Nuclear spin-lattice relaxation times for mixtures of ortho- and para-H$_2$: High ortho-H$_2$ concentration

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We investigate nuclear spin-lattice relaxation for high concentrations of ortho-H$_2$ in a para-H$_2$ matrix for temperatures above the ordering transition and lower than the onset of classical diffusion ($2 \lesssim T \lesssim 10$ K). We use diagrammatic representations of the moments of the electric quadrupole-quadrupole (EQQ) spectral functions which govern the relaxation. We find it practical to calculate the first three nontrivial moments of the EQQ autocorrelation functions. These spectral functions are then obtained via the principle of maximum entropy. The resulting functions predict an EQQ coupling constant of $\Gamma_{\text{eff}} = 0.92$ K. We find that much of the uncertainty in this prediction arises from difficulties in extrapolating data to infinite temperature and not from inherent inaccuracy in our moment analysis. We briefly discuss the implications of this calculation to related work.

I. INTRODUCTION

Solid para-hydrogen (p-H$_2$) with ortho-hydrogen (o-H$_2$) impurity has been the subject of continuing experimental and theoretical study since the early work of Reif and Purcell.[1] This material has proven to have a very rich range of behavior as one varies parameters such as the o-H$_2$ concentration and the temperatuare. This system is attractive to study because of the wealth of high quality experimental data and the relative simplicity of the interactions between o-H$_2$ molecules. For calculations of the longitudinal relaxation time T_1, one can simply ignore the host para-molecules and concentrate on the intermolecular interaction between o-H$_2$ molecules and effects of the lattice. Thus one can construct physically well justified and formally tractable models of this solid. Consequently, H$_2$ makes a good laboratory for testing theoretical models which frequently are applicable with appropriate modifications to other systems as well. Of course H$_2$ is an intrinsically interesting material in its own right. Beside trying to extend our understanding of the magnetic resonance properties of light molecular solids, the present study is relevant to laser fusion work.[2] It has been demonstrated that spin-aligned targets have a much larger cross section for fusion than unpolarized material. An understanding of spin-lattice relaxation is central to these problems. In the present work we make a first-principles high concentration NMR estimate of the EQQ coupling constant Γ_{eff} and calculate the EQQ autocorrelation functions to improved accuracy. We also illustrate the practicality of calculating unusually high order moments of spectral functions of the type encountered in spin dynamics.

We shall apply recently developed methods in two areas; methods for inverting moment problems (inferring spectral densities from a limited number of moments) and techniques for the practical extraction of high-order moments from complicated spin-spin interactions. Earlier calculations with moments have suffered from the arbitrariness of the researcher's choice of a fitting function with as many free parameters as known moments. This procedure is *ad hoc* at best, since the bias of the worker inevitably is manifested in the choice of fitting function. An alternative approach is to use probability theory to find a functional form which is consistent with the incomplete information (the few known moments) and which has the highest entropy (in the sense of information theory). Such a procedure has been developed by Jaynes[3] and specialized to the classical moment problem by Mead and Papanicolaou.[4] The maximum-entropy (maxent) method has been extremely successful in applications to solid state physics ranging from inferring nuclear magnetic resonance (NMR) line shapes for the dipolar-coupled lattice[5] to reconstructing electronic densities of states in disordered alloys[6] For calculating T_1 all the information required is contained in the electric quadrupole-quadrupole (EQQ) spectral functions. In this paper we use diagrammatic methods to obtain three nontrivial moments of these functions, and employ maxent to reconstruct them to find theoretical estimates of the relaxation time T_1.

