Dependence of the diffusion coefficient on the energy distribution of random barriers

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(Received 29 March 1995)

We study hopping transport of particles in the presence of randomly distributed energy barriers for diffusion. Exponential, Gaussian, and uniform distributions of barrier heights on square and simple-cubic lattices are investigated to uncover the influence of the form and width of the distributions. The temperature dependence of the characteristic time separating the initial regime of anomalous diffusion from the long-time normal diffusion is of Arrhenius form with an effective activation energy determined by the percolation threshold of the corresponding lattice. Our analytic results, derived within the framework of effective medium approximation, show that the asymptotic diffusion coefficient does not depend on the degree of disorder on a square lattice whereas on a cubic lattice it does. These predictions are confirmed by numerical simulations. The temperature dependence of the diffusion coefficient is also determined by the coordination number z of the lattice for "static" barrier disorder. On a square lattice it is of Arrhenius form and for $z \neq 4$ it deviates from it with increasing degree of disorder. It is always non-Arrhenian in the case of dynamically changing disorder.

PACS number(s): 05.40.+j

I. INTRODUCTION

Diffusion and conductivity in random media, such as amorphous solids and liquids, have received wide attention in recent years [1,2]. In particular, transport properties of test particles can be so strongly affected by randomness that the mean-square displacement (MSQD), $\langle R(t)^2 \rangle$, loses its usual linear dependence on time t and an *anomalous diffusion* law, $\langle R(t)^2 \rangle \approx t^{\nu}$, with $\nu \neq 1$ observed. Even if the randomness is not strong enough to lead to anomalous diffusion, interesting phenomena appear such as long crossover times to normal diffusion and considerable reductions of the asymptotic diffusion coefficients.

In a first-order description of particle transport in amorphous materials, randomness is usually introduced in terms of energetic rather than positional or geometric disorder. The basic models studied in this context fall into two classes, that of the randomly distributed site energies, i.e., the random trap model (RTM), or that of random barriers, the random barrier model (RBM). These two classes of randomness appear to have deeply different properties, most notably due to the total lack of correlated jumps of the particles in the former where each jump is independent of the preceding one. The differences also affect the theoretical methods of analysis of both models — in the RTM there exists an exact analytical result for the MSQD, whereas in the RBM as a rule no closed-form results are available, except in one dimension. A detailed presentation of most classic and recent studies and results may be found in the comprehensive review articles of Haus and Kehr [3] and Bouchaud and Georges [4].

In a recent work [5] we studied the RBM with a uniform distribution of barrier heights by means of Monte Carlo (MC) simulation in two (2D) and three (3D) dimensions, and we observed a transition from anomalous to regular diffusion of the particles at some (temperature-dependent) crossover time τ_c. With the crossover time τ_c versus temperature T relationship being of the Arrhenius type, it was suggested that the effective activation energy barrier is solely determined by the critical (threshold) concentration of *easy barriers* for particle transitions, which is given by the well known value for bond percolation. The barrier with the largest activation energy within this set of easy barriers then gives the effective activation energy for τ_c.

In the present work we corroborate this finding by investigating the RBM with three different probability distribution functions (PDF's), namely, an exponential, a Gaussian, and a uniform PDF for the barrier heights, and various degrees of disorder, σ, determined by the variance of the respective PDF. In all cases, one observes an initial regime of anomalous diffusion which becomes increasingly pronounced with decreasing temperature and growing σ. After a characteristic time τ_c diffusion turns to normal whereby we observe $\tau_c \propto \exp(-\frac{E_p}{k_B T})$ with E_p determined by the percolation threshold of the respective lattice.

One aim of this paper is to study the dependence of the asymptotic diffusion coefficient D_∞ on the form and, in particular, on the variance σ of the PDF. One of the approximate descriptions of the asymptotic diffusion coefficient is provided by the critical-path approach of Ambegaokar, Halperin, and Langer [6]. They pointed out that the asymptotic diffusion coefficient D_∞ is deter-

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mined by the effective activation energy that was characterized above.

In the simple version of the critical-path approach, *solely* the effective activation energy fixes D_∞, independent of the form of the PDF. Corrections to the simple version have been derived [7,8], but they do not allow one to see directly the influence of the variance σ of the probability distribution. Here we study directly the influence of σ, for the Gaussian and for the uniform PDF. We will see that no such influence exists for D=2 (coordination number 4), but it is present in D=3 (coordination number 6). This result is in contradiction to recent work of Limoge and Bocquet [9], who predicted such an influence, independent of the dimensionality.

Recently the numerical data for D_∞ of the RBM were compared with the predictions of the critical-path approach and of the effective-medium approximation (EMA) [10]. It turned out that for distributions of the barrier heights that are not too broad the simple critical-path approach does not describe well the simulation results for D_∞. A much better approximate description is provided by the EMA, for the uniform distribution of the activation energies and not too low temperatures, compared to the maximal energy of the PDF. Hence, we will also use the EMA in this paper to derive theoretical predictions for the asymptotic diffusion coefficients.

II. MODEL

As the model and the computational procedure have been described before [5] we shall sketch them here only briefly. Calculations are performed on a 2D square lattice and a 3D simple-cubic lattice where only jumps between adjacent sites are allowed. Since in this work we are mainly concerned with the case of static disorder, all barrier energies (saddle points) between neighboring sites are assigned values E_{ij} at random subject to a specific PDF at time $t = 0$, and they remain unchanged for the duration of the simulation.

