

Dipolar broadening in magnetically diluted lattices

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A method is presented for computing NMR line shapes at high temperatures for a system of magnetically diluted spins interacting via a dipolar Hamiltonian. We specialize to the case of a solid nonmagnetic host with spin- $\frac{1}{2}$ impurities randomly placed on a simple-cubic lattice. For low concentrations, an iterative procedure is developed to separate the broadening into homogeneous and inhomogeneous components. We find that, even in the dilute limit, a significant fraction of the spins contribute to a continuum (homogeneously broadened) band. An information-theoretic maximum-entropy technique is used to reconstruct the homogeneous component of the line shape from moments, and a version of the statistical theory is then employed to obtain the inhomogeneous component. Implications for hole-burning experiments are briefly discussed. For high concentrations, theoretical line shapes are obtained by use of configuration-averaged moments and maximum entropy, including up to the sixth Van Vleck moment. To test our results, we also calculated a line shape by diagonalizing the secular dipolar Hamiltonian for several configurations containing up to nine spins. For low concentrations we find reasonable agreement with the moment analysis. All of these methods are readily extended to any well-defined lattice structure and to other spin problems with a $1/r^n$ interaction.

I. INTRODUCTION

There have been many attempts to characterize the infinite-temperature NMR absorption spectrum for a magnetically inert host with identical magnetic impurities interacting via a dipolar spin Hamiltonian. Usually the investigator makes the additional assumption that these spins are randomly distributed on a lattice. In all these approaches, the authors make an (often implicit) assumption at the outset that all the broadening of the resonance line is due to either homogeneous or inhomogeneous processes.¹⁻⁷ It is our contention that for such a spin system this assumption, while computationally convenient, has never been justified. It is the purpose of this paper to investigate this point and to calculate the line shape for an arbitrary concentration of spins. To demonstrate the rationale for expecting both modes of broadening, consider two limiting types of configurations attainable to a randomly diluted spin system in the low concentration limit.

(1) Consider a simple cubic (sc) lattice with a lattice constant a . Now fill this lattice with spins in a superlattice with a lattice constant $c^{-1/3}a$, where c is the spin concentration. This system is an attainable, albeit improbable, configuration for the dilute lattice of spacing a . Such a system would exhibit only homogeneous broadening. By homogeneous broadening we refer to a band of energies where each spin is associated with all the energies equally. Indeed, within various scaling factors, such a sample would exactly reproduce the data of Engelsberg and Lowe⁸ for CaF_2 at $c=1$.

(2) Consider a pair of spins separated by a distance much smaller than the average interparticle spacing. As the dipolar interaction falls off as r^{-3} , where r is the spacing between the dipoles, such configurations exhibit

an enormous shift in Larmor frequency because of the comparatively huge local field the pair feels compared to the effects of all of the other spins. The resonance is thus so far removed from the other spins in the lattice that it may be considered completely isolated. Such a pair is inhomogeneously broadened. By inhomogeneous broadening we refer to the case where each spin is associated with a single energy and probing the system at that energy affects only that spin.

This elementary argument suggests that any real random magnetic alloy could have aspects of both configurations (1) and (2) discernible in the NMR absorption spectrum. Obviously both of these limiting configurations are improbable. Nevertheless, it is reasonable to expect some manifestation of both limits in the problem. Attempts to obtain line shapes assuming inhomogeneous broadening become difficult to justify at high concentrations where it is well known that homogeneous processes dominate. Similarly, the rationale for assuming purely homogeneous broadening becomes invalid for low concentrations where local configurations are the crucial determinant of the line shape. While both of these approaches have validity in extreme limits of concentration, neither is completely justified for intermediate concentrations, and we show that the assumption of completely inhomogeneous broadening is not precisely correct for any concentration, no matter how small.

In the rest of this paper we develop a method which can handle both modes of broadening and even estimate how much of the broadening is homogeneous, or inhomogeneous. We feel that the most promising approach to impurity averaging is a technique in which impurity configurations are simulated on a computer, then averages are performed on the ensemble so generated. This form of averaging allows an economical and excellent

characterization of the possible configurations attainable at all concentrations. It also gives additional insight into the contributions to the line shape on a configuration by configuration basis. To illustrate our approach without introducing unnecessary complications, we restrict our attention to spin $\frac{1}{2}$, though the method is more general.