Moment methods are applicable only to high o-H$_2$ concentrations: For sufficiently low random o-H$_2$ concentrations, ortho-molecules tend to become isolated or to form clusters with only a few molecules strongly influencing each other.[7] Using a procedure which we have developed for the dipolar lattice,[7] we have found that this clustering becomes important for the EQQ interaction around $c = 0.1$–0.2. We have used a computer to simulate an hcp lattie with o-H$_2$ randomly diluted in a para-background. By taking a coupling between o-H$_2$ molecules proportional to r^{-5} (with r the separation between a pair of spins) we can easily find what fraction of o-H$_2$ molecules "feel" an interaction from one another spin more strongly than the effects of the rest of the spins. Such spins cannot easily relax to an EQQ continuum, and add an inhomogeneous component to the EQQ spectral functions. These isolated molecular spins are not properly treated by configuration average moments. We illustrate the results of these simulations in Fig. 1. To handle lower concentrations ($c < 0.2$) one has to develop methods beyond the scope of this paper. We therefore re-
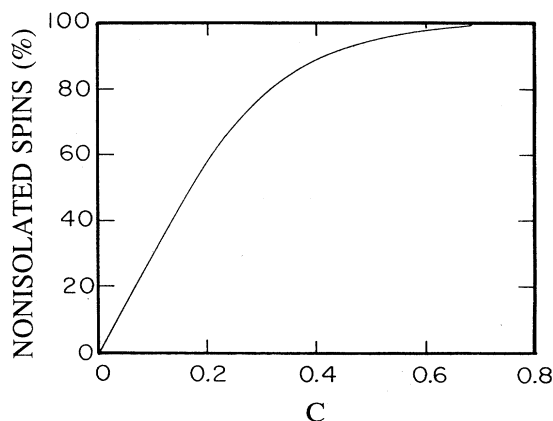
FIG. 1. The fraction of ortho-molecules not dominated by a single neighbor plotted vs the ortho-concentration c.

strict our attention to the high concentration regime and relegate our work on low concentrations to a future paper.

Earlier attempts to calculate the EQQ correlation functions have been of two types: the self-consistent theory of Myles and Ebner,[8] or moment work[9,10] with the first pair of nontrivial moments: M_2 or M_2 and M_4. The self-consistent theory has much to recommend it: In this approach the authors do not resort to the use of adjustable parameters, and they agree reasonably well with experiment. The complexity of the formalism however requires that the procedure be restricted to low order (only the second moment is reproduced properly by their correlation functions). Consequently, we expect to do considerably better using the information included in the fourth and sixth moments. Other work has involved the second moment or second and fourth moments. The first effort in this direction was by Moriya and Motizuki[9] using the second moment and a Gaussian fit. Harris[10] has calculated the second and fourth moments and observes that since the ratio of the fourth to squared second moments are not very different from three for the EQQ functions, a Gaussian approximation is reasonable. This argument is certainly qualitatively correct. However, for a more precise determination of relaxation times and the EQQ coupling constant it is necessary to go to higher order, especially for the $l = 2$ functions where $M_4/M_2^2 \approx 4.0 + 0.188/c$ for c the spin concentration, a significant departure from three and important since the $l = 2$ functions will turn out to be more important than the more nearly Gaussian $l = 1$ function. Hama and Nakamura[11] independently calculated the fourth moments and fit these to a product of a Hermite polynomial and a Gaussian. This form however has no theoretical justification, and has no more claim to validity than any other assumed form. So that we may obtain the advantages of maxent, we calculate the sixth moments of the EQQ functions, since the maxent procedure does not converge for the known second and fourth moments. Such convergence difficulties with maxent have been observed in earlier work,[5] and we believe this to be related to the lack of a sharp cutoff of the spectral functions in frequency

space. We emphasize that maxent is not an *ad hoc* procedure for solving moment problems: It is a general probability theoretic principle for making optimal inferences with problems of incomplete information.

The rest of this paper will be organized as follows: In Sec. II we discuss diagrammatic techniques for moment expansions. Section III deals with the results of the calculations, and we discuss the implications of this work to the EQQ coupling constant Γ_{eff} and other work.

II. METHODOLOGY

The relaxation of the nuclear spins in o-H_2 molecules is determined by the transverse spin fluctuations these nuclei feel from the molecular spin of their particular molecule. Consequently, a calculation of T_1 is largely an effort to characterize the spectrum of the molecular spin fluctuations. This is accomplished through the usual procedure of constructing autocorrelation functions of the multipole operators:[12]

$$G_\alpha(i,t) = \Theta(t)\langle A_\alpha(i,t) A_\alpha^\dagger(i,0)\rangle , \qquad (1)$$

