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Theory of nuclear spin relaxation in disordered systems: comparison of Bloembergen–Purcell–Pound models and Monte Carlo simulations

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Abstract

Two Bloembergen–Purcell–Pound (BPP) models for analysing nuclear spin relaxation data for translational diffusion in disordered systems are compared with Monte Carlo simulations. One model (the a-BPP model, 'a' standing for average) is commonly used for disordered systems and the other (the Cameron–Sholl BPP model) is more rigorously based and can distinguish between site- and barrier-energy disorder. Simulated relaxation data produced using Gaussian distributions of energy disorder are analysed using the models, and the parameters obtained from the fits are compared with the values used for the simulations. It is found that both models can give reasonable fits to the data. Both models also give reasonable agreement with the simulation parameters provided that the standard deviation of the energy distribution for the a-BPP model is interpreted as the average of the site- and barrier-energy standard deviations. Quantitative estimates are given of the accuracy of the parameters from the fits.

1. Introduction

The analysis of nuclear spin relaxation rates due to magnetic dipolar interactions between spins undergoing relative diffusion is often performed, for simple ordered systems, by using the Bloembergen–Purcell–Pound (BPP) model (Bloembergen *et al* 1948). The BPP model simply assumes an exponential correlation function for the magnetic dipolar fluctuations at a nuclear site. More accurate models have been developed for ordered systems which take into account the random walks of the diffusing species (see, for example, Sholl (1988)), but such detailed models are far more complex for disordered systems. A simple extension of the BPP model to disordered systems is obtained by averaging the exponential correlation function over an assumed distribution of activation energies arising from the structural disorder. This extension of the BPP model, to be referred to as the a-BPP model, is commonly used in analysing nuclear spin relaxation rates in disordered systems (see, for example, Barnes (1997)).

The a-BPP extension of the BPP model has little physical justification. An alternative extension of the BPP model to disordered systems, to be referred to as the Cameron–Sholl BPP (CS-BPP) model, has been proposed (Cameron and Sholl 1999a, Sholl 2000). This model is a more rigorous application of the BPP model to disordered systems which takes into account the Fermi–Dirac statistics for occupation probabilities of sites, and describes the jump probabilities of diffusing species away from a particular site correctly. The model can also incorporate both site-energy and barrier-energy disorder, unlike the a-BPP model for which the description of the energy disorder is not specified. The CS-BPP model has recently been applied to the analysis of relaxation data in a quasicrystalline material (McDowell *et al* 2001).

While the CS-BPP model is more rigorously based than the a-BPP model, it still involves the fundamental approximation of an exponential correlation function and does not take into account the random walk of the diffusing species on the disordered structure. The accuracy of assuming an exponential correlation function can be assessed in ordered structures by comparing the results with those from more rigorous models, but the accuracy of the a-BPP and CS-BPP models is not known for disordered structures. The aim of the present work is to assess the accuracy of these models by comparing their results with those obtained from Monte Carlo (MC) simulations.

The analytic forms of the BPP models are summarized in section 2. MC simulations of diffusion in disordered systems are more complicated than for ordered systems and the details of the simulation procedure used are described in section 3. The results of the simulations for some particular cases are compared with the results for the BPP models in section 4.

2. BPP models

The correlation function $G(t)$ for magnetic dipolar interactions is (see, for example, Girard and Sholl (1996))

$$G(t) = \sum_{\alpha,\beta} \frac{P_2(\cos\theta_{\alpha\beta})}{r_\alpha^3 r_\beta^3} P_{eq}(\boldsymbol{r}_\alpha) P(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, t) \tag{1}$$

where $P_{eq}(\boldsymbol{r}_\alpha)$ is the equilibrium probability of a pair of spins being separated by $\boldsymbol{r}_\alpha$, $P(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, t)$ is the probability that a pair of spins are separated by $\boldsymbol{r}_\beta$ at time t if they were separated by $\boldsymbol{r}_\alpha$ at time zero, and $\theta_{\alpha\beta}$ is the angle between $\boldsymbol{r}_\alpha$ and $\boldsymbol{r}_\beta$. The basic assumption in BPP theories is to approximate $P(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, t)$ by the probability of no jump of either spin in a time t. It is this assumption that gives an exponential correlation function in simple ordered systems. The physical meaning of the assumption is that the magnetic dipolar correlation is completely destroyed when a jump of either spin occurs.

