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Exact isolated and isothermal susceptibilities for an interacting dipole-lattice system*

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Relationships between the static isothermal susceptibility and the dynamic susceptibility as given by linear-response theory (isolated susceptibility) are investigated by means of an exactly soluble model of a two-level dipole moment interacting with phonons. Two forms of dipole-lattice interaction coupling are treated: coupling to lattice strain and coupling to lattice atomic displacements (piezoelectric coupling). In the case of piezoelectric coupling and for the temperature limits investigated, the isolated susceptibility follows closely the behavior predicted by a simple Debye theory with a one-phonon relaxation time predicted by the model. There are deviations from this behavior when the dipole-lattice coupling becomes strong. Static isolated susceptibilities for various cases are compared with the corresponding static isothermal susceptibilities. Two cases in which these two static susceptibilities differ are discussed: the case of strain coupling and that of piezoelectric coupling with a lower-frequency cutoff in the phonon spectrum which couples to the dipole. The occurrence of this difference is related to the nonergodic behavior of the polarization autocorrelation function which is in turn influenced by the existence of degeneracies in the model. It is further demonstrated that the addition of a symmetry-breaking term will remove the discrepancy between the two static susceptibilities at the expense, however, of creating a singularity in the dynamic isolated susceptibility associated with a low-lying zero-phonon absorption.

I. INTRODUCTION

In this paper we discuss some problems that arise in the theory of dielectric relaxation in solids. Actually these problems are of more general occurrence, being related to the longitudinal magnetic susceptibilities of paramagnetic systems and optical absorption by electronic impurities in insulating crystals. In order to keep the terminology definite, however, we adopt the example of dielectric relaxation. The problems discussed have more general interest than for dielectric relaxation in another sense: There exist long-standing fundamental questions concerning the theory of dynamic susceptibilities. In this connection we discuss the problem of the relationship between the isolated and isothermal susceptibilities through analysis of a class of models for which these quantities can be found exactly. That a difference between these susceptibilities exists has been repeatedly mentioned in the literature,[1-8] but it does not appear to be a well-known fact.

There are two ways which are commonly used to formulate the theory of dielectric relaxation: master equation and microscopic approaches. Master-equation methods are based on the assumption that there are Markovian[9] transitions (governed by constant transition probabilities per unit time) between states. All quantities appearing in the master equations are expanded up to terms linear in the external field and the linearized equations are solved for the deviation of the polarization from its equilibrium value. The proportionality factor between this deviation and the external field oscillating with a single frequency is the frequency-dependent susceptibility. An example of this approach is the Debye theory.[10,11]

For extremely slowly varying external fields the real part of the susceptibility approaches the isothermal static susceptibility, which in turn can be found by purely equilibrium-thermodynamics arguments. The master-equation approach is the customary way of extending the isothermal susceptibility to nonzero frequencies. The reason that the isothermal static susceptibility is recovered by this approach, in the zero-frequency limit, comes from the requirement of detailed balancing among the transition rates which appear in the master equations.[12]

The master-equations approach can be applied in almost all practical situations. The question remains, however, as to whether this approach is valid. If the conditions required for the existence of constant transition rates do not hold (i.e., the transitions are non-Markovian), then one cannot expect the master-equation approach to produce correct results. One must then resort to a more fundamental approach to the problem. An effort to do this is the microscopic approach.

A widely used formulation of the microscopic theory of dielectric or magnetic susceptibilities is the linear-response theory[13] of Kubo.[1,14] This theory is based on first-order time-dependent perturbation theory on the microscopic states of the system.[4,13] A feature of this approach is the fact that the thermal averages involved use the density matrix characteristic of the system before the external field is applied. The expression for the frequency-dependent susceptibility obtained in this way will be referred to as isolated or Kubo susceptibility.

It is not trivial to understand the relationship between this approach and that of the master equations. The latter have often been derived from the linear-response theory[15]; however, always with the help of simplifying assumptions and various approximations. The only frequency for which one knows exactly what the susceptibility ought to be is the frequency zero. We have already mentioned that the master equations give the correct isothermal static susceptibility. It is well known, however, that the corresponding result of the linear-response theory formally differs from the thermodynamic static value.[1–8] This has been recognized, for example, by Kubo,[1] who also discusses the conditions under which this difference is insignificant and points out that there is no such problem if the system is ergodic. It is, however, not easy to prove for an actual system, characterized by a certain Hamiltonian, that the condition of ergodicity is indeed satisfied in the Kubo sense. One tries, rather, to avoid this problem by assuming consciously or unconsciously that the system is ergodic. We shall discuss here cases in which such an assumption is incorrect. We use a simple nontrivial model for which both the Kubo susceptibility at all frequencies and the isothermal static susceptibility can be found exactly. The model consists of a two-level system, that is, a permanent electric dipole moment which can have two equilibrium orientations and which is linearly coupled with phonons. This model has been described in literature before,[16] but its application in the context in which it appears here is new. We discuss two nonergodic cases where the zero-frequency susceptibility as given by the Kubo formula is different from the isothermal static susceptibility. An ergodic version of the model is also discussed.

In Sec. II we first discuss some general conditions under which nonergodic behavior occurs. The model and the calculation of the susceptibilities are described in Sec. III. This is followed in Sec. IV by numerical results for various cases of dipole-phonon coupling. Our conclusions are summarized in Sec. V.

II. GENERAL CONSIDERATIONS

The Kubo or isolated susceptibility of a system which is characterized by the Hamiltonian H and the electric dipole moment operator M is given by

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

where ω is the frequency of the external field, ϵ the field switching parameter, and $M_i(t) = e^{iHt}M_i e^{-iHt}$; M_i being the ith Cartesian component of M. The symbols for the commutator and the thermodynamic average with respect to H have their usual meaning. For simplicity, we will discuss only one component of the susceptibility tensor, say $\chi^I_{ii}(\omega)$, and will drop the indices i, j from now on.

