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Validity of approximate methods in linear response theory for an interacting spin-phonon system*

R. Pirc† and B. G. Dick
Department of Physics, University of Utah, Salt Lake City, Utah 84112
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In order to gain insight into their degree of validity, certain commonly used approximate methods for finding dynamic susceptibilities are compared with the exact Kubo susceptibility for a linearly interacting spin-phonon system. Approximate methods investigated include: truncation or decoupling of equations of motion for the commutator and anticommutator Green's functions, and a memory-function method suggested by Götze and Wölfle. It is shown that approximate methods, while adequate for weak dipole-phonon coupling, can lead to conspicuous deviations from the exact susceptibility in certain frequency ranges. Results are also sensitive to the shape of the phonon spectrum. Ergodic and nonergodic cases are discussed.

I. INTRODUCTION

The dynamic dielectric response of a system characterized by a Hamiltonian H and dipole moment operator $\vec{M}$ is given by the Kubo (or isolated) susceptibility[1–3]

$$\chi^I_{ij}(\omega) = i \lim_{\epsilon \to 0} \int_0^\infty dt\, e^{i\omega t - \epsilon t} \langle [M_i(t), M_j(0)] \rangle , \qquad (1)$$

where ω is the frequency of the external probe field and $M_i(t) = e^{iHt} M_i e^{-iHt}$, M_i being the ith Cartesian component of $\vec{M}$. Two questions arise in connection with this expression.

First, does Eq. (1) give the susceptibility that one would measure under typical experimental conditions? Uneasiness in this regard is aroused by the known fact that for nonergodic systems the static ($\omega = 0$) limit of (1) differs from the static isothermal susceptibility. We have, in a recent paper[4] (PD), investigated this question for a class of models for linearly coupled dipole-lattice systems for which the isolated susceptibility (1) could be found exactly. We found that the conditions for the system to be ergodic were strongly related to the form of the dipole-lattice coupling. In particular, ergodic properties were found if the coupling was such as to allow the existence of Markovian transition processes in the system, which are responsible for the hydrodynamic-type (Lorentzian) behavior of the susceptibility at low frequencies. These are the processes which bring the system to thermal equilibrium. Conversely, if the coupling excluded the existence of Markovian processes the system was nonergodic. Furthermore, we concluded that the systems investigated were ergodic if they were free of degeneracy, as actual systems of interest usually are. For nonergodic systems the isothermal static susceptibility which can always be calculated formally is not a physically meaningful quantity due to the lack of hydrodynamic-type relaxation processes which would establish thermal equilibrium. On the other hand, the isolated susceptibility (1) may be meaningful in such cases, corresponding to photon absorption by acoustic phonons rendered optically active by the dipole. Equation (1) can thus describe two physically distinct types of linear response which in a general ergodic case will be superimposed on each other: namely, hydrodynamic relaxation and the phonon-mode absorption just mentioned.

The second question concerning Eq. (1) arises from the fact that it is seldom possible to evaluate it exactly. The validity of the approximations which are used to get around this fact is usually very difficult to judge. In particular, it is not obvious whether a certain approximation is part of a systematic chain of converging approximations, since higher steps in the sequence are so complicated to evaluate as to be inaccessible in practice. Thus the question arises whether an approximate method is capable of describing both types of linear response, and under which conditions, concerning the strength of the coupling and the range of frequency or temperature, it correctly represents the isolated susceptibility. To investigate this question we use in this paper a model which we have previously studied[4] and which will be described in the next section. Sections III and IV discuss two approximation methods. In Sec. V we analyze the validity of these approximate methods.

A preliminary report on the results given here has been presented elsewhere.[5]

II. THE MODEL AND THE EXACT ISOLATED SUSCEPTIBILITY

The model which we shall use has been discussed before in the literature[6] and we have treated it in some detail in PD to which the reader is referred for more detailed discussion. We present enough here only to have a convenient presentation of no-

tation. Our model will be a two-state electric dipole coupled to phonons with Hamiltonian

$$H=\frac{1}{2}\sum_q(\omega_q^2 Q_q Q_{-q}+P_q P_{-q})+\frac{1}{2}\sum_q F_q Q_q \sigma_z - pE\sigma_x e^{i\omega t}, \tag{2}$$

where the terms from left to right are the lattice phonon Hamiltonian, the dipole-phonon coupling term and, last, a term representing the interaction of an oscillating probe field E with the electric dipole moment of magnitude p. σ_i are Pauli spin matrices normalized so that $\sigma_i^2=1$. The frequencies, normal coordinates, and momenta of phonons are given by ω_q, Q_q, and P_q, and F_q is the dipole-phonon coupling coefficient. We will not consider a static transverse field along σ_z which was present in PD.