In this work we will use moment methods to deal with homogeneous broadening. The fundamental correlation or Green's function relevant to transverse relaxation experiments in dipolar coupled systems is the two-point linear-response function for sites i, j

$$G_{ij}(t) = \langle A_{1,1}(i, t) A_{1,1}^\dagger(j, 0) \rangle \Theta(t), \quad (1)$$

where $A_{lm}(i, t)$ are irreducible multipole operators⁷ in the Heisenberg representation for the site i at time t , $\Theta(t)$ is the Heaviside step function, and $\langle \dots \rangle$ denotes a thermal average. The experimentally measurable line shape is proportional to $G(\omega) = \sum_{ij} G_{ij}$, where ω means the Fourier transform of the time function. We find it convenient to work with the single-site functions $G_i = \sum_j G_{ij}$. The self-energy Σ_i associated with G_i is defined by the relation

$$G_i(\omega) = i / [\omega - \Sigma_i(\omega)]. \quad (2)$$

As discussed elsewhere,^{7,9,10} it is possible to completely characterize G and Σ by their spectral functions

$$\begin{aligned} A_i(\omega) &= \text{Re} G_i(\omega), \\ \Gamma_i(\omega) &= -\text{Im} \Sigma_i(\omega). \end{aligned} \quad (3)$$

The dispersive and absorptive parts of the Green's function and self-energy form Hilbert transform pairs and the moments of A_i and Γ_i are given by

$$\begin{aligned} M_n(i) &= \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega^n A_i(\omega), \quad n \geq 0 \\ L_n(i) &= \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega^{n-2} \Gamma_i(\omega), \quad n \geq 2. \end{aligned} \quad (4)$$

Relations between the self-energy and Van Vleck moments are readily obtained from the time domain version of Eq. (2). By forming equations of motion for the relevant operators, one can express the moments of Eq. (4) as lattice sums. Explicitly, the single-site moments are

$$\begin{aligned} L_2(i) &= M_2(i) = \frac{9}{16} \sum_j J_{ij}^2, \\ M_4(i) &= \frac{1}{256} \left[81 \sum_j J_{ij}^4 + 54 \sum_{\substack{j,k \\ jk \neq}} J_{ij}^2 J_{jk}^2 + 81 \sum_{\substack{j,k \\ jk \neq}} J_{ij}^2 J_{ik}^2 \right. \\ &\quad \left. + 27 \sum_{\substack{j,k \\ jk \neq}} (J_{ij} + J_{jk})^2 J_{ij}^2 \right], \end{aligned} \quad (5)$$

$$L_4(i) = M_4(i) - [M_2(i)]^2,$$

where $J_{ij} = \gamma^2 \hbar (1 - 3 \cos^2 \theta_{ij}) / r_{ij}^3$ and θ_{ij} is the angle between the external Zeeman field and the vector \mathbf{r}_{ij} which connects sites i and j . All sums are restricted to sites occupied by a spin, and $jk \neq$ means that no two indices are identical.

We note that there are several advantages to using the self-energy method. First, all terms in the self-energy moments scale in the same way with concentration. This is important for the diluted lattice because there are terms in the lattice sums for the Van Vleck moments $\{M_n\}$, which can dominate other terms in these moments. This makes it hard to extract more subtle information from the smaller terms. (The terms in question are single-site sums with the form J_{ij}^n , where n is the order of the moment, and J is the spin-spin coupling in the dipolar Hamiltonian.) It can be demonstrated that the self-energy function contains none of these dominating terms. It has also been shown that a small amount of structure in the self-energy can lead to a large amount of structure in the physically measurable quantity G . It should also be noted that in the concentrated lattice, it was found that the use of the self-energy as an intermediate step in the reconstruction led to the best agreement with experiment.¹¹

As a preliminary illustration of our method we calculate line shapes in two cases where it is possible to obtain closed form expressions for the line shape functions. Consider the probability density $P(M_2, c) dM_2$, the probability that for a given site M_2 has value in the range $[M_2, M_2 + dM_2]$ for concentration c . Then clearly, for $c \rightarrow 1$, this density takes the form

$$P(M_2, 1) = \delta(M_2 - M_{2,c}),$$

where $M_{2,c}$ is the second moment at any site in the concentrated lattice. The lowest-order maxent approximation for a line shape in terms of its second moment is

$$G(\omega, M_2) = (\pi/2M_2)^{1/2} \exp(-\omega^2/2M_2).$$

We may calculate the configuration average, which in this case is trivially

$$\bar{G}(\omega) = \int_0^\infty G(\omega, M_2) \delta(M_2 - M_{2,c}) dM_2 = G(\omega, M_{2,c}).$$

We see that for $c=1$ one recovers the familiar Gaussian fit to the line shape. The case of $c \rightarrow 0$ is more interesting. In this regime it can be shown that

$$P(M_2, c) = \frac{\delta}{(2\pi M_2^3)^{1/2}} e^{-\delta^2/2M_2},$$

where $\delta = (288\pi^3 c^2/243)^{1/2} \omega_d$, and $\omega_d = \gamma^2 \hbar / a^3$. The configuration average integral is easily evaluated and the result is a Lorentzian

$$\bar{G}(\omega) = \frac{\delta}{\omega^2 + \delta^2}.$$

This Lorentzian has half width at half maximum (HWHM)

$$\delta \approx 3.03 c \omega_d.$$

Thus, by using only the second moment, we obtain plausible line shapes in both concentration limits. While these simple calculations produce reasonable results in both limits, it is not obvious why the low-concentration line shape should be even qualitatively correct. As we argued above, we should expect manifestations of both

homogeneous and inhomogeneous broadening in the line shape, yet we have implicitly assumed the broadening to be purely homogeneous. Indeed, when the fourth moment is included in the calculation, the natural extension of the above method yields a completely spurious line shape with a cusp at the Larmor frequency. This is a consequence of the fourth moment's extreme sensitivity to rare (isolated) configurations. It turns out that the second moment is essentially insensitive to these same configurations, and thus yields the reasonable result given above for the second moment only case. To properly extend the calculation to the joint second- and fourth-moment reconstruction, we need to consider the broadening mechanisms in more detail.

