Frequency dependence of dielectric loss in condensed matter

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The dielectric response of condensed matter below microwave frequencies has been known to depart from the Debye behavior, sometimes to the point of being unrecognizable and yet the generally accepted interpretations of the departures have seldom deviated from the Debye philosophy of simple relaxation phenomena in noninteracting systems. It was recently recognized, from a synoptic view of the experimental data involving a wide range of materials, that there exists a remarkable universality of dielectric response behavior regardless of physical structure, types of bonding, chemical type, polarizing species, and geometrical configurations. This strongly suggests that there should exist a correspondingly universal mechanism of dielectric polarization in condensed matter. The present work proposes such a universal mechanism associated with the existence of some ubiquitous very-low-energy excitations in the system. These excitations exhibit an infrared-divergent-like response to transitions of the polarizing species induced by a time-varying electric field in the dielectric and give rise to the universal dielectric response.

I. INTRODUCTION

The dielectric response of solids and liquids has been the subject of intense investigation over a long period of time extending to this date, and pursued by physicists, chemists, and engineers alike. A detailed survey of the dielectric properties of a wide range of solids has been given recently by Jonscher.[1] It was observed[1] that the dielectric response functions in frequency or in time depart strongly from the Debye response for a large number of essentially dissimilar materials and fall into a remarkably common or "universal" pattern. In particular, the frequency dependence of the dielectric loss follows the empirical law

$$\chi''(\omega) \propto \omega^{n-1}, \quad \text{with } 0 < n < 1 \tag{1}$$

extending over several decades of frequency from low audio and subaudio to $\omega/2\pi \sim 10^9$ Hz. For some dielectrics, a broad loss peak may be found at lower frequencies. Genuine Debye behavior with the complex susceptibility given by $\chi(\omega) \propto (1+i\omega\tau)^{-1}$ is seldom observed in solids. The empirical law (1) emphasized by Jonscher is implicit also in several other empirical expressions presented in the past. These include the Cole-Cole, Cole-Davidson, and Havliak-Nigami forms[1] and their expressions are, respectively, $1/[1+i(\omega\tau)^{\beta}]$, $1/(1+i\omega\tau)^{\alpha}$, and $1/[1+i(\omega\tau)^{\beta}]^{\alpha}$. In the $\omega\tau >> 1$ limit these expressions all reduce to the empirical law (1) of Jonscher. Examples of the materials that obey the empirical law [Eq. (1)] include inorganic ceramics, ionic conductors, polymeric materials, inorganic crystalline, and amorphous materials including glasses, insulating or semiconducting, and organic and biological systems. By way of these examples we see that the frequency response (1) is similar for systems with permanent dipoles and with hopping charge carriers of electronic or ionic nature. It is valid in covalent, ionic, and molecular solids, in single crystals, polycrystalline, and amorphous structures; hence the behavior (1) is apparently independent of the particulars of the material. At higher frequencies, 10^9 Hz and up, quantum effects involving lattice mode excitations and/or electronic excitations become prominent and, as is well known, the response then differs from material to material, and as such will not be of interest to us in the present context.

The various types of dielectric response are summarized in Fig. 1. This figure is taken from a short summary of the present work published earlier.[2] We note the virtual absence of the pure Debye response; and the validity of the universal law of dielectric response, Eq. (1), in a remarkably wide range of physical and chemical situations, and over a very wide range of frequencies. In some types of dielectrics the universal response (1) is followed at low frequencies by a loss peak referred to as α and β peaks, or by another universal response with n typically between 0.1 and 0.3.

It is this state of affairs that has motivated us to seek a renewed understanding of these phenomena in terms of a common or "universal" characteristic across the entire spectrum of materials and to associate such a characteristic with some physically simple and "elementary" principles or properties. In Sec. II we shall present several elementary principles which when combined enable a derivation of the universal law (1) regardless of the physical, chemical, and geometrical properties of the solids, and also regardless of the nature of the electrically active species responsible for polarization, whether dipoles, elec-

