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Nuclear magnetic relaxation in disordered solids: a Monte Carlo study of metal–hydrogen systems

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Abstract. The dipolar nuclear magnetic relaxation rate associated with the hopping diffusion of atoms in a disordered solid is calculated by Monte Carlo methods. The model is intended to simulate the diffusion of hydrogen atoms trapped at interstitial positions in the matrix of metal atoms in amorphous alloys. The principal features of the model system are that the atoms hop on a spatially disordered array of traps and the trapping energy varies from trap to trap so that the diffusion of the hydrogen is characterized by a distribution of jump rates. The effective jump rate from a trap is assumed to have an Arrhenius dependence on temperature. Calculated at constant temperature, the characteristic peak in the relaxation rate, which occurs in ordered solids when the product of the average jump rate and the Larmor frequency is approximately unity, is found to be broadened and shifted in frequency, particularly when the occupancy of the traps is high. The long-range diffusion constant is also calculated and used to evaluate the effect of atom–vacancy correlations. It is found that the shifts in the relaxation peak cannot be accounted for solely by these correlation effects and it is suggested that multiple hopping of the more rapidly diffusing spins is a contributory factor.

The shifts have a profound effect on the temperature dependence of the relaxation rate when the distribution of jump rates is also dependent on temperature. The adjustments to the peak in the relaxation caused by the distribution are small when the temperature dependence is taken into account, showing that experiments involving only the temperature variation of the relaxation are unlikely to be a sensitive method for detecting the presence of a jump-rate distribution. This aspect of the results of the computer model is illustrated by comparison with experimental data.

1. Introduction

Measurement of nuclear magnetic dipolar relaxation is an effective method for investigating hopping diffusion in crystalline solids and its success has been accompanied by the development of increasingly comprehensive theories of the relaxation rate applicable over a wide range of spin concentrations [1–3]. This theoretical work has been reinforced by Monte Carlo simulation [4, 5] and it is now possible to interpret in some detail experimental measurements of the relaxation rate for spins hopping on particular lattices. On the other hand, owing to the complexity of the problem and the wide diversity of types of disorder, the theory of relaxation in non-crystalline solids has advanced more slowly and theoretical models with equivalent levels of detail have yet to be developed.

There is some evidence to show that in non-crystalline solids the structural disorder is, in itself, of minor importance to diffusion [6]. It is the variations of site and saddle-point energies arising from the structural disorder that are of more consequence. Addressing the problem of diffusion in a real amorphous material requires not only consideration of distributions of both site and saddle energies but also the possibility of correlations between

the values of the energies at neighbouring sites. In addition there are important aspects of hopping diffusion associated with the co-ordination of the sites and the proportion of vacancies. In these circumstances it may not be possible to adopt a general approach. Consequently, throughout this paper a particular example of diffusion is assumed, namely, the diffusion of hydrogen in metal-hydrogen systems based on transition-metal-alloy glasses. Because of the low mass, there is the possibility that quantum corrections to classical barrier crossing might be required at low temperatures. Gillan [7] has discussed the criterion for the transition from classical to quantum regimes in elemental metals containing interstitial hydrogen and concludes that the crossover temperature is typically about 200–250 K. It is difficult to assess whether quantum effects need to be taken into account in amorphous alloys and, in view of the fact that 200 K is well below the temperatures at which dipolar contributions have a principal role in the hydrogen nuclear magnetic relaxation, a firmly classical stance has been adopted in this paper.

In amorphous alloys the hydrogen atoms occupy interstitial sites in a random array of metal atoms and the energy binding a hydrogen atom to a particular site depends not only on the structural disorder of the alloy but also on the variation in chemical species of the metal atoms surrounding the site. Neighbouring sites must have similar chemical compositions, causing there to be some short-range order in the sense that particular values of site energies may be grouped together over dimensions of the order of a few atom spacings. In the interest of simplicity the present paper deals only with a distribution of site energies and ignores spatial correlations of the site energies and any variation in saddle energy.

The mobility of hydrogen in amorphous metal-hydrogen systems has been measured by several microscopic techniques including internal friction [8,9] and neutron quasielastic scattering [10]. The results of these experiments have been taken to indicate a distribution in the hopping rates of the hydrogen atoms, arising from the energy disorder. On the other hand, measurements of motion-dependent nuclear magnetic relaxation rates, particularly near the characteristic maxima, in many of these alloys can be interpreted by simple models not specifically related to the disorder [11–13]. The main question that needs to be addressed is the extent to which nuclear magnetic relaxation rates are susceptible to the presence of a distribution of diffusion hopping rates. Previous work by some of the present authors [13, 14] based on Monte Carlo simulations has shown that in these circumstances modest changes in the relaxation do occur at low hydrogen concentrations. However, most experiments have been conducted with high levels of interstitial site occupancy and, in consequence, the present paper, as well as describing the computer model in more detail, extends the earlier work to high concentrations. The application of the results to metal-hydrogen systems, including the effect of the spatial correlations mentioned above, has been considered elsewhere [15, 16]. The Monte Carlo method also complements some recent theoretical work on nuclear magnetic relaxation in amorphous hydrogen-bearing alloys [17].