The basic idea is as follows: We start by assuming that all of the spins in the diluted lattice contribute to the homogeneous line shape and we construct a line shape under this assumption. Next we note that certain close pairs of spins or nearly single spins are inhomogeneously broadened by so much that their frequencies lie outside of the homogeneous bandwidth. These spins are then removed from the homogeneous line shape and thus the ensuing homogeneous line shape is somewhat narrowed. This, in turn, means that even more spins may have inhomogeneous splittings that push them outside of the homogeneous bandwidth. The above process is iterated until it converges.

In some ways the above procedure is reminiscent of the real space renormalization-group techniques. However, in this case, the above procedure will remove all of the spins from the homogeneous bandwidth in the low-concentration limit if the spin-spin interaction falls off exponentially. In the present case the procedure converges to a finite fraction of homogeneous spins. The reason is that as more and more spins are removed from the continuum, the spins that are left form a more and more uniform system. Finally enough clusters of spins that are intrinsic to a random distribution are removed and the remaining spins form a rather evenly spaced system.

The remainder of this paper will be organized as follows: In Sec. II we review the theoretical tools necessary for this work. We will discuss the statistical theory in some detail from a point of view convenient for our purposes and present our approach in detail. In Sec. III we discuss our results, and compare them to explicit diagonalization of the truncated dipolar Hamiltonian, and other work.

II. METHOD

In this section we present a detailed account of our calculations. It is natural to separate the problem into two concentration regimes. For high concentrations the line shape may be constructed from configuration average moments. For low to intermediate concentrations we use a method combining moments and a method closely related to the statistical theory.

A. High concentrations

In the high- c regime each spin evidently feels the influence of many others and we are therefore in the

homogeneously broadened regime. For this range of concentrations configuration average moments are useful for obtaining the line shape. For reasons discussed above, we calculated line shapes from average self-energy moments, including up to the sixth, and performed a maxent reconstruction based on these moments. In fact, information theory has already been applied with average moments, but using only the second and the fourth.¹² In an earlier paper¹¹ it was seen that an excellent line shape could be obtained from a few self-energy moments L_n . In this work the required average moments were calculated from a paper of Hansen and Jensen.¹³ This approach was found to be useful down to $c \approx 0.4$, where inhomogeneous broadening becomes important. After obtaining the self-energy fit to Γ , we performed a Hilbert transform to get the full Σ , from which G was recovered using Eq. (2). The necessary lattice sums were calculated on a $7 \times 7 \times 7$ lattice, so that the central spin interacted with 342 other spins.

B. Low and intermediate concentrations

It is a formidable problem to obtain line shapes at high levels of dilution. In this regime, there is a very rich variety of spatial configurations the magnetic impurities can take. The amount of each form of broadening is evidently very sensitive to the particular local configuration and to the concentration. We outline a method for handling both of these modes of broadening simultaneously. We use an iterative technique to identify the spins in a particular simulated lattice which are inhomogeneously broadened. After characterizing the broadening of each spin, the line shape for the entire lattice can be treated in two separate parts, a homogeneous component and an inhomogeneous part. The process is then repeated over an ensemble of such simulated lattices. The moment methods outlined above work well for homogeneous broadening. For inhomogeneous broadening, these moments are inadequate for calculating a line shape, since they are dominated by a small number of improbable configurations. We apply a variation of the statistical theory^{1-2,14} to handle the inhomogeneous component as follows:

(1) We use a procedure described below to identify inhomogeneously broadened spins on a simulated diluted lattice.

(2) We assume that the only effect of spin i on spin j (both assumed isolated) is to shift the resonant frequency of the spin j by

$$\Delta\omega(i,j) = \frac{3}{4}\gamma^2\hbar\beta_{ij}[(1 - 3\cos^2\theta_{ij})/r_{ij}^3], \quad (6)$$

where θ_{ij} and r_{ij} are the same as in Eq. (5), and $\beta_{ij} = \pm 1$ with equal probability at high temperatures—specifying the “ m ” orientation of the two spins.

(3) These shifts are taken to be *additive*, so that the total frequency shift experienced by spin i is

$$\bar{\omega}_i = \sum_j' \Delta\omega(i,j), \quad (7)$$

where the prime means sum is restricted to inhomogeneous spins. The contribution to the line shape of spin i is then

$$G_i(\omega) = \delta(\omega - \bar{\omega}_i), \quad (8)$$

and properly normalized line shape for the entire collection of inhomogeneous spins is then

$$G(\omega) = N^{-1} \sum_i G_i(\omega), \quad (9)$$

where N is the number of inhomogeneously broadened spins in the lattice. Of course, for a macroscopic system, the δ functions become a continuous density, yielding a smooth approximation for the inhomogeneous part of the line shape.

