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A BPP (Bloembergen–Purcell–Pound) model for nuclear spin relaxation due to diffusion in disordered systems: combined barrier- and site-energy disorder

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Abstract. Nuclear spin relaxation rates due to magnetic interactions between diffusing spins in ordered systems are often interpreted in terms of an exponential correlation function (the BPP model). The common extension of this to disordered systems is to average the relaxation rate for a jump rate with energy E over a distribution $N(E)$ of energies in the disordered system. A more rigorous extension of the BPP model to disordered systems is described which incorporates simultaneous barrier- and site-energy distributions. An efficient computational scheme is developed to evaluate the triple integrals required. Results are presented for the correlation functions and relaxation rates for some typical values of parameters for both of the above extensions of the BPP model to disordered systems. There are significant differences between the results for the two models. The model presented here provides a means of analysing experimental relaxation data to deduce information about both barrier- and site-energy distributions.

1. Introduction

The nuclear spin relaxation rates due to magnetic dipolar interactions between spins undergoing relative diffusion depend on linear combinations of spectral density functions (see, for example, Sholl 1993). A theory of the spectral density functions is therefore necessary to relate observed relaxation rates to the microscopic details of the diffusion. The simplest approach for diffusion in ordered systems is the BPP model (Bloembergen *et al* 1948) which simply assumes an exponential correlation function proportional to $\exp(-t/\tau)$ where τ is the mean time for one of a pair of interacting spins to jump. The corresponding spectral density function is a Lorentzian function of frequency. It is also assumed that τ depends on temperature T according to the Arrhenius form $\tau = \tau_0 \exp(E/kT)$ where E is the activation energy for the diffusive jump of a spin. This model has been widely used in interpreting relaxation data on ordered systems because of its simplicity.

In disordered systems the structural disorder will produce a distribution of activation energies. The common extension of the BPP model for such cases has been to use a weighted average of the ordered BPP model with the weighting for each activation energy given by the appropriate energy distribution function (see, for example, Barnes 1997). There is, however, little justification for this procedure.

A physical basis for the assumption of an exponential correlation function is that $\exp(-t/\tau)$ is the probability of no jump of either of a pair of spins in a time t . The BPP model then describes a situation for which the correlation between a pair of spins is completely

destroyed when either of the spins jumps. This model has been extended to disordered systems (Cameron and Sholl (1999a), to be referred to as CS) for independent site-energy distributions and barrier-energy distributions. The energy of a site determines the occupation probability of the site according to the Fermi–Dirac distribution, and the height of the barrier energy between two neighbouring sites determines the rate of jumps between the sites. Some calculations by CS for the site-energy model and for the barrier-energy model showed that the results could be quite different to the common model of simply averaging the BPP model over a distribution of energies.

The purpose of this paper is to develop this CS model further. Any practical disordered system is likely to have both site-energy and barrier-energy disorder. It is therefore desirable that calculations can be performed for both such disorders occurring together. The computation of spectral density functions and relaxation rates in this case requires the numerical evaluation of triple integrals which can be extremely slowly convergent for low temperatures.

The basic theory of the correlation functions is described in section 2 and some numerical results are presented for both the present model (CS model) and the commonly used extension of the BPP model to disordered systems (BPP model) for the case of Gaussian energy distributions. An efficient method of calculating the spectral density functions and relaxation rates is described in section 3. Some results for relaxation rates for typical values of parameters are then shown and discussed.

2. Correlation functions

The model to be considered is a set of sites in a disordered structure for which the site-energy distribution is $N_s(E)$ and for which there is an energy barrier between adjacent sites with a 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

$$\Gamma(E, E_1) = \Gamma_0 e^{-(E_1 - E)\beta} \quad (1)$$

where $\beta = 1/(kT)$. The CS correlation function for magnetic dipolar interactions between spins diffusing on these sites is

$$G(t) = \frac{S}{c} \left\{ \int p(E) N_s(E) dE \left[\int N_b(E_1) e^{-(1-c)\Gamma(E, E_1)t} dE_1 \right]^Z \right\}^2 \quad (2)$$

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:

$$p(E) = \frac{1}{e^{(E-\mu)\beta} + 1}. \quad (3)$$

The chemical potential μ is related to c by

$$c = \int_{-\infty}^{\infty} p(E) N_s(E) dE. \quad (4)$$

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

$$G_{BPP}(t) = Sc \int N(E) e^{-2(1-c)Z\Gamma(E)t} dE \quad (5)$$

where $\Gamma(E) = \Gamma_0 \exp(-E\beta)$. A similar type of analysis has also been applied to the form of the average jump rate for disordered systems (Cameron and Sholl 1999b).