Equation (1) is based on a treatment in which the thermal ensemble averaging is that appropriate to the system before any perturbation is applied. Consequently it considers state-vector changes but not population changes. Thus Eq. (1) is not the same as an isothermal susceptibility, the static form, χ^T, of which follows from equilibrium statistical mechanics[1,3,5]:

$$\chi^T = \left[\frac{\partial\langle M\rangle}{\partial E}\right]_T = \int_0^\beta d\lambda \langle \tilde{M}(-i\lambda)\tilde{M}(0)\rangle , \qquad (2)$$

where $\tilde{M} = M - \langle M\rangle$.

The difference between (1) and (2) can be seen explicitly in an energy eigenstate (Lehmann) representation in which

$$\chi^I(0) = Z^{-1} {\sum_{l,m}}' \frac{e^{-\beta E_l} - e^{-\beta E_m}}{E_m - E_l} \, |\langle l|\, M|\, m\rangle|^2 , \qquad (3)$$

$$\chi^T = \chi^I(0) + \beta Z^{-1} \sum_{l,l'} e^{-\beta E_l} |\langle l|\, M|\, l'\rangle|^2 - \beta\langle M\rangle^2 . \qquad (4)$$

In (4) the sum over l and l' contains all states for which $E_l = E_{l'}$.

It has been shown formally by Wilcox[3] that $\chi^I(0) \le \chi^S \le \chi^T$ always holds. χ^S is the static adiabatic susceptibility. Since in experiments either χ^S or χ^T is usually the quantity measured, the hope is that in practical cases $\chi^I(0)$ becomes equal either to χ^T or χ^S. In particular, the condition for $\chi^I(0) = \chi^I$ clearly is either

$$\langle M\rangle^2 = Z^{-1} \sum_{l,l'} e^{-\beta E_l} |\langle l|\, M|\, l'\rangle|^2 \qquad (5)$$

or that both sides of (5) vanish. If this condition is not satisfied, and since $\chi^I(\omega)$ is presumably continuous for small ω, this would mean that susceptibilities measured under isothermal conditions would not be the same as the Kubo isolated susceptibility. The existence of this discrepancy is indicative of the nonergodicity of the system.

In order to gain a better insight into the low-frequency behavior of (1) we consider the Fourier transform of the correlation function $\langle \tilde{M}(0)\tilde{M}(t)\rangle$ which we will call $\chi_1(\omega)$:

$$\chi_1(\omega) = -i \lim_{\substack{u\to\infty \\ \epsilon\to 0}} \int_0^u dt\, e^{i\omega t-\epsilon t}\langle \tilde{M}(0)\tilde{M}(t)\rangle . \qquad (6)$$

By deforming the integration contour in the complex t plane as shown in Fig. 1, we can equate $\chi_1(\omega)$ to the sum of χ_2, χ_3, and χ_4. Noting that $\chi_4(\omega)$ vanishes and rearranging the difference $\chi_1 - \chi_3$ we obtain

$$\chi^I(\omega) = \frac{e^{\beta\omega/2}}{\cosh(\beta\omega/2)} \int_0^\beta d\lambda\, e^{-\omega\lambda}\langle \tilde{M}(-i\lambda)\tilde{M}(0)\rangle$$

$$+ i \tanh[\beta(\omega + i\epsilon)/2] \int_0^\infty dt\, e^{i\omega t - \epsilon t} \langle [\tilde{M}(t), \tilde{M}(0)]_+ \rangle . \tag{7}$$

A similar but less general result has been derived by Verboven[17] for the electrical-conductivity tensor.

For $\omega \to 0$ the first term of (7) reduces to χ^T. Therefore, the difference between χ^T and $\chi^I(0)$ can be written as

$$\chi^T - \chi^I(0) \equiv \beta K = \beta \tfrac{1}{2} \lim_{\epsilon \to 0} \epsilon \int_0^\infty dt\, e^{-\epsilon t} \langle [\tilde{M}(t), \tilde{M}(0)]_+ \rangle . \tag{8}$$

This result is more general than the corresponding form given by Kubo[1] or Suzuki[8] [from his Eqs. (1.6) and (1.7)]:

$$\chi^T - \chi^I(0) = \beta \{ \lim_{t \to \infty} \langle M(0) M(t) \rangle - \langle M \rangle^2 \} \tag{9a}$$

$$= \beta \lim_{u \to \infty} \frac{1}{u} \int_0^u dt \langle \tilde{M}(0) \tilde{M}(t) \rangle , \tag{9b}$$

because the limit in (9a) will only exist if the integral in (8) as a function of complex ϵ is regular for $\mathrm{Re}\,\epsilon > 0$.[18] This is not the case, for example, when the correlation function $\langle \tilde{M}(0) \tilde{M}(t) \rangle$, oscillates at large t.

One cannot derive Eqs. (9a) and (9b) from (8) for a general form of the correlation function. However, if the Lehmann representation is used to express the correlation function, it is easy to show that (9b) is equivalent to (8) but not to (9a). The derivation of Eq. (8) does not involve the Lehmann representation, which overemphasizes the discrete nature of the system in the sense that it implies that the limit $\epsilon \to 0$ can be taken before one passes to a continuum of states. This is not, in general, correct for continuous systems.

The conditions for K in (8) being zero are thus related to the large-t behavior of the correlation function. Consider three characteristic cases: (a) If, as $t \to \infty$, $\langle \tilde{M}(t) \tilde{M}(0) \rangle \to 0$, i.e., $\langle M(t) M(0) \rangle \to \langle M \rangle^2$, the system is ergodic. This is the case discussed by Callen *et al.*[19] (b) If $\langle \tilde{M}(t) \tilde{M}(0) \rangle$ oscillates as $\sum_j K_j e^{i \Delta_j t}$, where Δ_j are frequencies associated with some kind of a free precession of the polarization and K_j are the corresponding amplitudes, we have again $\chi^I(0) = \chi^T$. (c) If $\langle \tilde{M}(t) \tilde{M}(0) \rangle \sim C$, where C is some constant, it follows that

$$\chi^I(0) = \chi^T - \beta C, \tag{10}$$

so that C is the same as K defined in Eq. (8). This is, therefore, the only case for which nonergodicity occurs. Suzuki[8] has suggested a method of expressing K in terms of canonical averages involving all the constants of motion of the system.