We choose to write G in the form of Eq. (9) because it is computationally convenient. Given the positions i of the inhomogeneous spins, it is straightforward to calculate the sum in Eq. (9). The variation of the statistical theory outlined here is actually superior to the conventional version. In the original form of the statistical theory, it is assumed that *all* spins were isolated. In this approach, the statistical theory is applied only to the set of spins that *are* isolated, according to a well-defined criterion.

Two further remarks on the statistical theory are in order. First, we have performed calculations which indicate that keeping only pairs (i.e., modeling the spin system as an ensemble of isolated pairs) is inadequate, even at low concentrations. This is because in the central part of the line, cancellation of frequency shifts is important for obtaining a good line shape. Such cancellations obviously cannot occur for pair-only interactions. Also, this version of the statistical theory is done on a lattice, so that all effects of discreteness are properly reproduced. For low concentrations this point is moot, but for higher concentrations ($c > 0.1$) lattice effects are important. For pure inhomogeneous broadening, this version of the statistical theory is essentially exact.

To develop a criterion for homogeneous and inhomogeneous broadening we need to approximate certain relaxation rates. Consider a spin which is isolated from the continuum. As a consequence of its isolation, its HWHM is very small (such a spin is slightly broadened by the spins in the continuum band). We assume that the source of the spin's isolation is a large shift in its resonant frequency due to another spin very nearby, or a pair of adjacent spins. Denote this frequency shift for spin i , by Ω_i . We use the bubble approximation^{3,7} to estimate the relaxation rate for such a spin. We find

$$\Gamma_i = \frac{5}{6} L_{2c}(i) G(\Omega_i), \quad (10)$$

$G(\Omega_i)$ is the continuum (homogeneous) component of the Green's function evaluated at the frequency shift and L_{2c} is the same as in Eq. (5), except that the sum is restricted to the continuum. A similar result can be obtained for the relaxation rate of a spin in the continuum. A good approximation for this rate is

$$\Gamma_c = [G_c(0)]^{-1}, \quad (11)$$

where $G_c(0)$ is the value of the continuum component of the frequency Green's function at $\omega = 0$.

In order to proceed further, we introduce a few definitions: First, the definition of an *isolated* pair. Two

spins i and j form an isolated pair if

$$\begin{aligned} J^2(i, j) &> J^2(i, k) \quad \text{all } k \neq j, \\ J^2(j, i) &> J^2(j, k) \quad \text{all } k \neq i, \end{aligned}$$

and if the ratio of relaxation rate of the isolated spins to the continuum rate

$$\Gamma_i / \Gamma_c < \epsilon. \quad (12)$$

The terminology "isolated pair" is evidently sensible, since for small Γ_i / Γ_c such spins are very slow to relax, because they are only very weakly coupled to the other spins in the lattice compared to their mutual pair interaction. It is possible to show that in the dilute limit, about 60% of the spins satisfy conditions given by Eq. (11) above.

For certain configurations, one may also have an *isolated spin* which interacts more strongly with an isolated pair than with the rest of the spins in the lattice. The criterion for an isolated spin at site i is: (1) The effect of a particular isolated pair [as measured by its contribution to $L_2(i)$] on the spin i is greater than the rest of the lattice, and (2) $\Gamma_i / \Gamma_c < \epsilon$ where, $\Gamma_i = 5L_{2c}(i)G(\bar{\Omega}_i)/6$, $\bar{\Omega}_i$ is the frequency splitting experienced by spin i from the dominant pair. If a spin falls into neither of these two categories it is part of the continuum.

In the preceding definitions, ϵ is an as yet unspecified parameter; the ratio of relaxation rates for a given spin to the continuum rate. A criterion is introduced below for determining ϵ . Determination of ϵ roughly quantifies the separation of broadening into homogeneous and inhomogeneous components. We may form some preliminary ideas about what range of ϵ are reasonable. It is commonly expected that two nearest neighbors is the borderline for the existence of a continuum. For a sc lattice with coordination number 6, this crude estimate suggests $c = \frac{1}{3}$ as the concentration where inhomogeneous broadening becomes important. It turns out that our method is rather consistent with this rule. Another example to illustrate the meaning of ϵ is a one-dimensional coupled chain with nearest-neighbor interactions. We believe such a system to be near the boundary between homogeneous and inhomogeneous broadening. For this array of spins the ratio Γ_i / Γ_c is about $\frac{1}{2}$. This is fairly consistent with our calculations, as will be seen in Sec. II B.