The transition rates Γ_{ij} from site i to site j are given by the Arrhenius law,

$$\Gamma_{ij} = \Gamma_0 \frac{1}{z} \exp(-E_{ij}/k_B T), \tag{1}$$

where z denotes the coordination number of the lattice. Jumps that are made between two specific sites have exactly the same transition rate at any time during the calculation. Thus if a forward jump is made in a particular direction, then the backward jump (back to original position) should have the same rate as the forward jump. If the transition rates are converted into probabilities by dividing them by Γ_0, the difference of the sum over all neighbor sites from 1 gives the probability for the particle to make no jump whatsoever and remain on spot:

$$\frac{\Gamma_{ii}}{\Gamma_0} = 1 - \sum_{j(\neq i)} \frac{\Gamma_{ij}}{\Gamma_0}. \tag{2}$$

The following probability distributions for the activation energies were investigated:

(i) Exponential PDF,

$$\nu(E) = \frac{1}{\langle E \rangle} \exp\left(-\frac{E}{\langle E \rangle}\right). \tag{3}$$

The relevant parameter is then $\alpha = k_B T/\langle E \rangle$ and there is no additional dispersion parameter.

(ii) Gaussian PDF,

$$\nu(E) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(E - \langle E \rangle)^2}{2\sigma^2}\right]. \tag{4}$$

When combined with the Arrhenius law (1), there are now two parameters, namely $\alpha = k_B T/\langle E \rangle$ and the ratio between the dispersion parameter σ and the mean barrier height $\langle E \rangle$. The mean barrier energy is always kept constant at the value $\langle E \rangle = 0.5$. σ has been chosen such that values of $E < 0$ should occur with vanishing probability. We take 0.02659 as the smallest admissible probability. The largest possible σ equals thus 0.1667 and Gaussian PDFs with $\sigma = 0.0833, 0.0416, 0.0167$ have been studied.

(iii) Uniform PDF,

$$\nu(E) = \begin{cases} \frac{1}{2\sigma\langle E \rangle} & (1-\sigma)\langle E \rangle \leq E \leq (1+\sigma)\langle E \rangle \\ 0 & \text{otherwise,} \end{cases} \tag{5}$$

where E is a random number between 0 and 1. Also, the mean barrier energy is kept constant at the value $\langle E \rangle = 0.5$ and σ ranges in the interval 0 to 1. The dispersion parameter σ serves to control the width of the distribution, similar to the Gaussian case.

For the numerical simulation we build lattices of size 600×600. During the simulations we take care that the particle does not reach the boundary, provided it has been placed in the middle of the lattice at $t = 0$. We use the so called lattice growth technique. This implies that only the bonds of the lattice that are to be visited by the particle are asigned random energies according to the PDF [Eqs. (3)–(5)], and by drawing on a random number it is decided what step will be taken. Once these bond energies are defined they stay constant during the calculation. In subsequent steps we first ask if the four neighbors have been determined earlier or not. If they have been defined their values are directly used. If not, they are assigned energy values at that time, just like the previously visited bonds. We keep track of the particle coordinates as a function of time, from which the MSQD is calculated. The average values of the data are calculated from a large number of realizations. Depending on the inherent noise present the number of realizations utilized may vary from 1000 to 10 000 different ones.

III. EFFECTIVE-MEDIUM APPROXIMATION

Another approach for the calculation of the mean square displacement of a particle on a lattice with static random barriers is provided by the effective-medium approximation (EMA) [3]. The EMA for hopping transport

of particles was developed by Summerfield [11], Odagaki and Lax [12], and Webman [13]; for a review see [3]. The scheme followed by EMA is the following: One starts with the master equation for the probability $P(\mathbf{r}_i,t)$ of finding the particle at site $\mathbf{r}_i$ at time t,

$$\frac{d}{dt}P(\mathbf{r}_i,t)=\sum_{j\in i}[\Gamma_{ji}P(\mathbf{r}_j,t)-\Gamma_{ij}P(\mathbf{r}_i,t)]. \tag{6}$$

In the effective medium, the set of static jump frequences Γ_{ij} is replaced by a single, position-independent, but frequency-dependent, effective jump frequency $\tilde{\Gamma}_{eff}(s)$. The master equation reads then in the Laplace domain:

$$s\tilde{P}(\mathbf{r}_i,s)-\delta_{i,0}=\tilde{\Gamma}_{eff}(s)\sum_{j\in i}[\langle\tilde{P}(\mathbf{r}_j,s)\rangle-\langle\tilde{P}(\mathbf{r}_i,s)\rangle]. \tag{7}$$

From the solution of this equation the Laplace transformed MSQD is obtained as

$$\tilde{\langle r^2\rangle}(s)=za^2\tilde{\Gamma}_{eff}(s)/s^2 \tag{8}$$

whereby a denotes the lattice constant and cubic lattices are assumed. If the effective transition rate approaches a constant value in the limit $s\to 0$, the resulting MSQD is linear in time for large times,

$$\langle r^2(t)\rangle\longrightarrow_{t\to\infty} za^2\tilde{\Gamma}_{eff}(s\to 0)t\,, \tag{9}$$

and the asymptotic diffusion coefficient is given by $D_\infty=\tilde{\Gamma}_{eff}(s\to 0)$. Time-dependent MSQD in the RB model were investigated in the frame of the EMA in a recent paper [14].