The assumption in the form of $G_{BPP}(t)$ is that each site has an equal probability of occupation and that the probability of no jump away from a site in a time t is determined by the sum of the jump rates in each direction. The CS correlation function includes the effect of occupation probabilities of sites according to the Fermi–Dirac function, and that the probability of no jump of a spin away from a site in any direction in a time t is given by the product of the probabilities of no jump of a spin in each direction. The difference between the two assumptions regarding jumps away from a site can be understood by an example in which the rate of jumps away from a site is much faster in one direction than the others. The rate of escape of a spin from the site will be determined largely by this fast jump rate rather than the average jump rate. This effect is described correctly in the CS correlation function. The CS and BPP correlation functions are identical in an ordered system where the occupation probabilities of sites are the same for all sites and the jump rate is the same for all directions.

It is useful to write the above expressions in the following forms for computational purposes. It will be assumed that the energy distributions are Gaussians with mean energies E_s , E_b and standard deviations σ_s , σ_b for the site- and barrier-energy distributions respectively. A similar procedure could be followed for any other functional form of the energy distributions. The following changes of variable are made:

$$\begin{aligned}\sigma &= \sqrt{2}\sigma_s\beta & \sigma_1 &= \sqrt{2}\sigma_b\beta \\ u &= (E - E_s)/(\sqrt{2}\sigma_s) & v &= (E_1 - E_b)/(\sqrt{2}\sigma_b) \\ \bar{\mu} &= (\mu - E_s)/(\sqrt{2}\sigma_s) & t' &= t\bar{\Gamma}\end{aligned}$$

where

$$\bar{\Gamma} = \Gamma_0(1 - c) \exp[-(E_b - E_s)\beta].$$

Equations (2) and (4) then become

$$G(t') = \frac{S}{c} \left\{ \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{e^{-u^2}}{e^{(u-\bar{\mu})\sigma} + 1} F^Z(t' e^{\sigma u}) du \right\}^2 \quad (6)$$

$$c = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{e^{-u^2}}{e^{(u-\bar{\mu})\sigma} + 1} du. \quad (7)$$

The function $F(t')$ is

$$F(t') = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp(-v^2 - t' e^{-\sigma_1 v}) dv \quad (8)$$

which only depends on the parameter σ_1 . The correlation function $G(t')$ depends on the parameters c , σ and σ_1 . The scaled time t' corresponds to t in units of the reciprocal of the jump rate $\bar{\Gamma}$ for a particular direction for energies which are the means of the energy distributions. The functions $F(t')$, $G(t')$ are independent of the mean energies E_s and E_b . The difference between these mean energies is only relevant in the scaling of time t .

If only the barrier-energy distribution occurs (constant site energies), the correlation function $G(t') = S_c F^{2Z}(t')$. The BPP correlation function (5) expressed in this notation is $G_{BPP}(t') = S_c F(2Zt')$. For an ordered system, $\sigma_1 = 0$ and $F(t') = e^{-t'}$.

A comparison of $F^{2Z}(t')$, $F(2Zt')$ and $\exp(-2Zt')$ is shown in figure 1 for $Z = 4$ and $\sigma_1 = 0, 1.5$ and 3.0 . Increasing σ_1 corresponds to increasing σ_s and/or decreasing temperature. For non-zero σ_1 both $F^{2Z}(t')$ and $F(2Zt')$ initially decrease faster than the exponential for $\sigma_1 = 0$ and then decrease slower than it at longer times. The initial rapid decay corresponds to jumps from those sites with low activation energies. The function $F^{2Z}(t')$, corresponding to the CS model, decreases faster than $F(2Zt')$, corresponding to the BPP model, which reflects