In detail, our procedure is the following: A computer is used to simulate impurity configurations on a sc lattice. We sweep through the lattice, and for each site a random number R is obtained, $0 < R < 1$. If the random number for a given site is less than the spin concentration c , we occupy the site, otherwise it is left vacant. Simulations were performed for a variety of concentrations from $c = \frac{1}{1000}$ to $c = 1$. The following iterative scheme is employed to separate the line broadening and to obtain configuration averaged Green's functions.

(i) We use the simulation procedure outlined above to simulate a lattice with randomly distributed spins at concentration c .

(ii) For each occupied site in the lattice, we apply periodic boundary conditions (in effect making each site

in turn the “origin”) and calculate the ratio of Eq. (12) defined above. We then use the criteria for isolated pairs and isolated single spins so that each spin in the lattice could be classified as part of the continuum, part of a pair or a single isolated spin.

(iii) The procedure (ii) removes spins from the continuum. This can contribute to the isolation of more spins because the continuum second moment L_{2c} has been reduced. We therefore iterate (ii) until L_{2c} remains unchanged upon further iteration.

(iv) After iterating to convergence, we calculate the moments $L_{2c}(i), L_{4c}(i)$ and restrict the sums to the continuum lattice (i.e., the set of spins contributing to homogeneous broadening). These “continuum” (homogeneous) moments are then stored.

(v) The procedure (i)–(iii) is repeated many times to get a good sample of the joint distribution of moments $P(L_2, L_4)$. We saved these results at each step. It was also necessary to repeat (i)–(iii) for a wide range of ϵ for a later determination of what value of ϵ was appropriate.

(vi) The impurity averaged Green’s function is calculated in two steps. First we use maxent to treat the continuum spins, calculating an average continuum lattice Green’s function. This was just the ensemble average Green’s function over each of the continuum moments we generated. The pairs and isolated spins were treated differently. For each concentration and external Zeeman field configuration, the statistical theory was applied to the isolated spins in each lattice. The complete line shape was then taken to be the sum of the homogeneous and inhomogeneous shapes.

B. Parameter ϵ : Criterion of consistency

The parameter ϵ is determined by a criterion of consistency: The maxent approach to the moment problem produces a well-defined sequence of functional approximants given a finite set of moments. Of course, the more information (moments) known, the better the reconstruction—provided that we make use of all the information at our disposal. In particular, at low c , it is crucial to make use of the fact that the power moments of the spectral functions A and Γ are large because of unusual configurations which contribute in the remote tail of the line shape. If this information is neglected, maximum entropy can predict spectral functions with the additional weight near the origin which leads to entirely spurious line shapes. A naive application of maxent happens to work reasonably well for the reconstruction based on one moment, because the functional form maxent provided distributes the spectral weight required to produce the large moments almost uniformly in the part of the line of interest to us. For the two-moment reconstruction, the weight is placed incorrectly near the origin. Our difficulty can be resolved in one of two ways: (1) Find a way to include the information about the tail as a constraint on maxent, or (2) transform the problem so that the tail and neighborhood around the origin can be treated separately. We took the latter approach. To illustrate the point, it is worth examining the maxent fits for the one- and two-moment reconstructions.

The L_2 -only (Gaussian) reconstruction is dominated by the continuum homogeneously broadened configurations. This follows from the form the maxent fitting function takes:

$$G_{\text{Gauss}}(\omega) = (\pi/2L_2)^{1/2} e^{-\omega^2/2L_2}.$$

The effect of mutual isolated pairs (corresponding to large L_2) is negligible, such configurations merely introduce a very slowly decaying component in $G(\omega)$. Consequently they affect the relaxation rate in an unimportant way. By contrast, the joint reconstruction based on both the second and fourth moments is completely dominated by certain configurations involving very strongly interacting pairs. Such configurations lead to very rapidly decaying component in the Green’s function. This makes the predicted line shape absurdly sharp near the origin. So, to obtain a useful joint reconstruction, it is necessary to handle the inhomogeneous components separately.

We expect a Gaussian fit to the continuum component to be a fair approximation to the true Green’s function. This comes from two considerations: First, at $c=1$, the Gaussian approximation is reasonable, and for high c , the broadening must be completely homogeneous. Also, in diluted lattices, the line shape becomes even more Gaussian because there are effectively more continuum neighbors than in the concentrated lattice, and the central limit theorem may be invoked to infer a Gaussian shape. In principle, the two-moment reconstruction should be better than the Gaussian fit, simply because the extra moment provides additional information about the line shape. For $n \rightarrow \infty$ it should be exact, where n is the order of the fit. Consequently, a reasonable way to quantify the homogeneous and inhomogeneous components of broadening is to require that the single and joint reconstructions be consistent. This is not a rigorous criterion; there is no reason why the two fits should be identical. The usefulness of this criterion is great, however, because for ϵ too small, the two fits are extremely inconsistent. This is because the joint reconstruction is completely dominated by a few weird configurations. Such configurations occur, of course, yet their effect on the joint reconstruction is absurdly overweighted if ϵ is incorrectly chosen. The result of neglecting the inhomogeneous component (i.e., assuming purely homogeneous broadening) is illustrated in Fig. 1.