where $A_\alpha(i,t)$ denotes an irreducible multipole operator in the Heisenberg representation for site i at time t. The A_α are proportional to the operator analogues of the usual spherical harmonics Y_α for $\alpha = (l,m)$. $\Theta(t)$ is a step function to make the correlation function causal and $\langle \cdots \rangle$ denotes a thermal average. In this paper it is sufficient to restrict ourselves to consider only $J = 0$ (p-H_2) and $J = 1$ (o-H_2) because the splitting between these ground-state levels and higher J states is much larger than any other energies in the problem, at least for the zero pressure solid we concern ourselves with here.[13] There are five independent functions that are required for calculating T_1 at high temperatures.[8] These correspond to the choices $\alpha = 2\pm1$; $2\pm2,20$ and $1\pm1,10$. For high concentrations it is natural to use moment methods to approximate the correlation functions of Eq. (1). However, the direct calculation of moments of spectral functions with the van Vleck formula[14] is very cumbersome for high order moments and complicated spin-spin interactions such as the EQQ Hamiltonian. Several workers have introduced diagrammatic representations for these moments which are a great convenience in their calculation. A particularly successful diagrammatic method is the expansion developed by Reiter[15] originally for the Heisenberg magnet at high temperatures. As he and others[8,16] have demonstrated, this formalism is readily extended to any bilinear spin interaction. In this approach the vertices represent matrix elements of the Liouville operator in the space dual to the Hilbert space of spin states accessible to our system. To obtain useful formal expressions for the moments, one has to evaluate analytic expressions for the constituent vertices of the moment graphs, and construct all topologically distinct diagrams characteristic of a given order. For the sake of brevity we outline the construction of the graphs: Our discussion is intended to be illustrative, not exhaustive. Details of the method can be found in the literature.[16] In fact, we have already implemented this procedure for the second and fourth moment graphs for H_2 in Ref. 16. While the

present calculation is much more complex, the basic methodology is identical. The calculation was divided into several steps: First, we obtained all topologies for the sixth moment. By this we refer to the set of all possible combinations of six unlabeled bilinear vertices producing a closed graph and accounting for all possible time orderings. We find that there are 31 such topologies. These are reproduced in Fig. 2. We note (using the nomenclature of Ref. 2) that the diagrams fall into three categories; reducible [Fig. 2(a)], nonskeleton [Fig. 2(b)], and skeleton [Fig. 2(c)]. For each of these graphs we have to attach spin and site labels consistent with the usual rules for constructing these diagrams.[16,17] In the present work, we found that there are about 250 decorated graphs. To minimize the change for error, we wrote a simple computer program which examined all possible combinations of site and spin indexes and retained only

those combinations which were admissible (i.e., nonzero and not duplicated). In Fig. 3, we illustrate one decoration associated with a particular topology, the first diagram of Fig. 2(b). We give analytic expressions for the vertices Ω in Table I. The entries in Table I are readily obtained by forming equations of motion for the irreducible multipole operators for the EQQ Hamiltonian. For further details on these vertices see Ref. 8. Throughout this work we will use the convention that Greek indexes denote spin operators (in irreducible multipole form) and latin indexes denote sites on a hexagonal close-packed (hcp) lattice. Further, we will require that indexes χ, η, μ, ν, σ denote the m part of $l=2$ operators, while λ, ψ, ω represent the m part of $l=1$ operators. Thus the numerical value of Fig. 3 is just the sum over all indexes other than i and m of the analytic expression

$$\sum_{\substack{-2 \leq \chi, \eta, \mu, \nu, \sigma \leq 2 \\ -1 \leq \omega, \psi, \lambda \leq 1 \\ \langle jkl \rangle_{NN}}} \Omega_{m\lambda\chi}(ij)\Omega_{\lambda\mu\eta}(ik)\Omega_{\chi\psi\nu}(jl)\Omega^{*}_{\omega\mu\eta}(ik)\Omega^{*}_{\sigma\psi\nu}(jl)\Omega^{*}_{m\omega\sigma}(ij) , \tag{2}$$

where NN are nearest neighbors. The complete sixth moment for $\alpha = (1, m)$ is just the sum of all decorated graphs whch start and end with $(1, m)$ lines. The graph of Fig. 3 involves triple sums on sites, so that for o-H_2 concentrations c, each of these diagrams is proportional to c^3. There are actually many graphs which are proportional to c and c^2. Following a procedure first proposed by Abrahams and Kittel,[18] it is then evident that the average moments for the dilute lattice are of the form

