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Monte Carlo study of relaxation and diffusion in glassy systems

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Using a combination of Monte Carlo and analytical techniques we present an analysis of the random-walk problem of a particle diffusing in a system with energetic disorder. The particle is allowed to hop anywhere in the lattice and the rates vary exponentially with distance. We consider the number of new sites visited, the average energy, and diffusivity as a function of time and temperature. Deviations from mean-field theories are most pronounced at low temperatures when the relaxation can "freeze" at dead ends and deep traps. The Monte Carlo data can be summarized in terms of generalized analytical relations with a wide range of applications.

I. INTRODUCTION

An inherent feature of a glass is that both the ground-state energies as well as the excitation energies of its constituting elements are subject to a distribution much wider than one would expect for a system in thermodynamic equilibrium. Both the structure of the glass itself and the electronic excitations of its basic units are therefore subject to relaxation, towards equilibrium. The relaxation rate depends on the energy distribution of the sites involved in the diffusion process and the strength of intersite coupling.

The relaxation process can involve single-particle motion, the diffusion of two-level systems in glasses,[1] multiparticles, or spins such as in spin glasses,[1] for example. Even when the process does not involve many particle transitions or processes involving groups of atoms, the final equilibration dynamic can often be modeled in terms of *an effective single particle* undergoing random walk in a spatially and energetically disordered network. The connection between energy relaxation, random-walk, and spin-glass relaxation has been discussed recently in the paper by Larsen.[2]

In this paper we focus on the question of how fast an electronic excitation, an exciton or a charge carrier, generated at time $t=0$ at an arbitrary site of a glass loses energy by moving incoherently within the density of states (DOS) distribution of site energies. In doing so we draw heavily on previous work, both experimental[3,4] and theoretical,[5–8] establishing the existence of two types of relaxation regimes distinguished via the ratio of the spread of the site energies relative to kT. For a disorder parameter $\sigma/kT \lesssim 6$, σ being the width of the DOS, assumed of Gaussian shape, relaxation is aided by occasional thermally activated jumps of the excitation. The site-specific contribution to its total energy decay as $-\Delta\varepsilon \sim \ln t$ with a tendency to saturate at $(\delta\varepsilon)_\infty = \cong -\sigma^2/kT$.[6] For $\sigma/kT \gg 6$ thermally activated jumps are eliminated.

Therefore, a particle may be unable to escape from an even moderately deep state within the DOS. Relaxation is slowed down and has been predicted to follow a $\Delta\varepsilon \sim \ln\ln t$ law.[8] Both relaxation regimes have recently been discussed in relation to carrier hopping with the exponential distribution of tail state of amorphous inorganic semiconductors such as *a*-Si.[9] The "nonactivated relaxation" (NAR) mode, often termed the regime of pure hopping down motion, is realized at short times, while at a moderate degree of disorder particles enter the regime of "activated relaxation" (AR) after a critical time, called the segregation time t_S. For $t > t_S$ excitations redistribute by thermal excitation to transport states and subsequent recapturing in deeper states.

An exponential DOS realized in amorphous inorganic semiconductors[10] allows for approximate yet simple analytical treatments of the transition between both transport modes.[11] Unfortunately, its replacement by a Gaussian DOS, more appropriate for organic glasses,[12,13] renders the problem intractable in any simple terms. Movaghar and co-workers[5,7] have applied an effective medium approach (EMA) to treat the case of moderate disorder and extracted an asymptotic solution from an exact analytic calculation of the NAR relaxation case[7] without, however, being able to combine both relaxation regimes and the transition among these by an unified analytical approach. Bearing this difficulty in mind we have conducted a Monte Carlo (MC) computer study to unravel the complexities of excitation transport within a Gaussian DOS. Special emphasis will be placed on the rate of relaxation and transport as a function of site concentration, focusing on the question whether or not dilution of a hopping system leads to freezing in of the relaxation process, i.e., an AR→NAR transition, as does temperature reduction. A discussion of the results in terms of an extension of previous analytic approaches will lead to a unified description of diffusion and energy relaxation in disordered hopping systems with an arbitrary degree of disorder.

II. SIMULATION TECHNIQUE

The simulation system was a lattice of cubic symmetry with lattice constant a, consisting of $(101)^3$ point sites; see Ref. 14 for computational details. Dilution has been modeled by labeling the sites randomly as transporting or nontransporting sites via their energy. Imposing an energy difference of 3 eV between both restricts excitation transport to the former. A Gaussian DOS for the energies of the hopping sites has been established by picking random numbers from a Gaussian distribution of random numbers of width σ. After generating an excitation at random within the DOS the random walk is followed as a function of time. The motion is governed by an intersite jump rate

$$W_{ij}=\begin{cases}\nu_0\exp(-2\gamma R_{ij})\exp\left[-\dfrac{(\varepsilon_j-\varepsilon_i)}{kT}\right], & \varepsilon_j>\varepsilon_i\ ,\\ \nu_0\exp(-2\gamma R_{ij}),\quad \varepsilon_j<\varepsilon_i\ , & \\ R_{ij}=|\bar{R}_j-\bar{R}_i|\ , & \end{cases}\tag{1}$$

where ν_0 is a prefactor, and γ denotes the inverse decay length of the localized wave function, the time scale of the computation is set by $t_0=\frac{1}{6}[\nu_0\exp(-2\gamma a)]^{-1}$ which is the residence time of an excitation at an arbitrary site of an energetically degenerate system. Equation (1) implies intersite coupling via the exchange interaction, valid for triplet excitation in molecular solids and charge carriers. The neglect of an energy matching condition for downhill jumps is justified by low-temperature triplet transport studies in organic glasses[4] which suggests that energy dissipation does not limit the intersite hopping rate. This is readily explained in terms of the rich phonon spectrum of amorphous solids affording acceptor modes for virtually any quantum to be released in the course of a downward jump. Motion of an excitation is followed as a function of time employing previously tested MC programs[14,15] allowing an excitation to survey 342 acceptor sites from any site it momentarily occupies. The time frame of the computation covered 10 decades. It was subdivided into 200 logarithmically equidistant intervals. At the end of each interval the number of jumps $N(t)$ an excitation has executed, the number of new sites $\hat{S}(t)$ visited, the energy $E(t)$ of the site relative to the center of the DOS the excitation occupies, as well as the mean-square displacement $[\Delta r(t)/a]^2$, are stored. We checked that averaging near the individual events occurring within the time intervals has no effect on the statistics. The computation is terminated at $T=10^7 t_0$. Typically 3000 excitations per parameter set have been followed, the site energies being reset after every twentieth excitation.

