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A BPP model for nuclear spin relaxation in disordered metal–hydrogen systems

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Abstract

Nuclear spin relaxation rates measured for disordered metal–hydrogen systems are often interpreted using a BPP model with a distribution of activation energies. This model is analysed more rigorously, taking into account the Fermi–Dirac distribution for the probability of occupation of sites by hydrogen, and site- and barrier-energy models for the hydrogen jumps. The results show appreciable differences to the use of the simple BPP activation energy distribution model.

Keywords: Nuclear spin relaxation; Disordered; Metal; Hydrogen

1. Introduction

Measurements of nuclear spin relaxation rates can provide very useful information about diffusion of H in metal–hydrogen systems [1]. For simple ordered systems, the H or metal nuclear spin-lattice relaxation rates R (in either the laboratory or rotating frames) often have a characteristic form as a function of temperature T at fixed frequency ω: plots of $\log R$ vs. $1/T$ exhibit a maximum and have linear and symmetric asymptotic forms in the low- and high-temperature limits. This behaviour can be understood on quite general grounds [2] in terms of H diffusion between interstitial sites, with the mean diffusion jump rate Γ characterised by an Arrhenius form $\Gamma = \Gamma_0 \exp(-E_a\beta)$, where E_a is an activation energy and $\beta = 1/(kT)$. Detailed calculations of the relaxation rates can be made for this diffusion model [3], but a very simple model due to Bloembergen et al. [4] gives the correct qualitative behaviour and can provide approximate values of the diffusion parameters. This BPP model has been widely used in interpreting experimental relaxation data in many systems because of its simplicity and ease of use.

The forms of the relaxation rates as functions of temperature, frequency and H concentration are often quite different in disordered systems [1]. In ordered systems the asymptotic slopes of the $\log R$ vs. $1/T$ plots are of equal magnitude and opposite sign, whereas in disordered systems the low temperature side of the peak decreases more slowly with increasing $1/T$ and may not reach a linear asymptotic region. Attempts have been made (see, for example, Refs. [1,5–7]) to interpret such data in terms of a BPP model modified to include a distribution $N(E)$ of activation energies due to the structural disorder. The general form of the relaxation rate is assumed to be

$$R = \int N(E) R_{\mathrm{BPP}}(E)\, \mathrm{d}E \qquad (1)$$

where $R_{\mathrm{BPP}}(E)$ is the relaxation rate for the ordered BPP model for diffusion with a jump frequency Γ with an activation energy E.

The aim of this paper is to investigate the generalisation of the BPP model to disordered systems more thoroughly. Of particular interest is the application of the model as a function of H concentration following some quite detailed measurements by McDowell and Cotts [6] of ^{1}H spin-lattice relaxation in $\mathrm{Ni}_{0.33}\mathrm{Zr}_{0.67}\mathrm{H}_x$. The following generalisation of the BPP model considers the occupation probabilities of the interstitial sites as functions of temperature and concentration, together with some site-energy and barrier-energy distribution models for the H diffusion. It is shown that the results can be quite different to those from Eq. (1).

2. Theory

The essence of the BPP model in ordered systems is that the probability of no jump of an atom in a time t is $\exp[-Z(1-c)\Gamma_0 t]$, where Γ_0 is the mean frequency of attempted jumps of an atom to a particular one of the Z

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available nearest neighbour sites. The factor of $(1-c)$ takes account of the probability of the jump not being successful because the target site is occupied with probability c, where c is the fraction of interstitial sites occupied. The BPP model effectively assumes that the correlation between a pair of spins is destroyed when a jump occurs. The spherically averaged correlation function $G(t)$ for magnetic dipolar interactions may then be written as [3]

$$G(t) = cS\,\mathrm{e}^{-2Z(1-c)\Gamma t} \tag{2}$$

where the factor of two in the exponent occurs because either spin may jump, and the factor S is the lattice summation $S = \Sigma_\alpha\, r_\alpha^{-6}$, where the summation is over the interstitial site separations r_α. The corresponding spectral density function $J(\omega)$ is the Fourier transform

$$J(\omega) = 2\int_0^\infty G(t)\cos(\omega t)\,\mathrm{d}t \tag{3}$$

and the spin-lattice relaxation rates R_1 (laboratory frame) and $R_{1\rho}$ (rotating frame) are linear combinations of the spectral density functions [3].