Comparing Eqs. (10) and (4) we realize that in the Lehmann representation K is equal to

$$K = Z^{-1} \sum_{\substack{l, l' \\ (E_l = E_{l'})}} e^{-\beta E_l} | \langle l | M | l' \rangle |^2 - \langle M \rangle^2 \tag{11}$$

It may seem plausible that the states could perhaps be transformed by some unitary transformation in such a manner that all matrix elements $\langle l | M | l' \rangle$ with $E_l = E_{l'}$ including $l = l'$, would vanish so that K would also vanish. However, this would lead to the paradoxical result that the trace in formula (1) with $\omega = 0$ or (2) would not be invariant under a unitary transformation. That is, if the difference between (1) with $\omega = 0$ and (2) is nonzero in some representation it must be nonzero in all representations since it can be expressed as a trace.

The requirement that K should vanish is equivalent to Kubo's condition of ergodicity. It cannot be considered as an additional boundary condition on the correlation function, because that function itself is entirely determined by the Hamiltonian of the system.[9] In general, it is extremely difficult to prove that the function $\langle M(t) M(0) \rangle$ goes to $\langle M \rangle^2$ for large times, and one usually makes the assumption that this is so.

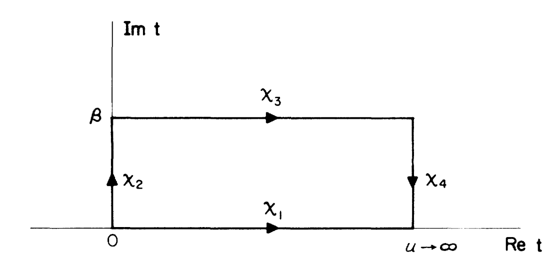

FIG. 1. Integration contour for formula (6).

III. SIMPLE MODEL FOR WHICH THE KUBO SUSCEPTIBILITY CAN BE CALCULATED EXACTLY

We consider a system of lattice defects coupled with the lattice vibrations. Each defect has only two states available, corresponding to two discrete orientations of an electric dipole moment. Assuming that the defects are well separated from one another, it is sufficient to study the microscopic Hamiltonian of the lattice with only one defect. This simply means that the defects are noninteracting. The Hamiltonian can then be written

$$H = -\tfrac{1}{2}\Delta \sigma_z + \frac{1}{2} \sum_q \{ \omega_q^2 Q_q Q_{-q} + P_q P_{-q} \} + \frac{1}{2} \sum_q F_q Q_q \sigma_z - pE\sigma_x e^{i\omega t} , \tag{12}$$

where σ_i, $i = x, y, z$, are the Pauli spin matrices with commutation relations $[\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k$. The symbols ω_q, Q_q, P_q stand for the frequency, normal coordinate, and momentum of phonons with wave vector q, where $[Q_q, P_{-q'}] = i\delta_{qq'}$. F_q is a defect-phonon coupling parameter. The last term describes the interaction with an oscillating external probe field E, p being the dipole moment of the defect. The parameter Δ has the meaning of an energy splitting due to some transverse static electric field. We will be mainly interested in the case with $\Delta = 0$. This is the familiar situation of an electric dipole interacting with an oscillating probe field and some relaxing medium, i.e., phonons, in the absence of any bias fields, which frequently is used in discussing the dielectric relaxation in solids.

The macroscopic dipole-moment operator M is clearly given by $M = p\sum\sigma_x$, where $\sum$ means the sum over all defects.

If $\Delta \neq 0$, Eq. (12) becomes identical to the model for a localized electronic impurity in insulating crystals which has been studied by Duke and Mahan.[16] For large ω, $\chi^I(\omega)$ corresponds to the optical absorption by the impurity. Following Duke and Mahan we assume that the phonons can be described by an isotropic Debye spectrum, and consider two cases of defect-phonon coupling:

$$F_q = d/V^{1/2}, \quad \text{piezoelectric coupling,} \tag{13a}$$

$$F_q = s\omega_q/(V^{1/2}\Omega), \quad \text{strain coupling.} \tag{13b}$$

Here, V is the volume of the crystal, Ω the Debye cutoff frequency, and d and s two constants describing the coupling with the lattice displacements and strains, respectively, at the defect site.

The Hamiltonian (12) without the external field can be diagonalized exactly.[16] It is convenient for this purpose to apply a canonical transformation of the form

$$\bar{H} = e^{-\hat{S}} H e^{\hat{S}}, \quad \text{with } \hat{S} = i\,\frac{1}{2}\sum_q \frac{F_q}{\omega_q^2} P_q \sigma_z \,. \tag{14}$$

The total Hamiltonian, including the external field, becomes

$$\bar{H} = -\tfrac{1}{2}\Delta\sigma_z + \frac{1}{2}\sum_q \{\omega_q^2 Q_q Q_{-q} + P_q P_{-q}\} - \frac{1}{8}\sum_q |F_q|^2/\omega_q^2 - pE(\sigma_+ e^S + \sigma_- e^{-S})\, e^{i\omega t}\,, \tag{15}$$

where

$$S = i\sum_q \frac{F_q}{\omega_q^2} P_q \,. \tag{16}$$

As usual, $\sigma_\pm = (\sigma_x \pm i\sigma_y)/2$.