Optimal consistency between the Gaussian and joint reconstructions is obtained at all concentrations for $\epsilon \approx 0.35$. There is some uncertainty in this, as mentioned above. A range of ϵ for which agreement is reasonable is

$$0.25 < \epsilon < 0.40.$$

For low concentrations, our line shapes are sensitive to the choice of ϵ . As indicated above, ϵ is determined by requiring consistency between the single and joint reconstructions. This specifies a good lower bound on ϵ . In Fig. 3 we illustrate the different constituents of the reconstructions for different ϵ . Tolerable consistency is obtained for $\epsilon \geq 0.25$. Optimal agreement is obtained for $\epsilon \approx 0.35$. We find that $\epsilon = 0.35$ is the optimal choice for all concentrations (of course this statement only has relevance for low concentrations, where some spins are

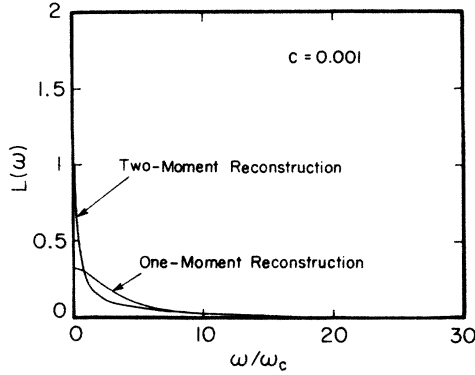


FIG. 1. Strikingly inconsistent line-shape functions for one- and two-moment reconstructions neglecting inhomogeneous broadening at $c=0.001$. In this and all other plots of line shapes, the line shape function is normalized to π , and the frequency is in reduced units of $\omega_c = c\omega_d$, where c is the spin concentration. Although it is difficult to see on this plot, the two moment reconstruction has a value of about 1.8 at the origin.

inhomogeneously broadened).

This works also clearly reflects the existence of a continuum for the dilute limit. We find that for any $\epsilon > 0$, the ratio of the homogeneous population to the total number of spins

$$\lim_{c \rightarrow 0} N_{\text{conti}} / N_{\text{total}}$$

is finite for all concentrations (down to $c=0.001$) and depends only on the value of ϵ chosen, and the assumption that the alloy is random. If a continuum did not exist, one could make the limit arbitrarily small by considering a sufficiently dilute lattice. For all very dilute cases we considered ($\epsilon < 0.01$) we found that about 10% of the spins were in the continuum for optimal ϵ .

III. RESULTS AND DISCUSSION

A. High concentrations

In Fig. 2 we present our line shape functions for high concentrations using average moments. For this concentration regime, the line shapes bear some interesting differences. The [100] case is flattened because of the strongly anisotropic dipolar interaction with spins in the first shell. The other two common directions [110] and [111] are much more Gaussian in appearance. We expect the average moment method to be valid for concentrations sufficiently high that isolated configurations are improbable. In practice, for a sc lattice, the great majority of line broadening is continuum in origin down to $c \approx 0.4$. In all graphs of line shape functions, frequencies are measured in units of $\omega_c = c\omega_d$, where ω_d is given in Sec. I. $L(\omega)$ denotes line shape functions in the figures.

B. Low concentrations

For the low-concentration limit, we predict a line width surprisingly consistent with other calculations.

The early work of Kittel and Abrahams¹⁵ and Anderson¹⁴ led to half-widths at half maximum of $\delta = 5.3 \omega_c$ and $\delta = 3.8 \omega_c$. We predict $\delta \approx 3.7 \omega_c$, in the notation of our figures. The plots of Fig. 3 are all for the [110] direction and for $c = 10^{-3}$. For low concentrations, the difference in line shapes is negligible for differing Zeeman field configurations—this is a consequence of the dipolar coupling J_{ij} having zero-angle average, and essentially all angles with respect to a given site being attainable for $c \rightarrow 0$.

Figure 4 illustrates our method for $c = \frac{1}{10}$ with Zeeman field along the [110] direction. $\epsilon = 0.35$ was again the maximally consistent choice, and about 30% of the spins were in the continuum. For high concentrations the continuum component continued to grow.

It is interesting to compare this work to average moments in the regime where they overlap ($c > 0.3$). For $c = 1$, there is a significant (but tolerable) discrepancy between the self-energy fit to L_2 , L_4 and experiment, whereas the three-moment reconstruction almost exactly reproduced experiment.¹² Fortunately, as the concentration decreases, the two-moment fit improves as the continuum part of the line becomes more Gaussian (Fig. 5).