The form of the correlation function in Eq. (2) involves a choice of origin for the starting position of one of a pair of interacting spins and a summation over the possible positions of the other spin with a weighting of c for the probability of occupation of the sites. The jump probability is the same for all sites and in all possible directions. This analysis needs modification for disordered systems.

In a disordered system with a normalised distribution $N_s(E)$ of site energies, the probability $p(E)$ of occupation of a site with energy E is given by the Fermi–Dirac distribution (see, for example, Ref. [8])

$$p(E) = \frac{1}{\mathrm{e}^{(E-\mu)\beta}+1} \tag{4}$$

where μ is the chemical potential. The chemical potential μ is related to the fraction c of interstitial sites occupied by

$$c = \int_{-\infty}^{\infty} p(E)N_s(E)\,\mathrm{d}E. \tag{5}$$

The atom jump rate from a site with energy E to a neighbouring site will depend on the barrier energy E_1 between the sites and whether or not the target site is vacant. Assuming that the occupation of each site is independent of the occupation of its neighbours, the probability of no jump of an atom to a particular neighbour in a time t is $\exp[-(1-c)\Gamma(E,E_1)t]$, where $\Gamma(E,E_1) = \Gamma_0\exp[-(E_1-E)\beta]$. The parameter Γ_0 is assumed independent of the site and the occupation of its neighbours.

The correlation function for disordered systems, analogous to Eq. (2) for ordered systems, is then

$$G(t) = \frac{S}{c}\left\{\int p(E)N_s(E)\,\mathrm{d}E\left[\int N_b(E_1)\,\mathrm{e}^{-(1-c)\Gamma(E,E_1)t}\,\mathrm{d}E_1\right]^Z\right\}^2 \tag{6}$$

where $N_b(E_1)$ is the normalized distribution of barrier energies. The summation S is taken over the average positions of neighbours of a site, ignoring correlations between these positions and jump rates $\Gamma(E,E_1)$. In the above expression the term $p(E)N_s(E)$ is the weighting of occupation of each of a pair of sites of interacting spins, the integral with respect to barrier energies E_1 is the probability of no jump of a spin to a particular neighbour in a time t, and this integral is raised to the power Z because of the Z possible directions for the jump. The value of Z is assumed to be the same at all sites. The integral over site energies is squared because either spin of the pair may jump. The factor of $1/c$ multiplying the expression occurs because $p(E)N_s(E)$ is normalised to c from Eq. (5), and the probability of occupation of one of the pair of sites must be normalised to unity. The ordered case described by Eq. (2) can be recovered by taking δ function distributions. When a pair of spins are nearest neighbours the number of possible jump directions should be reduced from Z but this effect is ignored in the BPP model.

Particular models that are often considered for diffusion in disordered systems are a site-energy model, in which all the barrier heights are assumed constant, and a barrier-energy model in which all the site energies are assumed constant. For the site-energy model the correlation function is

$$G_s(t) = \frac{S}{c}\left\{\int p(E)N_s(E)\,\mathrm{e}^{-Z(1-c)\Gamma(E,E_1)t}\,\mathrm{d}E\right\}^2 \tag{7}$$

where E_1 are the constant barrier energies. For the barrier-energy model

$$G_b(t) = cS\left\{\int N_b(E_1)\,\mathrm{e}^{-(1-c)\Gamma(E,E_1)t}\,\mathrm{d}E_1\right\}^{2Z}. \tag{8}$$

where E are the constant site energies.

It is of interest to note the dependences of the models on the concentration c. In the ordered case and the barrier-energy models, the parameter c occurs as an overall scaling factor and as a scaling of time with $(1-c)$. For the models including a site-energy distribution there is an additional c dependence through the Fermi–Dirac distribution.