In theoretical models of ordered systems it is usual to obtain the relaxation rate as a function of $\omega\tau$, where ω is the Larmor frequency and τ is the average interval between diffusion hops. The same perspective is adopted in the earlier parts of this paper, which describe the details of the simulation and the dependence of the relaxation on ω for a fixed value of τ . Since there is normally a one-to-one correspondence between τ and temperature in ordered systems, it is easy to translate from this dependence to the variation of the relaxation time with temperature, as measured in experiments. However it is found in the present work that for disordered systems this translation is no longer trivial because of the possibility that the distribution of jump rates is also temperature dependent. The later parts of the paper draw parallels between the effect of the change in the distribution

on the relaxation rate and the long-range diffusion and describe a method of obtaining the temperature dependence of the relaxation rate.

2. The Monte Carlo simulation

2.1. Background theory

Typically NMR experiments consist of measurements of the spin-lattice relaxation rate, either in the rotating frame ($T_{1\rho}^{-1}$) or at large static fields (T_1^{-1}), made with a view to obtaining the contribution to the rate that derives from the random fluctuations of the nuclear dipole coupling caused by the motion of the spin-bearing atoms. This paper will deal exclusively with the high-field rate. Even so, the method is equally applicable to $T_{1\rho}$. In the semiclassical model usually adopted [18], the dipolar relaxation rate for like spins is given by

$$T_1^{-1} = \frac{3}{2} \gamma^4 \hbar^4 I(I+1) [J_1(\omega) + J_2(2\omega)] \quad (1)$$

where the spectral densities, J , are the Fourier transforms of the time-dependent spin correlation functions, namely

$$J_m(m\omega) = 2 \int G_m(t) \cos(m\omega t) dt \quad m = 1, 2 \quad (2)$$

and the $G_m(t)$ are thermal averages over the spherical harmonics of the spin co-ordinates.

In earlier simulations of the dipolar relaxation rate for cubic systems [4, 5] the time-dependent probability, $P(\mathbf{r}_i, \mathbf{r}_j, t)$, that a pair of spins separated by \mathbf{r}_i at time zero is separated by \mathbf{r}_j after time t , was calculated. The correlation functions were then derived from this quantity. The aim of this complexity was to obtain the dependence of the relaxation rate on the product $\omega\tau$ to a high accuracy. This is not a pressing problem in the present case and we note that the correlation functions can be obtained directly in a computer model if the thermal average is replaced by a sum over a set of tagged spins. With this in mind we have calculated the $G_m(t)$ from

$$G_m(t) = \left(\frac{1}{N}\right) \text{Re} \sum_i \sum_j F_{m,i}(t) F_{m,i}(0) \quad (3)$$

where

$$F_{m,i} = (-1)^m (8\pi/15) Y_{2m}(\theta_{ij}, \phi_{ij}) / r_{ij}^3 \quad (4)$$

and i and j are two of the N interacting spins with time-dependent relative co-ordinates \mathbf{r}, θ, ϕ .

2.2. The disordered structure

The computer model consists of 1000 traps situated on a simple cubic lattice. Spins diffuse by making instantaneous hops to vacant near-neighbour traps. The determining factor of the relaxation is the jump rate, ν , which is proportional to the probability that a spin can leave a given trap. This probability is assumed to be associated with the site in question, to be independent of the direction of the hop and to be proportional to the number of

vacant neighbouring sites. The exact form of the distribution of trap energies in disordered metal-hydride systems is not known but a Gaussian distribution has often been assumed [19,20]. In the present work, the energy density, $f(E)$, is chosen to be constant between two limits, E and $E + \Delta E$, and zero beyond. In the computer algorithm it is more relevant to work in terms of jump rates so that the actual operational definition of the disorder was a distribution of jump rates $f(\nu)$ proportional to $1/\nu$. Simple differentiation shows this form of $f(\nu)$ arises if a simple Arrhenius relation between jump rate and energy exists and the pre-exponential factor is the same at all sites. It is also useful to define the effective width of the distribution in terms of W , which is the ratio of the greatest jump rate to the least. In the simulations W was given the values unity (no distribution), 10, 25 or 100. It should also be noted that absolute values of E/kT and the jump rates are not required since the latter appear in the expression for the relaxation rate only through the product, $\omega\tau$.

In spite of the fact that spatial disorder is of minor consequence, it is useful to include it since doing so removes the dependence of the relaxation rate on the direction of the magnetic field with respect to the lattice. In the present case it was introduced during the calculation of the spin correlation function by shifting the spins from their lattice positions. The shifts were random in magnitude and direction and, once chosen for a given site, remained constant for the whole simulation. To prevent overlap the maximum shift was limited to $\frac{1}{3}$ of a lattice spacing. The diffusing spins were not confined to the central 1000-site cube but could move beyond it in any direction, the only restriction being that periodic boundary conditions based on the central cube are observed. Computations were made at two spin-site ratios, namely 0.1 and 0.9, corresponding to 100 and 900 atoms, respectively.

The fraction of time for which a spin fills the i th trap is $\tau_i/\Sigma\tau_i$, where $\tau_i = 1/\nu_i$ and ν_i is the effective jump rate for that trap. Thus if initially the traps are seeded according to their respective τ_i the total trap energy of the spins should then remain constant. In an actual test, although the total energy fluctuated, there was no discernible trend. On the other hand the time taken for 100 spins distributed randomly on the traps to reach thermal equilibrium was about 200 jumps. No significant difference was apparent between correlation functions calculated after this thermal relaxation time had elapsed and those calculated immediately from seedings in thermal equilibrium. Of course, the problem is not so acute at high concentration. Nevertheless, all simulations were performed with the correct thermal equilibrium at the start.