As described in Cameron and Sholl (1999a) and Sholl (2000), the CS-BPP model considers a set of sites in a disordered structure for which the site-energy probability distribution is $N_s(E)$ and for which there is an energy barrier between adjacent sites with an independent distribution $N_b(E_1)$. A fraction c of the available sites are filled with atoms which diffuse by jumps from a site with energy E to a neighbouring site across a barrier with energy E_1 with a jump rate Γ given by

$$\Gamma(E, E_1) = \Gamma_0 \mathrm{e}^{-(E_1 - E)\beta} \tag{2}$$

where $\beta = 1/(kT)$ and the prefactor Γ_0 is assumed to be the same at all sites. The CS-BPP correlation function for magnetic dipolar interactions between spins diffusing on these sites is

$$G(t) = \frac{S}{c}\left\{\int p(E) N_s(E)\,\mathrm{d}E \left[\int N_b(E_1)\mathrm{e}^{-(1-c)\Gamma(E,E_1)t}\,\mathrm{d}E_1\right]^Z\right\}^2 \tag{3}$$

where Z is the average number of nearest-neighbour jumps from a site, S is the lattice summation $S = \sum_\alpha r_\alpha^{-6}$, and $p(E)$ is the Fermi–Dirac function

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

The chemical potential μ is related to c by

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

The corresponding correlation function for the a-BPP model averaged over a distribution $N(E)$ of activation energies is (Barnes 1997)

$$G_{BPP}(t) = Sc \int N(E) e^{-2(1-c)Z\Gamma(E)t}\, dE \tag{6}$$

where $\Gamma(E) = \Gamma_0 \exp(-E\beta)$. The relation between the energy distribution $N(E)$ and site and barrier energies is not specified in this model.

The corresponding spectral density functions $J(\omega)$ are the Fourier transforms of the correlation functions, and the nuclear spin relaxation rates are linear combinations of the spectral density functions (see, for example, Sholl (2000)). A numerical technique for evaluating the CS-BPP spectral density functions has been described by Sholl (2000).

3. Monte Carlo simulations

The MC simulations were performed for the diamond structure and for the simple cubic lattice to simulate diffusion in disordered systems with average coordination numbers of $Z = 4$ and 6, respectively. Diffusion is assumed to occur between the sites of these ordered structures with the disorder imposed on the jump rates of the diffusing species. Structural disorder could also be included in the simulations but was not considered because it involves additional parameters; it is sufficient to assess the validity of the a-BPP and CS-BPP models without including structural disorder, and the disorder in the jump rates is likely to be much more important than the structural disorder in explaining the form of relaxation rates in disordered systems.

In a simulation each site was allocated an energy according to the site-energy probability distribution and each direction to a nearest-neighbour site was independently allocated a barrier energy according to the barrier-energy distribution. Sites were then filled randomly with spins according to the site-energy distribution and the Fermi–Dirac distribution for a specific temperature T and average concentration c of atoms. The occupational probabilities of the sites then correspond to thermal equilibrium. It was verified numerically that the system remained in thermal equilibrium as diffusion proceeded. Periodic boundary conditions were used to ensure that no spins were lost from the system.

The diffusion for the site- and barrier-energy disorder was simulated in two ways: a discrete time method and a continuous time method. In the discrete time method, a spin and its jump direction to a nearest-neighbour site are chosen randomly at each MC cycle. If the target site for the jump is occupied, no jump occurs and the next cycle commences. If the target site is unoccupied, the jump is allowed to occur with probability Γ/Γ_{max} where Γ is the jump rate for the particular jump and Γ_{max} is the maximum jump rate for any jump in the particular simulation. The number N of MC cycles is related to the time t by $N = N_s \Gamma_{max} t$ where N_s is the number of spins in the simulation.