III. RESULTS

A valuable feature of MC simulation is that it allows keeping track of an excitation during its random walk across a sample. This provides a handle on the details of particle dynamics not generally amenable via experiment or analytic techniques that rely on an effective medium approach (EMA). A quantity of interest for the description of stochastic transport processes is the number of new sites $\hat{S}(t)$ an excitation has visited after a time t. In Fig. 1 we present plots of both $\hat{S}(t)$ and the total number of jumps $N(t)$, executed in an undiluted sample $(c=1)$ at temperatures $T=25$, 77, and 250 K, respectively, equivalent to disorder parameters $\sigma/kT=42$, 13.6, and 4.2, respectively, for $\sigma=90$ meV which is a realistic choice for organic glasses. While for $t/t_0\lesssim 10$, $N(t)\simeq\hat{S}(t)$, $N(t)$ increases faster than $\hat{S}(t)$ at longer times. Finally a linear t dependence is approached because the probability of an excitation to encounter a pair of energetically deep sites where it keeps oscillating without contributing to diffusion increases with time.

A first illustration of the interplay between nonactivated and activated excitation dynamics is contained in Fig. 2 showing $\hat{S}(t)$ versus $\log t/t_0$ at variable σ/kT. In the strong disorder case, $\sigma/kT=42$, thermally activated processes are eliminated and $\hat{S}(t)$ grows as

$$\hat{S}(t)\sim(\ln t/t_0)^{n_0}\ ,\tag{2}$$

where n_0 is an exponent.

As σ/kT decreased, thermally activated processes are turned on at progressively shorter times giving rise to an additional thermal contribution $\hat{S}^{(T)}(t)$ to $\hat{S}(t)$. $\hat{S}^{(T)}(t)$ no longer follows a logarithmic time dependence but varies as t^α, characteristic of dispersive transport, the dispersive transport, the dispersive parameter α decreasing with increasing temperature (α values are 0.6, 0.55, and 0.22 for $\sigma/kT=4.2$, 4.5, and 13.6, respectively). At long times, $\hat{S}^{(T)}(t)$ curves approach a linear t dependence signaling dynamic equilibrium characterized by a time-

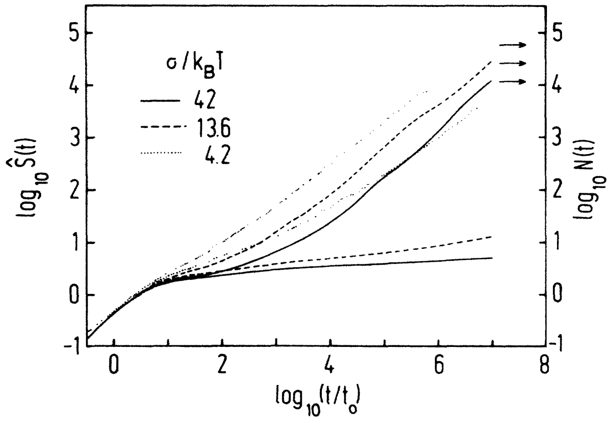

FIG. 1. Number of new sites $\hat{S}(t)$ an excitation has visited after a time t (left scale) and total number of hops executed, $N(t)$ (right scale) as a function of normalized times and degree of disorder. The t_0 is the dwell time of an excitation at an arbitrary site of an undiluted lattice composed of isoenergetic sites.

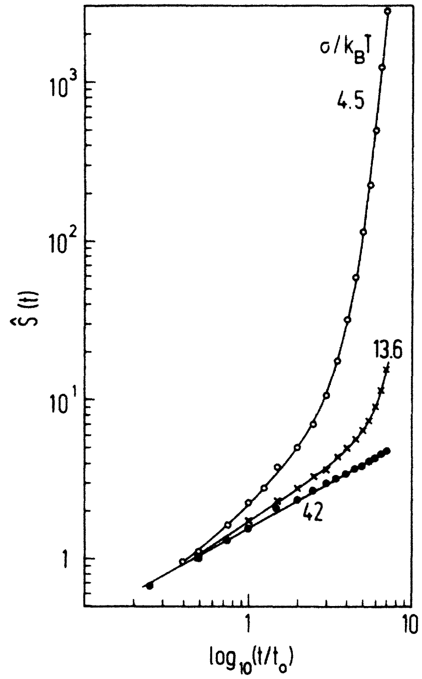

FIG. 2. $\hat{S}$ vs $\log t/t_0$ plotted on a double-logarithmic scale for different σ/kT. Data points in this and the following figures are taken from continuous computer printouts.

dependent distribution of hopping rates. As shown in Fig. 3, $\hat{S}^{(T)}(t)$ as a function of concentration reveals the expected decrease of α as the sample becomes more and more dilute. This illustrates the role of growing spatial disorder on the degree of dispersion of excitation transport in a system of both energetic and positional disorder. The variation of α with concentration prevents casting the dependence of $\hat{S}^{(T)}(c,t)$ into a simple analytic expression. We only note that for $t/t_0>10^2$,$\hat{S}^{(T)}(c,t/t_0=\text{const})$ rises superlinearly with c.

In summary we note that the functional dependence of $\hat{S}(t)$ is a criterion for distinguishing among activated and nonactivated excitation motion. At finite T the transition between both transport modes extends over several decades in time revealing the broad distribution of individual event times. For $\sigma/kT=4.5$, henceforth designated as the moderate-disorder case, activated dispersive motion dominates essentially the entire time frame of practical interest, while at $\sigma/kT=13.5$, henceforth termed the strong-disorder case, nonactivated motion prevails up to five or six decades in normalized time.

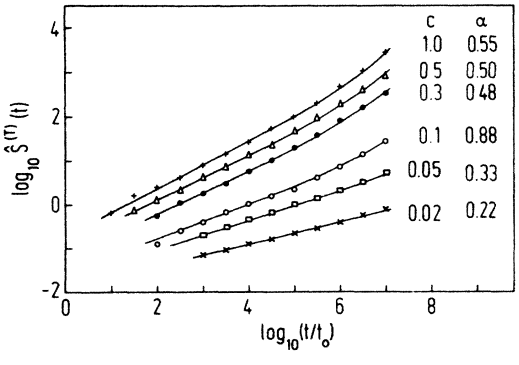

FIG. 3. Time dependence of $\hat{S}^{(T)}(t)$ resulting from thermally activated hopping ($\sigma/kT=4.5$). Parameter is the relative concentration c of transport sites, α is the dispersion parameter, inferred from the slopes.

Tamor[16] has computed the quantity $\hat{S}(t)$ versus t as a function of t using MC on a cubic lattice with nearest-neighbor hopping only and an exponential density of states. He finds an excellent fit to a dispersive law of the type $S(t)\sim t^{\alpha}$ where $\alpha(T)$ increases with temperature and approaches one above a critical temperature. His data suggest that the particle is "quasilocalized" even at finite T (low T) meaning that $\delta\hat{S}(t)/\Delta t\to 0$ as $t\to\infty$, or, in other words, that the diffusivity vanishes in the long limit. The quasilocalization in this case must be related to the nearest-neighbor hopping model. For infinite-range hopping as allowed in this paper the equilibrium long-time diffusivity must necessarily be finite for $T>0$.