3. Results

The expressions for the spin-lattice relaxation rates R_1 (laboratory frame) and $R_{1\rho}$ (rotating frame) are [3]

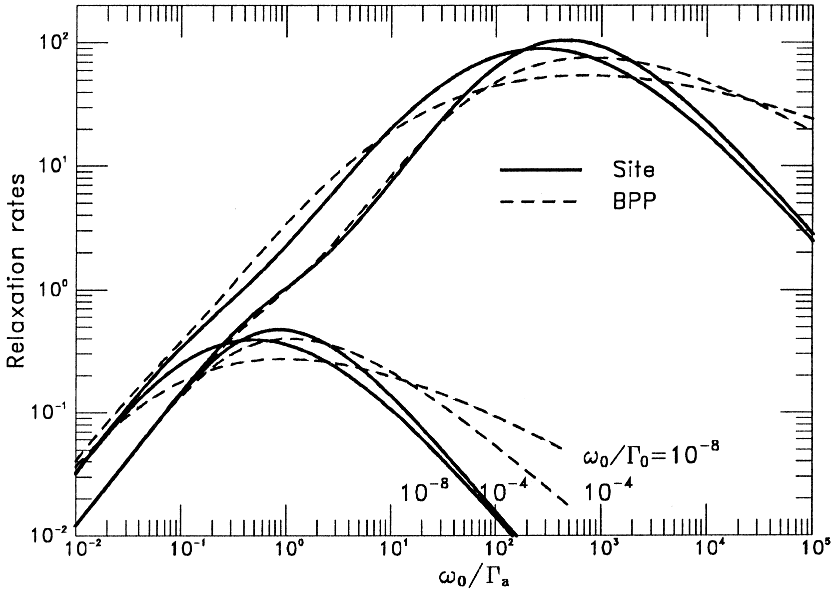

Fig. 1. Relaxation rates R_1 (curves with lower maxima) and $R_{1\rho}$ (curves with upper maxima), in units of $\omega_0/[\gamma^4 h^2 I(I+1)Sc]$, as a function of ω_0/Γ_a, for the BPP model of Eq. (1) and the site-energy model, with $c=0.5$, $\sigma/(\overline{E}_1-\overline{E})=0.12$ and $\omega_1/\omega_0=0.001$.

$$R_1=\frac{1}{5}\gamma^4 h^2 I(I+1)[J(\omega_0)+4J(2\omega_0)] \tag{9}$$

$$R_{1\rho}=\frac{1}{10}\gamma^4 h^2 I(I+1)[3J(2\omega_1)+5J(\omega_0)+2J(2\omega_0)] \tag{10}$$

where γ and I are the nuclear gyromagnetic ratio and spin quantum number, respectively, of the diffusing species, $\omega_0=\gamma B_0$ and $\omega_1=\gamma B_1$, where B_0 and B_1 are the static and rotating magnetic fields, respectively.

Calculations of the relaxation rates have been performed numerically for models with a normalised Gaussian distribution of energies

$$N(E)=\frac{1}{\sqrt{2\pi}\sigma}\,\mathrm{e}^{-(E-\overline{E})^2} \tag{11}$$

with mean $\overline{E}$ and standard deviation σ. The value of the number of nearest neighbours Z is assumed to be four, corresponding to tetrahedral interstitial sites.

