Temperature Behavior of Tracer Diffusion in Amorphous Materials: A Random-Walk Approach

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In this Letter we study the behavior, versus temperature, of tracer diffusion in random materials, for example, amorphous solids. By using a combined approach, using the analytical continuous-time random-walk theory and Monte Carlo simulations, we are able to propose a possible explanation for the nearly Arrhenian behavior observed in most amorphous solids by a compensation between site and saddle disorder.

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The diffusion and conductivity behavior of random systems have received wide attention for some years.[1] Nevertheless, there are few exact results available, particularly in dimensions higher than one. The most important one is due to Fisher[2] and states that, at least for not too strong a disorder, a random walk in dimensions higher than (or equal to) two gives rise to a classical diffusion behavior, i.e., $\langle R^2(t)\rangle > \propto t$, at large times. But the problem of the determination of the precise value of the diffusion coefficient, as well as the behavior at shorter times, remains unsolved for actual disorder. Conversely, there is now a significant amount of experimental data pertaining to actual materials, which allows one to compile a picture of the diffusion behavior in strongly disordered, amorphous matter. Despite the inherent disorder, diffusion appears to be nondispersive and the temperature behavior seems to be characterized by a well-defined activation energy.[3] In this Letter we propose an analytical approach which, despite some approximations, allows us to explain these contradictory results.[4]

Model.—As a first-order-level description, an amorphous material can be described as a random distribution of atoms in which diffusion nevertheless proceeds in most cases by a mechanism involving "defects," interstitials or vacancies, and defect jumps.[3]

In what follows we shall discard the geometrical part of the disorder of random materials, as it is well established that it has only irrelevant effects on diffusion behavior.[1] We want them to describe the random walk of a tagged particle jumping between sites of a regular lattice, whose energetic properties are randomly distributed. Both the sites and the saddle points will be "decorated" by energies chosen at random. The important point to realize is that, with respect to matter diffusion, amorphous systems are characterized by two kinds of disorder which have deeply different properties. These are, on the one hand, the site disorder, corresponding to the so-called random-trapping model and, on the other hand, the saddle disorder, corresponding to the random-hopping model. Unlike the case of electronic transport in disordered semiconductors, where specific cases fall into one or the other model, the transport of matter involves both of them simultaneously, giving rise to new effects.

In actual materials there are probably some correlations between the values of the energies on neighboring sites and saddle points. But in the context of the present theoretical modeling, it is relevant to consider them as uncorrelated variables.

The tagged particle will then be allowed to randomly move from site i to site j by a thermally activated Poissonian jump, the frequencies of which are given by $w_{ij} = \exp[-\beta(\epsilon_c^{ij} - \epsilon_s^i)]$. In what follows we shall use Gaussian distributions for the ϵ's, with means $\bar{\epsilon}_s$ and $\bar{\epsilon}_c$ and variances σ_s and σ_c, respectively, for site and saddle energies. The time-dependent diffusion coefficient is defined as

$$D(t) = \frac{1}{6}\frac{\delta}{\delta t}\langle R^2(t)\rangle_{\{\epsilon\}},$$

where R denotes displacement of the particle and $\langle\ \rangle$ stands for an average over tagged particles and configurational disorder. The usual D^∞ diffusion coefficient, when it exists, will be recovered as the limit at infinite time.

We used a combined analytical and numerical approach, the first based on the continuous-time random-walk approach (CTRW),[5] was applied to random systems by Scher and Lax,[6] and the second on numerical simulations by a peculiar Monte Carlo (MC) method.[7]

CTRW approach.—Let us define $P_n(s_{j_n}, s_{j_0}, t)$ as the probability of just arriving on the site number j_n as a result of the nth jump occurring exactly at time t. We also define $W(s_{j_n}, s_{j_{n-1}}, t)$ as the probability density of jumping from site number j_{n-1} to site number j_n at time t after the arrival in $s_{j_{n-1}}$. Both of these quantities depend of course on the particular realization $\{\epsilon\}$ of the energetic disorder on the lattice. Using standard methods of random walk, the configurational average of P is obtained after a Laplace transformation, $t \to u$, as

$$\langle \bar{P}_n\rangle_{\{\epsilon\}} = \sum_{s_{j_{n-1}}} \cdots \sum_{s_{j_1}} \left\langle \prod_{\nu=1}^{\nu=n} \bar{W}(s_{j_\nu}, s_{j_{\nu-1}}, u)\bar{P}(s_{j_0})\right\rangle_{\{\epsilon\}}. \quad (1)$$