The effective jump frequency, $\tilde{\Gamma}_{eff}(s)$, has to be determined from a *self-consistency* condition. Within the simplest approximation suitable for the random-barrier model, the so-called single-bond EMA, a single jump frequency Γ between a pair of neighboring sites (i.e., a single barrier height) is allowed to fluctuate and it is embedded into the effective medium [11–13]. In this case the corresponding master equation yields the self-consistency condition

$$\left\{\frac{\Gamma-\tilde{\Gamma}_{eff}(s)}{1-2[s\tilde{G}(\mathbf{0},s)-1][\Gamma-\tilde{\Gamma}_{eff}(s)]/[z\tilde{\Gamma}_{eff}(s)]}\right\}_{\rho(\Gamma)}=0, \tag{10}$$

where the brackets denote the average over the distribution of jump frequencies Γ (which corresponds to a distribution of barrier heights).

The initial site occupation probability $\tilde{G}(\mathbf{0},s)$ depends on the lattice type and it has been extensively studied in the literature [3]. In the present consideration its explicit form will not be needed since we focus on the long-time behavior $s\to 0$ of the MSQD, Eq. (8). In the limit $s\to 0$ one has $\lim_{s\to 0}s\tilde{G}(\mathbf{0},s)=0$, which holds for all types of lattices and in arbitrary dimensions. This largely simplifies the analytical treatment of Eq. (10), which reduces to

$$\int_{\Gamma_{min}}^{\Gamma_{max}}d\Gamma\rho(\Gamma)\frac{\Gamma_{eff}-\Gamma}{(z-2)\Gamma_{eff}+2\Gamma}=0, \tag{11}$$

where $\Gamma_{eff}\equiv\tilde{\Gamma}_{eff}(s\to 0)$ and $\rho(\Gamma)$ is the distribution density of the jump rate Γ. It should be noted that in the EMA result for the effective transition rate in the long-time limit, only the coordination number remains, and any direct influence of the dimensionality and the geometrical structure of the lattice is lost. This is typical of mean-field theories which become exact in high dimensionalities (say, $d>4$). A special case is the result for the square lattice, see the discussion below. The self-consistency condition Eq. (11) was already derived by Kirkpatrick [15] in the context of the random-resistor network. The distribution $\rho(\Gamma)$ is derived from the PDF of the energy levels Eq. (1) by the transformation

$$\rho(\Gamma)=\nu[E(\Gamma)]\left|\frac{dE}{d\Gamma}\right|. \tag{12}$$

For the uniform PDF of energy levels, the self-consistency condition can be explicitly evaluated. The distribution of the transition rates follows from (12) and (1); it is given by

$$\rho(\Gamma)=\begin{cases}\frac{\alpha}{2\sigma\Gamma} & \Gamma_{min}\le\Gamma\le\Gamma_{max}\\ 0 & \text{otherwise.}\end{cases} \tag{13}$$

The parameter $\alpha=\frac{k_BT}{\langle E\rangle}$ measures the relative thermal energy of the particle, and $\Gamma_{min}=\Gamma_0\exp(-\frac{1+\sigma}{\alpha})$, $\Gamma_{max}=\Gamma_0\exp(-\frac{1-\sigma}{\alpha})$ are the limiting jump rates in the case of uniformly distributed barrier heights. The parameter α used in this paper is twice the one used in Refs. [5,10]. Note that σ is restricted to the interval $(0,1)$. Using (13) the integral in Eq. (11) can be evaluated analytically, and the resulting self-consistency conditon solved with respect to Γ_{eff}. The result is

$$\Gamma_{eff}=\frac{2}{z-2}\Gamma_0\exp\left(-\frac{1}{\alpha}\right)\frac{\sinh(\frac{(z-2)\sigma}{z\alpha})}{\sinh(\frac{2\sigma}{z\alpha})}\,, \tag{14}$$

where it was assumed that $z>2$ [for $z=2$ by applying the l'Hospital rule to Eq. (14) one easily derives the one-dimensional result for Γ_{eff} — see below].

The influence of dimensionality on the transport properties of the random medium can now be studied explicitly. For the coordination number $z=4$, the effective rate is

$$\Gamma_{eff}=\Gamma_0\exp\left(-\frac{1}{\alpha}\right), \tag{15}$$

i.e., it is *independent* of σ. Thus it turns out that the asymptotic diffusion coefficient on a 2D square lattice, where z=4, is completely insensitive with respect to the degree of disorder in the barrier heights distribution and is equal to that in the perfect lattice with a single barrier height $E=\langle E\rangle$.

This finding deserves further comment. In the square lattice the prediction of the critical-path ap-

proach for the asymptotic diffusion coefficient is $D_\infty = \Gamma_0 \exp(-\langle E\rangle/k_BT)$, since the percolation threshold for bond percolation is exactly $p_c = 0.5$ in this lattice. Hence the result of the critical-path approach coincides with the EMA result. Gartner [16] could show that the result $D_\infty = \Gamma_0 \exp(-\langle E\rangle/k_BT)$ is exact for the 2D square lattice, as a consequence of the property of self-duality, and of the form (13) of the distribution of transition rates. For $z = 6$ in 3D, however, the result is qualitatively different. For the uniform PDF one obtains from Eq. (11)

$$\Gamma_{eff} = \frac{\Gamma_0 e^{(-\frac{1}{\alpha})}}{2}\left[\frac{e^{(\frac{\sigma}{\alpha})} - e^{(-\frac{\sigma}{3\alpha})}}{e^{(\frac{2\sigma}{3\alpha})} - 1}\right], \tag{16}$$

so that the effective jump rate Γ_{eff} now becomes σ dependent. In the case of vanishing degree of disorder, $\sigma \to 0$, Eq. (16) yields the old result $\Gamma_{eff} = \Gamma_0 \exp(-\frac{1}{\alpha})$ whereas for $\sigma \to 1$ (maximal disorder)

$$\Gamma_{eff} = \frac{\Gamma_0}{2}\left[\frac{1 - e^{-\frac{4}{3\alpha}}}{e^{\frac{2}{3\alpha}} - 1}\right]. \tag{17}$$