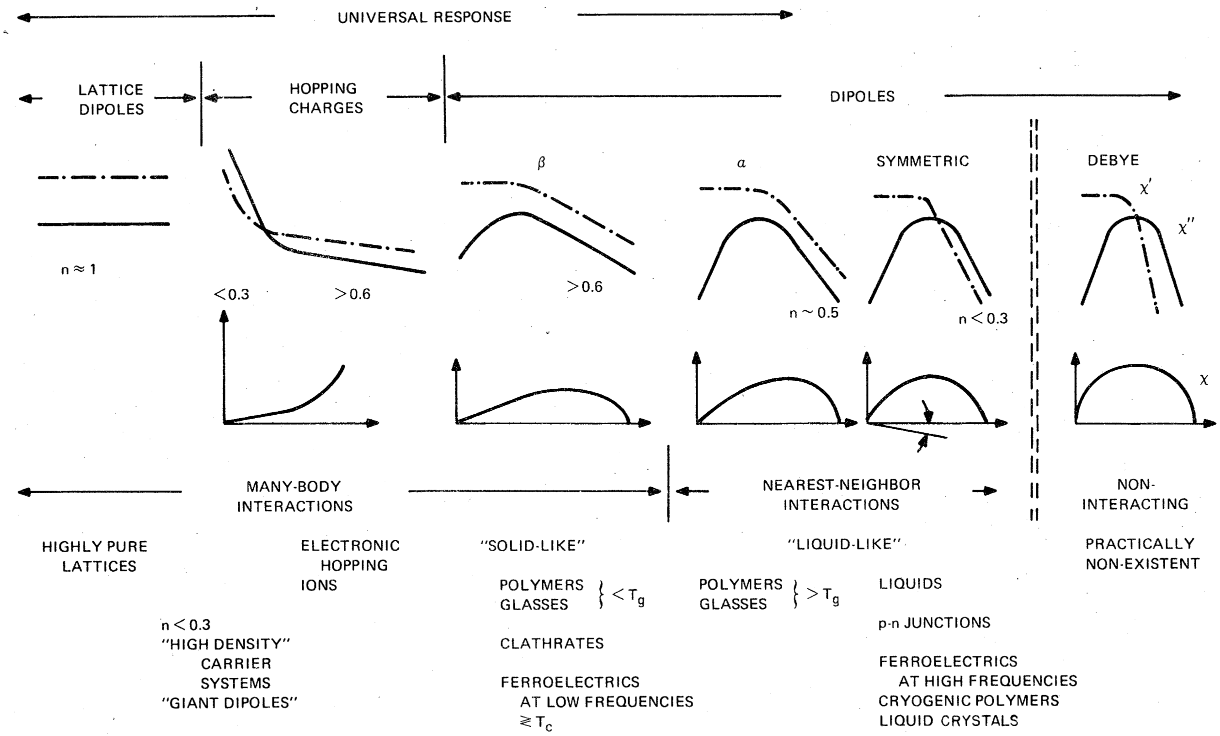

FIG. 1. Schematic representation of the various observed types of dielectric response over the entire range of solids. The upper set of diagrams represent the shapes of the logarithmic plots of $\chi'(\omega)$—chain-dotted lines, and $\chi''(\omega)$—solid lines, ranging from the ideal Debye through the α and β peaks and on to the universal dependence for charged carrier systems. The limiting forms of behavior are represented by the strong low-frequency dispersion with small values of n and by the limiting case of frequency-independent "lattice response" with $n \approx 1$. The lower set of diagrams represent the corresonding complex χ plots. The various types of materials obeying the respective types of response are shown and the presumed polarization mechanisms are indicated. This figure is taken from Ref. 2.

trons or ions. Then in Sec. III we discuss several examples of low-energy excitations expected in a host of systems that satisfy these elementary principles. In Sec. IV we consider the response of these states. Next, in Sec. V we derive the universal response (1) and the possible presence of a loss peak at lower frequencies. Finally, in Sec. VI we make some concluding remarks.

II. INFRARED DIVERGENCE AND THE UNIVERSAL LAW $\chi''(\omega) \propto \omega^{n-1}$

Infrared divergence phenomena, although not commonly observed in physics, have been seen in several instances. The most well-known case is in quantum electrodynamics where the infrared divergence manifests itself in a bremsstrahlung experiment[3] of a fast charged particle. In the realm of solid-state physics[4,5] an example of infrared divergence is thought to be provided by the peculiar shape of x-ray absorption edges of metals.[6] In another context (unrelated to the present work), Handel[7] has invoked also the infrared divergence principle to account for the origin of $1/f$ noise. He has considered in addition to photons, electron-hole pairs at the Fermi surface of a metal, phonons, and spin waves. These examples are by no means exhaustive but the subjects they cover demonstrate that infrared divergence is not uncommon. Excellent reviews on the subject are available.[4,5]

The features common to systems exhibiting the infrared divergence phenomenon are (a) the sudden application of a potential, or a sudden change of the potential or the Hamiltonian; and (b) availability of low-energy excitations of the system and its response to the sudden potential change dominated by the emissions of these low-energy excitations. In the time domain the phenomenon is the transient response[8,9] of the system to that abrupt change of potential. Infrared divergence occurs whenever the suddenly switched on potential V excites some low-energy excitations, with density of states $N(E)$ for excitation energy E, which is such that $V^2(E)N(E) \propto E$. In this instance there is an increasingly high probability of exciting decreasingly small energy excitations and this causes a power-law divergence of the response in the frequency domain. In the x-ray edge problem in metals an x-ray photon when absorbed, suddenly switches on a hole-core potential V for the conduction electrons. The low-energy excitations here are the electron-hole pairs.