The critical approximation in Scher and Lax's treatment

of transport in disordered systems consists in replacing the intricate n-site average by the n-product of n single-site averages according to

$$\left\langle \prod_{\nu=1}^{\nu=n} \overline{W}(s_{j_\nu}, s_{j_{\nu-1}}, u) \right\rangle \rightarrow \langle \overline{W}(s_{j_\nu}, s_{j_{\nu-1}}, u) \rangle^n , \quad (2)$$

defining now an average probability density of delay between jumps as

$$\Psi(s_{j_\nu}, s_{j_{\nu-1}}, t) = \langle W(s_{j_\nu}, s_{j_{\nu-1}}, t) \rangle . \quad (3)$$

In fact, the delay function, once taken on a regular lattice and averaged over the energetic disorder, depends only on the jump vector, $s = s_{j_\nu} - s_{j_{\nu-1}}$. The origin of the deeply different behaviors for the two kinds of disorder can be understood at that point: In the case of site disorder, each jump is independent of the preceding one, inasmuch as the site energies are independent variables. Therefore, the simple treatment implied by Eq. (2) is not at all an approximation, and we can expect this version of the CTRW treatment to give exact results. On the contrary, in the saddle-point problem one cannot decouple successive jumps, since any easy jump from i to j is likely to be followed by an easy jump in the reverse direction. The single-site approximation will be shown in that case to be only qualitative.

Taking, for the sake of simplicity, the case of nearest-neighbor jumps, the delay function for a process of Poissonian elementary jumps is now given by

$$\Psi(s,t) = \sum_j \left\langle w_{ij} \delta(s - a_{ij}) \exp\left(-t \sum_j w_{ij} \right) \right\rangle_{\{\epsilon\}} , \quad (4)$$

where site j is one of the nearest neighbors of i, and a is a jump vector. Strictly speaking, the delay density of the first jump is not given by the same function as the next one for the CTRW to be a stationary process in time. Indeed, if the process is stationary, one cannot know at the beginning of the observation whether the walker is just arriving on the initial site or not. Therefore, the delay density of the first jump has to be taken as a mean value with respect to all the possible arrival dates on the starting site.[8] In this manner the thermodynamical occupancy of this site will also be obeyed. But in the present context we will mainly check our results against MC simulations, where the initial conditions do not correspond to a stationary process but to a well-defined time origin. In such a case the right choice is then the same for all jumps. Equation (4) can be rearranged according to

$$\Psi(t) = -\frac{\delta}{\delta t} \left\langle \exp\left(-t \sum_j w_{ij} \right) \right\rangle_{\{\epsilon\}} .$$

Using the generating-function technique,[5] the usual diffusion coefficient D^∞ can be obtained as

$$D^\infty = \lim_{u \rightarrow 0} u \overline{D}(u) = \frac{a^2}{6\tau}, \quad \tau = \left\langle \left(\sum_j w_{ij} \right)^{-1} \right\rangle_{\{\epsilon\}} , \quad (5)$$

with τ the mean residence time on a site, if it is defined. In order to solve for D^∞ we need to introduce the following two approximations. (i) In the first we let $\beta \rightarrow 0$. In such a high-temperature regime, all the frequency factors $\exp(-\beta \epsilon_c^{ij})$ tend to become equal, so we are allowed to replace $\langle \Sigma^{-1} \rangle$ by $\langle \Sigma \rangle^{-1}$. It is now easy to calculate that

$$D_H^\infty = \exp[-\beta(\bar{\epsilon}_c - \bar{\epsilon}_s)] \exp[\tfrac{1}{2}\beta^2(\sigma_c^2 - \sigma_s^2)] . \quad (6)$$

(ii) On the other hand, for $\beta \rightarrow \infty$, the tagged particle will mainly escape a site by the easiest path, i.e., the lowest saddle. Therefore,

$$\left\langle \exp\left(-t \sum_j w_{ij} \right) \right\rangle_{\{\epsilon^{ij}, \epsilon^i\}} \approx \langle \exp(-t w^{\max}) \rangle_{\{\epsilon^{ij}_{\max}, \epsilon^i\}} .$$

But the density probability of $\epsilon^{ij}_{\max}$ is

$$\pi(\epsilon^{ij}_{\max}) = p(\epsilon^{ij} = \epsilon^{ij}_{\max}) \left(\int_{\epsilon_{ij}}^\infty p(\eta)\, d\eta \right)^{z-1}$$

for any elementary saddle energy distribution $p(\epsilon)$. Here, for a Gaussian one, we obtain

$$\pi(\epsilon) = p(\epsilon) \{ \tfrac{1}{2} \operatorname{erfc}[(\epsilon - \bar{\epsilon}_c)/\sigma_c \sqrt{2}] \}^{z-1} , \quad (7)$$

giving

$$D_L^\infty = \exp[-\beta(\bar{\epsilon}_c - \bar{\epsilon}_s)] \exp[\tfrac{1}{2}\beta^2(f\sigma_c^2 - \sigma_s^2)] , \quad (7')$$

with f being a slowly varying function of $\beta\sigma_c$ and of the coordination z amounting approximately to unity (see Table I). In both cases we used a jump-length value, and frequency factor, such that the infinite-temperature limit of D^∞ equals unity.

