

Spectral density functions for quadrupolar nuclear spin relaxation due to translational diffusion

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Abstract. The spectral density functions for relaxation of nuclear spins due to time-dependent electric quadrupole interactions are studied for diffusion of atoms on a crystal structure. It is shown that, for an arbitrary concentration c of diffusing atoms, the spectral density functions and consequent relaxation rates scale with concentration as $c(1 - c)$. The detailed form of the functions can be obtained simply from analysis of the low spin concentration limit, unlike the analogous case for magnetic dipolar relaxation. Some applications to metal-hydrogen systems are described.

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1. Introduction

Nuclear spin relaxation in condensed matter is often caused by fluctuating magnetic dipolar interactions between spins undergoing relative translational diffusion. An example is the relaxation of the proton magnetisation of hydrogen diffusing between interstitial sites in metals. For nuclei with spin $I > 1/2$, another common relaxation mechanism is fluctuating electric quadrupolar interactions between a nuclear quadrupole moment and the electric field gradient at the nuclear site which is time-dependent due to atomic diffusion. An example is the relaxation of the deuteron magnetisation of deuterium diffusing in metals.

Nuclear spin relaxation rates, for both the dipolar and quadrupolar mechanisms, may be expressed as linear combinations of spectral density functions which are the Fourier transforms of the correlation functions of the fluctuating magnetic dipolar or electric quadrupolar interactions (see for example, Abragam 1961, Wolf 1979, Kelly and Sholl 1992). The time-dependence of the correlation functions arises from functions describing the probability of a pair of nuclei having a particular separation at time t relative to the separation of a pair of nuclei at time zero.

It has been recognised for many years (Sholl 1967) that the probability functions for quadrupolar relaxation are different from those for dipolar relaxation. The dipolar interaction is a coupling between pairs of spins and so the relevant probability function describes the time evolution of the separation of a particular pair of spins. On the other hand, quadrupolar interaction is a coupling between a particular nucleus and the total electric field gradient due to the collective effect of all other diffusing atoms. The

relevant probability function in this case is therefore the probability that, relative to a particular quadrupolar nucleus, there is an atom at a particular separation at time zero and an atom (but not necessarily the *same* atom) at a particular separation at time t . At low concentrations of diffusing species the probability functions are the same for both the dipolar and quadrupolar cases. In general, the probability function for quadrupolar relaxation can be expressed as the sum of the dipolar probability function (a two-particle term) and a three-particle term which describes the probability of the final separation of atoms corresponding to a different atom to that for the initial separation.

For the dipolar case, methods have been developed for calculating the probability functions and spectral density functions for a range of physical systems (see for example, Sholl 1988). The quadrupolar case is more difficult because of the three-particle terms. It is known that the two- and three-particle terms tend to cancel for liquid metal systems (Sholl 1974). There has also been an attempt at deriving approximate results for diffusion in crystals (Barton 1982, Barton and Seymour 1982).

The purpose of this paper is to show the surprising result that, for diffusion in crystals, the quadrupolar spectral density functions for an arbitrary concentration of the diffusing species may simply be related to the case for a low concentration. Since the low concentration case is much easier to solve, the quadrupolar functions at arbitrary concentrations are much easier to treat than the corresponding dipolar functions. The analysis is presented in section 2 and the implications for analysing quadrupolar relaxation data are discussed in section 3.