In PD it is shown how the exact isolated susceptibility $\chi^I_{xx}(\omega)$ can be found for Hamiltonian (2). The result is given by

$$\chi^I(\omega)=i\lim_{\epsilon\to 0}\int_0^\infty dt\, e^{i\omega t-\epsilon t}(e^{I(t)}-e^{I(-t)}) \tag{3}$$

where we have set p equal to unity, and

$$I(t)=\sum_q \frac{|F_q|^2}{2\omega_q^3}[\bar{n}_q(e^{i\omega_q t}-1)+(\bar{n}_q+1)(e^{-i\omega_q t}-1)], \tag{4}$$

with $\bar{n}_q=(e^{\beta\omega_q}-1)^{-1}$ and $\beta=1/kT$. The subscripts on χ^I_{xx} have been dropped for convenience. In PD several special cases of Eq. (3) have been worked out. The phonon spectrum was obtained from an isotropic Debye model. Three forms of F_q were considered:

$$F_q=d/V^{1/2} \quad \text{(piezoelectric coupling)}, \tag{5a}$$

$$F_q=s\omega_q/V^{1/2}\Omega \quad \text{(strain coupling)}, \tag{5b}$$

and the additional case of piezoelectric coupling confined to a limited range of frequencies from Ω_1 to Ω_2. In (5a) and (5b), d and s are coupling constants, V is the crystal volume, and Ω is the Debye cutoff frequency.

In the present work we will use a modified form for the Debye density of phonon states,[7]

$$\rho(\omega)=\frac{3V\omega^2}{2\pi^2 c^3}[1-(\omega/\Omega)^2]^{1/2}, \quad \omega\le\Omega \tag{6}$$

where c is so defined as to preserve the notation used in PD, i.e., $c=(V_0/4\pi)^{1/3}\Omega/2$ with V_0 being the volume of the unit cell. The last factor of (6) introduces a Van Hove-type singularity at the cutoff frequency which is known to occur in a realistic spectrum at the zone boundary. The effects of this singularity on the dynamic susceptibility will be discussed in Sec. V. The advantages of using such a phonon density of states were pointed out to us by W. Götze.

III. DECOUPLING APPROXIMATIONS

A frequently used method to calculate isolated susceptibilities (1) is based on the properties of so-called double-time thermal Green's functions.[8] The essential point of the treatment lies in the fact that the Fourier transform of the retarded Green's function obeys an equation of motion which offers the opportunity for approximate solutions. We will use our model to point out the limits of applicability of this method which cannot be found in cases which are not exactly soluble.

We use the following standard notation for the Fourier transformed Green's function[8]:

$$\langle\langle A\,;\,B\rangle\rangle_\pm=-i\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{i\omega t}\Theta(t)\langle[A(t),B(0)]_\pm\rangle\,dt. \tag{7}$$

The upper and lower signs mean the anticommutator and the commutator, respectively, of any two operators A and B, and $\Theta(t)$ is the unit step function. Clearly, for our model with $M=\sigma_x$,

$$\chi^I(\omega)=-2\pi\langle\langle\sigma_x\,;\,\sigma_x\rangle\rangle_-. \tag{8}$$

It can further be shown that the imaginary part of the isolated susceptibility can also be directly obtained from the anticommutator Green's function,[9]

$$\mathrm{Im}\,\chi^I(\omega)=2\pi\tanh(\beta\omega/2)\,\mathrm{Im}\,\langle\langle\sigma_x\,;\,\sigma_x\rangle\rangle_+. \tag{9a}$$

It will be useful also to have the relationship

$$\mathrm{Im}\,\langle\langle\sigma_x\,;\,\sigma_x\rangle\rangle_+=\frac{-1}{2\pi}\coth\frac{\beta\omega}{2}\,\mathrm{Im}\,\chi^I(\omega) - \frac{1}{2}\lim_{t\to\infty}\langle[\sigma_x(t),\sigma(0)]\rangle_+\,\delta(\omega) \tag{9b}$$

where the δ-function term arises in nonergodic cases from the nonvanishing of the correlation function in Eq. (7) at $t\to\infty$. The functions (7) satisfy the equations of motion

$$\omega\langle\langle A\,;\,B\rangle\rangle_\pm=\frac{1}{2\pi}\langle[A,B]_\pm\rangle+i\langle\langle[A,H]\,;\,B\rangle\rangle_\pm, \tag{10}$$

which can be obtained by partial integration of (7) with $[A,H]=i(d/dt)A$. This equation introduces new Green's functions $\langle\langle[A,H]\,;\,B\rangle\rangle_\pm$ for which another equation of motion like (10) can be written. In this way, one can generate a sequence of equations of motion for a set of Green's functions. In general, both the sequence and the set are infinite so that to make progress the sequence is usually truncated by what is called a decoupling approximation.[9]

We apply one such method to the functions $\langle\langle\sigma_x\,;\,\sigma_x\rangle\rangle_\pm$. Using (10) with Hamiltonian (2) without the external field term, the sequence of equations of motion for the commutator function, for example, begins as follows:

$$\omega\langle\langle\sigma_x\,;\,\sigma_x\rangle\rangle_-=-i\sum_q F_q\langle\langle Q_q\sigma_y\,;\,\sigma_x\rangle\rangle_- \tag{11}$$

$$\omega\langle\langle Q_q\sigma_y;\ \sigma_x\rangle\rangle_- = -\frac{1}{2\pi}\,2i\langle Q_q\sigma_z\rangle + i\sum_{q'} F_{q'}\langle\langle Q_qQ_{q'}\sigma_x;\ \sigma_x\rangle\rangle_- + \langle\langle P_q\sigma_y;\ \sigma_x\rangle\rangle_- \ , \tag{12}$$

$$\omega\langle\langle P_q\sigma_y;\ \sigma_x\rangle\rangle_- = -\frac{1}{2\pi}\,2i\langle P_q\sigma_z\rangle + \frac{1}{2}\sum_{q'} F_{q'}\langle\langle[Q_{q'},P_q]_+\sigma_x;\ \sigma_x\rangle\rangle_- - i\omega_q^2\langle\langle Q_q\sigma_y;\ \sigma_x\rangle\rangle_- \ . \tag{13}$$