The main result obtained here is the observation of a possible compensation between the opposite effects of both kinds of disorder. Indeed in Eqs. (6) and (7') the σ_c^2 and the σ_s^2 terms which reflect the whole disorder of the system appear only through their difference. In this way the effect of the disorder upon diffusion is reduced and may even cancel out for $\sigma_s/\sigma_c = 1$ [low β, Eq. (6)] or $\sigma_s/\sigma_c = \sqrt{f}$ [high β, Eq. (7')]. In this case the behavior of D^∞ will become Arrhenian or nearly so due to the slight dependence of f on β. This is indeed the effect we conjectured some time ago.[7] The first approximation becomes naturally meaningless at increasingly low temperatures: The mean frequency involved in Eq. (5) using

TABLE I. Compensation between site and saddle disorder. $\bar{\epsilon}_i$ is 1800 K, $\sigma_i/\epsilon_i = 0.2$. We have given the ratio at compensation σ_s/σ_c, the apparent activation energy ϵ_{app}, and also the value of $\sqrt{f}$ (see text) for $\beta\sigma_c = 3.6$. fcc stands for face-centered cubic; bcc, body-centered cubic; and sc, simple cubic.

Lattice	z	σ_s/σ_c	ϵ_{app}	$\sqrt{f}$
fcc	12	0.47	1710	0.8
bcc	8	0.4	1730	0.7
sc	6	0.4	1784	0.6
3D	4	0.2	1805	0.39
2D	4	0.17	1800	0.39

this approximation will be dominated by lower and lower saddles according to $\langle w\rangle \approx \langle \exp(-\beta\epsilon_c+\beta^2\sigma_c^2/2)\rangle$. It will finally produce frequencies larger than 1 which correspond to negative saddle energies having no physical meaning, on the one hand, and also, as we shall see later, no effect upon long-range transport, on the other hand. It is easy to check that using truncated energy distributions one recovers at low temperatures $D^\infty = \exp[-\beta(\epsilon_c^{\min}-\epsilon_s^{\max})]$, where $\epsilon_s^{\max}$ and $\epsilon_c^{\min}$ represent the energies of the deepest trap and the lowest saddle, respectively. The low-temperature approximation produces essentially the same kind of results: Now the efficiency of the saddle disorder for compensating the site disorder is slightly reduced, but the overall trend is preserved. Moreover, the compensation in this approximation is no longer perfect: Since f is slightly β dependent, a ratio of disorder strength adjusted to produce an apparent perfect-lattice value, at one value of β, will not be optimum at another one and the Arrhenius behavior will be only approximate.

The origin of this effect lies in the nonindependence of the z variables w_{ij} which are accessible from a given site. All of them are related by the common site energy and therefore the variance of their distribution is not the sum of the site and saddle energy variances. The problem of a random walk on such a random lattice cannot be handled by a simple hopping model over random barriers.

In order to check for the limits of validity of the present model, we also performed a MC analysis. We used a slightly improved procedure[7] which allowed us to calculate the diffusion coefficient without any decrease in efficiency at high β, at the expense of the loss of the time behavior of $D(t)$. We directly obtained D^∞ values which can be compared to the CTRW ones. The results of these MC simulations on a fcc lattice are shown in Fig. 1 (see also Table I), and compared with the ones of the analytical model. In the figure the solid line represents both MC and CTRW values in the perfect lattice. They are of course identical within the statistical errors. The dashed line and the crosses represent the results in the case of pure site disorder. As expected, the CTRW method provides an exact result. This is no longer the case for a saddle disorder: The dash-dotted line represents MC values, the stars the high-T approximation, and the triangles the low-T one. As stated above, the high-T approximation is rapidly dominated by the highest frequencies, and so does not give accurate values except for the highest temperature range, but it reproduces the right curvature of D^∞ vs β. On the contrary, the low-T approximation gives a moderately accurate estimation of D^∞ values in a fairly large domain.