In order to evaluate the expressions (1), (2), (7) we consider the correlation function

$$C(t) = \langle \bar{\sigma}_x(t)\bar{\sigma}_x(0)\rangle = \langle \sigma_x(t)\sigma_x(0)\rangle = \langle \bar{\sigma}_x(t)\bar{\sigma}_x(0)\rangle, \tag{17}$$

where the second equality follows from the fact that $\bar{\sigma}_x = \sigma_x$, since $\langle\sigma_x\rangle = 0$ in our model. The thermal average indicated by $\langle\ \rangle$ is taken using (12) without the probe field. The time t in (17) can be complex. $C(t)$ is analytic if $0 < |\mathrm{Im}\,t| < \beta$.[20]

Using (15) and (17) we obtain

$$C(t) = [\cos(\Delta t) - i\tanh(\beta\Delta/2)\sin(\Delta t)]\, e^{I(t)}\,, \tag{18}$$

with

$$e^{I(t)} \equiv \langle e^{S(t)} e^{-S(0)}\rangle = \langle e^{-S(t)} e^{S(0)}\rangle \,. \tag{19}$$

The averages in (19) are taken only over the unperturbed lattice Hamiltonian. They can be calculated,[21] the result being

$$I(t) = \sum_q \frac{|F_q|^2}{2\omega_q^3}\, \{\bar{n}_q(e^{i\omega_q t} - 1) + (\bar{n}_q + 1)(e^{-i\omega_q t} - 1)\}\,, \tag{20}$$

with $\bar{n}_q = (e^{\beta\omega_q} - 1)^{-1}$. The expressions (18) and (20) are exact and independent of the particular form of the coupling constant F_q.

Using Eqs. (17)–(20) together with formula (1), we finally obtain for the contribution of one defect to the isolated susceptibility:

$$\chi^I(\omega) = i\lim_{\epsilon\to 0}\int_0^\infty dt\, e^{i\omega t - \epsilon t}\{\cos(\Delta t)[e^{I(t)} - e^{I(-t)}] - i\tanh(\beta\Delta/2)\sin(\Delta t)[e^{I(t)} + e^{I(-t)}]\}\,. \tag{21}$$

Henceforth we set $p = 1$.

To calculate the isothermal static susceptibility, we need the correlation function $C(t)$ for imaginary times $t = -i\lambda$. From Eqs. (2) and (18) it then follows that

$$\chi^T = 2\int_0^{\beta/2} d\lambda\, \cosh[\Delta(\tfrac{1}{2}\beta - \lambda)]\, e^{I(-i\lambda)}/\cosh(\beta\Delta/2), \tag{22}$$

where $I(-i\lambda)$ is obtained from (20) by simply replacing t by $-i\lambda$, and we have used the fact that the integrand is an even function of λ around $\lambda = \beta/2$.

IV. RESULTS FOR VARIOUS FORMS OF COUPLING

To proceed further we now have to consider various cases of frequency dependence of F_q and magnitude of the parameter Δ.

1. Piezoelectric coupling, $\Delta = 0$

Using Eq. (13a) and the Debye model for the acoustic-phonon spectrum, we change the sum in (20) into an integral, and write

$$I(t) = X(t) - iU(t), \tag{23}$$

where X and U are the real and imaginary part of I, respectively:

$$X(t) = A\int_0^\Omega \frac{dx}{x}\,[\cos(xt) - 1]\coth(\beta x/2)\,, \tag{24a}$$

$$U(t) = A\int_0^\Omega \frac{dx}{x}\,\sin(xt) = A\,\mathrm{Si}(\Omega t)\,. \tag{24b}$$

We have introduced a dimensionless coupling parameter $A = 3d^2/(4\pi^2 c^3)$, where c is the velocity of sound. The mode $q = 0$ should be absent from (20) in this case for reasons of translational invariance. This means that the lower limits in (24) are actually $\omega_{\min} = \pi c/L$, where L is the dimension of the crystal and the limit $L\to\infty$ is implicit.

The integral in (24a) cannot be calculated analytically. However, closed expressions can be obtained both in the high-temperature and the low-temperature limits[16]:

High temperature ($\beta\Omega \ll 1$):

$$X(t) = -\frac{2A}{\beta}\left[\frac{\cos(\Omega t)-1}{\Omega} + t\,\mathrm{Si}(\Omega t)\right] - 2A\sum_{k=1}^{\infty}\frac{2^{2k}}{(2k)!}B_{2k}\int_0^{\beta\Omega/2} dy\, y^{2k-2}\sin^2(yt/\beta)\,. \tag{25a}$$

Low temperature ($\beta\Omega \gg 1$):

$$X(t) = A\left\{\ln\left[\frac{\pi t/\beta}{\sinh(\pi t/\beta)}\right] + \mathrm{Ci}(\Omega t) - \ln(\Omega t) - \gamma\right\} + 4A\int_{\beta\Omega}^{\infty}\frac{dy}{y}\,\frac{\sin^2(yt/2\beta)}{e^y-1}\,. \tag{25b}$$

B_{2k} are the Bernoulli numbers and γ is the Euler constant. Si and Ci are the sine and cosine integral functions.[22]

It is easy to see from (18) and (25) that for large t the correlation function decays exponentially:

$$\beta\Omega \ll 1:\quad C(t) \sim \exp[A(2/\beta\Omega - i\pi/2)]\, e^{-\pi A|t|/\beta} \tag{26a}$$

$$\beta\Omega \gg 1:\quad C(t) \sim \exp\{A[\ln(2\pi/\beta\Omega) - \gamma - i\pi/2]\}\, e^{-\pi A|t|/\beta} \tag{26b}$$

This means that the anticommutator function in (7) also decays exponentially, and that the system is ergodic in this case.

The meaning of the decay constant $\pi A/\beta$ becomes clear if one calculates the transition probability per unit time between the two eigenstates $|\mu\rangle$, $|\nu\rangle$ of the operator $H_{ext} = -pE\sigma_x$ due to the perturbation $H' = \sum_q' F_q Q_q \sigma_z/2$. One finds in the lowest order of the perturbation theory that the transition rates at zero field are simply

$$w_{\mu\nu} = \lim_{E\to 0}\frac{\pi A}{2}\int_0^{\Omega} dx\, x(e^{\beta x}-1)^{-1}\delta(2pE - x) = \frac{\pi A}{2\beta} = w_{\nu\mu}\,, \tag{27}$$

and the relaxation time τ is given by $\tau^{-1} = w_{\mu\nu} + w_{\nu\mu} = \pi A/\beta$. Therefore, the exponential decay of the correlation function is entirely due to the lowest-order, i.e., one-phonon, processes. This remains true for large A, i.e., strong coupling with phonons. The correlation function decays for both positive and negative times. Irreversible behavior of the system, which is necessary to obtain dissipation, is achieved by considering only positive times in the Fourier transform in (1). The reason there is no periodic behavior of the system at large times (Poincaré cycles) is apparently due to the fact that the sum over all discrete states has been replaced by an integral over a continuum in (24), which means that we have used the so-called thermodynamic limit.