The particular decoupling approximation which we employ consists in terminating the pile-up of phonon operators in higher order Green's functions by writing

$$\langle\langle Q_qQ_{q'}\sigma_x;\ \sigma_x\rangle\rangle_- \approx \langle Q_qQ_{q'}\rangle\langle\langle\sigma_x;\ \sigma_x\rangle\rangle_- \approx \delta_{q,q'}\langle|Q_q|^2\rangle\langle\langle\sigma_x;\ \sigma_x\rangle\rangle_- \ , \tag{14}$$

$$\langle\langle[P_q,Q_{q'}]_+\sigma_x;\ \sigma_x\rangle\rangle_- \approx \langle[P_q,Q_{q'}]_+\rangle\langle\langle\sigma_x;\ \sigma_x\rangle\rangle_- \cong 0 \ . \tag{15}$$

Other decoupling terms, like for example $\langle Q_q\sigma_x\rangle\langle\langle Q_{q'};\ \sigma_x\rangle\rangle_-$, vanish.

There are two steps in this approximation: The first is to factor out or decouple pairs of phonon operators as thermal averages. Second, the averages over phonon operators are evaluated to zero order in the coupling strength. This means that the coefficients of decoupled Green's functions are evaluated to order F_q only. Note that the function $\langle\langle Q_qQ_{q'}\sigma_x;\ \sigma_x\rangle\rangle_-$ itself is not calculated to order F_q, because $\langle\langle\sigma_x;\ \sigma_x\rangle\rangle_-$ in (14) is kept as an unknown and thus contains arbitrary powers of F_q.

Using the decoupling approximation (14), (15) in (11)–(13) we can solve for $\langle\langle\sigma_x;\ \sigma_x\rangle\rangle_-$. The result is:

$$\langle\langle\sigma_x;\ \sigma_x\rangle\rangle_-^d = \frac{1}{2\pi}\,\frac{S_2(\omega)}{\omega - S_1(\omega)} \ , \tag{16}$$

where

$$S_1(\omega) \equiv \omega\sum_q \frac{|F_q|^2\langle|Q_q|^2\rangle}{\omega^2-\omega_q^2} \ ; \tag{17}$$

$$S_2(\omega) \equiv -2\omega\sum_q \frac{F_q\langle Q_q\sigma_z\rangle}{\omega^2-\omega_q^2} \ . \tag{18}$$

The average in (18) to linear order in F_q is $\langle Q_q\sigma_z\rangle = -F_{-q}/(2\omega_q^2)$. In zero order, $\langle|Q_q|^2\rangle = \coth(\beta\omega_q/2)/(2\omega_q)$. The superscript d in (16) refers to the decoupling approximation. Evaluating such thermal averages is to some extent arbitrary. Since the whole decoupling procedure is not a perturbation expansion, there is no clear criterion to decide the order in coupling parameter to which these averages should be evaluated.

In an analogous way we can find the anticommutator Green's function:

$$\langle\langle\sigma_x;\ \sigma_x\rangle\rangle_+^d = \frac{1}{2\pi}\,\frac{2}{\omega - S_1(\omega)} \ . \tag{19}$$

One cannot in practice understand the meaning of the decoupling approximation by introducing the decoupling either earlier or later in the sequence of equations (11)–(13) . . . . Decoupling earlier, e.g. $\langle\langle Q_q\sigma_y;\ \sigma_x\rangle\rangle_- = \langle Q_q\rangle\langle\langle\sigma_y;\ \sigma_x\rangle\rangle_-$, gives the trivial result $\langle\langle\sigma_x;\ \sigma_x\rangle\rangle_- = 0$. Decoupling at the three-phonon operator stage or higher would be a very formidable task and does not appear to have ever been carried out. We can, however, compare the expressions for the isolated susceptibility obtained from (16) and (19) with the exact result (3).

The sums in (17) and (18) are evaluated by using the coupling constants (5) and the modified Debye density of states (6). The results are:

$$S_1(\omega) = A\omega\int_0^\Omega dx\,x^n\coth(\beta x/2)\sqrt{1-(x/\Omega)^2}\,(\omega^2-x^2)^{-1} \ ; \tag{20}$$

$$S_2(\omega) = 2A\omega\int_0^\Omega dx\,x^{n-1}\sqrt{1-(x/\Omega)^2}\,(\omega^2-x^2)^{-1} \ , \tag{21}$$

where $n=1$ and $A = 3d^2/(4\pi^2c^3)$ for piezoelectric coupling while for strain coupling $n=3$ and A is to be replaced by B/Ω^2 with $B = 3s^2/(4\pi^2c^3)$.