The fact that $S(t)$ appears to obey a weaker time dependence, namely (2), than in Tamor's work is related to the temperature and the time regime. One has to distinguish several situations rather carefully. In the first place there is the situation $T\to 0$ where the particle experiences no returns at all to the origin. Here the sites become more and more depleted after each step and there is rigorously no long-time diffusion. The $(\ln t)^{n_0}$ with $n_0=d$, the dimensionality of the lattice is rigorously true in this limit. On the other hand for $T>0$, there is, strictly speaking, always a steady state with $D(t\to\infty)\neq 0$ so that in the strictly asymptotic domain $S(t)\sim t$ when $T>0$. This dependence may, however, be "experimentally" unattainable for finite times and the time law will behave as $S(t)\sim t^{\alpha}$ for a large portion of the curve. Indeed we can conclude that for times for which there is essentially no return to the "origin" (or closed loops), i.e., $t<t_s$, the $(\ln t)^{n_0}$ law characteristic of $T\to 0$ is the correct representation. As time progresses and loop processes take place, $t>t_s$ and we crossover from the NAR to the AR regime when approaching a steady state, a gradual change to t^{α}, and finally t should take place. Finally, one should also note that it is very difficult to distinguish (2) from t^{α} as $\alpha\to 0$ or $T\to 0$.

The similarity between diffusion on a disordered lattice and an effective fractal lattice has been discussed in the work of Tamor. The nature of diffusion and trapping on real fractal lattices has been investigated by Blumen *et al.*[17]

The energy of the relaxing excitations relative to the center of the DOS and normalized to σ is portrayed in Fig. 4(a) which demonstrates that increasing the degree of disorder in an undiluted sample has no effect on the short-time relaxation yet reduces the rate of relaxation at longer times. In accord with intuitive reasonging Figs. 4(b) and 4(c) show that the rate of relaxation is slowed down upon sample dilution. In the moderate disorder case, $\langle E(t)\rangle/\sigma$ approaches a $\ln t$ law at long times. Anticipating the result of the data analysis to follow (Sec. IV) we note that the relaxation pattern observed for

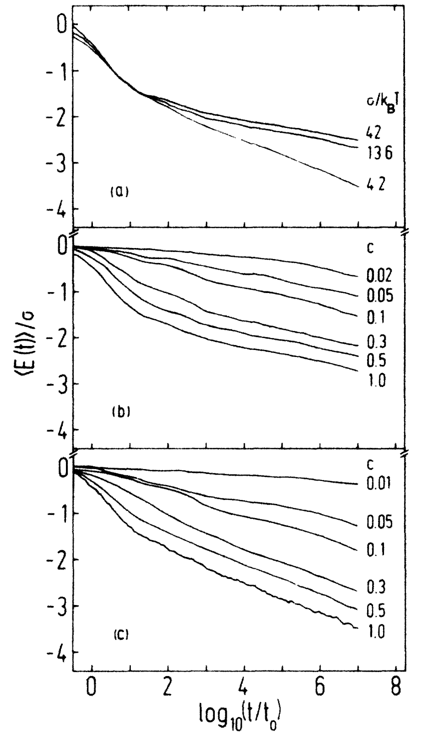

FIG. 4. Computer printouts for the mean energy $\langle E \rangle$ of an excitation, normalized to the Gaussian width σ of the DOS, as a function of time and concentration. Comparison of $\langle E(t)\rangle/\sigma$ for undiluted lattices and $\sigma/kT=42$, 13.6, and 4.2 (a), respectively, (b) and (c) show $\langle E(t)\rangle/\sigma$ for $\sigma/kT=13.6$ and 4.5, respectively, at various concentration c.

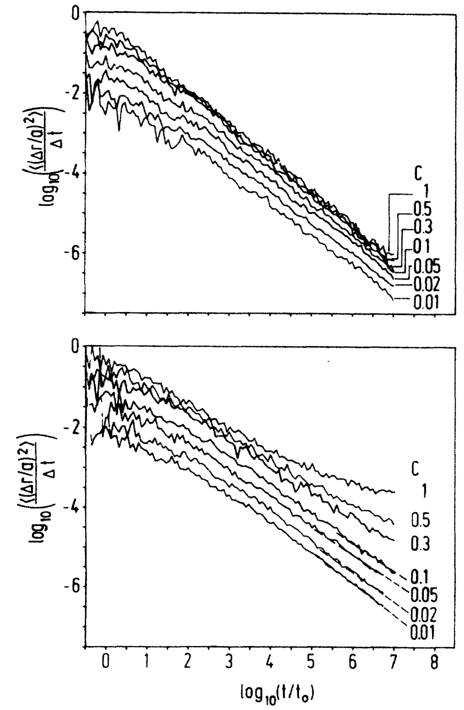

FIG. 5. Mean-square displacement of an excitation per time interval Δt as a function of time and concentration and for $\sigma/kT=13.6$ (upper plot), $\sigma/kT=4.5$ (lower plot).

$\sigma/kT=42$ and 13.6 is of the $\ln\ln t$ type and thus a signature of the freezing effect occurring in the low-T/large disorder case.

Analysis of the energy relaxation function is to some extent hampered by small-amplitude oscillations seen in the computer printouts for $E(t)/\sigma$. Their correlated appearance at different concentrations rules out insufficient MC statistics as a potential reason. Instead, we have to consider that the structure of the simulation lattice gives rise to metastabilities as far as jump statistics and, concomitantly, energy relaxation is concerned. If, for instance, an excitation becomes temporarily localized at a low-energy dimer site within which it keeps oscillating, the probability of escape from one of the sites is reduced because the probability of occupying the escape site is reduced. The fact, that the oscillations vanish if $\Delta E(t)/\alpha$ is plotted versus $\hat{S}(t)$ (see discussion) supports this notion.

The velocity at which an electronic excitation or a charge carrier generated in an amorphous structure is transported is governed by the time derivative of its mean-square displacement, $D(t)=d[\Delta R^2(t)]/dt$. While being constant in the case of Gaussian transport, $(\alpha=1)D(t)$ decays with time if motion is dispersive. We present in Fig. 5 plots of $d[(\Delta R^2(t)]/dt$ as a function of time on a log-log scale for $\sigma/kT=13.6$ and $\sigma/kT=4.5$, respectively. In both cases $D(t)$ can be represented to a good approximation by power laws. We note, however, that the slopes approach the value dictated by $D(t)\sim d\hat{S}(t)/dt\sim t^{\alpha-1}$ only in the long-time limit. This illustrates that inferring the time-dependent diffusivity of an excitation from its mean-square displacement rather than from $d\hat{S}(t)/dt$ is an approximation rigorously justified only at longer times. For $\sigma/kT=4.5$ and $c\geq 0.1$, $D(t)$ tends to saturate at long times indicating that the system is approaching dynamic equilibrium. In the strong-disorder case α approaches unity in the long-time limit. It is, however, obvious that in a real experiment probing transport of triplet excitations in diluted systems the asymptotic law may not be reached within their intrinsic lifetime.