$$\overline{M}_6(c) = \delta c + \epsilon c^2 + \zeta c^3 . \tag{3}$$

The sums of the type indicated in Eq. (2) were quite tedious as is evident by the large number of spin and site
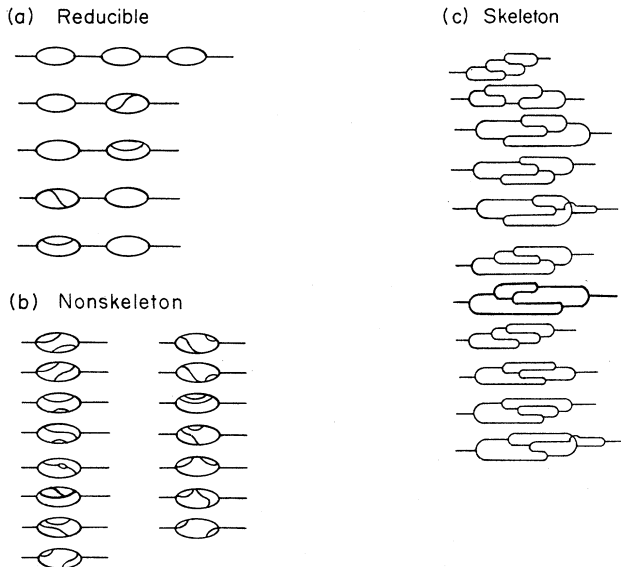
indexes. In fact, the evaluation of some of these graphs required a supercomputer. All diagrams were evaluated in a nearest neighbor approximation, which has been justified by Hama and Nakamura,[11] and Harris.[10] For $c = 1$ we find that the difference between nearest and second nearest neighbors is $\approx 1\%$. This is fortunate, since some of the diagrams would be virtually intractable beyond nearest neighbors.

III. RESULTS AND DISCUSSION

Harris[10] has shown that there is little angular anisotropy in the correlation functions G_α for fixed l and different m. Consequently it is acceptable to make the simplifying assumtion of working with only two independent EQQ spectral functions corresponding to the choice of $G_{1,m}$ and $G_{2,m}$ for any m. The results of summing the aforementioned diagrams are summarized in Table II. For convenience, we have also included the results for the second and fourth moments as well. Using the nomenclature of Table II, a moment of order n and of specific l may be written in the form

$$M_n = \sum_{i=1}^{n/2} c^i a_{i,n} . \tag{4}$$

We have numerically evaluated the average moment expressions of Tables II for several concentrations and used

(a) Reducible

(c) Skeleton

(b) Nonskeleton

FIG. 2. Undecorated graphs required for the sixth moment.
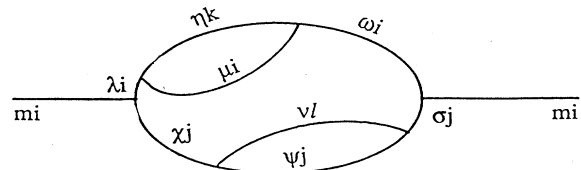

FIG. 3. An example of a decorated graph. The analytic expression associated with this diagram is given by Eq. (2).

TABLE I. Nonzero EQQ vertices

$$\Omega_{\alpha\beta\gamma}(j) \equiv \alpha i \quad \overset{\beta i}{\underset{\gamma j}{\frown}} \quad ,$$

$$F_{mn}(ij) = (70\pi)^{1/2}\Gamma_0(a/r_{ij})^5 C_{mn}[Y_4^{n+m}(\Omega_{ij})]^*/9 ,$$

and

$$\alpha_1 = 1, \quad \alpha_0 = \sqrt{2}, \quad \beta_1 = 3\sqrt{2}, \quad \beta_0 = \sqrt{6}, \quad \beta_{-1} = -2\sqrt{3} .$$