At low temperatures, $\alpha \to 0$, Eq. (17) then yields

$$\Gamma_{eff} = \frac{\Gamma_0}{2}\exp\left(-\frac{2}{3\alpha}\right), \tag{18}$$

reflecting an increased mobility of the tracer because of disorder. At high temperature, on the contrary, Eq. (17) yields $\Gamma_{eff} = \Gamma_0$, as one should expect. In one dimension one has $\Gamma_{eff} = \Gamma_0 \exp(-\frac{1}{\alpha})\frac{(\frac{\sigma}{\alpha})}{\sinh(\frac{\sigma}{\alpha})}$ so that with growing σ the diffusion coefficient decreases, i.e., large barriers cause many more delays than what is gained by the particle at the low barriers.

For the case of the Gaussian or the exponential PDF of the energies, the self-consistency condition Eq. (11) can only be evaluated by numerical integration. In the case of the Gaussian distribution one obtains for the distribution of the transition rates

$$\rho(\Gamma) = \frac{k_BT}{\Gamma}\exp\left[-\frac{[k_BT\ln(\frac{\Gamma_0}{\Gamma}) - \langle E\rangle]^2}{2\sigma^2}\right], \tag{19}$$

and for the exponential distribution (which in the present work does not depend on σ) one has

$$\rho(\Gamma) = \frac{\alpha}{\Gamma}\left(\frac{\Gamma}{\Gamma_0}\right)^\alpha. \tag{20}$$

In the latter case it is expedient to decompose the fraction in Eq. (11) into two parts and to perform an integral over $(\Gamma/\Gamma_0)^\alpha$ explicitly; the remaining integrand then contains the power $(\Gamma/\Gamma_0)^{\alpha+1}$ and no convergence problems appear during numerical integration. The integration can be done by standard routines. The results of the numerically determined effective transition rates Γ_{eff} will be presented together with the results of the simulations.

IV. NUMERICAL RESULTS

Figure 1 displays the behavior of the MSQD $\langle R(t)^2\rangle$ as a function of time for several different α values. In this, and in subsequent figures, we plot the data with the temperature T as the explicit parameter, implying that $k_B = 1$, and that T is measured in units of $\langle E\rangle$ As given after Eq. (3), $\alpha = k_BT/\langle E\rangle$. The heights of the barriers are chosen at random according to the exponential PDF [Eq. (3), Fig. 1(a)], the Gaussian [Eq. (4), Fig. 1(b)], and the uniform PDF [Eq. (5), Fig. 1(c)]. We present data for the range of up to 10^7 MC steps, and in one case up to 10^8 MCS. For the Gaussian and the uniform PDF we choose here the case of maximal degree of disorder, $\sigma = 0.1667$ and $\sigma = 1.0$, respectively. For the exponential distribution the degree of disorder is fixed by the width of the distribution which is given by $\langle E\rangle$. In all three cases one observes very similar behavior. At early times and at small temperatures, $T \le 0.115$, there is a distinct regime, different from the diffusive $\langle R^2\rangle \propto D_\infty t$, in agreement with earlier results [5]. At a crossover time τ_c, depending on the temperature T, one goes over to the classical diffusion regime, manifested by a slope 1 in the log-log plots of Fig. 1. For the case of the exponential PDF and square lattices this is qualitatively different from the case of exponentially distributed *site* disorder where the diffusion coefficient goes to zero in all dimensions and only subdiffusive behavior may exist at temperatures, lower than a critical temperature, $k_BT_c = \langle E\rangle$ [17]. Evidently, as the temperature is decreased, linearity is achieved after longer and longer times.

In Figs. 2(a)–2(c) we show in semi-log scale the respective plots of the crossover times τ_c versus inverse temperature. Although the exact position of τ_c could be determined only graphically as an intersection of the tangents to the $\langle R^2\rangle$ curves in the early-time subdiffusive and the long-time diffusive regimes which may give rise to errors, the Arrhenian nature of the τ_c vs T relationship is clearly evident from the plots. While the slopes for the Gaussian and the uniform distributions are very nearly equal to 0.5, for the exponential PDF we obtain a slope of ≈ 0.3453.

All these data strongly support a picture, put forward in a previous work [5], which relates the effective activation energy, derived from the Arrhenius plots of the crossover times, to the critical concentration of low enough barriers (percolating channels) on the lattice in concern. It may be conceived that, as the particle starts at some random position, it is localized at low temperatures in some valley of low-energy barriers, surrounded by high boundary barriers, which acts as an effective trap. As long as the temperature is low most of the jumps are consumed for visiting the same sites in the valley again and again. The probability for escape from this localized region, however, albeit very small, is realized after a period τ_c and a measurement of the MSQD in time units, larger than τ_c, would produce the expected linear dependence on time.