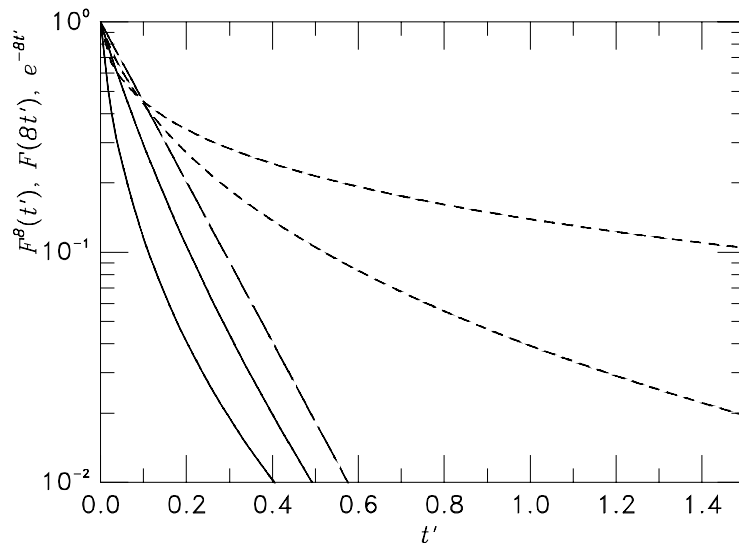


Figure 1. A comparison of $F^8(t')$ (CS model, solid curves), $F(8t')$ (BPP model, short-dashed curves) and $\exp(-8t')$ (long-dashed line). The curves with the smallest difference from the exponential for each model are for $\sigma_1 = 1.5$ and the other curves are for $\sigma_1 = 3.0$.

the possibility of a spin being able to jump along the fastest jump path in the CS model, rather than jumping according to the average jump rate as in the BPP model.

The form of the correlation function $G(t')/(Sc)$ is shown in figure 2 for $Z = 4$ and some values of σ , σ_1 and c . The two upper curves for large t' in figure 2 are for σ and σ_1 equal to 3 and

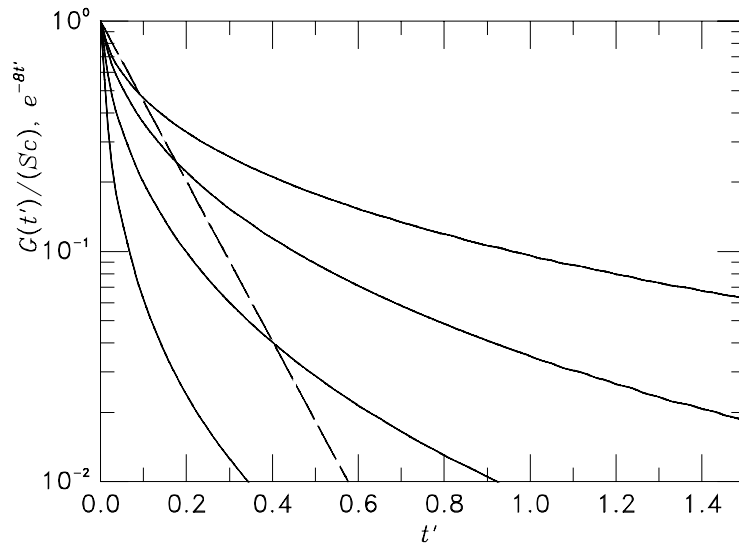


Figure 2. The correlation function $G(t')/(Sc)$ (solid curves). From left to right, the curves are for: $\sigma = 3.0, \sigma_1 = 1.5, c = 0.1$; $\sigma = 1.5, \sigma_1 = 3.0, c = 0.1$; $\sigma = 1.5, \sigma_1 = 3.0, c = 0.9$; $\sigma = 3.0, \sigma_1 = 1.5, c = 0.9$. The dashed curve is $\exp(-8t')$.