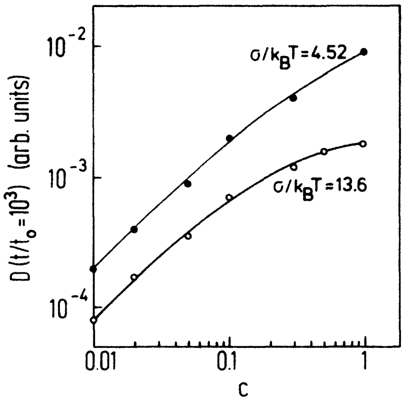

FIG. 6. Mean diffusivity of an excitation after a time $t/t_0=10^3$ as a function of concentration.

We finally show in Fig. 6 that at a given time the diffusivity scales linearly with concentration for $c < 0.1$ and begins leveling off for $c \gtrsim 0.1$. This is clear evidence against the existence of a percolation threshold at times where the transporting particles have not yet reached dynamic equilibrium.

IV. DISCUSSION

A. The strong-disorder case

The large body of MC data collected for disorder parameters $\sigma/kT = 42$ and 13.6, where the nonactivated relaxation (NAR) regime is strictly or approximately realized, allows detailed comparison with the analytic $T \rightarrow 0$ version of the Movaghar, Ries, and Grünewald[8] (MRG) relaxation theory for a Gaussian DOS. While this theory predicts a short-time behavior identical to that following from the EMA at arbitrary T, the asymptotic long-time behavior should obey a characteristic double logarithmic time dependence

$$\left[\frac{\Delta E}{\sigma}\right]^2 \alpha \ln \ln(\nu_0 t)^{\alpha_0(t)} , \tag{3a}$$

where

$$\alpha_0(t) = (n/6)[\ln(\nu_0 t)]^{d-1} \bar{F} . \tag{3b}$$

n is the site density, d is the dimensionality of the lattice, and $\bar{F} = \int \exp(-2\gamma R_{ij}) d\mathbf{R}_{ij}$ is the spatially averaged overlap factor controlling the jump rate. More rigorous analytic treatment yields a proportionality factor of about 3.5 in Eq. (3a). From the $T = 0$ theory for the energy of an excitation and its diffusivity it follows immediately that the dependence on time and concentration is given by a function of the form

$$t(n) = n \int_0^\infty d\mathbf{R}(1 - e^{-\nu_0 F(R) t}) . \tag{4}$$

Evaluation of the integral leads to a scaling relation between the relative concentration $c = na^3$ and the reduced time $t\nu_0 = t_1$. In the short-time limit a linear scaling law $t_1 \rightarrow ct_1$ is recovered, while in the long-time limit, $t_1(c) \rightarrow c[\ln(t_1)]^3$. This implies that at short times, $E(t)$ curves should only exhibit a parallel shift only if plotted versus ln(time), while at long times their slopes should also change. In the latter case universality is restricted to plots of $[\langle E(t) \rangle / \sigma]^2$ versus ln ln(time).

Plotting the $\langle E(t) \rangle / \sigma$ data for $\sigma/kT = 42$ on a $(E/\sigma)^2$ versus $\ln \ln \nu_0 t$ scale (Fig. 7) confirms the functional relationship implied by the $T = 0$ theory and shows that the asymptotic long-time behavior is quantitatively recovered. For $\sigma/kT = 13.5$ deviations are noted at times where thermally activated transitions become important leading to a faster decay of $\langle E(t) \rangle / \sigma$. Relaxation curves for variable concentration tail off asymptotically into a family of parallel shifted straight lines again in corroboration of theory. Unfortunately, the nonvanishing thermal contribution to relaxation at σ/kT in the long-time limit, precludes a rigorous test of the $c(\ln t_1)^3$ scaling relation. Nevertheless, an approximate check is provided by extrapolating those sections of the $[\langle E(t) \rangle / \sigma]^2$ versus $\ln \ln \nu_0 t$ plots that are parallel to the asymptotic part of the "ideal" $\sigma/kT = 42$ curve. The abscissa intercepts $\ln \ln(\nu_0 t_c)$ yields $4\pi/3(\gamma a)^{-3} \ln(\nu_0 t)^3 = 0.9 \pm 0.2$ independent of concentration for $1 \geq c \geq 0.02$. Without further documentation we note that the changes in the functional dependence of $\hat{S}(t)$ as a function of concentration, implied by Eq. (2), can also be accounted for in terms of the above scaling argument. We thus conclude that the MRG $T \rightarrow 0$ relaxation theory provides a quantitative description for energy relaxation in systems with strong energetic disorder and variable concentration, or, more generally, variable coupling among the sites active in transport. Nevertheless, we wish to add a cautionary note regarding uniqueness of the functional form of $\langle E(t) \rangle / \sigma$. The weak time dependence implied by a double-logarithmic law precludes distinguishing among Eq. (3) and a relation of the form $\langle E \rangle / \sigma \sim \ln \ln \nu_0 t$ on the basis of the quality of a data fit alone. Plotting MC data on a $\langle E \rangle / \sigma$ versus $\ln \ln \nu_0 t$ scale would reveal a similarly good qualitative fit for $c \geq 0.3$, systematic deviations being noticeable only for lower concentrations. It is the *quantitative* agreement which demonstrates the superiority of Eq. (3).

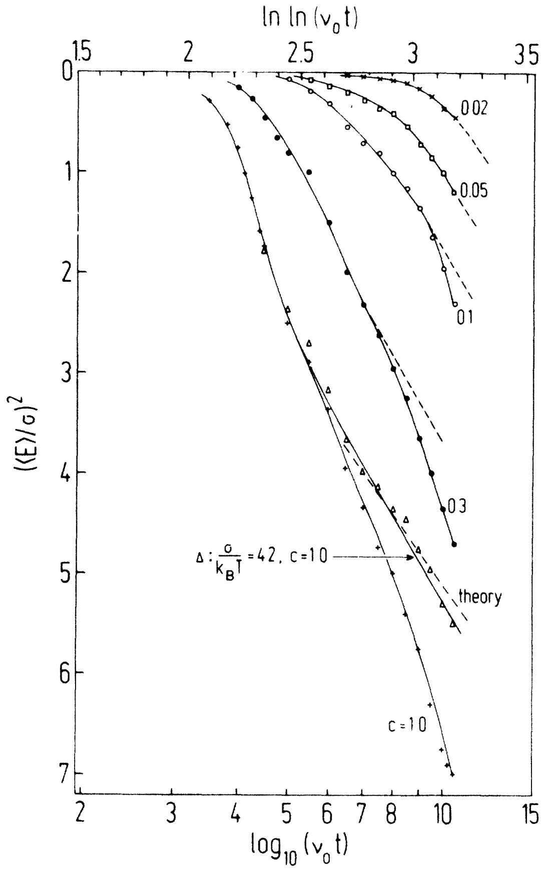

FIG. 7. $(\langle E \rangle / \sigma)^2$ vs $\ln \ln \nu_0 t$ for $\sigma/kT = 42$, $c = 1$, and $\sigma/kT = 13.6$ at variable concentration, respectively. The dash-dotted curve is the asymptotic behavior predicted by the analytic $T > 0$ theory.