It is interesting to note that if the correlation function is replaced by its asymptotic value (26) over the entire range of time, and using (18) with $\Delta = 0$ to find $I(t)$, which is then inserted into Eq. (21), one obtains for $A \ll 1$ the well-known Debye relaxation formula $\chi^I(\omega) = \chi^T/(1 - i\omega\tau)$, where $\chi^T = \beta$.

The isolated susceptibility, Eq. (21), can now be written as

$$\chi^I(\omega) = 2\int_0^{\infty} dt\, e^{i\omega t} e^{X(t)}\sin[U(t)]\,. \tag{28}$$

This Fourier transform can only be calculated numerically. The results for several values of A for the high- and the low-temperature cases are shown in Figs. 2 and 3. The imaginary part of $\chi^I(\omega)$ for small values of A has the typical Debye shape with a maximum at $\omega \approx 1/\tau$. There are apparent deviations from this behavior at larger values of A.

At higher frequencies, the real part of the isolated susceptibility becomes negative. This behavior is also characteristic of a damped harmonic

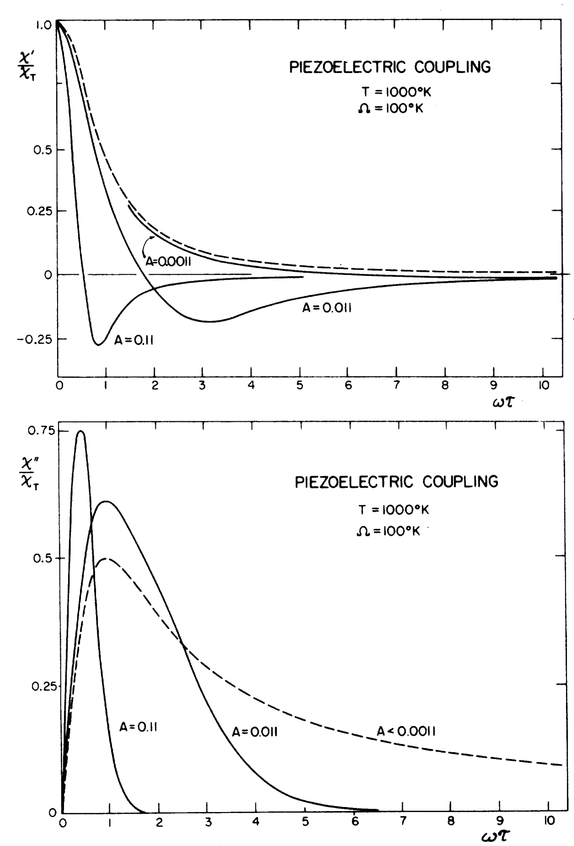

FIG. 2. Real and imaginary parts, χ' and χ'', of the exact isolated susceptibility, Eq. (28), for piezoelectric coupling and various values of the coupling parameter A (solid lines). Dashed lines: Lorentzian curve (Debye theory) with $\tau = \beta/\pi A$. For $A < 0.0011$, χ'' becomes indistinguishable from the Lorentzian on these graphs.

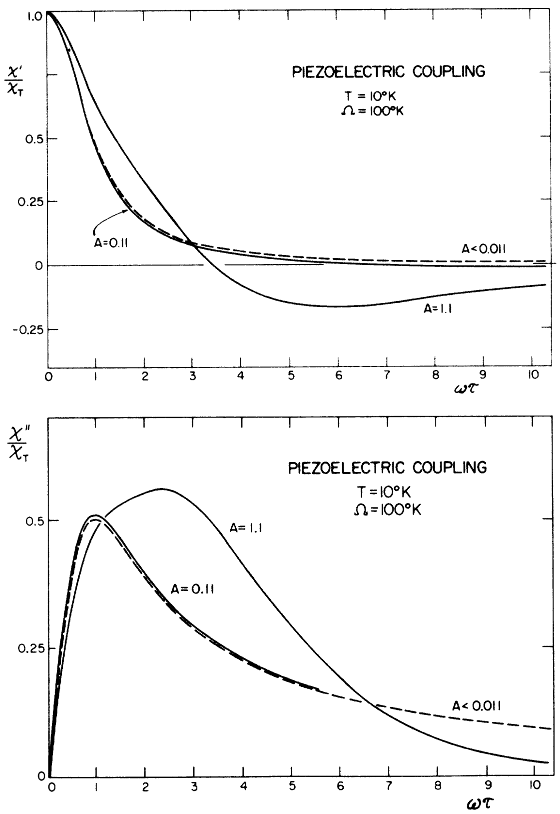

FIG. 3. Same model as that of Fig. 2 but for low temperature.

oscillator as opposed to the simple exponential decay which always follows from the Markovian master equations. In this case, the total system, i.e., defects plus the lattice, behaves like a harmonic oscillator with a characteristic frequency of the order of the cutoff frequency.