The simultaneous introduction of both disorders in MC simulations also produces a compensation effect with the site disorder decreasing and the saddle disorder increasing D^∞. We cannot naturally check the validity of this compensation for large $\beta\epsilon$ values, due to the inherent statistical fluctuations becoming too large at large

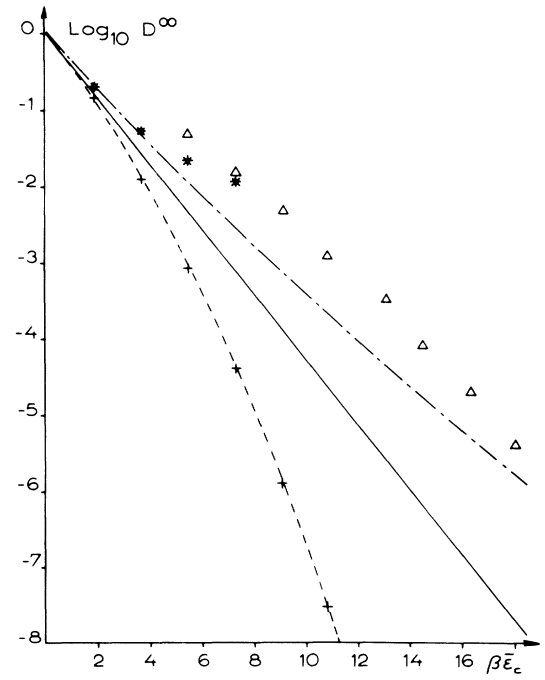

FIG. 1. Arrhenius plot of D^∞ on a randomly decorated fcc lattice, in both Monte Carlo simulations (lines) and CTRW model (symbols), $\bar{\epsilon}_s=0$. $\sigma_c=\sigma_s=0$: solid line, both models. $\sigma_c/\bar{\epsilon}_c=1/3$, $\sigma_s=0$: dash-dotted line, MC; stars, CTRW high-T approximation; and triangles, CTRW low-T approximation. $\sigma_c=0$, $\sigma_s/\bar{\epsilon}_c=1/3$: dashed line and crosses.

$\beta\epsilon$. Nevertheless, in all cases, and in the whole range explored (8 orders of magnitude), we found a perfect compensation; i.e., we recovered D^∞ values identical to the ones of the perfect-lattice case, and a well-defined thermally activated behavior for a constant value of the ratio σ_s/σ_c whatever the value of $\beta\epsilon$. These values are given in Table I for various lattices, the coordination z varying from 12 to 4. We also give the similar ratio as foreseen by the low-temperature CTRW approximation, which is nothing but the square root of the f function in Eq. (7'). Here we chose the value $\beta\sigma_c=3.6$ to display it; it would be slightly different for different values. The CTRW approximation clearly gives too large an effect to the saddle disorder in compensating for the effects of the site disorder. The origin of this partial failure is also clear: The effects of saddle disorder are overestimated by the CTRW approach, in both approximations, since back and forth jumps over easy saddles are counted in the same manner as others. But because of mutual canceling they do not contribute to long-range diffusion. As they represent an increasing part of the jumps at large β, the estimated mobility becomes correlatively too large.

A second difference between the simulations and the analytical model concerns the activation energy. It is foreseen by the CTRW in the high-T approximation to be the same at compensation as in the absence of disor-

der, contrary to the simulations which show a small but systematic decrease of it with increasing z. The simulation value is always smaller than the CTRW one. In the low-T approximation the slight dependence of f on β also produces a T-dependent activation energy, even at compensation, at variance with the MC results.

The last point we now have to discuss concerns the extent to which the observed compensation acts in actual amorphous materials. Of course it cannot be claimed to explain fully the observed trend, but we note the following points:

(1) The very existence of both distributions acting simultaneously always implies [see Eqs. (6) and (7')] a reduction of their individual effects and opens the way to some compensation, more or less complete.

(2) The criterion for exact compensation is rather stringent. For example, with respect to the Arrhenian behavior, our MC results show no curvature over 8 orders of magnitude. In actual experiments the domain covered for D^∞ is mostly limited to 3 to 4 orders or less. In such cases undetectable curvatures can easily be obtained for ratios σ_s/σ_c no longer strictly equal to, but not too different from, the critical value.

(3) In actual materials both disorders are probably interrelated through the structure of the medium and cannot be taken as independent variables. Numerical simulations on more realistic amorphous media should yield some alterations to the present simple model, but cannot alter, we believe, the essence of the present proposal for the mathematical results underlined in point (1) should be valid for wide classes of disorder.

In the present Letter we proposed an original interpretation of the behavior of diffusion in strongly disordered materials. The main physical ingredient of the present model is the simultaneous introduction of site disorder, which tends to trap the diffusing particle, and of saddle disorder, which tends to enhance the mobility of it. With respect to the diffusion at infinite time, D^∞, we have shown that both effects can compensate each other to a high level. By comparison with Monte Carlo simulations we have shown that the continuous-time version of the random-walk theory is able to give a satisfactory explanation, although not completely quantitative, of the behavior of D^∞ in the presence of both disorders.

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