Analysis of the MC data affords a possibility of getting deeper insight into the statistics of the relaxation by introducing the number of sites and excitation visits in course of its random walk as a variable not explicitly constrainted in the analytic treatment. Plotting $\langle E\rangle/\sigma$ as a function of $\hat{S}$ (Fig. 8) demonstrates that for $\hat{S}>1$, $\langle E\rangle/\sigma$ varies as $\ln\hat{S}$, the slope decreasing by about a factor of 2 upon reducing c from 1 to 0.05. It indicates that the incremental energy loss an excitation suffers per jump to a site not visited before decreases in proportion to $\hat{S}$. Since this behavior is independent of T (see also Sec. IV B) it proves that the dilution of states an excitation faces in the course of NAR does not only slow down its motion but imposes a tendency towards hopping at constant average energy which, however, will not be reached at realistic times for large σ/kT. It is remarkable that for $\sigma/kT=42$, where the $\langle E\rangle/\sigma\sim\ln\hat{S}$ law is strictly obeyed, an excitation has lost an energy of $\sim 2.3\sigma$ after having visited above five new sites, requiring seven decades in normalized time. Considering the logarithmic time dependence of $\hat{S}(t)$ (see Fig. 2) we conclude that the total number of new sites a particle can visit in course of a real-time experiment over the time frame $t_0<t<10^{14}t_0$ is of order 10 only.

Deviations from the $\langle E\rangle/\sigma\sim\ln\hat{S}$ relation are noted for $\hat{S}<1$ and $\hat{S}\gtrsim 4$. The latter indicates the onset of thermally activated hopping processes (see Sec. IV B). For $\hat{S}\lesssim 1$, $\langle E\rangle/\sigma$ is $\propto\hat{S}$ as expected, since an excitation on average started at the center of the Gaussian DOS will on average have three nearest-neighbor sites it can jump to without restriction.

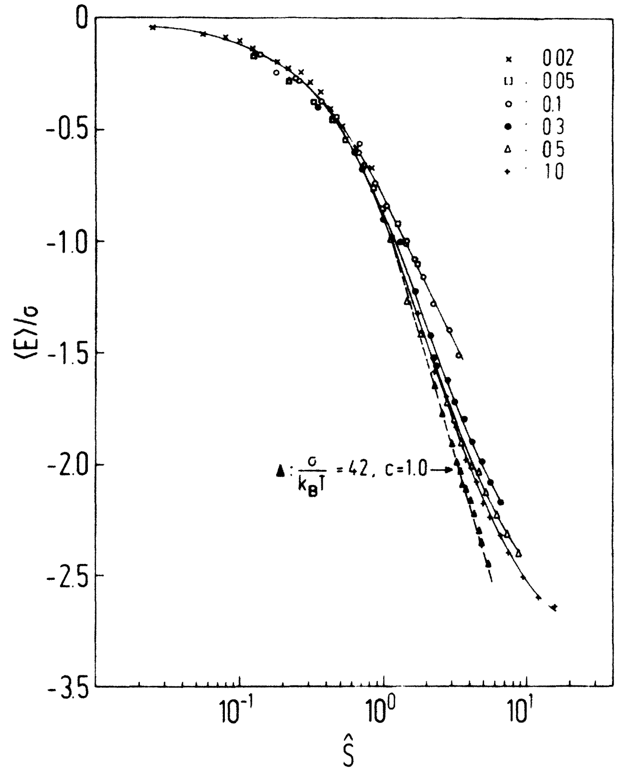

FIG. 8. $\langle E\rangle/\sigma$ vs $\hat{S}$ plotted on a lin-log scale for $\sigma/kT=13.6$ for various relative concentrations. For comparison the data set for $\sigma/kT=42$, $c=1$ is included.

B. The intermediate-disorder case

The changes in the relaxation pattern that occur upon increasing σ/kT from 13.6 to 42 are best seen by comparing plot of $\langle E\rangle/\sigma$ versus $\hat{S}$ (Figs. 8 and 9). The transition from the nonactivated to the activated relaxation regime, barely noticeable in the $\sigma/kT=13.6$ data, is now clearly visible via the change in slope of $\langle E\rangle/\sigma$ versus $\ln\hat{S}$ curves as the fact that $[\langle E\rangle/\sigma]$ versus $(\hat{S})$ continues to follow a logarithmic dependence. Although onset of thermally excited motions depresses the overall time scale of the relaxation process, it slows down the rate of relaxation if expressed in terms of the energy released to the lattice per new site visited. Raising T temporarily elevates an excitation to an energetic level from where its chances for finding relaxation paths is increased, yet by the same token does thermal agitation counteract energy dissipation. *It is remarkable that apparently the* $\langle E\rangle/\sigma\sim\ln\hat{S}$ *law is retained suggesting that it is specific for a given* DOS. An increase in T may be considered as a renormalization of the DOS a relaxing excitation is able to survey. We conjecture that this functional dependence is related to the form of the DOS. The analytical treatment of Sec. V will support this notion.

Figure 9 also indicates that (i) decreasing σ/kT leaves the NAR regime unaffected, (ii) approach of dynamic equilibrium, where the mean energy of an excitation equilibrates at $\langle E_\infty\rangle/\sigma\simeq\sigma/kT$ sets in for $\hat{S}$ of order of 10^3, and (iii) reducing the site concentration causes an upward shift of the segregation energy E_S at which the

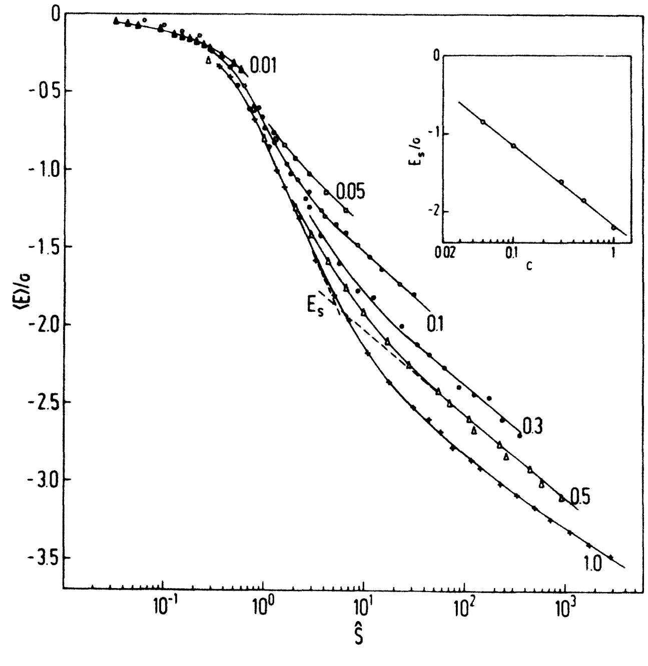

FIG. 9. $\langle E\rangle/\sigma$ vs $\hat{S}$ plotted on a lin-log scale for $\sigma/kT=4.2$ and variable concentration. The inset shows the variation of the segregation energy E_S with concentration. E_S is defined via the intersection of asymptotes as indicated.