An effective energy barrier, E_p, may be determined such that the concentration of all barriers with height

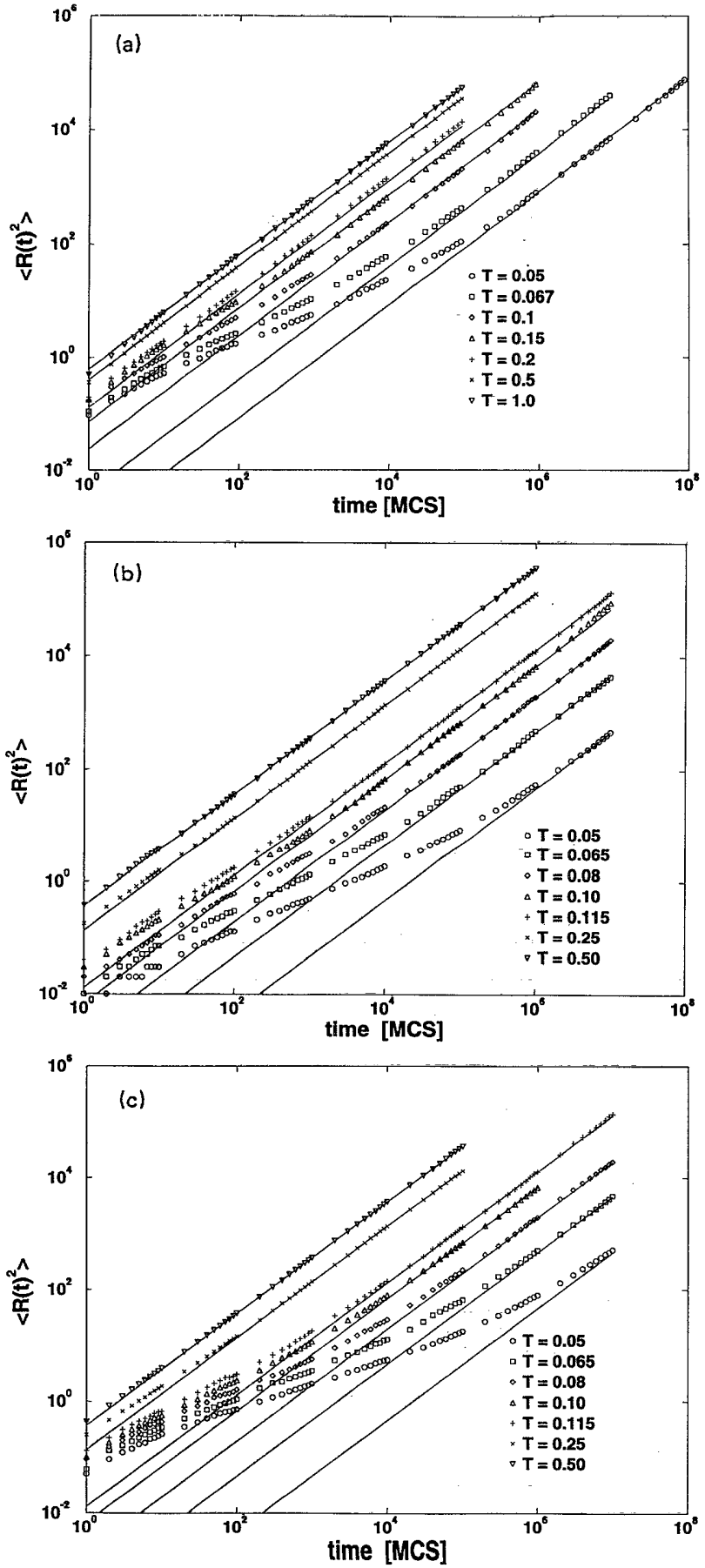

FIG. 1. Log-log plot of the mean-square displacement $\langle R^2 \rangle$ as a function of time (measured in MC steps) for several different temperatures on a square lattice with frozen-in disorder with (a) exponential PDF of the barrier heights, (b) a Gaussian distribution of barriers and $\sigma = 0.1667$, and (c) uniform PDF and $\sigma = 1.0$. Symbols denote simulational data, full lines correspond to the EMA results according to Eq. (9). The parameter T plotted here corresponds to the parameter α via $\alpha = k_B T/\langle E \rangle$, implying that we use $k_B = 1$, and that T is measured in units of $\langle E \rangle$.

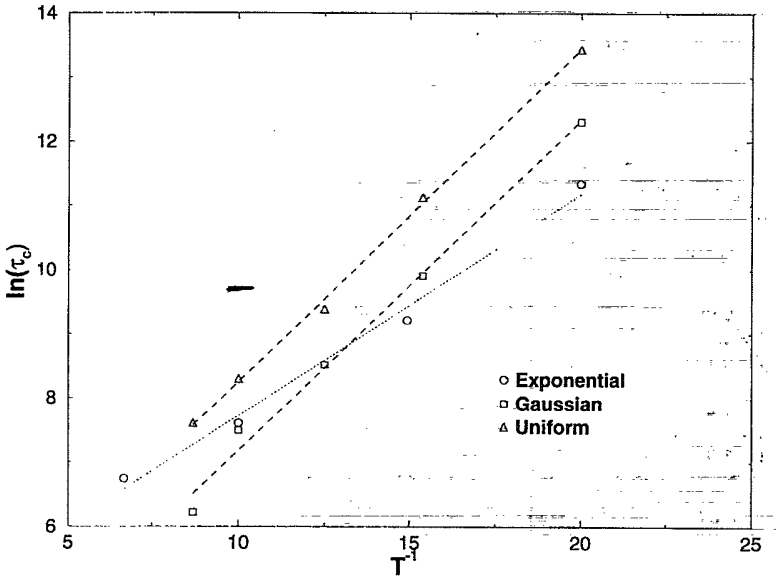

FIG. 2. Arrhenius plots of the measured crossover times τ_c vs inverse temperature for the data shown in Fig. 1. The slopes, determined by the least-square method, are 0.3453 — exponential PDF, 0.514 — Gaussian PDF, and 0.518 — uniform PDF.