2.3. The correlation functions

The two spin correlation functions in equation (3) were calculated at the start of the simulation and, as each diffusion jump occurred, the change in these functions was evaluated. The correlation decays were smoothed by taking the average of 5 and 50 diffusion runs on the same lattice in the case of the 900- and 100-spin simulations respectively.

In the computational algorithm the natural unit of time is the number of successive jumps. In an ordered system all the spins will jump, on average, in time τ , the interval between jumps of each individual spin. Thus the interval between successive jumps in algorithm-converted real time is τ/N , where N is the number of spins and τ is 100 or 900 successive jumps for the two systems considered. In a later part of the paper we have occasion to use a different jump rate but, for the present, we continue with this definition of real time.

The Fourier transformation to the relaxation rate given in equation (2) cannot be made accurately by direct integration at values of $\omega\tau$ very much greater than unity owing to the residual small fluctuations of the correlation decay with an average period somewhat less than the decay constant. In the crystalline case this may be remedied with the aid of known

analytic expressions for the long- and short-time limits [5]. This method is not possible in the present simulation, especially as the main effect of the disorder is to change the long-time limit of the correlation function. Our alternative is to fit the correlation with a sum of exponential functions by visual trial and error and subsequent minimization of the sum of the squares of the deviations. Fitting procedures involving up to three exponentials were handled in this way. The advantage is that the Fourier transform may be found analytically from the fitted functions. The amplitudes and the decay constants of the individual exponentials do not have any particular physical significance as several different sums will give very similar final smooth curves.

3. Results of the simulation of the dipolar relaxation

The simulation program calculates the time-dependent spin correlation functions, $G_1(t)$ and $G_2(t)$ from which the dipolar relaxation rate is obtained by Fourier transform. Following Torrey's work [1], it has generally been the custom to present the dipolar relaxation rate, T_1^{-1} , as a graph of ωT_1^{-1} against $\omega\tau$, since then the characteristic maximum near $\omega\tau = 1$ is clearly demonstrated. The results of present simulations are shown in this way in figures 1 and 2. The units of T_1^{-1} are arbitrary computer units since our main concern is to show how T_1^{-1} changes with the distribution. However, the maximum value is essentially determined by the initial, $t = 0$, magnitude of the correlation function, that is, the average dipolar coupling of a static array of spins. The initial values of the correlation functions agree with those found by Crouch [12] in a simulation also based on a cubic lattice, and Crouch reports that his curves are consistent with earlier work [4].

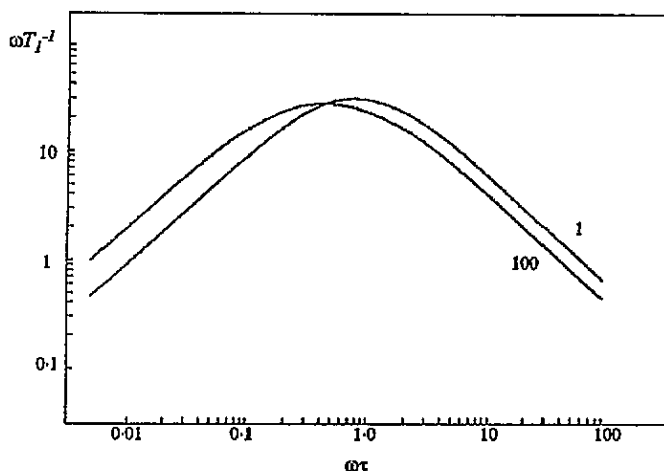


Figure 1. The calculated relaxation rate T_1^{-1} in arbitrary computer units for a spin-site ratio of 0.1. The quantity ωT_1^{-1} is shown as a function of $\omega\tau$, where ω is the Larmor frequency and τ is the average interval between hops. The jump-rate distribution is indicated by its width parameter W , defined in the text as the ratio of the greatest to least jump probabilities. Curves are shown for $W = 1$ (no distribution of jump rates) and $W = 100$.

It is well established that the decay of the correlation is not exponential even when there is no spread in jump rate [1]. The general form of T_1^{-1} found for zero spread, $W = 1$, is

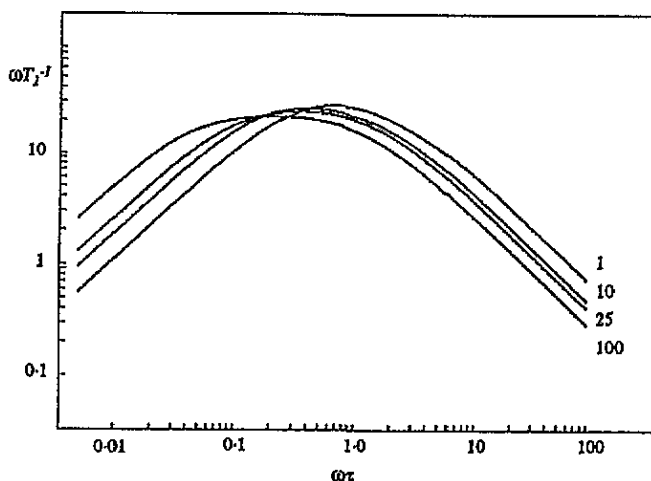


Figure 2. The calculated relaxation rate T_1^{-1} in arbitrary computer units for a spin-site ratio of 0.9. The quantity ωT_1^{-1} is shown as a function of $\omega\tau$, where ω is the Larmor frequency and τ is the average interval between hops. The jump-rate distribution is indicated by its width parameter W , defined in the text as the ratio of the greatest to least jump probabilities. Curves are shown for $W = 1$ (no distribution of jump rates) and $W = 10, 25$ and 100 .