NAR→AR transition occurs. E_S values, defined via the intersection of the $\langle E \rangle/\sigma$ versus $\ln\hat{S}$ slopes characterizing the NAR and AR regimes, vary logarithmically with c (see the inset of Fig. 9).

Analyzing E_S as a function of c and T allows a criterion for occurrence of the NAR→AR regime to be established. The fact that $\partial(\langle E_S \rangle/\sigma)/\partial\ln\hat{S}$ remains virtually constant upon reducing c clearly demonstrates that dilution does not induce an AR→NAR transition as one might surmise by qualitatively comparing of $\langle E(t,c) \rangle$ plots for moderate and strong disorder (Fig. 4). Instead, the quantitative relation between E_S and c, included in Fig. 9, can be translated into a relation between c and the number of hopping sites N_S at $E < E_s$ that are accessible via nonactivated jumps:

$$N_s = c(2\pi\sigma^2)^{-1/2} \int_{-\infty}^{E_s} \exp[-(E-E_s)^2/2\sigma^2] dE \ . \tag{5}$$

It turns out that $c_s = N_s/N = 0.013 \pm 0.003$ for $0.02 < 0 < 1$. This is the accord with the notion that the NAR→AR transition is determined by the competition between nonactivated downhill jumps and activated uphill jumps, the probability for the former being solely a function of N_s. At a given temperature $\langle E_s(c) \rangle$ must therefore be determined by the condition $N_s(cE_s) = \text{const}$.

Since uphill jumps are activated, E_s at constant c must experience an upward shift upon increasing T and the segregation time t_s after which the mean energy of an excitation has dropped to E_s must decrease accordingly. Meanwhile we know both from theory[4,6,18,19] and experiment[20,21] that the interplay between nonthermal and thermal transitions among the localized states of a Gaussian DOS leads to a non-Arrhenius T dependence of the mean hopping rate after attainment of dynamic equilibrium. It relates to the fact that the mean energy within a Gaussian DOS at which excitations settle in the long-time limit and which on average is the activation energy required for transport varies as σ^2/kT.

Indeed the long-time diffusivity within a Gaussian band has been evaluated explicitly using analytical and MC technqiues. From Ref. 7 we have that

$$D_\infty(T) = D_0 \exp[-(T_0/T)^2] \ , \tag{6a}$$

where T_0 is a constant proportional to the width σ of the DOS. The crossover time t_r to equilibrium varies as $t_r^\alpha D_\infty = \text{const}$ and $\alpha = 0.45$ (see Ref. 7). The present MC results, shown in Fig. 10, confirms the applicability of this concept to the entire time domain relevant for activated jump processes. It documents that the segregation time or equilibration time obeys the relation

$$t_S(c)/t_0 = A(c) \exp \left[\frac{+(\sigma/kT)}{(\sigma/kT)_0} \right]^2 \tag{6b}$$

with $kT_0 = 0.21\sigma$ for $c = 0.5$. The data points for $c = 1$ suggest that varying c leaves $(\sigma/kT)_0$ unaffected $[A(c=1) \approx 10^2]$. The slope parameter $(\sigma/kT)_0$ yields a characteristic temperature $T_0 = 2440\sigma$ (T in K, σ in eV), which is the equivalent of the activation energy in a conventional Arrhenius expression. Numerically T_0 is about a factor of 3 less than the value found for diffusion T_0 in the $t \to \infty$ limit. This is due to the fact that at the beginning of thermally activated processes an excitation is sampling easy activated transitions only.

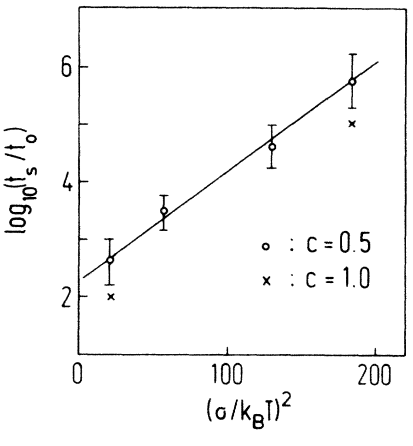

FIG. 10. Log-lin plot of the normalized segregation time t_S/t_0 vs $(\sigma/kT)^2$.

The condition that during an experimental time scale no NAR→AR transitions occurs, is $t_s/t_0 > t_{\text{expt}}/t_0$. Taking $t_{\text{expt}}/t_0 = 10^{12}$ yields $\sigma/kT > 23$ equivalent to $T \leq 50$ K for $\sigma = 0.1$ eV which is a typical value for the width of the DOS charge carriers in random organic solids.[20,21]

We end this section by comparing MC and EMA results. In doing so we draw on the scaling relation contained in the EMA in the limit $T = 0$, namely, $t_1 \to ct\nu_0\bar{F}$. It implies that upon varying the concentration energy relaxation curves $-\langle E(t) \rangle/\sigma$ should experience a parallel shift along the time axis when plotted on a $\ln\nu_0 t$ scale the slope remaining virtually unaffected. Although Fig. 11 bears out common features quantitative differences are, however, evident at low c. Recalling that the EMA does not properly account for the freezing in of energy relaxation in the $T \to 0$ limit because it notoriously overestimates relaxation paths, we attribute the discrepancies

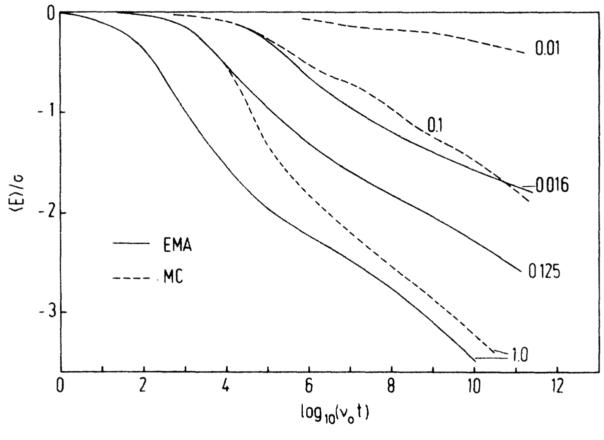

FIG. 11. Comparison of the rate of energy relaxation predicted by the effective medium theory (EMA) with the MC result for $\sigma/kT = 4.5$. Parameter is the concentration.