In the continuous time method, all possible (unblocked) jump frequencies Γ_i are first calculated for the current stage of the particular simulation at the beginning of each MC cycle. The sum Γ_{tot} of all these frequencies is then stored. The time Δt to the next spin jump

somewhere in the system is then calculated from a random number X between 0 and 1 using $X = 1 - e^{-\Gamma_{tot} t}$, since $e^{-\Gamma_{tot} \Delta t}$ is the probability of no jump in a time t. The jump i that actually occurs is chosen with probability Γ_i / Γ_{tot}.

In both methods it is more efficient to follow the diffusion of vacancies rather than spins for $c > 0.5$. It was verified that the discrete time and continuous time methods gave consistent results. Another check on the simulation procedures was to compute the average jump rate and compare it with the known analytic form (Cameron and Sholl 1999b). With regard to the comparative efficiency of the two methods, the continuous time method has the disadvantage of requiring the calculation of Γ_{tot} at each MC cycle, but has the advantage that a successful jump always occurs. The discrete time method has less computation at each cycle but can result in many cases with blocked jump attempts. It was found that the discrete time method was more efficient at low concentrations of spins or vacancies and that the continuous time method was more efficient at higher concentrations.

The correlation function (1) was calculated at regular time intervals in a simulation. The form of $G(t)$ is difficult to obtain accurately at long times since this requires very long simulations. This difficulty was overcome by noting that the asymptotic form is expected to be proportional to $t^{-3/2}$ since the correlation is a result of three-dimensional diffusion. This asymptotic limit was verified numerically and the proportionality constant obtained in each simulation. To obtain the corresponding spectral density function $J(\omega)$, the Fourier transform of $G(t)$ can then be evaluated accurately and efficiently by integrating the numerical form of $G(t)$ up to the time at which the $t^{-3/2}$ behaviour is reached and integrating the analytic asymptotic form for larger t.

MC simulations of nuclear spin relaxation rates for diffusion in disordered systems have previously been carried out by Adnani *et al* (1994) and Hua *et al* (1995, 1997). The work of these authors did not use the Fermi–Dirac function for the equilibrium distribution of spins and discussed the results in terms of the average jump rate, which was obtained numerically from the simulations. Analytic expressions for the average jump rate are now available (Cameron and Sholl 1999b). The correlation functions obtained were fitted to a sum of exponentials rather than by the more rigorous procedure of obtaining the correct asymptotic limit as used in the present work.

4. Results

The approach used to assess the accuracy of the BPP models was to first use MC simulations with a choice of diffusion parameters to calculate the correlation functions $G(t)$, spectral density functions $J(\omega)$, and relaxation rates R_1 in the laboratory frame and $R_{1\rho}$ in the rotating frame as functions of temperature. The R_1-relaxation data were then fitted using the a-BPP and CS-BPP models by varying the diffusion parameters and using a numerical least-squares fitting procedure. The accuracy of the BPP models can then be assessed by the quality of the fits obtained to both the R_1- and $R_{1\rho}$-data, and, in particular, by how well the original parameters used in the simulation are reproduced by the fits.

All simulations were performed assuming a Gaussian $N(E) = (2\pi\sigma^2)^{-1/2} \exp[-(E - \overline{E})^2/(2\sigma^2)]$ for the energy probability distributions. Subscripts s and b will be used to denote parameters referring to site energies and barrier energies, respectively. The difference between the mean barrier energy and mean site energy is $E_a = \overline{E_b} - \overline{E_s}$. E_a will also denote the mean energy for the energy distribution in the a-BPP model. A value of $E_a = 0.5$ eV was used in all of the simulations.