1.5, and the two lower curves are for 1.5 and 3 respectively. For each pair of curves the upper curve is for $c = 0.1$ and the lower curve for $c = 0.9$. The differences between these pairs of curves shows that disorder in the site energies has a different effect on the correlation functions to disorder in the barrier energies. The differences between the curves of each pair shows that the correlation functions depend significantly on the spin concentration c due to the effect of the Fermi–Dirac function. The BPP correlation function (5) does not show this c dependence, nor does it distinguish between disorder in the site- and barrier-energy distributions. All of the correlation functions for disordered systems in figure 2 show similar qualitative behaviour to the curves for the BPP model in figure 1 but the quantitative forms are different and depend on c . The results for the case of only a barrier-energy distribution (solid curves in figure 1) are quite different and show that the BPP model is not consistent with a distribution of barrier energies.

3. Relaxation rates

The expressions for the spin–lattice relaxation rates R_1 (laboratory frame) and $R_{1\rho}$ (rotating frame) for magnetic dipolar interactions between like spins can be expressed as

$$R_1 = \frac{M_2}{3Sc} [J(\omega_0) + 4J(2\omega_0)] \quad (9)$$

$$R_{1\rho} = \frac{M_2}{6Sc} [3J(2\omega_1) + 5J(\omega_0) + 2J(2\omega_0)] \quad (10)$$

where the second moment M_2 and the spectral density function $J(\omega)$ are

$$M_2 = \frac{3}{5} \gamma^4 \hbar^2 I(I+1) Sc \quad (11)$$

$$J(\omega) = 2 \int_0^\infty G(t) \cos(\omega t) dt = \frac{2}{\Gamma} \int_0^\infty G(t') \cos\left(\frac{\omega}{\Gamma} t'\right) dt'. \quad (12)$$

In these expressions γ is the gyromagnetic ratio and I the spin quantum number of the diffusing spins and ω_0 , ω_1 are the resonant frequencies of the spins in the static and rotating fields, respectively.

The computation of the relaxation rates for a particular set of parameters σ_s , σ_b , $E_b - E_s$ that specify the energy disorder, and for a specific temperature T , involves the numerical evaluation of a triple integral arising from the Fourier transform (12) and the double integral in the expressions (6) and (7) for $G(t')$. A direct numerical evaluation of the triple integral is extremely slow for low temperatures. An efficient computational method is needed for fitting experimental data since the calculations need to be performed for many sets of parameters in the fitting procedure. The following method is a rapid practicable scheme for all temperatures. The function $F(t')$ defined by equation (8) is first computed for a set of values of t' defined by $t' = \exp[(\sigma_1 + 0.8)t_i]$ with the values of t_i equally spaced. The values of $F^Z(t_i)$ are stored in an array and required values of $F^Z(t'e^{\sigma u})$ needed in computing $G(t')$ are computed from the stored array by interpolation. The 0.8 in the above exponential is an empirical value. The Fourier transform (12) is calculated by numerical integration over successive periods of the cosine until desired accuracy is reached. The infinite integrals in equations (6) and (8) are evaluated over a range of sufficient numbers of standard deviations to ensure the required accuracy.

Some examples of calculated relaxation rates, in units of M_2 , for typical values of parameters are shown in figures 3 and 4 for the CS and BPP models. The calculations are all for a resonant frequency of 30 MHz and $\omega_1 = 0.002\omega_0$. All of the results for the