in overall agreement with previous work [4, 5] and has the correct asymptotic behaviour at both $\omega\tau \gg 1$ and $\omega\tau \ll 1$. The effect of an increasing spread in jump rate is to cause both a change in shape of the correlation function and a general reduction in its rate of decay. The slower parts of the correlation decay are enhanced, the greatest change being observed at high concentrations and wide distributions. As a result the peak in the relaxation rate is both broadened and shifted. In the dilute case the maximum shifts from $\omega\tau = 0.74$ at $W = 1$ to $\omega\tau = 0.4$ at $W = 100$. In the concentrated case it occurs at $\omega\tau = 0.63, 0.32$ and 0.18 for $W = 1, 25$ and 100 respectively. The width of the peak for the $W = 100$ distribution, as measured by the ratio of $\omega\tau$ at the higher and lower asymptotes, is 2.8 and 1.3 times the width at zero spread for the 0.9 and 0.1 concentrations respectively. These widths are measured at the same relative fraction of the maximum relaxation rate.

Even though these are large effects it is proper to raise the possibility that the simulation has not accounted for long decay times caused by slow-moving spins. In the simulations the maximum number of jumps was 1000 in the dilute system and between 20 000 and 40 000 in the concentrated system. For the narrower distributions this is more than adequate to allow for a period in the simulation where the correlation function fluctuates about zero. However, the decay is not so complete for the $W = 100$ distribution at the 0.9 atom-site ratio and a small positive fraction of about 0.002 of the initial value remains. Although this amplitude would appear to be negligible it is worth considering what contribution to the relaxation rate curves it could make if the decay time were very long.

In the high-frequency limit, where the period of the oscillations of the cosine term in the Fourier transform is much shorter than the correlation decay constant, the relaxation rate is proportional to the first time derivative of the correlation function. An estimate of the error involved in fitting to this slope from a comparison of separate simulations indicates a probable error of less than 5%. At the low-frequency limit the relaxation rate is proportional to the area under the correlation decay since the sinusoidal term may be treated as a constant. In the example mentioned above, the greatest decay constant found from the simulation is

$\sim 10\tau$, so the missing area in the tail of the correlation decay is about 2% of the whole. On the other hand, if it is assumed that τ relates to the motion of the most rapidly diffusing spins rather than the mean, the longest possible decay constant is 100τ . The missing area would then be increased by a factor of 10, resulting in the possibility of a 20% increase in the relaxation rate at low $\omega\tau$ and in the width of the peak. We regard an error of this magnitude as acceptable in the context of the present paper. The true error is likely to be considerably smaller.

Interestingly these results reveal that the presence of a jump-rate distribution is clearly discernible only in concentrated samples. Examination of the computer output shows that the pattern of jumps is different in dilute and concentrated systems. In the former the spins principally occupy the deeper traps, which are relatively widely separated in comparison with the nearest-neighbour distance. Diffusion takes place by means of a spin leaving a trap and hopping through several shallower traps before meeting another deep one. The total displacement is of the order of the average separation and, consequently, several hops are required in general for the dipolar coupling of a particular spin to be lost. The process involves a number of very different trap depths with the result that the divergence from the average of the time taken is reduced. On the other hand, in the concentrated system each spin becomes uncorrelated in one jump. The spins no longer sample several different jump rates while becoming uncorrelated and this is reflected in the relatively broader relaxation curve.

Even though averaging over a combination of hops does not apply, concentrated systems are not free from averaging effects. A different sort of averaging occurs because of the spatial proximity of traps of different depth and the pair-like nature of the dipolar coupling. A large contribution to the total spin correlation function originates from pairs of spins with different jump rates and, since pair correlations are destroyed when either entity of the pair jumps, the full effect of the deeper traps is attenuated. This averaging between the time constants of 'slow' and 'fast' spins cannot be seen in the hopping process but can be tested by the use of approximate correlation functions in the following way. Only a brief description is given.

If the dipolar coupling involved independent spins rather than pairs, a reasonable approximation to the total correlation functions could be obtained by first assuming that the auto-correlation functions of the individual spins are exponentials and then integrating over the distribution of jump rates, $g(\nu)$. That is, the correlation functions would have the form

$$G(t) = G(0) \int g(\nu) \exp(-\nu t) d\nu \quad (5)$$

where $G(0)$ is the initial value. This integral can be dealt with directly within the confines of the present model by taking the Fourier transform to obtain the relaxation rate. The result, when $g(\nu)$ corresponds to the $W = 100$ distribution, is a relaxation curve similar to the $W = 100$ curve in figure 2 but having about twice the width, as defined in the way indicated above.