2. Theory

The spectral density functions $J^{(p)}(\omega)$ for quadrupolar relaxation are the Fourier transforms of the correlation functions

$$G^{(p)}(t) = \langle F^{(p)}(0)F^{(p)*}(t) \rangle \quad (1)$$

where $F^{(p)}(t)$ are the electric field gradient (efg) functions at a nuclear site at time t (Wolf 1979) and the diagonal brackets denote an ensemble average. It will be assumed that the total efg at a site may be written as the sum of contributions from atoms at crystal sites so that

$$F^{(p)} = \sum_i u^{(p)}(\mathbf{r}_i). \quad (2)$$

The correlation function may then be written as

$$G^{(p)}(t) = c \sum_{i,j} u^{(p)}(\mathbf{r}_i)u^{(p)*}(\mathbf{r}_j)P(\mathbf{r}_i; \mathbf{r}_j, t) \quad (3)$$

where c is the probability, at time zero, of an atom at \mathbf{r}_i (assumed the same for all sites), and $P(\mathbf{r}_i; \mathbf{r}_j, t)$ is the probability that there is an atom at \mathbf{r}_j at time t given that there was an atom at \mathbf{r}_i at time zero. The vectors are all relative to a quadrupolar nucleus at the origin, which may diffuse in the time t . The atom at \mathbf{r}_j at time t may be the same as that at \mathbf{r}_i at time zero, or it may be a different atom that was at some other site at

time zero. The analogous correlation functions for magnetic dipolar relaxation may be written in a similar form to equation (3) where the particles at the origin and at \mathbf{r}_i are a pair of interacting spins undergoing relative diffusion. But in this case, the atom at \mathbf{r}_j at time t must be the *same* as that at \mathbf{r}_i at time zero because the magnetic dipolar interaction is between a pair of spins.

The following analysis of the quadrupolar probability function is similar to that used by Kutner (1981) in discussing tracer and chemical diffusion. First consider the case of a quadrupolar nucleus fixed at the origin with the sources of efg diffusing on a separate structure. An example is relaxation of fixed metal nuclei due to hydrogen diffusing on interstitial sites where each hydrogen produces an efg at a metal site. A differential equation for $P(\mathbf{r}_i; \mathbf{r}_j, t)$ is

$$\frac{dP(\mathbf{r}_i; \mathbf{r}_j, t)}{dt} = \Gamma \sum_{\mathbf{r}'_j} \left[P(\mathbf{r}_i; \mathbf{r}'_j, \bar{\mathbf{r}}_j, t) - P(\mathbf{r}_i; \mathbf{r}_j, \bar{\mathbf{r}}'_j, t) \right] \quad (4)$$

where $P(\mathbf{r}_i; \mathbf{r}'_j, \bar{\mathbf{r}}_j, t)$ is the probability of an atom at \mathbf{r}'_j and no atom at \mathbf{r}_j at time t and subject to the initial condition for an atom at \mathbf{r}_i . The sites \mathbf{r}'_j are the set of sites which are nearest neighbours of \mathbf{r}_j to which an atom at \mathbf{r}_j may jump and Γ is the mean jump rate of an atom to an unblocked site. The initial condition is

$$P(\mathbf{r}_i; \mathbf{r}_j, 0) = \delta_{\mathbf{r}_i, \mathbf{r}_j} + c(1 - \delta_{\mathbf{r}_i, \mathbf{r}_j}) = c + (1 - c)\delta_{\mathbf{r}_i, \mathbf{r}_j} \quad (5)$$

where c is the fraction of sites occupied by atoms.

The functions on the right hand side of equation (4) satisfy

$$P(\mathbf{r}_i; \mathbf{r}'_j, \bar{\mathbf{r}}_j, t) + P(\mathbf{r}_i; \mathbf{r}'_j, \mathbf{r}_j, t) = P(\mathbf{r}_i; \mathbf{r}'_j, t) \quad (6)$$

$$P(\mathbf{r}_i; \mathbf{r}_j, \bar{\mathbf{r}}'_j, t) + P(\mathbf{r}_i; \mathbf{r}_j, \mathbf{r}'_j, t) = P(\mathbf{r}_i; \mathbf{r}_j, t) \quad (7)$$

where $P(\mathbf{r}_i; \mathbf{r}'_j, \mathbf{r}_j, t)$ is the probability of atoms at \mathbf{r}'_j and \mathbf{r}_j at time t given there was one at \mathbf{r}_i at time zero. The differential equation (4) therefore becomes

