{aligned} \tag{19}$$

or

$$\begin{aligned}D_2 &= \frac{16 D_s}{\pi^4 (1-p)^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^4}\int_0^{\infty} x^3 \exp(-x) \\ &\quad \times \left[1-\exp\left(-\frac{\pi^2 (2n+1)^2}{2x^2}\frac{\tau_s}{\tau_f}(\ln p)^2\right)\right] dx,\end{aligned} \tag{20}$$

where $x = -(L/a)\ln p$.

Introducing the dimensionless parameter $A = \pi^2 (\ln p)^2 \tau_s / 2\tau_f$ and changing the integration variable $x = b_n \sqrt{z}$, where $b_n = \sqrt{A}(2n+1)$ one can perform the summation over n to get

$$D_2 = \frac{a^2 A}{\pi^2 \tau_f}\int_0^{\infty} \frac{z[1-\exp(-1/z)]\,dz}{\sinh(\sqrt{Az})}. \tag{21}$$

At $A \gg 1$ one can neglect the exponent in the nominator of Eq. (21). Then

$$D_2 = D_s/(1-p)^2. \tag{22}$$

At $A \ll 1$ one can expand this exponent to get $D_2 = D_f$. One can also get the next term at small A. Thus,

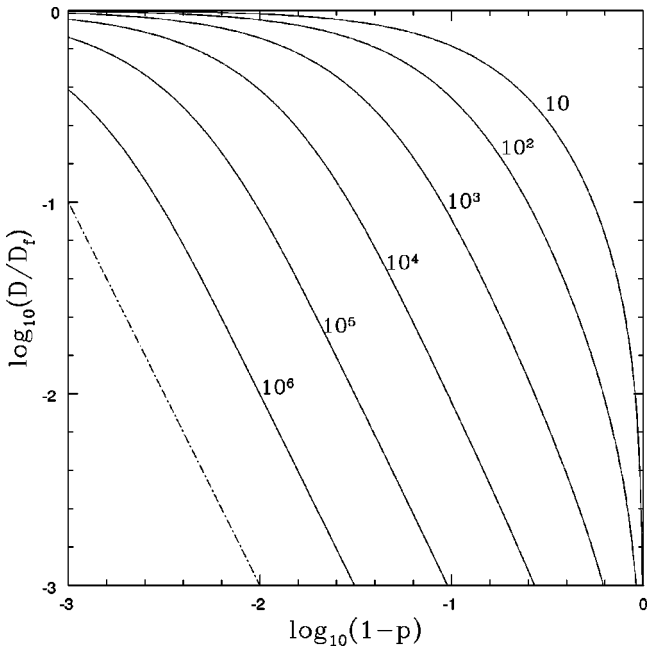

FIG. 1. The function D/D_f is plotted vs $1-p$ at different values of τ_s/τ_f in the double logarithmic scale. The function $(1-p)^{-2}$ is shown by the dot-dashed straight line.

$$D_2 = D_f\left\{1 - \frac{2\sqrt{A}}{\pi^2}\int_0^\infty \sqrt{z}\left[\frac{1}{z} - 1 + \exp\left(-\frac{1}{z}\right)\right]dz\right\}. \tag{23}$$

Calculating the integral in Eq. (23) one gets

$$D_2 = D_f(1 - 0.479\sqrt{A}) = D_f[1 - 1.06\sqrt{\tau_s/\tau_f}(1-p)] \tag{24}$$

at $A \ll 1$. Here we expand $\ln(p)$ at $1-p \ll 1$.

Note that the linear dependence in $1-p$ in the second term of Eq. (24) means that the deviation of D_2 from D_f at $1-p \ll 1$ is proportional to the ratio of the mean displacement of a particle $\sqrt{D_f\tau_s}$ during the time τ_s to the typical size of a white cluster $(1-p)^{-1}$.

The scaling arguments in some different form than Eq. (1) can be applied to the one-dimensional case as well. It can be written in a form

$$D_2 = D_f F\left(\frac{1-p}{h^m}\right), \tag{25}$$

where $h = \tau_f/\tau_s$ and $F(z)$ is an analytical function. Eq. (25) has the same form as Eq. (1) except that $s=0$. This relation is defined at $p \leqslant 1$ and $1-p \ll 1$. In the same way as before, we put $F(0)=1$. At large values of $(1-p)/h^m$ one has $D \sim h/(1-p)^q$. It follows that $mq=1$ which is analogous to the relation $s+mq=1$ that is valid in general case. We know from Eq. (22) that $q=2$. At $1-p \ll 1$ one can write $A = \pi^2(1-p)^2\tau_s/2\tau_f$. Then one gets that $m=1/2$ in agreement with the scaling relation. The exponent t has no meaning in the one-dimensional case.

Finally, we present the solution for the effective diffusion coefficient D which is valid at all values of p within the interval $0 \leqslant p \leqslant 1$. It has been shown that $D=D_1$ if $p/(1-p)^2 \ll \tau_s/\tau_f$. On the other hand $D=D_2$ if $(1-p) \ll 1$. Thus, the two approximation have a wide region of overlap $(p\tau_f/\tau_s)^{0.5} \ll (1-p) \ll 1$. In this region $D_1 = D_s p/(1-p)^2$ and $D_2 = D_s/(1-p)^2$. Thus, one can get a result which is exact everywhere if $\tau_s \gg \tau_f$. This result is pD_2. Finally,

$$D = \frac{a^2 A p}{\pi^2 \tau_f}\int_0^\infty \frac{z[1-\exp(-1/z)]dz}{\sinh(\sqrt{Az})}. \tag{26}$$

This result has been derived above for the site problem. One can see, however, that it remains unchanged for the bond problem as well.

The diffusion coefficient D/D_f as given by Eq. (26) is plotted in Fig. 1 versus $(1-p)$ in the double logarithmic scale at different values of τ_s/τ_f. The function $(1-p)^{-2}$ is also shown there as a dot-dashed line. One can see that at the large values of τ_s/τ_f the curves have wide regions which are parallel to this line. In these regions the diffusion coefficient increases as $(1-p)^{-2}$.

In conclusion, we have presented a novel problem which fills a gap between the diffusion and percolation in the case when the motion of the random media is very slow. We have considered the dc transport only. It would be interesting to study a frequency-dependent transport under the same conditions.

We thank B. D. Laikhtman and A. V. Plukhin for a fruitful discussion. This work was supported by the US-Israel Binational Science Foundation, Grant No. 9800097.

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