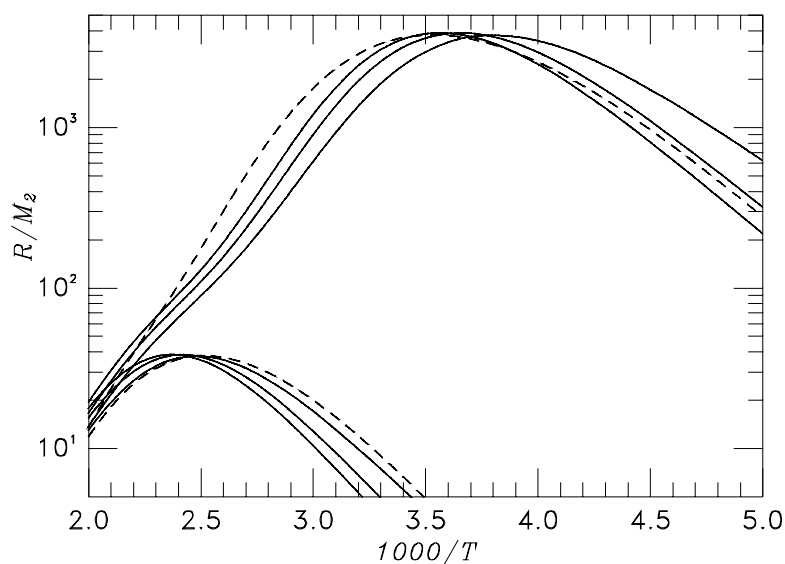


Figure 3. Calculated relaxation rates R_1 (curves with lower maxima) and $R_{1\rho}$ (curves with upper maxima) for a resonant frequency of 30 MHz and $\omega_1 = 0.002\omega_0$ and for the CS model (solid curves) and the BPP model (dashed curves). The parameters for the CS rates are $\sigma_s = 0.03$ eV, $\sigma_b = 0.06$ eV, $E_b - E_s = 0.5$ eV, $\Gamma_0 = 3.00 \times 10^{13}/(1 - c)$ Hz and $c = 0.1, 0.5$ and 0.9 (for curves from right to left). The parameters for the BPP rates are $\sigma = 0.06$ eV, $\bar{E} = 0.5$ eV, $\Gamma_0 = 1.0 \times 10^{14}/(1 - c)$ Hz and $M_2(\text{BPP}) = 1.21M_2$.

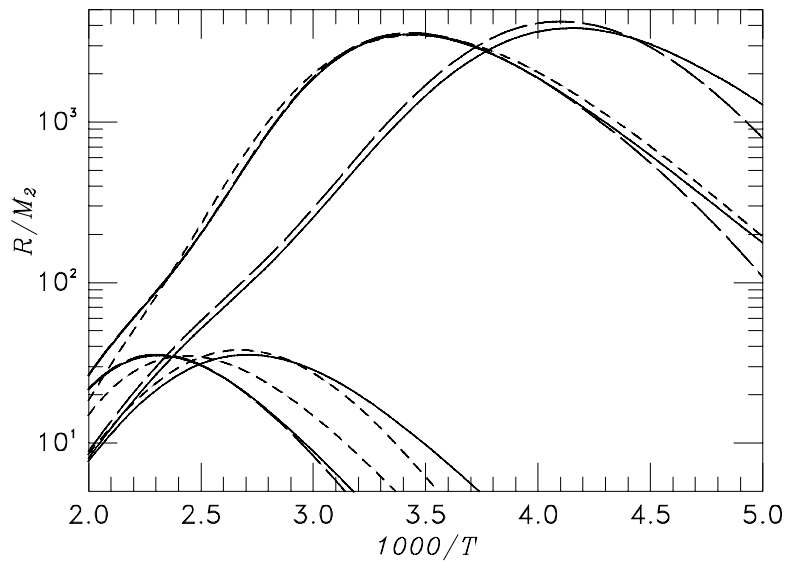


Figure 4. Calculated relaxation rates as for figure 3. The parameters for the CS model (solid curves) are $\sigma_s = 0.06$ eV, $\sigma_b = 0.03$ eV, $E_b - E_s = 0.5$ eV, $\Gamma_0 = 3.0 \times 10^{13}/(1 - c)$ Hz and $c = 0.1, 0.5$ and 0.9 (for curves left to right). The parameters for the BPP model (short-dashed curves) are $\sigma = 0.05$ eV, $\Gamma_0 = 6.3 \times 10^{13}/(1 - c)$ Hz and $M_2(\text{BPP}) = 1.11M_2$.

CS model have $E_b - E_s = 0.5$ eV and all of the results for the BPP model have a mean distribution energy $\bar{E} = 0.5$ eV. The value of the prefactor frequency for the CS calculations is $\Gamma_0 = 3.0/(1 - c) \times 10^{13}$ Hz. The CS results in figure 3 are for $\sigma_s = 0.03$ eV, $\sigma_b = 0.06$ eV and $c = 0.1, 0.5$ and 0.9 . The values of the BPP parameters σ , Γ_0 and M_2 have been chosen to give a reasonable fit to parts of the CS results. The value of M_2 was adjusted to fit the maximum CS rates, σ was chosen to give comparable broadening of the curves and Γ_0 was chosen to give a reasonable fit to the position of the CS R_1 maximum for $c = 0.9$. The factor of $1/(1 - c)$ included in the choice of Γ_0 above corresponds to eliminating simple site-blocking effects which would shift the curves along the $1000/T$ axis for different c . For the BPP model this is the only c -dependent effect and the BPP results in figure 3 are therefore independent of c . For the CS model there are additional spin concentration effects arising from the effects of the Fermi–Dirac distribution.