$E \leq E_p$ is p_c. As shown previously [18], E_p is simply given by

$$\int_0^{E_p} \nu(E)dE = p_c, \tag{21}$$

where $\nu(E)$ is the PDF of the energy barriers and p_c depends on the coordination number of the lattice z and on the space dimension. On a square lattice $p_c = 0.5$ for the case of bond percolation [19]. Inserting Eq. (3) with $\langle E \rangle = 0.5$ into Eq. (21) one obtains $E_p = 0.5\ln(2) \approx 0.3466$ which nearly coincides with the value of the slope in Fig. 2(a). For the other two PDF's one has, similarly, $E_p = 0.5$ which agrees favorably with the slopes measured from the respective Arrhenius curves for τ_c [Figs. 2(b) and 2(c)]. In a recent paper [14] the crossover between anomalous and normal diffusion was investigated by a time-dependent EMA for the uniform PDF of energies. The analytic results derived from the EMA were in agreement with the previous numerical results [5]. At temperatures when the thermal energy of the particle is high enough [cf. the $\langle R(t)^2 \rangle$ curves for $T = 0.25$ and $T = 0.5$ in Fig. 1], all bonds (channels) are practically conducting and the regular diffusion relationship is recovered.

It is to be expected that this picture will be affected by the degree of disorder present in the random medium. Increasing dispersion σ enhances the differences in the energetic landscape with deeper valleys and higher ridges present which will be experienced by the tracer particle at low temperature. In Fig. 3 we present MSQD vs t data at $\alpha = 0.1$ and for various σ in the Gaussian (a) and uniform (b) PDF. Qualitatively both plots look very similar. With increasing degree of disorder σ the subdiffusive regime is progressively more pronounced whereas at sufficiently long times all curves merge to a *single* curve with slope one.

It is interesting to note also that the early-time regime of anomalous diffusion in Fig. 3 may be subdivided into an initial period when the slope of the MSQD is nearly unity, and a subsequent interval which is marked by a reduced slope of the $\langle R(t)^2 \rangle$ vs t relationship. This latter slope is seen from Fig. 3(b) to decrease steadily with increasing degree of disorder σ. While the onset of this subsequent period of highly correlated and localized movement seems to coincide roughly with the number of time units (MC steps) needed for a particle to perform a nonzero MSQD on a regular lattice (cf. the cases with lowest σ in Fig. 3), the crossover times τ_c from anomalous to normal diffusion appear to be independent of the degree of disorder σ whatsoever. Indeed, since both the Gaussian and uniform PDF are symmetrical, at any σ there will be a concentration of low barriers with height $E \leq \langle E \rangle$ equal to the percolation threshold p_c and the effective stay time in a valley of low energy barriers will be determined by the largest barrier height among the low ones, $\tau_c \propto \exp(\frac{\langle E \rangle}{k_B T})$.

We now turn to the discussion of how the asymptotic diffusion coefficient D_∞ depends on the degree of disorder, i.e., on the form and the width of the PDF of the barrier heights. The EMA results for D_∞ were utilized to insert straight lines of slope 1 into Figs. 1(a)–1(c), 3(a) and 3(b), and 4. In almost all cases one observes very good agreement between the EMA predictions and the simulation results for long times.

Figures 1(b) and 1(c) show that the *asymptotic* behavior of the MSQD of particles is identical for the Gaussian and uniform distribution of barriers on square lattices. The asymptotic diffusion coefficient is simply given by $4\Gamma_0 \exp(-\langle E \rangle / k_B T)$, cf. Eq. (15). It was already pointed out in Sec. III that for square lattices and symmetric PDF of the energy the EMA result coincides with the critical-path result.

As Fig. 1(a) shows, D_∞ depends less strongly on α for the exponential PDF than in the other two cases. When the critical-path approach is applied to predict D_∞ for this case, one expects a critical energy of $E_p = -\langle E \rangle \ln 2$,

as derived for the crossover behavior, cf. Eq. (21). The expression $D_\infty = 4\Gamma_0 \exp(-E_p/k_BT)$ does not agree with the EMA and the simulation results. The critical-path prediction is 30–20 % larger than the EMA results, with a reduced difference at smaller α values. We conclude that for this PDF the critical-path prediction is not exact, except perhaps in the limit $\alpha \to 0$.

The dependence of the MSQD on the width σ of the Gaussian and the uniform distribution was examined in Figs. 3(a) and 3(b) for square lattices. One observes that the asymptotic diffusion coefficient does not depend on σ, in agreement with the EMA results. See also the discussion in Sec. III. Figure 4 demonstrates that D_∞ does depend on σ in d=3 and for the uniform distribution of barrier heights, again in agreement with the EMA predictions. It is interesting to note that the diffusivity is enhanced by increasing the width of the distribution. The qualitative reason for this behavior is discussed in Sec. V. In the case of the full width $\sigma = 1$ of the distribution of activation energies there appears a difference between the EMA prediction and the simulation results. Luck [20] has calculated the difference between the EMA and an exact perturbation expansion. For the small value of the parameter α used, this difference becomes visible in the simulation data, see also [10].

The results for the dependence of the asymptotic diffusion coefficient D_∞ on the width of the distribution are at variance with the predictions of Limoge and Bocquet [9]. Comments on this disagreement are also made in Sec. V.