This version of the correlation function, usually in a form that gives the relaxation rate directly, has been used on several occasions to analyse experimental data [21-23]. It is not the best approximation since, in the case of pair correlations, the single integral should be replaced by a convolution over pairs. The convolution cannot be evaluated so readily since it involves consideration of the spatial distribution of the pairs. We have been able to obtain an approximate numerical solution corresponding to $W = 100$ and the random spatial distribution of the present model. The rate constants in the convolution are now

the averages for the spin pairs and the distribution, $g(\nu)$, is modified. This results in a relaxation curve with a width more consistent with the outcome of the simulation. The method is satisfactory only when the spin-site ratio is of the order of unity, and attempts to deal with the dilute case by modifying $g(\nu)$ to include only the deeper traps results in a relaxation curve of different shape from that found by computer simulation.

4. Relation to the diffusivity

The disorder not only causes a change in shape of the spin correlation function but also a general increase of its decay constant in relation to the average jump rate, that is, a shift in the peak in the relaxation curves towards lower values of $\omega\tau$. In ordered systems such shifts of the peak, which occur as the concentration increases, are ascribed to atom-vacancy correlations, particularly the increased probability at finite concentrations of an atom retracing the path of its preceding jump. An alternative way of examining these correlations is through the long-range diffusion. For the random walk of a single atom the long-range diffusion constant, D , is defined through the relation

$$\langle r^2 \rangle = na^2 = a^2t/\tau = 6Dt \quad (6)$$

where $\langle r^2 \rangle$ is the mean square distance jumped in time t , n the number of jumps in the same time, a the mean jump length and τ the mean residence time on a site. At this concentration in the present model each hop is independent of the previous one since the site energies are independent variables. To account for the atom-vacancy correlations at larger concentrations it is usual to include a further concentration-dependent factor in this equation.

At this point a distinction must be drawn between ordered and disordered systems. When there is no site disorder the probabilities of a forward and backward jump are equal. This is not so in the disordered case, where the differences in site energy and the accompanying jump-rate distribution destroy this equality. For example, there is a greater likelihood of a return to the original position when an atom hops from a deep trap to a shallow one than there is for the reverse process. Thus the correlation factor is likely to depend on the jump-rate distribution as well as the concentration, c . In the present model, where there is a definite choice of distribution frequency, this may be accommodated by the inclusion of the parameter W in the functional form of the correlation factor. That is, the diffusion constant may be written

$$6D = f(c, W)a^2/\tau = f(c, 1)a^2/\tau_d. \quad (7)$$

Here $f(c, W)$ is the coefficient that denotes the reduction in the diffusion constant caused by the correlations. The second equality in the expression has been included because we find it convenient to define a diffusion-related mean jump interval, τ_d , which can be used to link the diffusion constant and the relaxation rate. In this equation $f(c, 1)$ is the value of $f(c, W)$ when there is no energy distribution.

In order to determine D , the total mean square displacement $\langle R^2 \rangle = N\langle r^2 \rangle$ of the spins was calculated in a series of simulations equivalent to those that gave the relaxation rate. For independently hopping spins the mean square displacement in n successive computer hops is na^2 and this value was found to within 1% in the dilute system, $c = 0.1$, whether a jump-rate distribution was present or not. We therefore conclude that, at this low concentration,

$f(c, W)$ is unity and successive jumps are essentially uncorrelated. A different result was found for the concentrated system, $c = 0.9$. As shown in figure 3, $\langle R^2 \rangle$ becomes linear in time after an initial transient of the order of τ . Even in the case where there is no energy disorder the slope of the linear part falls below the value applicable to independent hops. At long times the reduction is about 30% for $W = 1$ and ascribing this reduction to the presence of the correlation effects leads to a magnitude for $f(c, 1)$ of 0.7, which is consistent with the results of calculations of $f(c, 1)$ for nearest-neighbour jumps on simple cubic lattices [24, 25]. The behaviour at shorter times, of the order of τ , is more germane to the relaxation. Since $\langle R^2 \rangle$ is not linear in time over this period it is not possible to give a constant value for $f(c, 1)$. Redefining it as $\langle R^2 \rangle / na^2$ measured at $t = \tau$ gives $f(c, 1) = 0.88$. Figure 3 also shows that $f(c, W)$ decreases as the width of the distribution increases. In fact it is possible to bring the curves in the figure into close coincidence at times greater than τ by adjusting the time scale for each curve by a suitable factor. The scaling factor is 0.49 for the $W = 100$ curve compared with the curve representing no distribution. Again due to the slightly different shapes of the curves in the non-linear region this factor is somewhat larger, about 0.53, for coincidence at times of the order of τ .

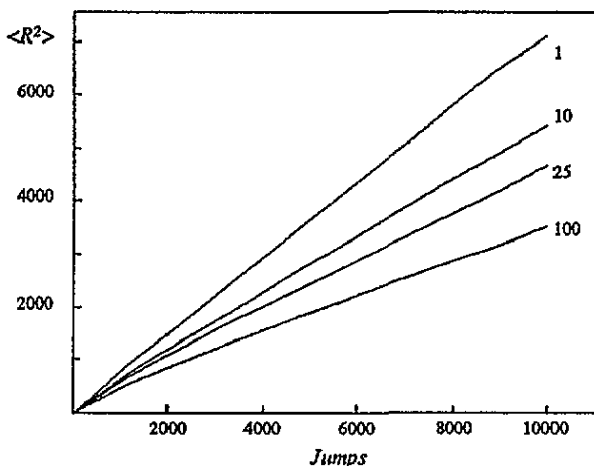


Figure 3. The total mean square distance, $\langle R^2 \rangle$, travelled by all spins initially in the base cube is shown as a function of the number n of hops. The spin-site ratio is 0.9. $\langle R^2 \rangle$ is essentially linear in n after an initial period of the order of the average interval τ between jumps. The figure shows that the diffusivity falls as the width W of the jump-rate distribution increases. The value of W is given against each curve in the figure. The reduction is due to atom-vacancy correlation effects, which depend not only on the concentration of the spins but also on the distribution.