α	β	γ	$\Omega_{\alpha\beta\gamma}(ij)$
10	$2m$	$2n$	$\sqrt{6}m F_{mn}(ij)$
11	$2m$	$2n$	$-\sqrt{3}\sqrt{6-m(m-1)}F_{m-1,n}(ij)$
1 -1	$2m$	$2n$	$\sqrt{3}\sqrt{6-m(m+1)}F_{m+1,n}(ij)$
20	$1m$	$2n$	$3\sqrt{2}m F_{mn}(ij)$
21	$1m$	$2n$	$-\beta_m F_{m-1,n}(ij)$
2 -1	$1m$	$2n$	$\beta_{-m}F_{m+1,n}(ij)$
22	$1m$	$2n$	$2\sqrt{3}\alpha_m F_{m-2,n}(ij)$
2 -2	$1m$	$2n$	$-2\sqrt{3}\alpha_{-m}F_{m+2}(ij)$

TABLE II. Coefficients of Eq. (4).

n (order)	a_1	a_2	a_3
		(a) $l = 1$	
2^{a}	280		
4^{a}	22 040	189 600	
6	799 200	3.186×10^7	1.960×10^8
		(b) $l = 2$	
2^{a}	168		
4^{a}	5304	113 760	
6	50 411	1.159×10^7	1.153×10^8

[a]References 10 and 11.

$$T_1 = A + B/T \tag{6}$$

which is valid for $B/T \ll A$. (For the values of A and B calculated by these authors this means $T \gg 2$ K, which is adequately satisfied by the data we analyze.) Hama and Nakamura[11] performed infinite temperature extrapolations by using Eq. (5). We will use their extrapolations of the data of Amstutz et al.[20] for comparisons with our theory. We note however, that there is appreciable uncertainty in this procedure: In fact, a comparison of the extrapolated experimental values and our spectral functions lead to predictions of Γ_{eff} varying by $\approx 5\%$.

The maxent approach to the moment inverse problem leads to the following functional form to which the theoretical moments must be fitted:[4]

$$G(\omega) = \exp\left[-\sum_{i=1}^n \lambda_i \omega^i\right]\bigg/\lambda_0 . \tag{7}$$

In this equation λ_i refers to undetermined Lagrange multipliers which are determined by the condition that G have the desired moments, and n is the number of known moments. Since the functions we are dealing with are even, all odd λ vanish. In Table III(a) and III(b) we present the λ_i as a function of concentration. We measure frequencies in units of $[M_2(c)]^{1/2}$, and the spectral functions so obtained are normalized to unity. Table III(a) contains the Lagrange multipliers for the $l = 1$ functions, Table III(b) for $l = 2$. These functions are then used in conjunction with Eq. (6) to find T_1, and to estimate the EQQ parameter in the solid state, Γ_{eff}. We illustrate these functions for several different concentrations

maxent to reconstruct the $l = 1$ and $l = 2$ spectral functions. These functions are related to T_1 by the usual formula:

$$T_1^{-1} = \tfrac{3}{2}\omega_d^2 \sum_{m=-2}^2 m^2 G_{2,m}(m\omega_0)$$

$$+ \tfrac{2}{3}\omega_c^2 \sum_{m=-1}^1 m^2 G_{1m}(m\omega_0) , \tag{5}$$

where $\omega_c = 7.15 \times 10^5$/sec and $\omega_d = 3.62 \times 10^5$/sec are frequencies characterizing the coupling between the molecular and nuclear spin systems, ω_0 is the frequency at which the nuclear spins resonate, and G_α is normalized to π in Eq. (4). The present work has been carried out in the infinite temperature limit, which is all that is practical within the present formalism. Thus comparisons with experimental data must involve a procedure for extrapolating the data to the infinite temperature limit. Harris and Hunt[19] and Harris[10] have obtained the leading order terms in a high-temperature expansion for the second moments for the EQQ functions. They find that the temperature dependence of T_1 takes the approximate form

TABLE III. Reduced moments and lagrange multipliers for spectral functions.