Eventually in Fig. 5 we compare the temperature dependence of the asymptotic diffusion coefficient D_∞ for

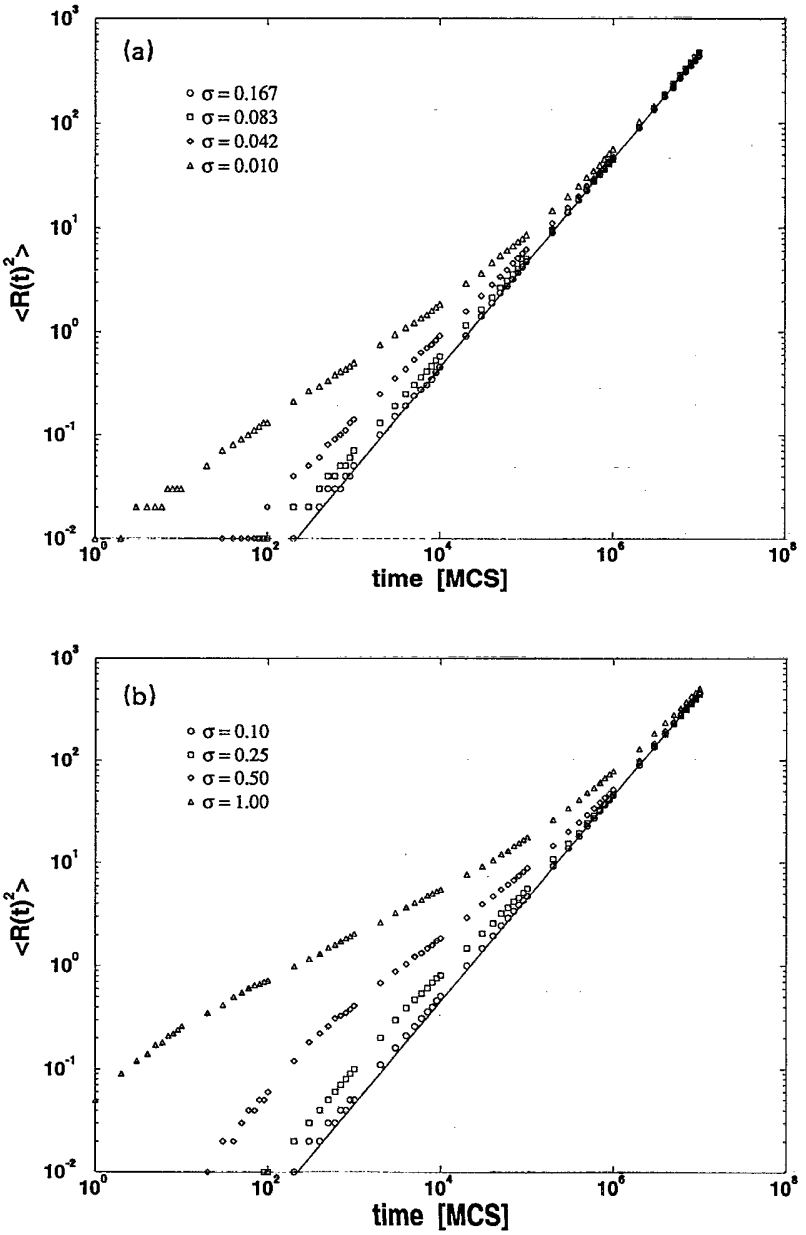

FIG. 3. Log-log plot of the mean-square displacement $\langle R^2 \rangle$ as a function of time (measured in MC steps) on a square lattice for several different values of the variance σ and $T = 0.05$: (a) Gaussian PDF; (b) uniform PDF. Symbols denote simulational data, full lines correspond to the EMA results according to Eq. (9).

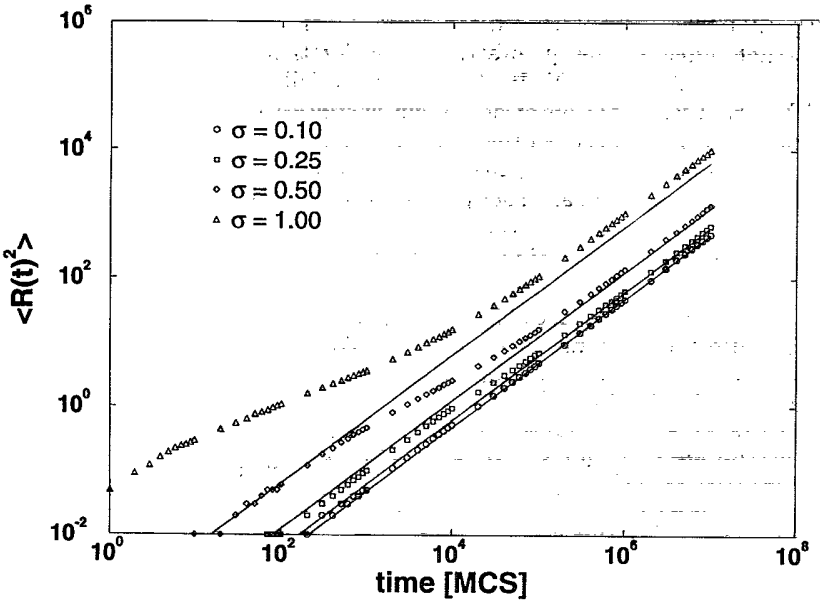

FIG. 4. The same as in Fig. 3 with uniform PDF for the cubic lattice.

the cases of static (frozen-in) and *dynamic* disorder. As an example, we choose the uniform PDF for which also our previous data [5] in the case of dynamic disorder, i.e., the barrier height changes at random upon each attempted jump of the particle, are shown. Evidently, on the square lattice $z = 4$ in 2D the D_∞ vs T relationship for static disorder is of purely Arrhenius type with a single effective activation energy ≈ 0.49, which coincides within the error limits with the average barrier height $\langle E \rangle = 0.5$. An upward curvature of $D_\infty(T)$ for the RBM is observed if the barrier heights change at the same rate as jumps of the particle are performed. We believe that this is an important finding which distinguishes qualitatively static from dynamic disorder. It may be related to the numerous experiments on viscosity in glass-forming melts where the well known non-Arrhenian curve of the viscosity vs temperature dependence changes abruptly to an Arrhenian-like with the onset of vitrification in the undercooled melt [18].