In general agreement with the results for cubic lattices [4], the maxima in the relaxation curves for $W = 1$ occur at $\omega\tau = 0.74$ and $\omega\tau = 0.63$ in the dilute and concentrated systems respectively. The ratio of these values is 0.85, showing that the shift in the maximum between these two systems can be ascribed to the atom-vacancy correlations. In spite of some difference in shape, the overall decay of the spin correlation function near τ is the same in each case for a given mean square displacement of the spins. A new feature of the simulations is that this is apparently no longer true when disorder is present. The equivalent of comparing spin correlation functions at equal root mean square displacements is to scale τ according to equation (7) using the data of figure 3. That is, τ_4 replaces τ , and the result is shown in a new plot of the relaxation curves for $c = 0.9$ in figure 4. Whether the scaling

is made at long or short times, shifts in the relaxation maxima towards low $\omega\tau$ persist. The scaling is sufficient to bring only the asymptotes at large $\omega\tau$ into near coincidence. In terms of the correlation functions this implies that their initial decays are similar, but overall there remains a tendency for the spin correlation to decrease more slowly as W increases.

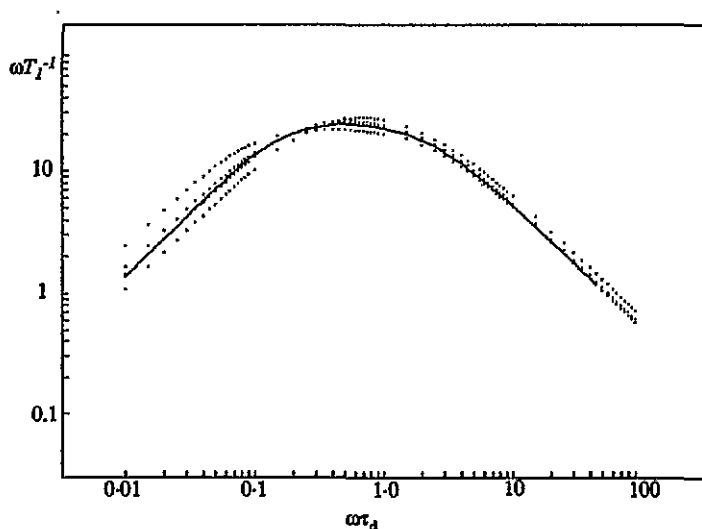


Figure 4. The relaxation curves of figure 2, now shown as dotted curves, are plotted as a function of $\omega\tau_d$, where τ_d is an average jump rate derived from the long-range diffusion and takes into account the effect of the atom-vacancy correlations. The solid curve shows a typical modification to the relaxation curves if W is temperature dependent. The conditions under which this curve has been derived are explained in the text.

In ordered materials the decay constant of the correlation function is approximately equal to the average interval between hops to within a factor of two and the differences that exist between dilute and concentrated spin systems can be reconciled with the effects of atom-vacancy correlations [4]. The relatively longer decays when disorder is present cannot be accounted for in the same way and appear to be intrinsic to the disordered state. It is difficult to establish the reason for the reduced rate from the simulation but it seems likely that it arises from multiple hopping. Because of the short-range nature of the dipolar coupling the contribution of a given spin to the correlation function in a concentrated system essentially disappears when that spin hops. The initial decay of the spin correlation tends to take place through the movement of those spins with the greater probability of making a jump. They may make further jumps, which increase the mean square displacement without adding significantly to the diminution of the correlation, in the average time required for a single hop of a spin with a low probability of hopping. Thus in relation to the diffusion the decay of the spin correlation is biased towards the movement of those spins with low jump rates.

5. Dependence on temperature

Most experiments explore the temperature dependence of the relaxation rate and the simulated relaxation curves may be used to interpret such measurements if the distribution of

jump rates is known to be independent of temperature. Unfortunately, a constant distribution of this type is unusual. A more typical example, which can be discussed in the framework of the present model, is one in which the energy disorder is independent of temperature and, because of the activated nature of the diffusion, the jump-rate distribution is temperature dependent. Retaining the condition that all hops have the same pre-exponential factor, the parameter W has the form

$$W = \tau_2/\tau_1 = \exp[(E_2 - E_1)/kT] = \exp(\Delta E/kT) \quad (8)$$

where E_1 and E_2 are the extremes of the energy distribution and τ_1 and τ_2 are the corresponding jump intervals. One way of dealing with this equation is to replace temperature by some other variable related to the diffusion and clearly the most straightforward substitution is to use a replacement with a temperature variation similar to the right-hand side. For example, if τ_d is given by

$$\tau_d = \tau_0 \exp(E_a/kT) \quad (9)$$

where E_a is a temperature-independent activation energy

$$\ln W = (\Delta E/E_a) \ln(\tau_d/\tau_0). \quad (10)$$

It is then possible to obtain W as a function of τ_d independently of temperature for a given choice of $\Delta E/E_a$ and τ_0 .