c	μ_4	μ_6	λ_0	λ_2	λ_4	λ_6
			(a) $l = 1$			
1	2.699	10.42	2.46	0.661	-0.107	1.33×10^{-2}
0.75	2.793	10.93	2.30	0.907	-0.213	2.38×10^{-2}
0.5	2.98	11.98	2.02	1.42	-0.436	4.67×10^{-2}
0.2	3.823	17.10	1.21	4.19	-1.62	0.170
			(b) $l = 2$			
1	4.22	26.77	1.85	1.37	-0.241	1.45×10^{-2}
0.75	4.28	27.60	1.84	1.38	-0.242	1.44×10^{-2}
0.5	4.41	29.25	1.82	1.41	-0.244	1.41×10^{-2}
0.2	4.97	36.84	1.71	1.57	-0.265	1.42×10^{-2}

in Fig. 4. We also show the Gaussian fit for comparison for both $l = 1$ and $l = 2$.

We take the $c = 1$ data to make our best estimate of Γ_{eff}. Since we are effectively calculating T_1 for an "average" site (in the sense of configuration average moments), it is important that this distribution have a small width. Clearly this width is a minimum at $c = 1$, the limit of translational invariance. Also, inspection of the data at $c = 1$ shows that a fairly reliable linear extrapolation as required by Eq. (5) is possible. We find a surprisingly high value of $\Gamma_{eff} \approx 0.92$ K, in contrast to the accepted experimental value of ≈ 0.83 K. There are several kinds of error in the present problem which account for this discrepancy. We believe the main source of error to be the extrapolation to infinite temperature: this depends upon the rapid convergence of a high-temperature expansion and upon the uncertainty in the experimental data. These effects cannot be estimated to better than about 5%, and as we mentioned above, using several different concentrations we found about a 5% variation in the estimated Γ_{eff}. Other sources of error are the intrinsic limits imposed by incomplete information (only six moments) and computational approximations including the neglect of second and further neighbors and angular anisotropy in the moments. All of these effects amount to about a 10% imprecision in the estimate of Γ_{eff}.

Taking $\Gamma = 0.92$ K we find reasonable agreement with the data of Amstutz et al.[20] We illustrate this in Fig. 5. For concentrations $\lesssim 0.4$ we note a dramatic change in
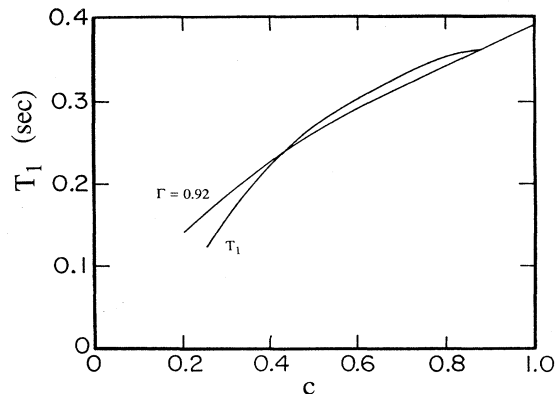
FIG. 5. Comparison of experimental T_1 and the present calculation with $\Gamma_{eff} = 0.92$. The experimental T_1 values are taken from Ref. 11 which provides an infinite temperature extrapolation of the data of Ref. 20.

the slope of the theoretical T_1 versus c curve. This also is reflected in the experimental data. In the concentration range $0.2 < c < 0.4$, there is still reason to believe that the EQQ interaction provides a mechanism for the rapid thermalization of the molecular spins. So we conclude that the change in slope around $c = 0.4$ is a consequence of the increasing variety of spatial configurations experienced by the ortho molecules, while relaxation via the EQQ interaction is still dominant. For concentrations less than ≈ 0.2 however, isolation of the spins leads to a qualitative change in the physics as the EQQ interaction becomes quenched by the dilution. As we indicated in the Introduction, it is not correct to interpret the relaxation purely in terms of the average moments for that regime.

In view of our rather high value for Γ_{eff} we are led to compare our results to those of Hama and Nakamura,[11] who report a Γ_{eff} of 0.81 K which is closer to experiment. First we note that the functional form chosen to fit the fourth moment in their paper is completely arbitrary, and other equally reasonable choices can produce significantly different results. Also, it is not obvious how to extend their approximation to higher order, their fit is *not* an expansion of the spectral densities on a complete set, so that it is not clear that in the limit of an infinite number of moments that such a function would converge to the exact solution. Consequently we regard their excellent agreement with experiment as being somewhat fortuitous.