The real and imaginary parts of $S_1(\omega)$ and $S_2(\omega)$ for $\omega = \omega + i\epsilon$ with $\epsilon \to 0_+$ are calculated by standard procedure. We obtain for the imaginary parts:

$$S_1''(\omega) = -(\pi/2)A\omega^n\coth(\beta\omega/2)\sqrt{1-(\omega/\Omega)^2}\times\Theta(1-|\omega/\Omega|) \ ; \tag{22}$$

$$S_2''(\omega) = -\pi A\omega^{n-1}\sqrt{1-(\omega/\Omega)^2}\,\Theta(1-|\omega/\Omega|) \ . \tag{23}$$

The real part of S_2 is given by

$$S_2'(\omega) = \pi A(\omega/\Omega)[1-\sqrt{1-(\Omega/\omega)^2}\times\Theta(|\omega/\Omega|-1)] \text{ (piezoelectric coupling)} \ , \tag{24}$$

$$S_2'(\omega) = -\pi B(\omega/\Omega)[\tfrac{1}{2}-(\omega/\Omega)^2+(\omega/\Omega)^2\sqrt{1-(\Omega/\omega)^2}\times\Theta(|\omega/\Omega|-1)] \quad \text{(strain coupling)} \ . \tag{25}$$

The real part of $S_1(\omega)$ is found from (20) by numerical integration with the integral interpreted as a principal-value integral.

We can now derive two versions of the isolated susceptibility in the decoupling approximation, χ_{d+} and χ_{d-}. From (8) and (16) the real and the imaginary parts of the commutator version of the susceptibility are:

$$\chi_{d-}'(\omega) = \frac{S_1'S_2'' - (\omega - S_1')S_2'}{(\omega-S_1')^2+(S_1'')^2} \ ; \tag{26}$$

$$\chi_{d-}''(\omega) = \frac{S_1'S_2' - S_1''S_2' - \omega S_2''}{(\omega-S_1')^2+(S_1'')^2} \ . \tag{27}$$

From the anticommutator Green's function (19) and

(9) we obtain:

$$\chi''_{d+}(\omega)=\frac{2\tanh(\beta\omega/2)S_1''}{(\omega-S_1')^2+(S_1'')^2}=-\frac{\omega S_2''}{(\omega-S_1')^2+(S_1'')^2}\,, \tag{28}$$

where the last result follows from the explicit forms of S_1'' and S_2'' as given by (22), (23). The real part of $\chi_{d+}(\omega)$ can only be found by performing a numerical Hilbert transform of (28).

By comparing (27) and (28) we realize that the decoupling approximation yields two different results for the isolated susceptibility depending on whether we use the commutator or the anticommutator version. Clearly, this is an inadequacy of our decoupling approximation because no such difference is possible if $\chi^I(\omega)$ is calculated exactly. This is not a special feature of our model because the method is applicable to any system and the use of commutators or anticommutators is equally justifiable. In fact, both versions of this method have been used for more general spin-phonon systems.[9,10] If fermion or boson operators appear in the Green's function, the natural choice seems to be the anticommutator and commutator, respectively. However, there is no *a priori* reason for not using the alternative method in such cases. It can be shown that the difference between (27) and (28) will be negligible at high temperatures ($\beta\Omega \ll 1$), however, it can become quite important at low temperatures. We will return to this problem in our discussion of numerical results.

IV. THE MEMORY FUNCTION APPROXIMATION OF GÖTZE AND WÖLFLE

Using the analytic properties of $\chi^I(\omega)$ with ω complex, Götze and Wölfle[11] (GW) have shown that in general $\chi^I(\omega)\neq\chi^I(0)$ for $\mathrm{Im}\omega\neq 0$. They introduced a new analytic function, also called the memory function,[12]

$$N(\omega)=\frac{\omega\chi^I(\omega)}{1-\chi^I(\omega)/\chi^I(0)}\,, \tag{29}$$

which in view of the above properties of $\chi^I(\omega)$, is nonsingular and can be expected to have a smoother behavior than χ^I itself. Therefore, $N(\omega)$ might be easier to calculate by some perturbation expansion than $\chi^I(\omega)$.

Knowing $N(\omega)$, one can find $\chi^I(\omega)$ from the inverse relation

$$\chi^I(\omega)=\frac{N(\omega)}{\omega+N(\omega)/\chi^I(0)}\,. \tag{30}$$

It is then assumed that the system is ergodic so that $\chi^I(0)$ is exactly equal to the isothermal static susceptibility

$$\chi^I(0)=\chi^T=p\,\partial\langle\sigma_x\rangle/\partial E\big|_{E=0}\quad\text{(ergodic)}\,. \tag{31}$$

That the longitudinal susceptibility behaves like Eq. (30) in the low frequency (hydrodynamic) range has been suggested by Kadanoff and Martin.[13] Mori[14] has used a projection operator technique to derive a formal expression for $N(\omega)$ which, evaluated to second order in the dipole-phonon coupling strength, is the same as $N_{GW}(\omega)$ below in Eq. (33).

Following the ideas of GW we calculate $N(\omega)$ approximately in the lowest order with respect to the coupling parameter. We expand (30) as

$$\omega\,\chi^I(\omega)=N(\omega)+O(N^2)\,, \tag{32}$$

noting that for weak coupling $N(\omega)$ is approximately given by the left hand side of (32) with $\chi^I(\omega)$ being calculated to the order F_q^2 only. This approximate $\chi^I(\omega)$ will be denoted as $\tilde{\chi}^I(\omega)$. The calculation of $\tilde{\chi}^I(\omega)$ is accomplished by considering the equation of motion (11) for the Green's function $\langle\langle\sigma_x;\,\sigma_x\rangle\rangle$ which together with (32) leads immediately to

$$N_{GW}(\omega)=\omega\tilde{\chi}^I(\omega)=2\pi i\sum_q F_q\langle\langle Q_q\sigma_y;\,\sigma_x\rangle\rangle$$

$$=2\omega\sum_q\frac{F_q\langle Q_q\sigma_q\rangle}{\omega^2-\omega_q^2}=-S_2(\omega)\,. \tag{33}$$

The Green's function in (33) has been calculated to the order F_q from Eqs. (12), (13). The notation N_{GW} is used to emphasize the fact that (33) has been obtained from (32) and not from (29).