Equation (9) is not strictly obeyed in the present model. As mentioned earlier the jump rate distribution is skewed with respect to the energy distribution by the factor $1/\nu$, so there is a temperature-dependent shift of the mean jump rate. The effect has already been noted in relation to random walk on a lattice with site energy disorder [26]. In that case the mean jump interval increases faster than $\exp(E/kT)$, where E is the average site energy, and the diffusion constant has a corresponding divergence. In addition, particularly at high concentrations, there is the effect of the atom-vacancy correlations, which also contribute to the temperature dependence of τ_d . It is therefore necessary to appeal to experiment in order to obtain justification for the use of equation (9). Typical relaxation measurements occupy the temperature range 200–450 K and the aim is to show that the mean interval departs little from the Arrhenius form over this restricted range. For example, internal friction measurements on hydrogen-loaded metallic glasses are consistent with a spread of activation energies of the order of 0.08 eV about a mean of $\frac{1}{4}$ – $\frac{1}{3}$ eV [8, 9]. On the basis of these data, W changes by a factor of 10 and the mean jump interval departs by less than 1% from an Arrhenius dependence over the above temperature range. As indicated above the effective activation energy of the mean jump interval is different from the mean energy of the distribution. A similar argument holds for the effect of the atom-vacancy correlation and it is possible to infer that errors deriving from the assumed form of equation (9) are less than those incurred in typical relaxation experiments.

Given that equation (9) is a satisfactory form for τ_d equation (10) can be used to obtain a curve of T_1^{-1} against τ_d , which includes compensation for the change in W . The output of the computer simulation is essentially a family of curves connecting T_1^{-1} , W and τ_d so that the desired curve is the locus through this family that gives T_1^{-1} as a function of τ_d while simultaneously satisfying equation (8). Rather than carry out the large number of curves required for a smooth locus we have interpolated between successive curves in figure 4. In keeping with the logarithmic relation between T_1^{-1} and τ_d , interpolation was carried out according to the following rule:

$$\ln(s/s_2)/\ln(s_1/s_2) = \ln(W/W_2)/\ln(W_1/W_2) \quad (11)$$

where s is the relaxation rate T_1^{-1} and the subscripts 1, 2 refer to two successive curves obtained from the simulation. The locus through the curves corresponding to $c = 0.9$ calculated on this basis with $\Delta E/E = 0.3$ is shown as a solid line in figure 4. The value of τ_0 was chosen to give $W = 10$ on the low-frequency side of the peak and $W = 100$ when $\omega\tau_d$ is about 30.

The extent of the data from the simulation imposes a limitation on the qualitative nature of the loci that can be constructed. In order to achieve loci that extend over the greater part of the $\omega\tau_d$ range of figure 4 it is necessary to restrict W to less than about 25 on the low-frequency side of the peak and $\Delta E/E$ to less than 0.5. In order to improve this range, it would be necessary to carry out the simulation at much higher values of W . Within this restriction it turns out that all the loci generated with $\Delta E/E$ in the range 0.2–0.5 have a shape similar to the curve for $W = 1$. This is a consequence of the fact that the dotted curves in figure 4 are almost coincident at large $\omega\tau$, which in turn arises from the shifts of the relaxation curves ascribed to the effects of multiple hops. In principle values for E_a may be obtained by comparing these loci with experimental measurements of the temperature variation of the relaxation rate.

It is also possible to deal with the curves of figure 2 in the same way with similar results. Because of the general shift of the curves towards low $\omega\tau$ the peaks of the loci that now have $\omega\tau$ as a variable tend to have a narrower width than those described above. Consequently, applied to experimental measurements of the relaxation rate, each of the loci generated this way give a value for the activation energy of the average jump interval lower than the equivalent E_a . The difference in activation energy of τ_d and τ reflects the change in the atom–vacancy correlations caused by the increase in W that occurs as the temperature decreases.

The similarity between the loci that include the temperature dependence of W and the relaxation curve for $W = 1$ results in a predicted temperature dependence for the relaxation rate almost symmetrical about the peak rate. That is, the relation $\ln(T_1^{-1}) \propto \pm E_a/kT$ is approximately true well above and below the peak, respectively. This result is quite different from theoretical predictions of relaxation rates in amorphous alloys [17] in which it turns out that the temperature dependence on the low-temperature side of the peak is generally smaller. It is possible to achieve a similar temperature dependence, but with a smaller difference in variation above and below the peak, by making the simulated relaxation curves coincide at their peak values before constructing the loci. A possible explanation of the difference between simulation and theory is that the latter does not account for the shifts found in the simulations. The theoretical predictions do not agree in detail with the outcome of measurements on disordered alloys, whereas we will show below that it is possible to obtain agreement between the simulated and experimental relaxation rates providing that more than one relaxation channel is assumed to operate at low temperatures.

