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Journal of Alloys and Compounds 253–254 (1997) 425–427

Journal of ALLOYS AND COMPOUNDS

Measuring distributions of jump rates in disordered metal–hydrogen systems by nuclear magnetic relaxation

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Abstract

Monte Carlo calculations of the nuclear magnetic relaxation rate in a disordered metal–hydrogen system having a distribution of jump rates are reported. The calculations deal specifically with the spin-locked rotating-frame relaxation time $T_{1\rho}$. The results demonstrate that the temperature variation of the rate is only weakly dependent on the distribution and it is therefore unlikely that the jump rate distribution can be extracted from relaxation measurements in which temperature is the main variable. It is shown that the alternative of measuring the relaxation rate over a wide range of spin-locking field strengths at a constant temperature can lead to an evaluation of the distribution.

Keywords: Monte Carlo calculations; Metal–hydrogen systems; Nuclear magnetic relaxation

The individual hydrogen sites in disordered metal–hydrogen systems, for example amorphous alloys, may have different structural and chemical environments which result in a range of binding and barrier energies. In order to use nuclear magnetic relaxation to measure the diffusion in such systems it is necessary to know how the relaxation rate depends on the distribution of jump rates which arises from this variation in energy. Additionally there is the separate and interesting question of whether it is possible to extract the jump rate distribution from such measurements. In this context the relaxation process involves random fluctuations of the nuclear spin dipole–dipole coupling caused by the diffusion and has the characteristic times, T_1, in high external magnetic fields and $T_{1\rho}$ in the so-called rotating frame. The experimental conditions are such that it is usually satisfactory to describe these relaxation rates by well-known semi-classical expressions [1], of which the one for $T_{1\rho}$ is

$$T_{1\rho}^{-1} = (\tfrac{3}{8})\gamma^4 h^2 I(I+1)[J^0(2\omega_1) + 10J^{(1)}(\omega_0) + J^{(2)}(2\omega_0)]$$

where the spectral densities, J, are the Fourier transforms of the spin dipolar correlation functions, $G^{(m)}(t)$, with $m = 0,1$ or 2. Here $\omega_0 = \gamma B_0$ is the Larmor frequency and $\omega_1 = \gamma B_1$, where B_1 is the strength of the radiofrequency magnetic field, the spin-locking field, along which the spins relax in the rotating-frame. Typically, $\omega_0 \sim 40$ MHz, $B_0 \sim 10$ kGauss and $B_1 < 100$ Gauss and, under those circumstances where the first term in $T_{1\rho}^{-1}$ is near its maximum value, it is usually possible to neglect the terms in ω_0. For simplicity this approximation will be made here. Finding the relaxation rates then amounts to calculating the time-dependent spin correlation functions, $G^{(m)}(t)$ and, particularly for disordered systems, this can conveniently be done by Monte Carlo (MC) methods.

We have reported MC calculations of $G^{(1)}$ and $G^{(2)}$ for spins diffusing on a disordered array of sites in an earlier paper [2] and here we extend them to include $G^{(0)}$ and $T_{1\rho}$. The calculations assume that the local jump rates, ν_s, are related to the site energies, E, through $\nu_s = \nu_0 e - ^{E/kT}$ and the site energies have a uniform distribution, of width δE, about the central value of E. There is no distribution of saddle point energies. The jump rate distribution is then $\rho(\nu_s) = kT/\nu_s \delta_E$ and the ratio of the maximum to minimum jump rate is $r = e^{\delta E/kT}$. The model, the details of which may be found in Ref. [2], allows us to calculate the time dependence of the $G^{(m)}(t)$ and, after Fourier transform, $T_{1\rho}$ at any temperature. A representative set of results for a spin/site ratio, $c = 0.5$, is shown in Fig. 1. It should be noted that $\rho(\nu_s)$ and r are temperature dependent even when δE is constant, so in this figure the width of the jump rate distribution has been defined by the parameter, r_0, the value of r at the temperature, T_0, at which $\omega_1\tau = 1$, where $\tau = 1/\nu$ and ν is the mean jump rate. The temperature, T, is given in terms of a reduced temperature, $\theta = T/T_0$, and the mean value of E is $10kT_0$.

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0925-8388/97/$17.00
PII S0925-8388(96)03083-6