The expression (33) is then substituted into (30) using (31); the resulting approximate expression for $\chi^I(\omega)$ will be called χ_{GW}.

$$\chi_{GW}(\omega)=\frac{\tilde{\chi}^I(\omega)}{1+\tilde{\chi}^I(\omega)/\chi^T}=-\frac{S_2(\omega)}{\omega-S_2(\omega)/\chi^T}\,. \tag{34}$$

Like the decoupling approximation, this procedure clearly produces an approximation which contains terms of all orders in F_q. It differs from the exact susceptibility but it may, under some circumstances, be a good approximation. It has the advantage that it is simpler to find in practice than it is to perform the decoupling scheme.

If the approximate $\tilde{\chi}^I(\omega)$ in (34) happens to be more singular than the exact $\chi^I(\omega)$, the resulting χ_{GW} will contain singularities which are not present in the exact susceptibility. As pointed out by GW, the method is not useful in such cases. In our model, this occurs if the Debye density of phonon states does not contain the square-root factor in (6), as will be demonstrated later.

V. COMPARISON OF SUSCEPTIBILITIES AND DISCUSSION

A. Piezoelectric coupling

It is of interest to first investigate the static limits of χ_{GW} and χ_{d+}. The $\omega\to 0$ limit of (34) will be given by the isothermal static susceptibility χ^T if, for example, $S_2''(\omega)\to$ const and $S_2'(\omega)\propto\omega$ for small ω. From (22)–(25) it can be seen that this behavior

is found in the ergodic piezoelectric coupling case.

In a recent paper, Götze and Schlottmann[15] have shown that χ^T, which appears as an unknown parameter in (34), can be determined self-consistently by employing the general sum rule

$$\tfrac{1}{2}\langle[\sigma_x, \sigma_x]_+\rangle = 1 = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \coth\left(\frac{\beta\omega}{2}\right)\chi''(\omega) + \frac{1}{2}\lim_{t\to\infty}\langle[\sigma_x(t), \sigma_x(0)]_+\rangle . \quad (35)$$

This result follows by integration over all ω of the anticommutator form of Eq. (7) with $A = B = \sigma_x$ and using relation (9b).

In the ergodic case the last term in (35) is zero. To calculate χ^T self-consistently, we replace $\chi''(\omega)$ by the imaginary part of Eq. (34). Using Eqs. (22) and (23) and introducing an integration variable $y = \omega/\Omega$ leads to the transcendental equation for χ^T_{GW}:

$$1 = \frac{\chi^T_{GW}}{\beta} + \frac{A}{2}\int_{-1}^{+1} dy \frac{y(1-y^2)^{1/2}\left[\coth\left(\beta\frac{\Omega}{2}y\right) - \frac{2}{\beta\Omega y}\right]}{y^2\left[1 - \frac{2\pi}{\chi^T_{GW}\Omega}\right] + \left(\frac{\pi A}{\chi^T_{GW}\Omega}\right)^2} . \quad (36)$$

This equation can be solved numerically. The result for $A = 0.1$ appears as $\chi_{GW}(0)$ in Fig. 1 as a function of $\beta\Omega$.

It is interesting to compare this self-consistent χ^T_{GW} with the exact $\chi^I(0)$ and with $\chi'_{d+}(0)$. The latter quantity can be found numerically from the Kramers-Kronig relation

$$\chi'_{d+}(0) = \frac{1}{\pi}\int_{-\infty}^{\infty} d\omega \frac{\chi''_{d+}(\omega)}{\omega} \quad (37)$$

with $\chi''_{d+}(\omega)$ given by Eq. (28). For further comparison we have included also the static susceptibility calculated using equilibrium statistical mechanics to second order in F_q, an often used approximation. From Eq. (22) of PD with $\Delta = 0$ we find

$$\chi'_2(0) = \beta + 2\int_0^{\beta/2} d\lambda\, I(-i\lambda) . \quad (38)$$

These quantities also appear in Fig. 1.

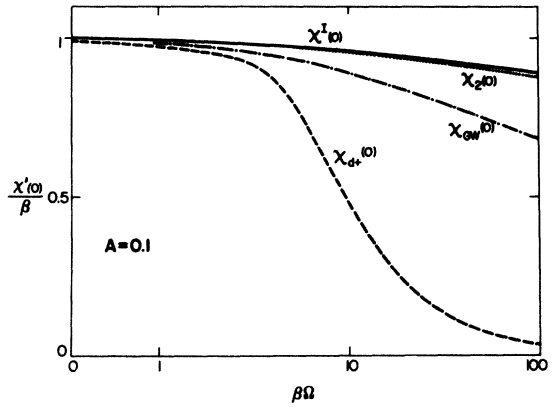

FIG. 1. Static susceptibilities for piezoelectric coupling in various approximations. $\chi_2(0)$ is based on equilibrium statistical mechanics and $\chi^I(0)$ is the exact static susceptibility. The others are based on approximations to the dynamic isolated susceptibility.