Some results are presented in Figs. 1 and 2 for the relaxation rates, in units of $\omega_0/[\gamma^4 h^2 I(I+1)Sc]$, as a

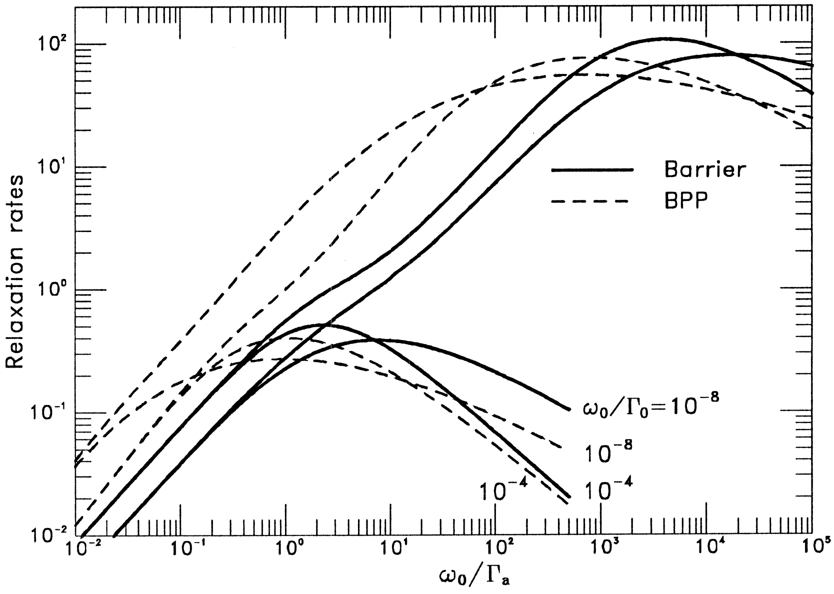

Fig. 2. As for Fig. 1 for the barrier-energy model.

function of ω_0/Γ_a, where $\Gamma_a = Z(1-c)\Gamma_0 \exp[-(\overline{E_1} - \overline{E})\beta]$ is the average jump rate of a spin from a site with energy barriers corresponding to the means of the energy distributions. The figures correspond to scaled plots of experimental relaxation rates as a function of reciprocal temperature. For a BPP model of an ordered system such a plot would give a universal curve independent of concentration c and frequency ω_0, for a given ratio ω_1/ω_0 in the case of $R_{1\rho}$. For disordered systems the additional parameters required are c and ω_0/Γ_0 [9], as well as parameters describing the energy distributions.

The results in Fig. 1 are for a site-energy distribution model corresponding to Eq. (7) and those on Fig. 2 for a barrier-energy model corresponding to Eq. (8). In both cases $\sigma/(\overline{E_1} - \overline{E}) = 0.12$, $\omega_1/\omega_0 = 0.001$ and $c = 0.5$. Results are shown for $\omega_0/\Gamma_0 = 10^{-4}$ and 10^{-8}. In the case of the site-energy model the chemical potential μ was first calculated for each c and T (corresponding to a particular value of ω_0/Γ_a), and this value then used in Eq. (7). The BPP results from Eq. (1) are also shown and these are the same in both figures because this model does not distinguish between site- and barrier-energy models.

Features of relaxation rate data that are often of interest are the magnitudes of the maximum relaxation rates and the temperatures at which these maxima occur. Some results for these parameters for the rotating frame relaxation $R_{1\rho}$ are shown in Figs. 3 and 4. The BPP model for an ordered system gives the maximum of the relaxation rate in the rotating frame as $0.15\omega_0/\omega_1$ in the units used in Figs. 1 and 2, so that the corresponding line in Figs. 3 and 4 would be $150c$. The position of this maximum for the ordered system is at $\omega_0/\Gamma_a = \omega_0/\omega_1 = 1000$, independent of c and ω_0/Γ_0.

4. Discussion and conclusion

A comparison between the relaxation rates calculated from the present theory with those from the BPP theory in Figs. 1 and 2 for $c = 0.5$ shows that, while the curves are all qualitatively similar in form, there are substantial differences in detail. For the site-energy model in Fig. 1 the BPP model shows much more broadening in the curves and asymmetry between the asymptotic forms on either side of the peaks. For the barrier-energy model in Fig. 2 the BPP model shows similar broadening to the results for the barrier-energy model, but the values of the maxima and their positions are quite different. Results for other values of spin concentration c show similar behaviour. The BPP values of the maximum relaxation rates, and their positions, as functions of c, show similar behaviour to the site-energy model as shown in Fig. 3, but again the magnitudes of the values are quite different. For the barrier-energy model in Fig. 4 there are significant differences between the BPP and barrier-energy maxima as functions of c in the form of the curves as well as the magnitudes. The maxima in the relaxation rates for all of the models are less than the corresponding values for the BPP results in an ordered system. For the ordered system the position of the maximum is when ω_0/Γ_0 is a constant. This is not the case for disordered systems, as can be seen