Calculations were performed for concentrations $c = 0.1$, 0.5, and 0.9 of diffusing nuclei on the simple cubic lattice and on the diamond structure. The MC simulations used 22^3 sites

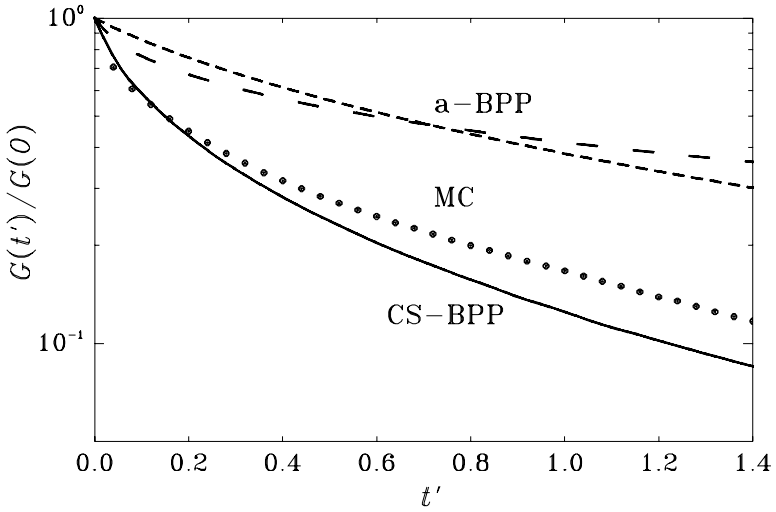

Figure 1. Comparison of the normalized correlation function from a MC simulation with the a-BPP and CS-BPP models for the same parameters and conditions: tetrahedral structure, $c = 0.1$, $\sigma_s = 1.5kT$, $\sigma_b = 3kT$. The a-BPP curves are for $\sigma = 1.5kT$ (short-dash curve) and $\sigma = 3kT$ (long-dash curve). The parameter $t' = (1 - c)\Gamma_0 t \exp(-E_a/kT)$.

for the simple cubic lattice with $c = 0.1$ and 1000 sites for other c. The number of sites used for the tetrahedral structure were 16^3 for $c = 0.1$ and 1000 for other c. It was verified that there was no significant change in the results for a larger number of sites. Results for the correlation function $G(t)$ were averages of at least 30 different simulations for the same set of parameters.

An example of a correlation function as a function of dimensionless time, given by $t' = (1 - c)\Gamma_0 t \exp(-E_a/kT)$, is shown in figure 1. The a-BPP and CS-BPP results are for the same parameters as the MC simulations. The a-BPP model does not distinguish between site- and barrier-energy distributions, so results are shown for both values of the standard deviations. The BPP correlation functions depend only on the combination σ/kT rather than σ and T separately. All of the curves in figure 1 are qualitatively similar and show decay slower than exponential. There are, however, quantitative differences between the curves which indicate that fitting the relaxation data by varying the diffusion parameters will give different parameters to those used for the simulations. (Figure 1 showing the CS-BPP curve is analogous to figure 2 in Sholl (2000). The latter figure is incorrect.)

Examples of simulated relaxation rates and fits to the R_1-data are shown in figures 2 and 3. The parameters varied in the fits were: E_a, Γ_0, σ_s, and σ_b for the CS-BPP model; and E_a, Γ_0, and σ for the a-BPP model. The $R_{1\rho}$-curves shown for the BPP models are for these parameters obtained from the R_1-fits. The curves are not fitted to the MC $R_{1\rho}$-data. The quality of the fits to the data is reasonable for both models, but is better for the CS-BPP model. The fit in the low-temperature region is the least satisfactory, which suggests that the BPP models are less reliable there. The low-temperature region is also the region for which the MC simulations and the calculations for the models are most time-consuming. The effort necessary to perform the calculations in this region would not therefore seem to be worthwhile, and fitting to experimental data would be more efficiently done by excluding such low-temperature data. The simulations and calculations for the models are also more time-consuming for larger amounts of disorder in the energy distributions. For example, the data in figure 3 required considerably more computing time than those in figure 2 because of the larger values of the standard deviations.