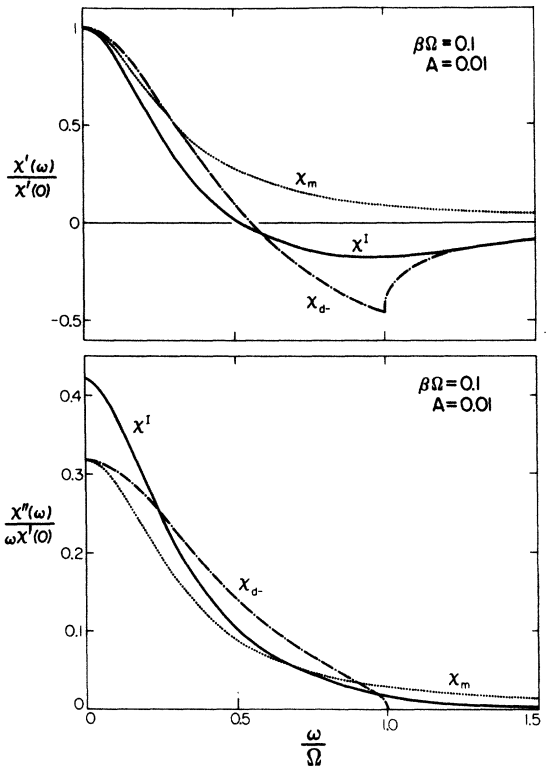

FIG. 2. Real and imaginary parts of approximate susceptibilities for moderate piezoelectric coupling and high temperature. χ_{d-}, χ_{d+}, and χ_{GW} are indistinguishable in this case.

Note that $\chi_2(0)$ is the most accurate approximation in this case. χ^T_{GW}, the self-consistent version of the static susceptibility from Eq. (36), is a good approximation only at high temperatures. For $\beta\Omega < \pi A$ it can be shown that this approximation breaks down because of a singularity of $\chi_{GW}(\omega)$ near $\omega = \Omega$ due to the vanishing of the denominator in Eq. (34). $\chi'_{d+}(0)$ is not a useful approximation except at very high temperatures where it equals β. $\chi'_{d-}(0)$ is equal to β for all β.

To investigate the frequency dependence of various approximate susceptibilities, we have numerically calculated $\chi_{d-}(\omega)$, $\chi_{d+}(\omega)$ and $\chi_{GW}(\omega)$ and plotted them together with the exact $\chi^I(\omega)$ in Figs. 2 and 4. For further comparison the simple Lorentzian form

$$\chi_m(\omega) = \frac{\chi^T}{1 + i\omega\tau} \quad (39)$$

is also included. Here, $\tau^{-1} = \pi A/\beta$ is the one-phonon relaxation rate as has been shown in PD. The subscript m on χ_m is a reference to the fact that the susceptibility (39) results, for a two level system, from a treatment of Markovian master equations.[16]

Figure 2 shows the exact and approximate susceptibilities for high temperature ($\beta\Omega = 0.1$) and moderate coupling. In order to exhibit the low frequency behavior of $\chi''(\omega)$ in Figs. 2 and 4 we have in each case plotted the quantity $\chi''(\omega)/(\omega\chi^T)$. Note that χ''_{d-}, χ''_{d+}, and χ''_{GW} are indistinguishable in this case, as are also $\chi'_{d-}(\omega)$, $\chi'_{d+}(\omega)$, and $\chi'_{GW}(\omega)$. This can be understood by comparing (16) and (34) using the fact that the χ^T in (34) calculated self consistently from (36) is very close to β in this case and $S_2(\omega) \cong \beta S_1(\omega)$ by (20) and (21). The real parts of approximate susceptibilities become negative at large frequencies in agreement with the exact result. There is, however, a discontinuity in the slope of χ'_d at $\omega = \Omega$ which is due to the sharp cutoff of χ''_{d-} at the same frequency as discussed below. If a simple Debye model for the phonon spectrum is used instead of the modified form (6), χ'_{d-} contains a singularity in the neighborhood of $\omega = \Omega$ which is due to the vanishing of the denominator in (27) at ω slightly above Ω. Both χ'_{d-} and χ''_{d-} can have very large values for $\omega < \Omega$ but no singularities occur in this region. (See Fig. 3.)

Numerical calculations show that in the limit of small coupling ($A < 0.001$) all approximate methods together with χ_m become very close to the exact χ^I at all frequencies below Ω except in a narrow range near Ω.[17] Above Ω, the real parts are still a very good approximation to $\chi^I(\omega)'$, the imaginary parts of χ_d and χ_{GW} being equal to zero in this region.