2. Strain coupling, $\Delta = 0$

The function $I(t)$ in Eq. (21) is now written as

$$I(t) = Y(t) - Y(0) - iV(t). \qquad (29)$$

Using Eq. (13b) and introducing $B = 3s^2/(4\pi^2 c^3)$ we derive

$$Y(t) = \frac{B}{\Omega^2}\int_0^\Omega dx\, x\cos(xt)\coth(\beta x/2), \qquad (30a)$$

$$V(t) = \frac{B}{\Omega^2}\int_0^\Omega dx\, x\sin(xt) = B\left[\frac{\sin(\Omega t)}{(\Omega t)^2} - \frac{\cos\Omega t}{(\Omega t)}\right]. \qquad (30b)$$

The function $Y(t)$ in the high- and the low-temperature limits is given as follows:

$\beta\Omega \ll 1$:

$$Y(t) = \frac{2B}{\beta\Omega}\,\frac{\sin(\Omega t)}{(\Omega t)} + 2B\sum_{k=1}^{\infty}\frac{(-1)^k(\beta\Omega)^{2k}}{(2k)!}B_{2k}\frac{\partial^{2k}}{\partial(\Omega t)^{2k}}\left[\frac{\sin(\Omega t)}{\Omega t}\right], \qquad (31a)$$

$$Y(0) = \frac{2B}{\beta\Omega} + B\sum_{k=1}^{\infty}\frac{2^{2k}}{(2k)!\,(2k+1)}B_{2k}\left(\frac{\beta\Omega}{2}\right)^{2k-1}; \qquad (31b)$$

$\beta\Omega \gg 1$:

$$Y(t) = B\left[\frac{\sin(\Omega t)}{(\Omega t)} + \frac{\cos(\Omega t)}{(\Omega t)^2} - \left(\frac{\pi}{\beta\Omega}\right)^2 \operatorname{cosech}^2(\pi t/\beta) - \frac{2B}{(\beta\Omega)^2}\int_{\beta\Omega}^{\infty} dy\, y\,\frac{\cos(yt/\beta)}{(e^y - 1)}\right], \qquad (31c)$$

$$Y(0) = B\left[\frac{1}{2} + \frac{\pi^2}{3\beta^2\Omega^2}\right] - \frac{2B}{(\beta\Omega)^2}\sum_{n=1}^{\infty} e^{-\beta n\Omega}\left[\frac{\beta\Omega}{n} + n^{-2}\right]. \qquad (31d)$$

Asymptotically, the correlation function now behaves as

$$C(t) \sim e^{-Y(0)}, \qquad (32)$$

and hence remains finite as $t \to \infty$. According to our general analysis in Sec. II, the system should be nonergodic in this case. It follows from Eq. (8), or from (9a), which is valid in this case, that the difference between χ^T and $\chi^I(0)$ is simply given by

$$\chi^T - \chi^I(0) = \beta e^{-Y(0)}. \qquad (33)$$

In Fig. 4 we have plotted $\chi^I(\omega)$ for $B = 1.1$ and low temperature ($T = 1$ °K). The real part of the Kubo susceptibility at zero frequency is only a few percent of the isothermal static susceptibility in this case.

The fact that $C(t)$ approaches a finite value at large times is due to the absence of the one-phonon processes at $E = 0$, which alone were responsible for the exponential decay in the previous case. If one were to use the master equations here, one would have to consider transitions in higher orders. It turns out, however, that the matrix element for the next higher process in the third order is exactly zero. The lowest nonzero transitions can occur in the fifth order. Unless the coupling is extremely strong, or the temperature very high, the relaxation rates for the case of Fig. 4 will be very small, typically of the order $\tau^{-1} \sim 10^{-50}$ sec^{-1}. This means that the usual Debye relaxation is extremely slow in this case. In performing a static measurement one would have to wait for times $t \sim 10^{50}$ sec, much longer than the age of the universe, for the system to come into thermal equilibrium after each infinitesimal change of the external field. It seems that in this case the isothermal static susceptibility has little physical meaning. Clearly, in deriving χ^T from equilibrium considerations one does not ask how fast the system can reach

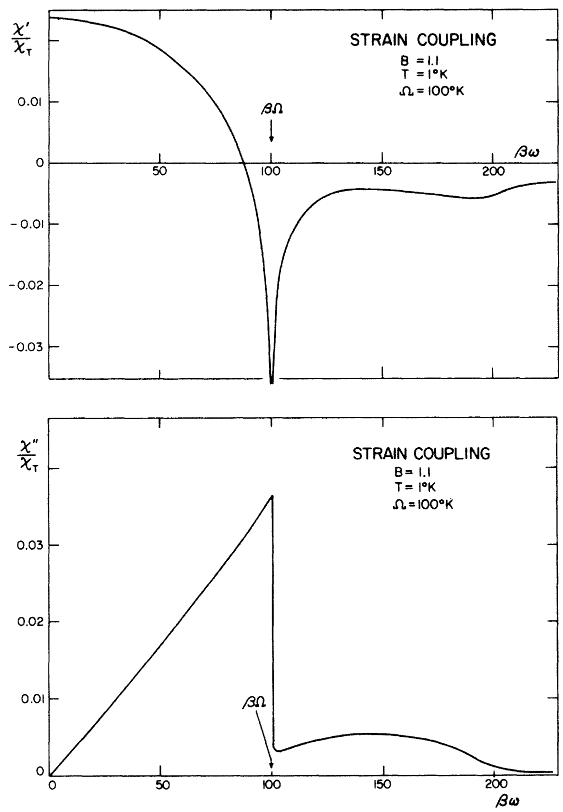

FIG. 4. Real and imaginary parts, χ' and χ'', of the isolated susceptibility in the strain-coupling case at low temperature. χ^T is given by Eq. (22).

equilibrium. One implicitly assumes that there must be some mechanism of relaxation which helps to establish the equilibrium. If so, the same mechanism should be incorporated into the isolated susceptibility, but this would then change the whole behavior of $\chi^T(\omega)$ at low frequencies.

The fact that $\mathrm{Re}\chi^I(\omega)$ in Fig. 4 does not fall abruptly to zero in a narrow frequency interval of the order of $\sim 10^{-50}\ \mathrm{sec}^{-1}$ suggests that linear-response theory deals with much faster relaxation processes than the extremely slow rates described above in connection with the master equations. In this regard it is interesting to note that if one calculates the one-phonon transition rates for the strain-coupling case and includes, *ad hoc*, a quantum of the oscillating probe field in the energy splitting, $2pE$, in the spirit of harmonic perturbation theory, the result for small ω and vanishing E is

$$w_{\mu\nu}(\omega)=\lim_{E\to 0}\frac{\pi B}{2\Omega^2}\int_0^\Omega dx\, x^3(e^{\beta x}-1)^{-1}\times\delta(2pE+\omega-x)\approx\frac{\pi B\omega^2}{2\beta\Omega^2}\,. \qquad (34)$$

Such a transition rate would be much larger than the fifth-order processes already at very small frequencies. If $\chi^I(\omega)$ is calculated by standard approximation methods, frequency-dependent rates such as (34) occur. We intend to discuss this point in a future publication.