$$\frac{dP(\mathbf{r}_i; \mathbf{r}_j, t)}{dt} = \Gamma \sum_{\mathbf{r}'_j} \left[P(\mathbf{r}_i; \mathbf{r}'_j, t) - P(\mathbf{r}_i; \mathbf{r}_j, t) \right] \quad (8)$$

since $P(\mathbf{r}_i; \mathbf{r}'_j, \mathbf{r}_j, t) = P(\mathbf{r}_i; \mathbf{r}_j, \mathbf{r}'_j, t)$. But equation (8) is the same as the differential equation for the random walk of a *single* atom on the structure. The physical explanation of this result is that as c increases, the number of successful jumps decreases because of site blocking, but the number of atoms that can be found at \mathbf{r}_j increases. These two effects cancel so that the time evolution of $P(\mathbf{r}_i; \mathbf{r}_j, t)$ is independent of c .

The first term c on the right hand side of the initial condition (5) has the solution $P(\mathbf{r}_i; \mathbf{r}_j, t) = c$ to equation (8). This constant term does not lead to relaxation and may be ignored. The second term of the initial condition gives a solution that is $(1 - c)$ times the probability function for a random walk of an atom starting at \mathbf{r}_i .

The correlation function (3) may therefore be written as

$$G^{(p)}(t) = c(1 - c) \sum_{i,j} u^{(p)}(\mathbf{r}_i) u^{(p)*}(\mathbf{r}_j) P(\mathbf{r}_i; \mathbf{r}_j, t) \quad (9)$$

where $P(\mathbf{r}_i; \mathbf{r}_j, t)$ is the solution of equation (8) with the initial condition $P(\mathbf{r}_i; \mathbf{r}_j, 0) = \delta_{\mathbf{r}_i, \mathbf{r}_j}$. The correlation function is therefore $c(1 - c)$ times the correlation function for a single atom undergoing a random walk on the structure. The spectral density functions and nuclear spin relaxation rates may therefore be simply expressed in terms of the corresponding theory for the low spin concentration limit.

The above analysis is not applicable to the case of the probability functions for magnetic dipolar relaxation because the symmetry condition following equation (8) is not then valid. In the dipolar case the atom at \mathbf{r}'_j must be the *same* as that at \mathbf{r}_i initially, whereas \mathbf{r}_j is the location of *any* atom.

Similar analysis may also be applied to the case of the quadrupolar nuclei diffusing on the same lattice as the sources of the efg. An example is relaxation of deuterium for deuterium diffusing on interstitial sites in a metal. The differential equation (4) needs modification in this case because of the diffusion of the relaxing nucleus and because of site-blocking effects. The equation becomes

$$\frac{dP(\mathbf{r}_i; \mathbf{r}_j, t)}{dt} = \sum_{\mathbf{r}'_j} \left[W(\mathbf{r}'_j, \mathbf{r}_j) P(\mathbf{r}_i; \mathbf{r}'_j, \bar{\mathbf{r}}_j, t) - W(\mathbf{r}_j, \mathbf{r}'_j) P(\mathbf{r}_i; \mathbf{r}_j, \bar{\mathbf{r}}'_j, t) \right] \quad (10)$$

where $W(\mathbf{r}'_j, \mathbf{r}_j)$ is the jump frequency for atoms with a separation \mathbf{r}'_j to a separation \mathbf{r}_j . Either of the atoms may jump and $W(\mathbf{r}'_j, \mathbf{r}_j)$ includes Kronecker delta terms which exclude jumps which would result in both atoms at the same site. The symmetry conditions (6) and (7) are still valid and $W(\mathbf{r}'_j, \mathbf{r}_j) = W(\mathbf{r}_j, \mathbf{r}'_j)$, so that equation (10) becomes

$$\frac{dP(\mathbf{r}_i; \mathbf{r}_j, t)}{dt} = \sum_{\mathbf{r}'_j} \left[W(\mathbf{r}'_j, \mathbf{r}_j) P(\mathbf{r}_i; \mathbf{r}'_j, t) - W(\mathbf{r}_j, \mathbf{r}'_j) P(\mathbf{r}_i; \mathbf{r}_j, t) \right]. \quad (11)$$