V. CONCLUDING REMARKS

We have used MC simulational technique to study the diffusion properties of particles in a random environment modeled within the framework of the random barrier model. A general feature of diffusion in amorphous media, namely, the transition from subdiffusive to normal diffusive regime at crossover times, which reveal an Arrhenian dependence on temperature, has been interpreted in terms of percolation theory. Consistent results

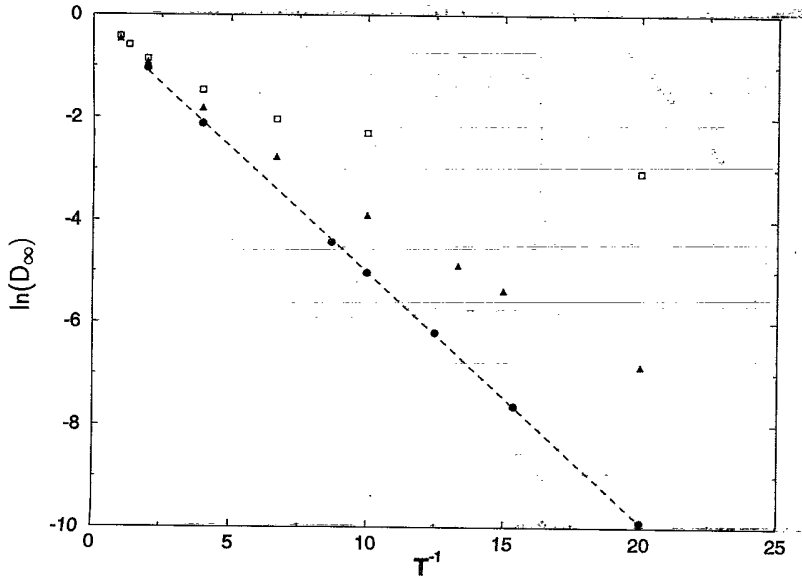

FIG. 5. Arrhenius plot of the diffusion coefficient D_∞ for the case of static disorder (full circles) and dynamic disorder (empty squares) of barriers on a square lattice. The slope of the dashed line is ≈ 0.49. Full triangles denote the case of static disorder on a cubic lattice.

have been obtained for different PDF of the energy barrier heights which separate adjacent sites. In all cases a single effective energy barrier governs the transition to normal diffusion, and this barrier is directly related to the percolation threshold p_c of bond percolation.

We have studied the influence of the *distribution* of energy barriers on the asymptotic diffusion coefficient D_∞. Does the form or the width of the distribution influence this coefficient? We have derived D_∞ by the effective-medium approximation and have estimated it by long-time MC simulations. The theoretical predictions were in very satisfactory agreement with the simulation results. We found that the answer to the above question depends on the coordination number z, or on the dimensionality of the lattice. In square lattices with z=4, D_∞ is given by the median barrier height, if the distribution is symmetric about it. It is independent of the degree of disorder, i.e., it does not depend on the width of the distribution in the two cases where the width can be varied. In the simple-cubic lattices where $z = 6$, the asymptotic diffusion coefficient does depend on the degree of disorder. In this case D_∞ is enhanced by increasing disorder. This is in qualitative agreement with the prediction of the critical-path approach. Namely, for $z > 4$ the bond percolation threshold yields values of the critical barrier that are below the median value. In these lattices, where there exist easy paths extending over the infinite lattice, the critical barriers are lowered when the width of the distribution is increased. In contrast, in $d = 1$ diffusion is progressively hindered by increasing the width of the energy barrier distributions.

The qualitative behavior of the temperature dependence of D_∞ depends both on z and on whether the random environment changes with time or not. For static disorder on a lattice with $z = 4$ we observe an Arrhenian dependence of the diffusion coefficient on temperature in sharp contrast to the case of dynamic disorder where a non-Arrhenian relationship is found. Limoge and Bocquet [9] postulated compensatory effects between the influence of random barriers and of random traps on the temperature dependence of the asymptotic diffusion coefficient. Their predictions were based on approximate calculations for the random-barrier and for the random-trap model. They assert a dependence of D_∞ in the random-barrier case on the width of the distribution, independent on the coordination number or dimensionality. This assertion is in contradiction to our results, which show a dependence on dimensionality. It remains to be examined whether the postulated compensatory effect between the random barriers and the random traps really exists in two- or three-dimensional lattices.

ACKNOWLEDGMENTS

This project was supported by EU grant Copernicus, No. CIPA-CT93-0105. One of us, A.M., is indebted to Professor K. Binder at the Institute of Physics, Johannes-Gutenberg University, Mainz, Germany, during a stay supported by the Deutsche Forschungsgemeinschaft (DFG) under Grant No. 436-BUL-113/45.

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