IV. CONCLUSION

In this paper we have calculated the high-temperature autocorrelation functions for $o\text{-}H_2$ at high temperatures and obtained a new estimate of the EQQ coupling constant Γ_{eff} based on high-concentration nuclear relaxation data. We also have illustrated the practical calculation of a sixth moment for a complicated spin-spin coupling. In this paper we only have addressed the high-concentration
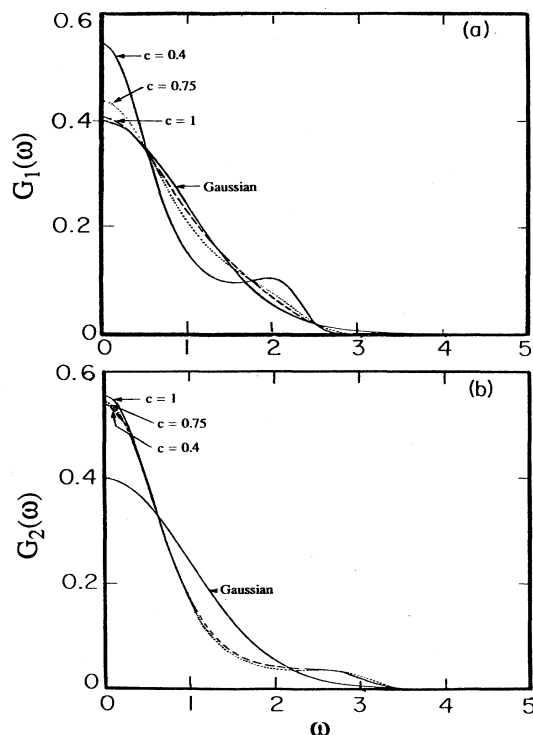

FIG. 4. Frequency dependent EQQ spectral functions reconstructed from configuration averaged moments for several concentrations. (a) depicts the $l = 1$ functions, (b) illustrates $l = 2$.

regime, much work remains to be done to gain a thorough understanding of the more complicated low-c solid. We are currently looking into this problem.

ACKNOWLEDGMENTS

[1] F. Reif and E. M. Purcell, Phys. Rev. **91**, 631 (1953).

[2] P. C. Souers, *Hydrogen Properties for Fusion Energy* (University of California Press, Berkeley, 1986).

[3] E. T. Jaynes, *Papers on Probability, Statistics and Statistical Physics* (Reidel, Dordrecht, Holland, 1983); Phys. Rev. **106**, 620 (1957).

[4] L. R. Mead and N. Papanicolaou, J. Math. Phys. **25**, 2404 (1984).

[5] P. A. Fedders and A. E. Carlsson, Phys. Rev. B **32**, 229 (1985).

[6] A. E. Carlsson and P. A. Fedders, Phys. Rev. B **34**, 3567 (1986).

[7] D. A. Drabold and P. A. Fedders, Phys. Rev. B **37**, 3440 (1988).

[8] C. Ebner and C. Myles, Phys. Rev. B **12**, 1638 (1975), and references therein.

[9] J. Moriya and K. Motizuki, Prog. Theor. Phys. **18**, 183 (1957).

[10] A. B. Harris, Phys. Rev. B **1**, 3495 (1970).

[11] J. Hama and T. Nakamura, Prog. Theor. Phys. **44**, 303 (1970).

[12] P. A. Fedders, Phys. Rev. B **11**, 995 (1975).

[13] Isaac A. Silvera, Rev. Mod. Phys. **52**, 395 (1980).

[14] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

[15] G. F. Reiter, Phys. Rev. B **5**, 222 (1972).

[16] D. A. Drabold, Phys. Rev. B **37**, 565 (1988).

[17] C. W. Myles and P. A. Fedders, Phys. Rev. B **9**, 4872 (1974).

[18] E. Abrahams and C. Kittel, Phys. Rev. **90**, 238 (1953).

[19] A. B. Harris and E. Hunt, Phys. Rev. Lett. **16**, 845 (1966).

[20] L. I. Amstutz, H. Meyer, and S. M. Myers, J. Phys. Chem. Solid **30**, 2693 (1969).