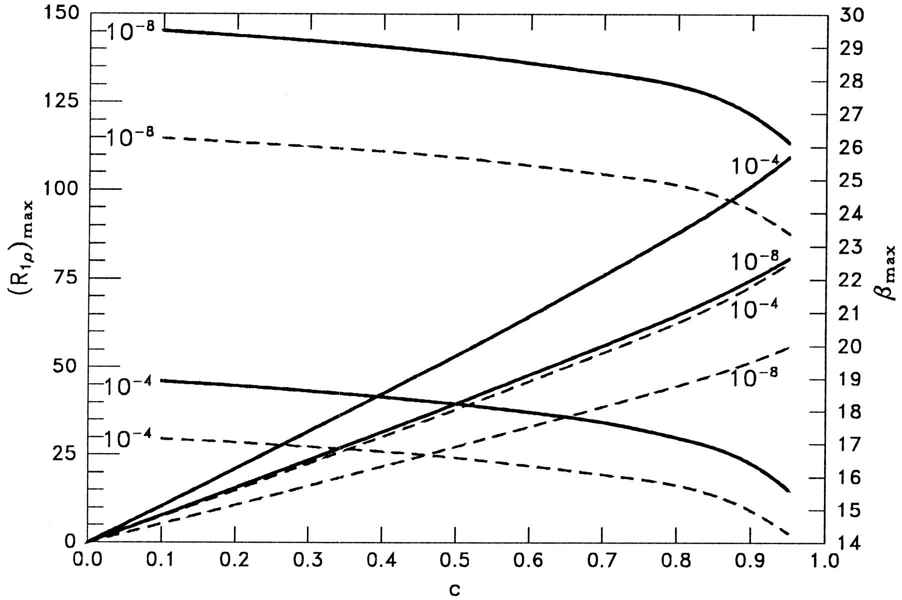

Fig. 3. Values of the maximum relaxation rate $R_{1\rho}$, in units of $\omega_0/[\gamma^4 h^2 I(I+1)S]$, and the value of $\beta = (\overline{E_1} - \overline{E})/(kT)$ at which the maximum occurs, as functions of spin concentration c, for the BPP model (broken lines) and the site-energy model (solid lines). The curves commencing at the origin are the maximum relaxation rates (left-hand scale) and the other curves are the values of β_{max} (right-hand scale). The values of ω_0/Γ_0 for each curve are shown on the figure.