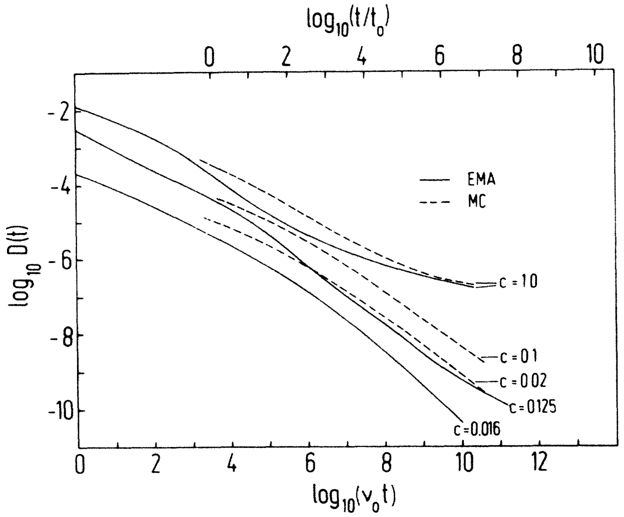

FIG. 12. Comparison of the diffusivity as a function of time predicted by EMA and the time derivative of the mean-square displacement of an excitation inferred from simulation. Parameter is the concentration.

seen in Fig. 11 to the spurious neglect of dead ends in the network of random walks in diluted systems. This neglect becomes more severe as the actual number of relaxation paths occurring in a real system is reduced by either eliminating thermally assisted hops or by dilution. While in the former case the system tends to become completely localized at $T \rightarrow 0$, concentration-inhibited relaxation favors hopping transport at an elevated energy level within the DOS (see above). As a consequence, the diffusivity calculated by EMA approaches a t^{-1} law at low c in formal analogy to the $T \rightarrow \infty$ case while MC data indicate the occurrence of dispersive transport. We note, however, that the shortcomings of EMA are less severe regarding diffusivity (Fig. 12) than they are regarding energy relaxation.

V. ANALYTICAL CONSIDERATIONS

The MC results and discussion presented above have uncovered a series of important empirical relationship which deserve closer examination from an analytical point of view. The most important relation found is the approximate proportionality

$$[\langle E(\hat{S})\rangle/\sigma]^2=\gamma(T)\ln\hat{S} \tag{7}$$

with a proportionality constant $\gamma(T)$ which depends on T. Let us attempt to derive the relationship between $\langle E\rangle$ and $\hat{S}$ analytically by first considering the $T \rightarrow 0$ limit. We argue that after having performed $\hat{S}$ steps (necessarily new sites at $T \rightarrow 0$), the average energy lost between the $(\hat{S}+1)$ and the $(\hat{S})$ step can be anywhere in the energy distribution up to the energy $E(\hat{S})$; thus

$$\bar{E}(\hat{S}+1)-E(\hat{S})=\int_{-\infty}^{\bar{E}(\hat{S})} dE'\,E'\rho(E') \,, \tag{8}$$

where $\rho(E)$ is the density of states. For a Gaussian of width σ the integral on the right-hand side (rhs) can be done analytically and expanding the left-hand side (lhs) as a continuum we have

$$\frac{\delta E(\hat{S})}{\delta\hat{S}}=\frac{\sigma}{(2\pi)^{1/2}}e^{-E^2/2\sigma^2} \,. \tag{9}$$

In the limit $\hat{S} \rightarrow \infty$ (long times) we obtain

$$E^2(\hat{S})/2\sigma^2=\ln\hat{S} \tag{10}$$

which is almost the empirical MC result (7). To check the consistency of (10), we now use the MC result for $\hat{S}(t)$ versus t as given by (2), and indeed recover the *exact asymptotic analytical law* (3) and plotted in Fig. 7 for the MC data provided that the exponent n in Eq. (2) is $n=3$. The scaling with site concentration is also given by (3). The deviations between the analytic and empirical observation are obviously well within the possible errors associated with asymptotic long times, temperature effects, and deviations from perfect linearity in the MC plots of Fig. 8. Finite-T effects can be included in (10) by adding to the rhs a term due to activated processes and given by

$$\Delta\left[\frac{d\bar{E}}{\delta\hat{S}}\right]\simeq\int_{E(\hat{S})}^{\infty} dE'\,E'e^{-E'/kT}\rho(E') \,. \tag{11}$$

The next question concerns the relationship between this result and the MC result (2) which gives $\hat{S}(t)$ as a function of t. Can we derive this analytically? First let us ask the following question: Can we derive a rigorous relation between the mean-squared displacement $[\Delta r(t,\varepsilon)/a]^2$ also written as $\langle R^2(\varepsilon,t)\rangle$ and $E(\varepsilon,t)$ using the $T=0$ theory from Ref. 8. For convenience we have defined ε as the start energy of the particle.

First we note that from the very basic integral equation for $E(\varepsilon,p)$ and $D(\varepsilon,p)$ given in Ref. 7 it follows that

$$\frac{\delta E}{\delta t}(\varepsilon_i,t)=\varepsilon_i\frac{\delta G_{ii}^0(t)}{\delta t}+\sum_l\int_0^t d\tau\, G_{ii}^0(\tau)W_{il}\frac{\delta E_l}{\delta t}(t-\tau) \,, \tag{12}$$

where $G_{ii}^0=\exp(-t\sum_l W_{il})$ and W_{ij} are the jump rates. We can relate this equation to the analogous one for the diffusivity if we write, for the configurational average of the first-order term of Eq. (60) in Ref. 8,

$$\begin{aligned}\left\langle\sum_l R_{il}^2W_{il}\exp\left[-\sum W_{il}t\right]\right\rangle&=D_i^0(t)\\&\simeq\bar{r}_0^{\,2}(\varepsilon_i,t)\frac{\delta}{\delta t}\langle G_{ii}^0(t)\rangle_i(-1)\end{aligned} \tag{13}$$

and neglect the time dependence of $\bar{r}_0^{\,2}$ as defined by (13). We also note that in the long-time limit, the initial energy dependence also disappears so that $E(\varepsilon_i,t)$ and $D(\varepsilon_i,t)$ are independent of ε_i as $t \rightarrow \infty$.

From (12) and the corresponding one for $D(\varepsilon,t)$ we thus obtain in the present (very good) approximation the general relation

$$\frac{-\delta E}{\delta t}(\varepsilon,t)\simeq\frac{6\bar{\varepsilon}}{\bar{r}_0^{\,2}}\Delta D(\varepsilon,t) \tag{14}$$

which is valid as long as we can neglect the time dependence of $\bar{r}_0^{\,2}$ from (13) and where ΔD is the time-dependent part, i.e., $\Delta D=[D(t)-D(t\to\infty)]$. This relation (up to weak functions of time and energy) should be valid even at finite T. Indeed Eq. (14) is even more accurate if the initial energy dependence is averaged over with some distribution function. Equation (14) can be verified at $T=0$ by using the results derived in Ref. 8 for $E(\varepsilon,t)$ and $D(\varepsilon,t)$.