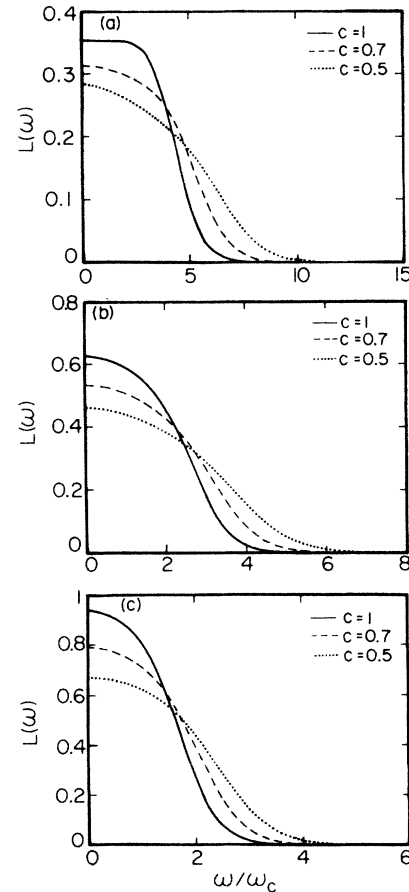


FIG. 2. Line-shape functions at high concentrations and for different Zeeman field configurations. (a) Illustrates the line shapes for the [100] direction, (b) corresponds to [110], and (c) to [111].

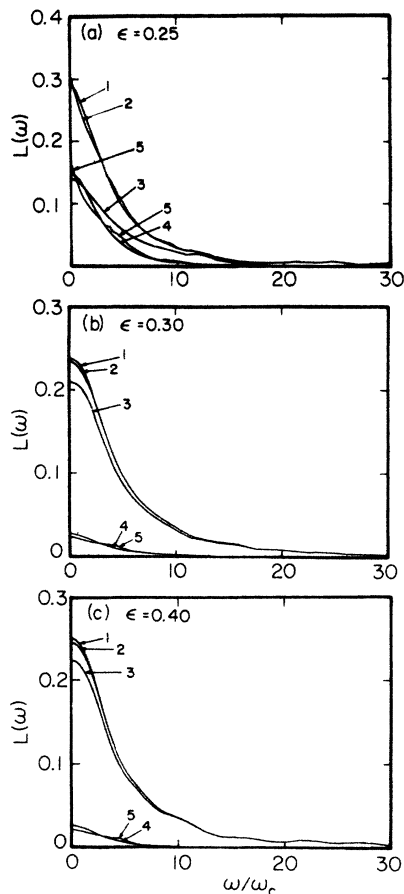


FIG. 3. Line shapes for different ϵ corresponds near the optimally consistent value of 0.35. All plots are for $c=0.001$. (a) Depicts the case of $\epsilon=0.25$, where 37% of the spins are homogeneously broadened. Note the sharp feature in the two moment reconstructions. (b) $\epsilon=0.35$ has 9% of the spins in the continuum. (c) $\epsilon=0.40$ has 6% in the continuum. 1, composite one-moment reconstruction; 2, composite two-moment reconstruction; 3, inhomogeneous; 4, homogeneous one moment; 5, homogeneous two moment.

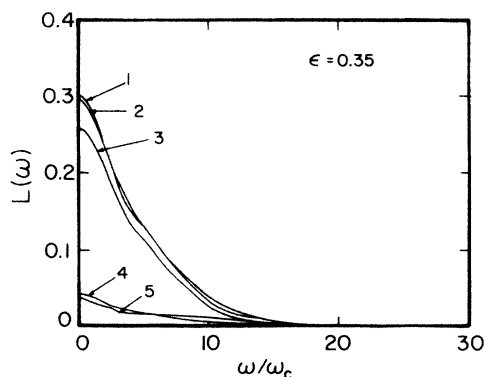


FIG. 4. Line shape for $c=0.1$ and [110]. Here $\epsilon=0.35$, and 15% of the spins are in the continuum. 1, composite one-moment reconstruction; 2, composite two-moment reconstruction; 3, inhomogeneous; 4, homogeneous one moment; 5, homogeneous two moment.

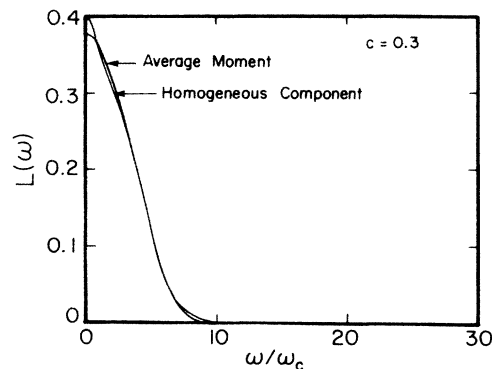


FIG. 5. Comparison of continuum component of line shape and average moments ($c=0.3$, [110]).

As an independent test of our work, we formed the Green's function by diagonalizing the secular dipolar Hamiltonian for several configurations. Because of the prohibitive size of the matrix to diagonalize, even for a moderate number of spins, we present our results only for a very dilute lattice ($c=0.001$), where any particular spin is influenced primarily by a few neighboring spins. We applied periodic boundary conditions to reduce edge effects, and performed the indicated diagonalization for up to nine spins. As we illustrate in Fig. 6, the agreement between the moment analysis and the simulation is reasonable. We are inclined to accept the moment work as the better predicted line shape, since it was computationally feasible to work with many more spins, and easier to configuration average to convergence. The fair agreement between the two methods does suggest that for the dilute limit most of the broadening of the line is inhomogeneous. This is because only inhomogeneous broadening could be well represented by nine or less spins.