The reason that $C(t)$ remains finite as t goes to infinity can be related to the existence of degenerate states in the system. If one uses the Lehmann representation to calculate $C(t)$ one finds time-independent terms with matrix elements $\langle l|M|l'\rangle$, with $E_l=E_{l'}$, which are the nonoscillating part of $C(t)$ and hence the contributors to K of Eq. (11). At low temperatures, the degeneracy of the ground state is responsible for the nonergodic asymptotic behavior of $C(t)$. The commutator function which appears in the Kubo susceptibility (1), $[C(t)-C(-t)]$, decays in the strain-coupling case only as $1/t$, in contrast with the exponential decay of $C(t)$ itself in the piezoelectric coupling case.

3. Piezoelectric coupling with two cutoff frequencies $\Delta=0$

The one-phonon processes which gave the exponential decay of $C(t)$ in case 1 can be removed by eliminating the coupling with the low-frequency phonons. Let us therefore assume that $F_q=d/V^{1/2}$ only if $\Omega_1<\omega_q<\Omega_2$, and zero otherwise, where Ω_2 corresponds to Ω in the previous case, and Ω_1 is a lower cutoff frequency. This is an artifical model for which it would be difficult to find any physical justification. It corresponds to the defect interacting with the phonons through a filter with upper and lower frequency cutoffs.

With this assumption. Eqs. (24b) and (25b) become:

$$U(t)=A[\mathrm{Si}(\Omega_2 t)-\mathrm{Si}(\Omega_1 t)]; \qquad (35)$$

$\beta\Omega_1\gg 1$:

$$X(t)=A\left[\mathrm{Ci}(\Omega_2 t)-\mathrm{Ci}(\Omega_1 t)-\ln\left(\frac{\Omega_2}{\Omega_1}\right)-4A\int_{\beta\Omega_1}^{\beta\Omega_2}\frac{dy}{y}\,\frac{\sin^2(yt/2\beta)}{(e^y-1)}\,.\right] \qquad (36)$$

We only consider the low-temperature case. It can easily be shown that for large times $C(t)$ again approaches a constant value,

$$C(t)\sim e^{-A\ln(\Omega_2/\Omega_1)} \qquad (37)$$

which is temperature independent.

The results for $\chi^I(\omega)$ with $\Omega_1=0.4\Omega_2$ are given in Fig. 5. The situation is similar to the strain-coupling case, and many of the conclusions reached there still apply. It is interesting to note that this is a case in which there is a continuum of phonon states but for which nevertheless $C(t)$ does not approach zero for long times. The low-frequency,

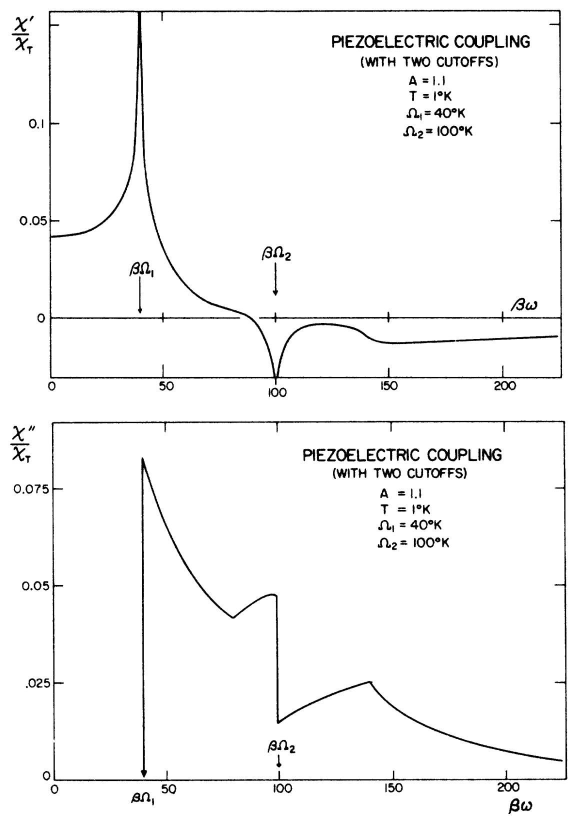

FIG. 5. Isolated susceptibility for the piezoelectric coupling case with two cutoff frequencies and low temperature.

long-wavelength phonons are responsible for the decay of $C(t)$ to zero in (26a) and (26b), not the continuum of phonon states. In the piezoelectric example the infinite size of the model system, i.e., the existence of phonons of infinite wavelength, rather than the infinity of its number of degrees of freedom itself is essential for the ultimate vanishing of the correlation function $C(t)$. In the case of strain coupling neither the existence of a continuum of phonon states nor the infinite size of the system can make $C(t)$ approach zero.

4. Symmetry-breaking terms in the Hamiltonian

It has been suggested[23] that the addition of arbitrary small symmetry-breaking terms to the Hamiltonian will remove the degeneracies and hence lead to the desired static limit of $\chi^I(\omega)$. In our model this can be achieved by taking $\Delta \neq 0$ in (15) and (21). We should then consider $\chi^I(\omega)$ in the limit of small Δ.

We consider the strain-coupling case only. For large times, the correlation function now oscillates as

$$C(t) \sim \frac{1}{2\cosh(\beta\Delta/2)}\, e^{-Y(0)}\left[e^{\beta\Delta/2}e^{-i\Delta t} + e^{-\beta\Delta/2}e^{i\Delta t}\right], \quad (38)$$

and from the conclusions of Sec. II it follows that both static limits should be the same.