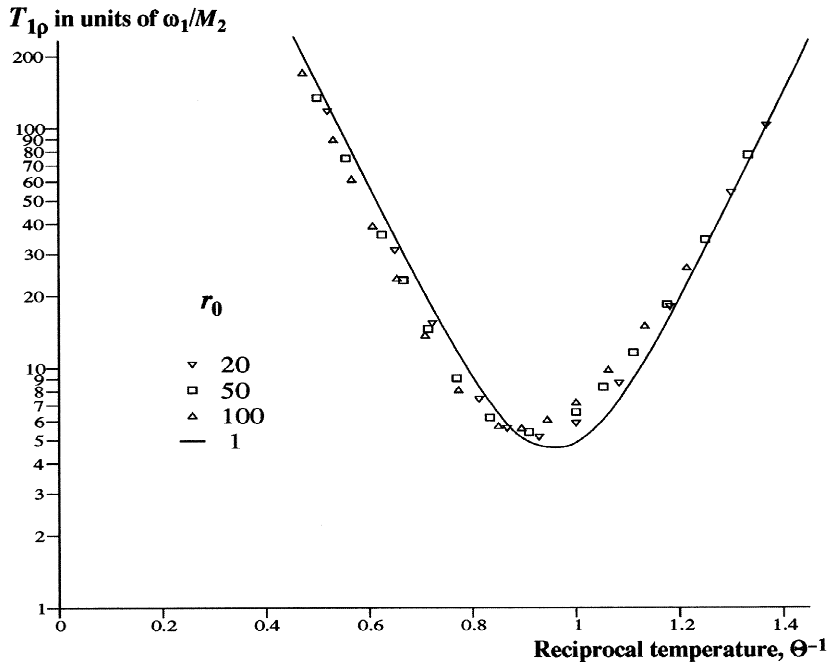

Fig. 1. Calculated values of $T_{1\rho}$ over a range of reduced temperature, θ, are given as data points. The distribution of jump rates in each case is given in terms of the parameter, r_0, defined in the text. The solid line gives $T_{1\rho}$ at $r_0=1$, namely when there is no distribution, $T_{1\rho}$ is in units of ω_1/M_2, where M_2 is the second moment of the dipolar local field under static conditions.

In spite of the large variation in r_0, the $T_{1\rho}$ curves are remarkably similar apart from shifts in the position of the minimum and changes to the asymmetry in the slopes at the extremes of temperature. Essentially the same behaviour has been observed for T_1 in our earlier work [2] and in other calculations of $T_{1\rho}$ based on distributions of site energies [3,4]. This behaviour arises principally from the temperature dependence of r since we are able to show that calculations with r held independent of temperature lead to much greater changes. It has been reported [3] that distributions of saddle point energies have a greater effect than distributions of site energies but the few calculations we have made with the former to not bear this out, particularly at low spin/site ratios where the spins tend to take paths involving the lower saddle points. The calculations create a basis for the discussion of experimental measurements, which typically have had temperature as a variable, but they also show that it is unlikely that accurate values of the parameter r can be extracted from the measured temperature dependence of $T_{1\rho}$.

In spite of these weak temperature effects, $G^{(0)}(t)$ itself depends significantly on the jump rate distribution. All the correlation functions were found to depend on time in very similar ways for a given value of r. Even for small values of r the variation of the correlation function with time departs from the simple exponential form with $G^{(0)}(t)$ remaining relatively large in the tail of the decay. The magnitude in the tail increases when either r or c increases. The general effect is well documented in our earlier paper [2]. Fourier transform leads to a spectral density function, $J^{(0)}$, which is best described in terms of the dimensionless parameter, $\omega_1\tau$. At small $\omega_1\tau$, $J^{(0)}$ approaches an asymptotic value but, as $\omega_1\tau$ increases, $J^{(0)}$ decreases, passing a point at which its slope is -1, and which, for $r=1$ (no distribution), is near $\omega_1\tau=1$. The actual value of $\omega_1\tau$ at this slope and the value of the asymptote depend strongly on r. The asymptote of $T_{1\rho}$ at small $\omega_1\tau$ is T_2, the motionally narrowed spin–spin relaxation rate, and it is quite feasible to measure both $T_{1\rho}$ over a wide range of B_1 (say 1 to 100 Gauss) and T_2 at a

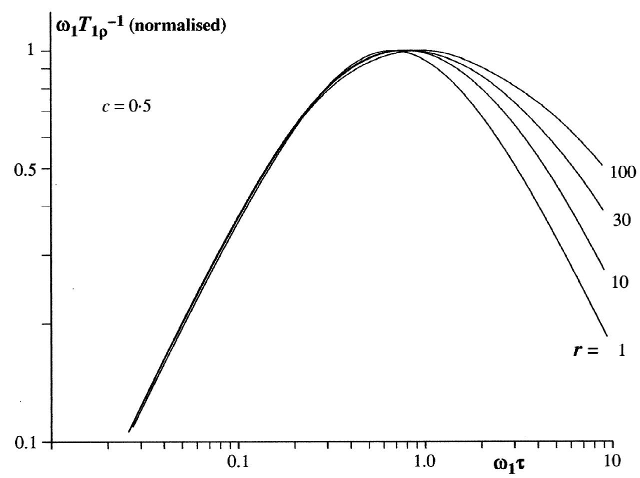

Fig. 2. Calculated values of the product $\omega_1 T_{1\rho}^{-1}$ as a function of $\omega_1\tau$ for various distributions designated by the parameter r given in the text. In order to allow better comparison with experiment as explained in the text, $\omega_1 T_{1\rho}^{-1}$ has been normalised to the same value of $\omega_1 T_2^{-1}$ and the same maximum value in each case. This process involves shifts of the curves with respect to $\omega_1\tau$. Consequently, only the curve for $r=1$ has its true position on the abscissa.

given temperature (constant r and τ). In order to fit the experimental data to the MC calculations, it is better to plot the product $\omega_1 T_{1\rho}^{-1}$, which has the asymptote $\omega_1 T_2^{-1}$ and a maximum where $J^{(0)}$ has the slope -1. These values may be used as normalisation factors in the fitting procedure. The very significant effect of a jump rate distribution on such normalised plots, as obtained from the MC calculations, is shown in Fig. 2. We have made some measurements (to be published later) of $T_{1\rho}$ over a range B_1 which confirm the feasibility of extracting a value of r from experimental data by fitting to these MC results. It should be noted that the equivalent experiment using T_1 requires a wide range of ω_0, which is not normally available in typical nuclear magnetic relaxation spectrometers.

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