The parameters for the BPP curves in figure 3 are $\sigma = 0.05$ eV, $\Gamma_0 = 1.0 \times 10^{14}/(1 - c)$ Hz and $M_2(\text{BPP}) = 1.21 M_2$. The BPP fit to the CS results is quite good for the R_1 results for $c = 0.9$, or for the high-temperature $R_{1\rho}$ results for $c = 0.1$, or for the low-temperature region of the $R_{1\rho}$ curves for $c = 0.5$. It is not, however, possible to choose parameters for the BPP model that give a good fit to both R_1 and $R_{1\rho}$ curves over the entire temperature range for any of the values of c . The CS model therefore gives different types of functions to the BPP model in general.

The relaxation rates for the CS model shown in figure 4 are for the same parameters to those in figure 3, but with the standard deviations of the energy distributions reversed to $\sigma_s = 0.06$ eV and $\sigma_b = 0.03$ eV. It can be seen by comparing the results for $c = 0.1$ and 0.9 in figures 3 and 4 that interchanging the site- and barrier-energy distributions produces quite different relaxation results. The BPP model does not distinguish between these distributions. The fit of the BPP results to the CS curves is for $\sigma = 0.05$ eV, $\Gamma_0 = 6.3 \times 10^{13}/(1 - c)$ Hz and $M_2(\text{BPP}) = 1.11 M_2$. The fit is reasonable over the entire temperature range for R_1 and $R_{1\rho}$ with $c = 0.9$.

The value of $\bar{E} = 0.5$ eV for the BPP results in figures 3 and 4 is the same as that for $E_b - E_s$ for the CS results. The BPP fit value of $\sigma = 0.05$ eV in both figures is close to the larger of σ_s and σ_b in each case. The BPP values of Γ_0 are a factor of two or three different from the CS values and the fitted BPP values of M_2 are larger. This result that the BPP model gives lower maxima than the CS model (for the same M_2) is consistent with the results found by CS for separate site- and barrier-energy models.

The examples shown in figures 3 and 4 suggest that the fitting of experimental data using the CS model will lead to fitting parameters that are similar in magnitude to those that would be obtained from a fit using the BPP model. However, the CS model can provide information on both barrier- and site-energy distributions, unlike the BPP model which can only provide information on a single-energy distribution for which a physical interpretation is not clear.

4. Discussion and conclusions

The extension of the BPP model to diffusion in disordered systems described here has a more rigorous basis than the commonly used phenomenological extension that averages relaxation rates over a distribution of jump rate energies. This CS model also allows fitting of experimental data to distinguish between site- and barrier-energy distributions. The efficient computational procedure described provides a practical approach for analysing the data. The theory could easily be extended to energy distribution functions other than Gaussians and to relaxation due to unlike spins, which involves a different combination of similar spectral density functions.

The CS model, however, is based on the assumption that the magnetic dipolar correlation

between a pair of diffusing spins is destroyed when either of the pair of spins undergoes a jump. This approximation ignores the effect of return jumps of a spin and correlated diffusion of spins following the first jump. In ordered systems the effect of this approximation can be assessed by comparing the results from the BPP model to the exact results for particular diffusion models. The use of the BPP model in this case can lead to values of the prefactor Γ_0 that are in error by as much as 60%, the approach of the relaxation rates to asymptotic limits is described incorrectly and small deviations from Arrhenius behaviour could be incorrectly inferred (Sholl 1993). Nevertheless, the use of the BPP model in analysing relaxation data on ordered systems does not in general produce major errors in deducing activation energies and can give a moderately good fit to experimental data.

It is highly desirable that a similar comparison of the results of the present CS extension to the BPP model is made with the results of more rigorous calculations of spectral density functions and relaxation rates for disordered systems. Such methods could include Monte Carlo simulations (Hua *et al* 1995) or a rigorous analysis of small finite systems (Girard and Sholl 1996).

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