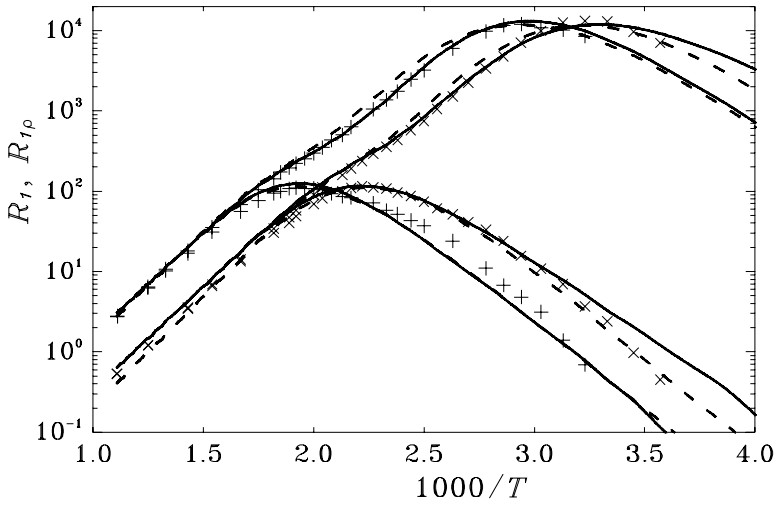

Figure 2. The relaxation rates R_1 and $R_{1\rho}$ (in units of the second moment M_2) from the MC simulations and the fits using the a-BPP (dashed curves) and CS-BPP (solid curves) models. The MC results are shown by symbols: $+(c = 0.9)$ and $\times(c = 0.1)$. The simulations are for $E_a = 0.5$ eV, $\sigma_s = 0.03$ eV, $\sigma_b = 0.06$ eV and $\Gamma_0 = 3 \times 10^{13}/(1 - c)$ s^{-1}. The parameters for the fits are given in table 1.

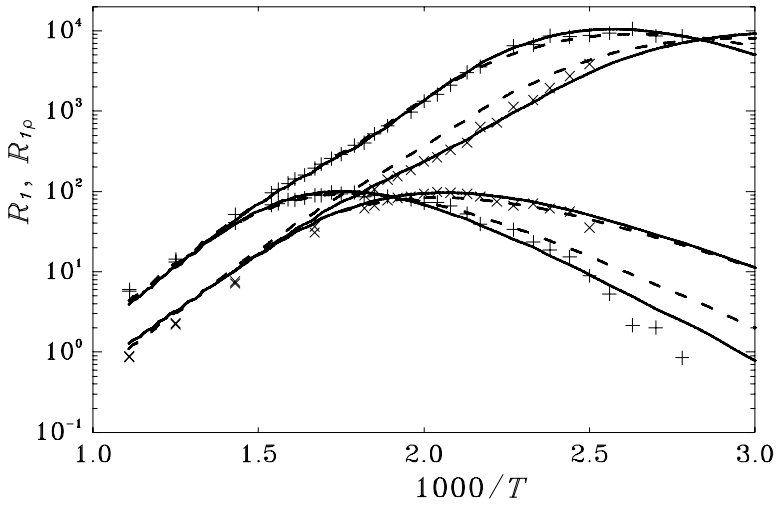

Figure 3. As for figure 2, but with $\sigma_s = \sigma_b = 0.0875$ eV.

The values of the fitted parameters are compared in table 1 with the starting values of the parameters for the cases in figures 2 and 3, and for a range of other starting parameters. All of the data in table 1 are for the tetrahedral structure and values of $c = 0.1$ and 0.9. Calculations were also performed for $c = 0.5$ and for diffusion on a simple cubic lattice. The agreements with the starting parameters in these cases were similar to those presented in table 1.

The values of E_a, σ_s, and σ_b from the fits using the CS-BPP model agree with the starting values of these parameters typically to within 10%. The values of σ from the fits using the a-BPP model are close to the corresponding means of the starting values of σ_s and σ_b. The

Table 1. Comparison between the starting parameters for the MC simulations and the parameters deduced by fitting the BPP models to the R_1-relaxation rates. Units are eV for energies and standard deviations, and 10^{13} s^{-1} for Γ_0.