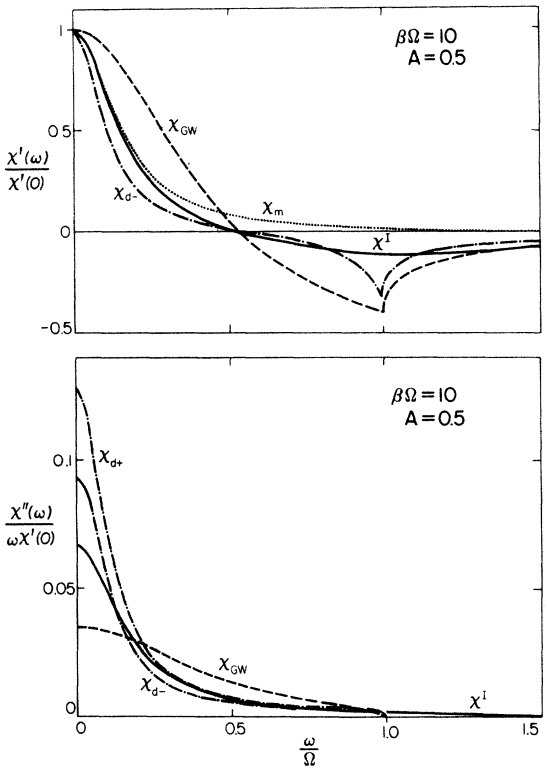

FIG. 4. Real and imaginary parts of approximate and exact susceptibilities for strong piezoelectric coupling and low temperature.

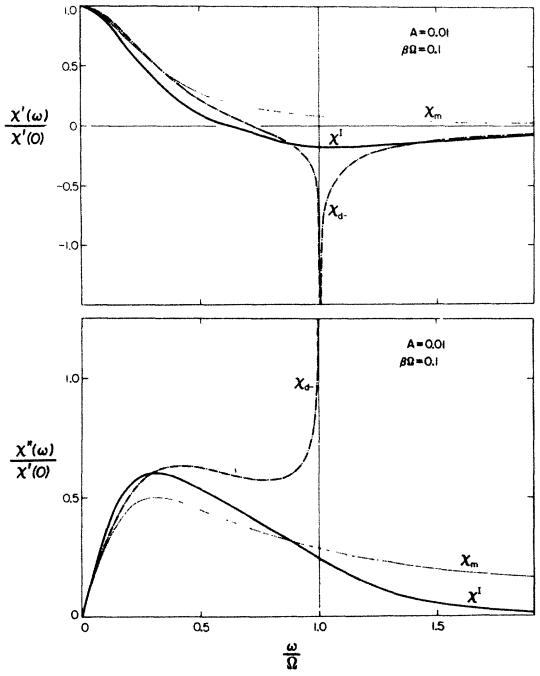

FIG. 3. Same parameters as Fig. 2, but calculated using a simple Debye spectrum instead of the modified form of Eq. (6).

Figure 4 shows the low temperature results ($\beta\Omega = 10$) for strong coupling ($A = 0.5$). There is now a large difference between χ'_{d-} and χ'_{GW} at low frequencies due to the fact that $\chi^T_{GW} < \beta$. Again, for $\omega > \Omega$ both approximate real parts converge towards $\chi^I(\omega)'$. We can clearly distinguish between the commutator version of the decoupling approximation, χ''_{d-}, and its anticommutator counterpart, χ''_{d+}.

A general feature of both the decoupling and GW approximations is that they always give good results for the real part of the susceptibility at large frequencies ($\omega > \Omega$) even for strong coupling. This suggests that the equation of motion method which is used to derive χ_d and N_{GW} in χ_{GW} is equivalent to an asymptotic expansion of $\chi^I(\omega)$ for large ω. As already mentioned in connection with (10), integration of (7) by parts produces an equation for the Green's function with a new Green's function appearing in it. Repeated partial integration, which is a standard method for obtaining asymptotic ex-

pansions of nonsingular Fourier integrals, produces an asymptotic expansion of (7) or, alternatively viewed, a sequence of equations of motion. The decoupling method is a truncation of this asymptotic expansion with a special treatment of the remainder term. It is not understood why this truncation yields a good representation of $\chi^I(\omega)$ at low frequencies. The termination of the asymptotic expansion at the lowest order, that is at $|F_q|^2$, is responsible for the vanishing of χ_d'' and χ_{GW}'' for $\omega > \Omega$. This termination limits the relaxation processes to one-phonon transitions which become forbidden by energy conservation for $\omega > \Omega$.

B. Strain coupling

The decoupling approximation can be applied to this case without difficulty. The static limit of χ_{d-}' turns out to be

$$\chi_{d-}'(0) = \frac{h(T)}{1 + \frac{2\Omega}{\pi B} h(T)} , \tag{40}$$

where

$$h(T) = (\pi\Omega/2)\left(\int_0^{\Omega} dx\, x \coth(\beta x/2) \sqrt{1 - (x/\Omega)^2} \right)^{-1} . \tag{41}$$

For high temperatures ($\beta\Omega \ll 1$), $h(T) \cong \beta$. Except for very strong coupling (large B), the static limit (40) will be much different from the isothermal static susceptibility χ^T as expected for this nonergodic case. This is due to the lack of Markovian transitions between the two states of the dipole. As shown in PD the one-phonon relaxation rate τ^{-1} is zero in this case and the first non-vanishing, five-phonon rate is estimated to be negligible. For the same reason, the Lorentzian expression (39) cannot be used in this case.