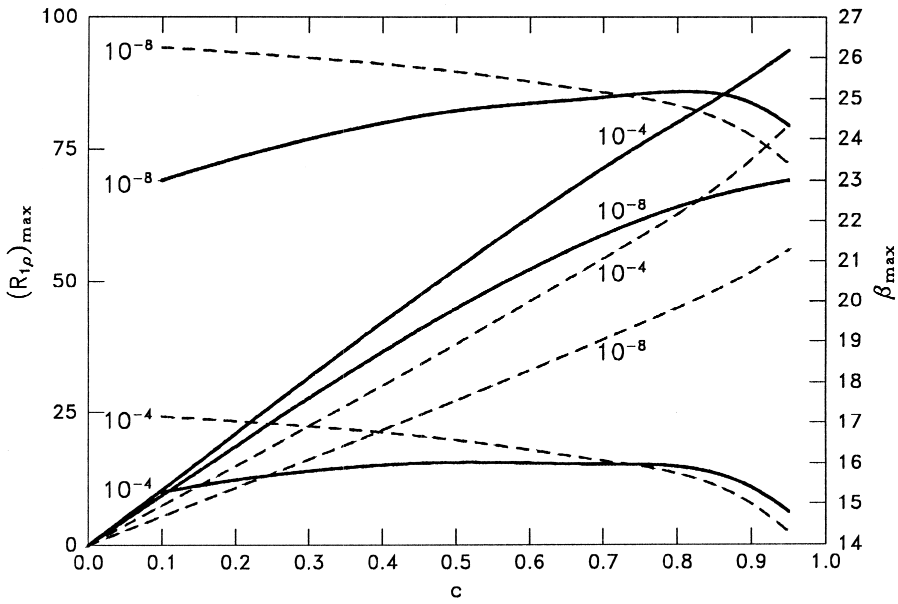

Fig. 4. As for Fig. 3 for the barrier-energy model.

in the figures, and the position of the maximum depends on the values of ω_0/Γ_0 and c.

Similar conclusions follow for results calculated for other values of the standard deviation σ. As the value of σ is decreased the relaxation rates for all the models tend towards the form for the BPP model for an ordered system as expected. The differences between the BPP and present models, therefore, increase with increasing disorder. There would, therefore, appear to be serious discrepancies in the simple BPP model of Eq. (1) for disordered systems.

The present model based on Eqs. (7) and (8) has a sounder physical basis than Eq. (1) but it still involves approximations. In particular, it assumes that the correlation between a pair of diffusing spins is destroyed as soon as one of the spins jumps. The importance of the return jumps and the contributions to the relaxation from diffusion to other sites needs further investigation. It is, however, of interest to note that the result in Figs. 1 and 2, that a distribution of barrier energies is more effective in producing broadening of the relaxation peaks than a distribution of site energies, is consistent with an analysis of finite disordered systems for low spin concentrations [9], although some Monte Carlo calculations have shown the reverse behaviour [10] and the behaviour may depend on the spin concentration. A detailed comparison of the results from the present models with calculations by other methods is highly desirable to clarify the effect of the approximations in deriving Eqs. (6)–(8).

The concentration dependence of the maximum relaxation rates and their positions shown in Figs. 3 and 4 can be compared with the concentration-dependent measurements of McDowell and Cotts [6] for ^{1}H rotating frame relaxation in $Ni_{0.33}Zr_{0.67}H_x$. The present modifications of the BPP model cannot explain their data with a single set of concentration-independent parameters. Their results showed a much greater relative change in the position of the peak with concentration than is the case for any of the curves in Figs. 3 and 4, and the values of their maximum relaxation rates showed structure between $c = 0.25$ and 5 that is not present in the present results. This suggests that these features are a consequence of parameters such as the the details of the site- or barrier-energy distributions being concentration dependent.

The modifications to the BPP theory described here provide a relatively straightforward method and a more rigorous approach than Eq. (1) for analysing relaxation data in disordered systems. There is the possibility of distinguishing between site- and barrier-energy disorder and of examining the consequences of combinations of these on the relaxation rates. The more general model of Eq. (6) could be used with a set of parameters for both types of disorder together to obtain the best fit to data. A practical difficulty with this generalisation is the number of parameters involved and also the computational effort needed in this general case. The use of Eq. (6) involves the computation of a triple integral to obtain the spectral density functions, compared with only double integrals for the site- or barrier-energy models separately. Even in these simpler cases the computational time can be significant for higher frequencies, although this difficulty can be overcome in practice by neglecting the $J(\omega_0)$ and $2J(2\omega_0)$ terms in Eq. (10) in regions away from the rotating-frame relaxation peak where they are small.

Frequency-dependent measurements of relaxation rates in disordered systems are especially valuable. As shown in Figs. 1–4, measurements at different frequencies provide additional information, unlike the case for ordered systems. The rotating-frame relaxation is especially important in this regard as it may provide a greater range of frequencies than the laboratory frame [10]. Analysis of the data as a function of frequency at fixed temperature and spin concentration would then eliminate any temperature or concentration-dependent effects on the nature of the disorder.

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