c	MC	CS-BPP	a-BPP
0.1	$\sigma_s = 0.03$, $\sigma_b = 0.06$	0.032, 0.059	0.047
	$E_a = 0.5$, $\Gamma_0 = 3.3$	0.51, 1.1	0.51, 1.5
0.9	$\sigma_s = 0.03$, $\sigma_b = 0.06$	0.033, 0.062	0.043
	$E_a = 0.5$, $\Gamma_0 = 30$	0.54, 6.8	0.52, 12
0.1	$\sigma_s = 0.06$, $\sigma_b = 0.03$	0.052, 0.034	0.048
	$E_a = 0.5$, $\Gamma_0 = 3.3$	0.48, 0.71	0.53, 1.3
0.9	$\sigma_s = 0.06$, $\sigma_b = 0.03$	0.066, 0.027	0.048
	$E_a = 0.5$, $\Gamma_0 = 30$	0.54, 11	0.53, 11
0.1	$\sigma_s = 0.045$, $\sigma_b = 0.045$	0.051, 0.048	0.048
	$E_a = 0.5$, $\Gamma_0 = 3.3$	0.49, 0.98	0.52, 1.4
0.9	$\sigma_s = 0.045$, $\sigma_b = 0.045$	0.058, 0.054	0.042
	$E_a = 0.5$, $\Gamma_0 = 30$	0.57, 14	0.56, 6.1
0.1	$\sigma_s = 0.075$, $\sigma_b = 0.1$	0.075, 0.092	0.085
	$E_a = 0.5$, $\Gamma_0 = 3.3$	0.54, 2.0	0.58, 3.1
0.9	$\sigma_s = 0.075$, $\sigma_b = 0.1$	0.056, 0.087	0.073
	$E_a = 0.5$, $\Gamma_0 = 30$	0.54, 5.4	0.56, 15
0.1	$\sigma_s = 0.1$, $\sigma_b = 0.075$	0.13, 0.070	0.090
	$E_a = 0.5$, $\Gamma_0 = 3.3$	0.48, 2.9	0.61, 3.0
0.9	$\sigma_s = 0.1$, $\sigma_b = 0.075$	0.090, 0.068	0.075
	$E_a = 0.5$, $\Gamma_0 = 30$	0.58, 7.1	0.52, 4.9
0.1	$\sigma_s = 0.0875$, $\sigma_b = 0.0875$	0.081, 0.083	0.075
	$E_a = 0.5$, $\Gamma_0 = 3.3$	0.57, 3.6	0.59, 3.7
0.9	$\sigma_s = 0.0875$, $\sigma_b = 0.0875$	0.070, 0.072	0.078
	$E_a = 0.5$, $\Gamma_0 = 30$	0.58, 5.9	0.55, 8.9

accuracy of the deduced values of E_a and the mean of the standard deviations is again typically within 10%. The fitted values of the jump rate prefactor Γ_0 are too small by a factor of up to approximately five for both the BPP models.

5. Conclusions

The comparison between the MC simulations of the relaxation rates with the fits using the a-BPP and CS-BPP models for the range of parameters studied show that both of the models can produce reasonable fits to the relaxation data, except for the low-temperature regime. It would therefore be preferable in using the models for fits of experimental relaxation data to exclude data in the low-temperature region, especially in view of the considerable computational effort needed to calculate the theoretical values there.

Within the constraint of assuming Gaussian distributions for the energy distributions, the values of the parameters obtained from the fits suggest that the CS-BPP model can give standard deviations and the difference between the mean energies for the site- and barrier-energy distributions for relaxation data fits to typically within 10%. The a-BPP model cannot provide information on site and energy distributions separately, but appears to give reasonable values of the averages of the standard deviations of the distributions, and the energy difference between the means again to typically within 10%. Both models give values of the prefactors for the jump rates that are typically too small by a factor of up to five. These quantitative

results show that the BPP models are likely to be quite reasonable in analysing relaxation data on disordered systems to within these accuracies.

The a-BPP and CS-BPP models have been used by McDowell *et al* (2001) to analyse proton relaxation data in a metallic icosahedral quasicrystal. A difficulty with fitting these data was that the relaxation rates in the laboratory and rotating frames could not be fitted simultaneously with a single set of parameters. The relative values of the maximum rates in the laboratory and rotating frames could not be reproduced by the BPP models. The comparison of the MC simulations with the results from the BPP models show that both of the models do reproduce the relative values of these maximum rates well. The source of the anomaly in the relative maxima in the above case is therefore not due to the approximations in the BPP models.

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