For the case T strictly$=0$, we can in principle derive an even more accurate relationship between $D(\varepsilon,p)$ and $E(\varepsilon,p)$ using (12) and (13). This is, however, beyond the scope of the present paper.

The neglect of the time dependence of the $\bar{r}_0^2$ term as expressed by approximation (13) is clearly justified when looking at the diffusivity $D(\varepsilon,t)$. The reason is that a quick estimate using the exact result indicates that one is neglecting terms of order $(\ln t_1)^m$, $1<m<3$, in comparison to a factor of $\sim t^{-1}$ at $T=0$. This clearly becomes a problem when we are now looking at $\langle R^2(t)\rangle$, since the integrated diffusivity is itself a function of $(\ln t_1)$ or even weaker as expressed by (3). We conclude, therefore, that the general relation (14) in the long-time limit, together with the complete neglect of time dependence of $\bar{r}_0^2$, is reasonable for $D(\varepsilon,t)$ but not for $\langle R^2(t)\rangle$, where indeed the $\bar{r}_0^2(t)$ effects dominate the time dependence. In view of the above remarks and the fact that MC also measures $\hat{S}(t)$ as expressed by (2), it is now important to attempt a rigorous derivation of $\hat{S}(t)$ at $T\to 0$. This we shall now demonstrate.

A. The numbers of new sites visited at $T=0$

At $T=0$, every site visited in the presence of energetic disorder, is necessarily a new site. If between the Nth and $(N+1)$th jump the energy lost is expressed as $\int_{-\infty}^{E_N}\rho(\varepsilon')d\varepsilon'$ as shown in (9), then the effective site density $\rho_N(\varepsilon)$ which the particle sees after N steps is of order (Gaussian ρ)

$$\rho_N(\varepsilon)\sim\exp(-N^2\varepsilon_N^2/2\sigma^2)\ , \tag{15}$$

where E_N is the average energy relaxed between the N and $(N+1)$th step. Since every site is a new site the mean-squared distance moved should behave as

$$\langle R_S^2\rangle=\tfrac{1}{3}\sum_{n=1}^{S}r_n^2\ , \tag{16}$$

where S is the number of new sites visited and r_n^2 is the mean-distance squared corresponding to the nth jump. This distance clearly grows with n since the number of available sites is decreasing after each jump. Indeed, using (19) we have

$$\bar{r}_m^2\sim\frac{1}{\{n\exp[(-m\bar{\varepsilon}_m)^2/2\sigma^2]\}^{2/3}}\ , \tag{17}$$

where n denotes the total density of sites and should not be confused with the index m. At $T=0$, the sum on the rhs of (16) is dominated by the last term in the series, so that

$$\langle R_S^2\rangle\sim\frac{1}{n^{2/3}}\exp\left[\frac{S\varepsilon_S}{\sigma}\right]^2\frac{1}{3}\ . \tag{18}$$

For a Gaussian we have already evaluated $\bar{\varepsilon}_S$ using (a) and we have

$$\bar{\varepsilon}_S=\frac{\sigma}{(2\pi)^{1/2}}e^{-(E_S^2/2\sigma^2)}\ . \tag{19}$$

Substituting (19) into (18) it now follows that ($S=\hat{S}$ is the number of new sites visited)

$$\hat{S}\sim[\ln(n^{2/3}\ln\langle R_S^2\rangle)]^{1/2}e^{E_S^2/2\sigma^2}\ , \tag{20}$$

where E_S is the total energy relaxed after $\hat{S}$ steps. Transforming the rhs into time space using the exact analytical asymptotic formula for $E(\varepsilon,t)$, (3a) gives us immediately

$$\hat{S}(t_1)\underset{t\to\infty}{\sim}\alpha_0(\ln t_1)^{\bar{d}}\ , \tag{21}$$

where $\alpha_0=c/6\bar{F}$, and consistent with the deductions made previously on the basis of (3) and (10). Indeed (21) could also have been derived using (10) and (3a).

Let us now compare (21) with the MC result given by (2). The functional forms clearly agree except that the value of the exponent n_0 in (16) and (2) and its apparent concentration dependence do not (for a three-dimensional lattice $\bar{d}=3$). The MC simulations suggest at low c an effective, fractal dimensionality $1<\bar{d}<2$, with $\bar{d}(c)$ changing with concentration. Since (21) is rigorously true for a $\bar{d}$-dimensional system in the asymptotic regime and in this case $\bar{d}=3$ and furthermore the concentration scaling of (2) does not appear to be quite right in the sense that $n_{\text{expt}}\to 3$ as $c\to 1$, we suggest that the MC calculations were most likely not strictly in the asymptotic domain as far as the quantity $\hat{S}(t_1)$ is concerned. The data in Fig. 3 indicate that at low concentration, $\hat{S}(t)$ is always less than 10 indeed often of order ~ 5. The analytic results are clearly referring to the strict asymptotic regime when $\hat{S}(t)$ is necessarily a larger number. In this case there are of course several sources of "error." In the first place the replacement of the sum (16) by its largest term is an approximation which however can be remedied. A further improvement could also be achieved for the intermediate time domain by substituting into (20) the more complete expression for $E(\varepsilon,t)$ given in Ref. 8. We shall not pursue this in the present paper.

Altogether we can now conclude that we have a very satisfactory understanding of diffusion and energy relaxation in a system with energy disorder including now also the very low-T region. This has been achieved using a combination of MC and analytical techniques. The MC work has brought out the importance of temperature effects even at very low temperatures. It has given us a hint on how to incorporate these effects in the analytical framework without too many complications [see Eqs. (7) and (3a) together with (8) and (11)]. In this paper we have also introduced, in the analytical theory, the very important concept of the number of new sites visited $\hat{S}$ and the important equation (16); therefore we can now complete the connection $\bar{E}(\hat{S})\to\langle R^2(\hat{S})\rangle\to\hat{S}\to t$. We have also shown that the approximation used in Ref. 7 and very frequently used in the literature namely Eq. (13) must be handled with care when discussing the time dependence of $\langle R^2(\varepsilon,t)\rangle$ rather than $D(\varepsilon,t)$. In the former case Eq. (13) and the neglect of the dependence of $\bar{r}_0^2$ as used in (14) can be misleading since $\bar{r}_0^2$ may be a stronger function (or of the same order) than the remaining term. The exact evaluation of $\langle R^2(\varepsilon,t)\rangle$ at $T\rightarrow 0$ is, however, no problem and can be carried out using Eq. (60) of Ref. 8 when necessary. Temperature effects (low T) and electric fields can now easily be included in the above analytical analysis. This we propose to do in a future paper.

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