The initial condition (5) is still valid, so that the correlation function may again be written as equation (9). The function $P(\mathbf{r}_i; \mathbf{r}_j, t)$ can be obtained from the differential equation (11) which is the equation for the low spin concentration limit analogous to equation (8), but which in this case includes the jump probabilities $W(\mathbf{r}'_j, \mathbf{r}_j)$.

3. Discussion

The results of the previous section show that the correlation functions for quadrupolar relaxation at any concentration c are a scaling factor $c(1 - c)$ multiplying the functions for the low concentration limit. This result also applies to the spectral density functions and relaxation rates. The implications of this result for the relaxation rates is that the relaxation rates for different c simply scale as $c(1 - c)$ and that the maxima in the rates as a function of temperature will occur at the same temperature for all c .

An example is the quadrupolar relaxation of ^{45}Sc in ScH(D)_x (Barnes et al. 1997). For a model in which only H(D) nearest neighbours of a Sc nucleus contribute to the efg at the Sc site, Barnes et al. showed by a direct evaluation of the efg that the correlation function satisfied the $c(1 - c)$ scaling for $t = 0$, where $c = x/2$ for this structure. The time-dependence of the correlation function was evaluated in the low concentration limit

from random walk theory. The resulting correlation function agreed very well with the results of Monte Carlo simulations, as expected from the general result derived above. The relaxation data for Sc hydrides and deuterides was reasonably consistent with the maximum relaxation rate being proportional to $c(1 - c)$ and with the maximum rate occurring at the same temperature for all c . In this case the complications of the theory of diffusion of many atoms at arbitrary values of c can be straightforwardly taken into account by using results from the simple random walk of a single particle.

A second example is the quadrupolar relaxation of deuterium in metal-hydrogen systems. In this case the low concentration limit corresponds to the relative diffusion of two deuterium atoms on the structure such that the site blocking effects of the two atoms are taken into account. This model has been solved within the context of magnetic dipolar relaxation by Sankey and Fedders (1979) and Barton and Sholl (1980) for the cubic lattices. The resulting spectral density functions have been parametrised by Sholl (1988). If the efg due to a deuterium atom is assumed to arise from a point charge then the efg functions $u^{(p)}(\mathbf{r})$ are proportional to the corresponding magnetic dipolar functions. According to the theory in the previous section, the dipolar spectral density functions for the low concentration limit can then be used to analyse the quadrupolar deuterium relaxation data for any deuterium concentration c . The corresponding quadrupolar relaxation functions would involve a factor of $c(1 - c)$ but would otherwise be proportional to the dipolar results.

The theory in section 2 has assumed atoms diffusing amongst a fixed set of sites which is an inappropriate model for liquids. The results cannot therefore be applied to quadrupolar relaxation in liquid metals.

4. Conclusion

It has been shown that quadrupolar relaxation rates due to an arbitrary concentration c of diffusing species can be calculated rigorously by simply calculating the corresponding relaxation rates in the low concentration limit and scaling these results by a factor $c(1 - c)$. The complications of analysing the diffusion of many particles do not need to be addressed. This result does not apply to the analogous case of dipolar relaxation.

The model used has assumed that there is a fixed set of sites amongst which atoms diffuse at any concentration c . This may not necessarily always be the case. For example, it is known that hydrogen generally occupies tetrahedral sites in some metal-hydrogen systems, but that some octahedral site occupation can also occur at high concentrations (see for example Barnes 1997). It has also been assumed that the efg produced at a nuclear site is a simple addition of the efg from individual sites. It is possible that the efg from a site at high concentrations may be modified by interaction effects. Either of these effects would require modification of the above theory.

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