C. Discussion

A distinct advantage of simulating randomly diluted lattices is that the investigator is forced to deal with the problem on a configuration by configuration basis. This

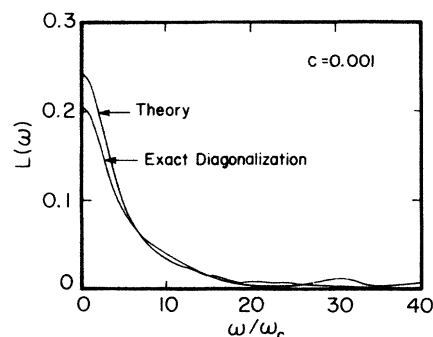


FIG. 6. Comparison of diagonalizing the secular spin-spin interaction, forming the Green's function directly, and the result of our method. Both plots are for $c=0.001$ and the [110] orientation of the Zeeman field.

forced us to find the configurations responsible for strange line shapes such as Fig. 1. It also enabled us to quantify the different components in a meaningful way. The iterative procedure we outlined is evidently not easily implemented in any other fashion.

We have also calculated distributions of relaxation rates for inhomogeneously broadened spins contributing to different parts of the NMR line shape. A typical cause of inhomogeneous broadening in this problem is the presence of spins at small separations compared to the average interspin distance. Such spins experience a huge shift in Larmor frequency because of the local field each element of the pair feels from the other. It is interesting to consider such distributions, because in a hole-burning experiment¹⁶ one can excite a small band of frequencies in the line shape, and observe the decay of the "hole." Hole lifetimes τ_{hole} are of the order

$$\tau_{\text{hole}}^{-1} \approx \int_0^\infty d\Gamma \Gamma \rho(\Gamma).$$

We have calculated such rate densities for two different parts of the line. For the case of $c = \frac{1}{1000}$, we considered the range $1 < \omega/\omega_c < 5$, and $15 < \omega/\omega_c < 30$. The results are shown in Fig. 7 and ω_c is defined in Fig. 1.

In work on inhomogeneous broadening of distorted solids, Kanert *et al.*¹⁷ used a configuration averaging scheme somewhat similar to ours. These authors used a computer to generate an ensemble of simulated lattices with a fixed number of magnetic impurities in each lattice. In a finite lattice this suppresses local fluctuations in concentration that are relevant to the line shape. These fluctuations are of order $n^{1/2}$, where n is the number of spins. The measure of the effects on physically measurable quantities is $\approx n^{-1/2}$. A more correct approach is to form an ensemble of lattices each of which having its sites occupied with probability c . The distinction between these two ensembles is analogous to the difference between the canonical and grand canonical ensembles in statistical mechanics. For the infinite lattice limit, the two ensembles evidently coincide. For the finite lattices we are compelled to work with however, we feel it is more appropriate to use our "grand canonical ensemble."

The foregoing work also raises an important point about the use of maximum entropy. Information theory provides a powerful method of dealing with inverse problems of many kinds. However, to get useful results based on incomplete information, one must be sure to include

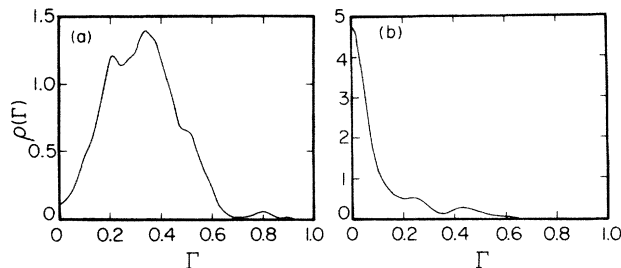


FIG. 7. Densities of relaxation rates for different parts of the line shape for the dilute limit. (a) Depicts the range $1 \leq \omega/\omega_c \leq 5$. (b) Obtained for $15 \leq \omega/\omega_c \leq 30$. The wiggles are probably a consequence of too few simulations, particularly in (a).

all the information available. It is very easy to use maximum entropy, leaving out an apparently insignificant bit of information, only to find that the results depend crucially on that information. In this work, we had to separate the forms of broadening because the joint reconstruction of the Green's function tended to put too much spectral weight in near the origin, rather than in the tail to account for the large moments caused by inhomogeneously broadened configurations.

The preceding work could be continued in several ways. Another system of interest is solid molecular hydrogen. It is closely analogous to the dipolar case, except that the dominant part of the spin Hamiltonian is the electric-quadrupole-quadrupole interaction in the hydrogen problem. We are currently pursuing this problem. It is also straightforward to simulate clustering, by requiring the probability for occupation to be site dependent.

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