The isolated susceptibility at low temperatures is obtained from Eq. (21) with $I(t)$ given by formula (29) and $V(t)$, $Y(t)$, $Y(0)$ given by Eqs. (30b), (31c), and (31d), respectively. The result is

$$\chi^I(\omega) = e^{-Y(0)}\tanh(\beta\Delta/2)\left(\frac{2\Delta}{\Delta^2-\omega^2} + i\pi[\delta(\omega-\Delta) - \delta(\omega+\Delta)]\right) + 2e^{-Y(0)}\int_0^\infty dt\, e^{i\omega t}e^{Y(t)}\{\cos(\Delta t) \times \sin V(t) - \tanh(\beta\Delta/2)\sin(\Delta t)[1-\cos V(t)]\} \quad (39)$$

Numerical results for $\Delta = 0.15\Omega$ are shown in Fig. 6. It is clear that $\chi^I(0)$ is indeed equal to χ^T in this case. However, the frequency dependence of $\chi^I(\omega)$ at low frequencies has been changed drastically. There is now a singularity at $\omega = \Delta$, which is due to the first term of (39). The δ-function

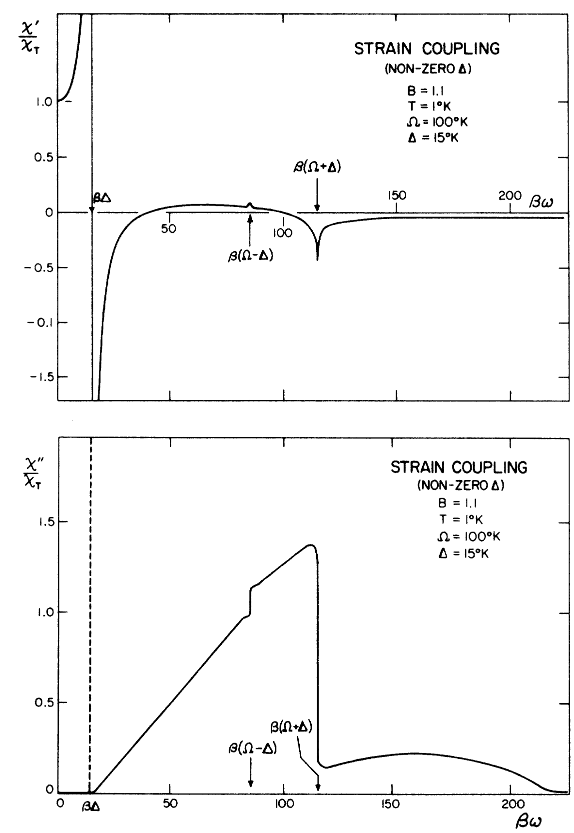

FIG. 6. Isolated susceptibility for strain in the presence of symmetry-breaking term (with $\Delta = 15\,°\mathrm{K}$) in the Hamiltonian. The dashed vertical line indicates a δ-type singularity corresponding to a zero-phonon absorption line.

term in the imaginary part of the susceptibility is physically equivalent to a zero-phonon line. The static susceptibility is equal to the transverse isothermal susceptibility, which for very weak coupling becomes $\chi^T_{\text{transv}} \simeq 2\tanh(\beta\Delta/2)/\Delta$, and for $\Delta \to 0$ becomes equal to the longitudinal isothermal susceptibility. However, the singularity at $\omega = \Delta$ remains even when $\Delta \to 0$. Clearly, the model no longer corresponds physically to the problem of dielectric relaxation. It describes, rather, the optical absorption of an impurity with extremely small energy splitting Δ between the ground state and the first excited state. The singularity vanishes only if $\Delta \to 0$ before ω goes to zero, but this brings us back to the case 2 discussed earlier. We conclude that the symmetry-breaking term does indeed lead to the desired static limit for the susceptibility, but at the same time totally changes the physical character of the model.

V. CONCLUSION

The isolated susceptibility of a system of noninteracting electric dipoles, coupled with lattice vibrations, is strongly dependent upon the form of the dipole-lattice coupling. When the dipole is coupled with the lattice displacements (piezoelectric coupling), the low-frequency dielectric susceptibility strongly resembles the usual Debye relaxation, at least in the weak-coupling limit. At frequencies larger than the phonon cutoff frequency, the system shows features similar to those of a damped harmonic oscillator. The zero-frequency isolated susceptibility is always equal to the isothermal static susceptibility in this case. This fact is related to the ergodic behavior of the polarization autocorrelation function $\langle \tilde{M}(t)\tilde{M}(0)\rangle$ at large times which decays exponentially with a time constant determined by the one-phonon transitions between the two states of the dipole.

In the strain-coupling case, the real part of the isolated susceptibility at zero frequency differs from the isothermal susceptibility. The difference depends strongly on the coupling strength and is, in general, smaller if the coupling is large or the temperature high. The nonergodic behavior is apparently due to the absence of one-phonon processes at zero-energy splitting between the states of the dipole. This allows the correlation function to approach a finite value at large times. The isothermal susceptibility is always larger than the isolated susceptibility because it contains the contributions from the perturbed statistical factors in addition to the perturbed states of the system. The extra contribution contains matrix elements between degenerate states of the system, in particular, the ground state of the system, which is important at low temperatures. At low temperatures, the transitions between the states of the dipole are extremely slow and it takes unreasonably long times for the system to reach thermal equilibrium. Therefore, it is not clear whether or not it is physically meaningful to include the pertrubed statistical factors in the calculation of the susceptibility for degenerate systems. However, in most situations degeneracy will be absent owing to defect interactions, random strains, fields, etc., and the model Hamiltonian for the system should contain this feature in order for either the microscopic or master-equation approach to be meaningful. Behavior similar to the strain case is found in the case of piezoelectric coupling which is effective only within a phonon frequency range with a lower cutoff.

The addition of an arbitrary small symmetry-breaking term to the Hamiltonian restores ergodic behavior to the system. This procedure, however, has no value as a general way of making an arbitrary system ergodic because the behavior of the system is radically changed. In the present case it is marked by the appearance of a low-lying zero-phonon line and an associated singularity in the real part of the susceptibility.

In another paper we plan to use the exact expressions for the isolated susceptibilities found here in an effort to judge the validity of various approximation methods which are commonly used to evaluate expression (1), which cannot normally be evaluated exactly.

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