An interesting problem arises in connection with the method of GW. As noted before, the method has been developed for ergodic systems with $\chi^I(0) = \chi^T$. However, the arguments of GW[11] leading to Eq. (29) are valid as well for the nonergodic systems for which $\chi^I(0) \neq \chi^T$. Thus, it seems plausible that the function $N(\omega)$ defined in terms of the exact $\chi^I(\omega)$ in (29) must be nonsingular also in the nonergodic case and that Eq. (30) can again be used as in Eqs. (32)–(34) for generating an approximation to $\chi^I(\omega)$. The result is Eq. (34) with χ^T replaced by $\chi^I(0)$. The real and imaginary parts of $S_2(\omega)$ are obtained from Eq. (25) and (23) with $n = 3$, respectively. At low frequencies $S_2''(\omega)$ is now proportional to ω^2 and $S_2'(\omega)$ to ω. The zero frequency limit of $\chi_{GW}(\omega)$ in the strain coupling case would be

$$\chi_{GW}(0) = \frac{\chi^I(0)}{1 + \frac{2\Omega}{\pi B} \chi^I(0)} . \tag{42}$$

$\chi^I(0)$ could, like χ^T in (34), be treated as parameter to be evaluated self-consistently as done in the last section with χ^T. Notice from (42) that $\chi^I(0)$ calculated in such a way is not equal to $\chi_{GW}(0)$. Its physical meaning is not clear. More importantly, it is not clear how such a self-consistent calculation could be performed. The sum rule (35) in this nonergodic case now includes the last term on the right hand side of (35). This term along with the $\chi^I(0)$ which is to be determined self-consistently comprise *two* unknown parameters, since the limit of $\langle [\sigma_x(t), \sigma_x(0)]_+ \rangle$ as t goes to infinity, is not known to us.

In Fig. 5 we have plotted χ_{d+} and χ_{d-} along with χ^I for a nonergodic strain coupling case. There are marked discrepancies between the exact χ^I and the two decoupling approximations.

C. Conclusions

The applicability of approximate methods investigated here depends on the properties of the system through the shape of the phonon spectrum and the strength of the dipole-phonon interaction. As expected, for weak coupling, all methods are good approximations to the isolated susceptibility in a wide frequency range. The simplest to apply is the Lorentzian approximation which, however, fails in representing the real part of the susceptibility at frequencies larger than the cut-off frequency Ω. Also, this approximation is not appli-

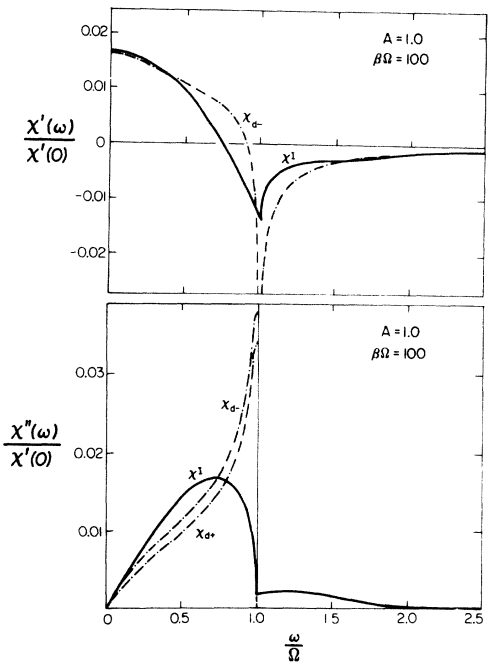

FIG. 5. Decoupling approximation and exact susceptibilities for a strong strain coupling case at low temperature.

cable in the nonergodic strain coupling case. The decoupling approximations and the method of Götze and Wölfle give, in general, good results for the real parts of the isolated susceptibility at large frequencies but are poor approximations to the imaginary part near and above the cutoff frequency. For $\omega \sim \Omega$ the degree of accuracy of the imaginary part is much better when a modified Debye spectrum of the form (6) is used instead of the usual Debye spectrum. For $\omega = 0$ all the approximations treated were worse than a simple second order calculation based on equilibrium statistical mechanics.

The decoupling approximations and the method of GW are characterized by certain factorization schemes for the Green's function (7) in the frequency picture which lead to the results (16), (19), and (34). The factorization occurs in the lowest nonzero (second) order with respect to the coupling strength. This is responsible for the nonphysical sharp cutoff in the imaginary part of the susceptibility at $\omega = \Omega$. Factorization schemes can be interpreted as a crude extension of the simple Lorentzian result (39) by introducing *ad hoc* frequency-dependent relaxation rates $S_1(\omega)$ or $S_2(\omega)/\chi^T$ in lieu of τ^{-1}. A constant relaxation rate τ^{-1} is only meaningful if the irreversible time evolution of the polarization can be adequately described by Markovian master equations. These equations are only approximately satisfied in some systems in a certain range on the time scale, and have to be replaced, in general, by the integral (non-Markovian) equations.[18] The discrepancy between the commutator and anticommutator decoupling method results suggests that the factorization methods implicitly introduce irregularities into the time behavior of the correlation function $\langle A(t)\, B(0)\rangle$ figuring in (7) since a properly behaved correlation function can only lead to identical results in both cases.

To improve the decoupling approximations and the GW method, one is tempted to develop more complicated schemes through various corrections to the functions $S_1(\omega)$ and $S_2(\omega)$ in (16), (19), and (34) in higher order of the coupling strength, for example, by including the perturbed phonon frequencies ω_q into S_1 and S_2, etc. However, it is not clear whether such schemes would lead to the correct time dependence of the correlation function. To avoid this difficulty one should consider a perturbation expansion with a factorization scheme in the time picture by writing the correlation function in a form which has the correct limit for both short and long times. We will discuss one such method and its application to a more general model of spin-phonon interaction in a future publication.

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