6. Comparison with experiment

The inference that can be drawn from the simulation, namely that the temperature variation of the relaxation rate is not sensitive to the distribution of jump rates, offers an explanation of the fact that in many experiments it is possible to fit the data to standard relaxation models over the greater part of the range of temperature measured [11–13]. The changes in activation energy sometimes reported [11] appear to be genuine and not the result of mismatch with theory, since a single value is found in the vicinity of the peak relaxation rate. A particular difficulty with the experiments is that departures from the theoretical variation of

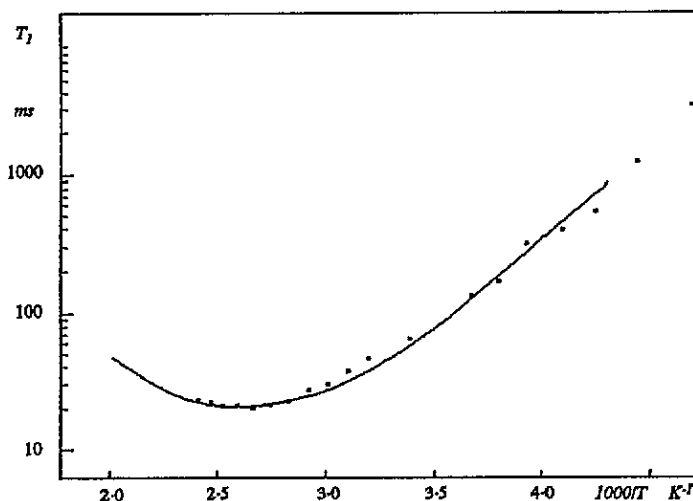


Figure 5. The solid line shows the results of the computer model for $\Delta E/E = 0.3$ compared with the experimental values of the hydrogen nuclear magnetic relaxation time, T_1 , in an $\text{Ni}_{35}\text{Ti}_{65}\text{H}_{150}$ metallic glass as given by Crouch [12]. A Korringa contribution to the relaxation rate, T_{1c}^{-1} , given by $T_{1c}T = 72 \text{ s K}$ has been subtracted from the raw data. The computer curve has been adjusted to give coincidence at the minimum in T_1 and by choosing the average activation energy E_a to be 0.26 eV.

the relaxation rate are observed at low temperatures. Such departures in crystalline metal-hydrogen systems are well established to be due to other relaxation processes, typically the interaction of the nuclear and conduction electron spins [27]. Unfortunately in amorphous alloys the experimental data are often not extensive enough to provide an unequivocal identification and this has led to different interpretations of the data. For example, data on amorphous nickel-titanium alloys [22] have been analysed along the lines suggested by equation (5), whereas it has been pointed out [13] that an interpretation without recourse to a distribution of jump rates is possible if other relaxation channels are taken into account. In other cases distributions have been assumed to account for minor deviations from simple theory [21].

In order to demonstrate the relation between the simulation and experiment we have chosen to fit computer-generated loci to the measured dipolar relaxation of interstitial hydrogen in an $\text{Ni}_{35}\text{Ti}_{65}$ alloy glass. In view of the likely presence of second relaxation channels the experimental data in figure 5 have been corrected to allow for a contribution to the relaxation rate from the conduction electrons. The curve in figure 5 has been obtained from the solid curve in figure 4 by adjusting E_a and bringing the computer-generated and experimental minimum relaxation times into coincidence. The activation energy comes out to be 0.26 eV and ΔE is 0.078 eV. If the correction for the electronic contribution is not made, the same simulated curve with the same value of E_a still fits the data near the minimum but the experimental points fall below the calculated curve at temperatures less than 250 K. As indicated above, the shape of the generated curve is not very sensitive to the value of ΔE and it is possible to fit the data equally well with ΔE up to 0.11 eV and E_a increasing to 0.28 eV. Some indication that the locus corresponding to the solid line in figure 4 is similar to the computer-generated curve for $W = 1$ can be obtained from the result that the best fit of the latter to the same set of data gives $E_a = 0.25 \text{ eV}$. The general agreement between the computer calculation and earlier relaxation-rate theories can

be demonstrated by noting that fitting Torrey's [1] calculated relaxation curves to the same data also gives 0.26 eV.

The reason that similar parameters fit the corrected and uncorrected data arises from the small adjustment necessary to the vicinity of the minimum relaxation time. This is only about 20%. Equivalent fits can be made to all the data of T_1 in hydrogen-loaded amorphous alloys obtained by Crouch [12] and Wolney Filho [28] and it seems reasonable to conclude that the simulated relaxation rates along with a secondary contribution rather than an asymmetric temperature variation can provide an explanation of the experimental observations.

Finally it should be noted that the implication of the computer simulations is that the best method of detecting the presence of a distribution of jump rates is to measure the frequency dependence of the rate at a fixed temperature. Unfortunately the range of frequency required makes such an experiment technically difficult and it is probably for this reason that measurements are carried out with temperature as the variable. It may be necessary to adopt a different approach and, in this connection, we note that the correlation functions that govern T_1 and the spin-locked rotating-frame relaxation time, $T_{1\rho}$, are similar in form. The principal differences, which make measurements of $T_{1\rho}$ particularly advantageous, are that the radio-frequency (RF) field strength replaces the Larmor frequency and experiments over a wide range of RF field strengths do appear to be technically feasible. In fact we are currently engaged in such measurements and intend to interpret them by means of a suitable modified version of the present simulations.

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