In Secs. III–VI we shall argue that within a broad classification of dielectrics, according to a scheme to be outlined, there exist states which, for convenience, we shall refer to as correlated states. Low-energy excitation (and de-excitations) of the correlated states with excitation (de-excitation) energy E consists of transition from one correlated state to another and is the analogue of the electron-hole pair excitation in the x-ray edge problem.

The charged particles or dipoles responsible for polarization in the dielectrics undergo quantum transitions, including changes in their positions (orientations), between preferred states in an abrupt manner by hopping or jumping movements such that the time $1/\nu$ taken by the actual transition is negligible in comparison with both (i) the time spent on average in the respective preferred states, and (ii) the time characteristic of the low-energy excitation of the correlated states. The condition (i) is invariably satisfied in solid dielectrics. That condition (ii) is also satisfied will become clearer after we have considered the nature of the correlated states.

Due the charged particle (dipole) transition a potential is suddenly switched on which acts on the correlated states. The low-frequency response of the dielectric to this potential involves the emission of low-energy excitations of the correlatred states. We shall argue that the low-energy excitations of these correlated states have a density of states $N(E) \propto E$, and that the potential change V has little or no E dependence. It follows that the conditions for an infrared divergent dielectric response of the correlated states are justified. The mean number $\bar{n}$ of correlated state excitations is then

$$\bar{n} \propto bV^2 \int_0^{E_c} \frac{E\,dE}{E^2} ,$$

which diverges logarithmically, where E_c is the upper "cutoff" of the correlated state excitation energy which can be considered as the energy above which the correlated state excitations no longer have the density of states $\propto E$. The Fourier transform to the time domain of the universal relation (1) is $i(t) \propto t^{-n}$, i.e., the widely observed Curie–von Schweidler law[1] of depolarization. It is interesting to note that the infrared divergence problem when considered in the time domain as a transient response problem[8,9] does lead to the time decay of the response function for large times as $S(t) \propto t^{-n}$. The derivation of the complete dielectric response will be deferred to Sec. IV, after we have discussed the correlated states in a broad classification of dielectrics in Sec. III.

III. CORRELATED STATES

In Sec. II we connected the "universal law", Eq. (1) to an infrared divergent response of correlated states. For this interpretation to follow it is necessary for such states to be prevalent in dielectrics and have characteristic response times long in comparison to the switching of the Hamiltonian. In this section, we discuss several examples of such correlated states which can reasonably be expected to be present in many dielectrics. Parenthetically, the purpose of this section is to give enough insights into these correlated states and their excitations so that the reader can, if he desires, have a better feeling for them. These discussions are not the core of this work but serve as useful illustrations. One should note from the onset that although the examples that we will detail are quite general, they are by no means exhaustive. Further note that these correlated states are certainly not familiar nor are their excitations "elementary".

A. Dielectrics with electron self-trapping states

The concept of local electron self-trapping largely arises from the observation that by and large if a particular electronic state is singly occupied the atom or atoms principally associated with this state will adjust their positions in such a way as to lower the one-electron energy level of this state relative to its value when unoccupied. A traditional example is provided by those ionic solids where strong local Coulomb interactions between the electron and lattice constituents induce a local lattice distortion leading possibly to the self-trapping of the electron and the formation of a small polaron. This tendency is not simply restricted to ionic materials but is much more general. Well-known examples lying outside the usual small polaron mechanism are provided by the reconstruction of semiconductor surfaces[10,11] and electron pairing states in amorphous glasses.[12] The origin of the self-trapping in former instance is essentially a dehybridization energy[10,11] arising from concepts inherent in covalency and stereochemistry. The electron-lattice interaction may be strong enough to make it energetically much more favorable to self-trap electrons in pairs rather than singly and such systems have been described by Anderson[12] through a negative U Hubbard model. Let us restrict our attention for the moment to the negative U electron pairing states which should be important due to the prevalence of diamagnetic systems in nature. In this instance several subgroups of possible correlated states can be identified with properties leading to the desired behavior in χ'' where, in each case, the response time of these states is expected to be acceptably slow due to the lattice coordinates involved.

As noted in the previous paragraph, in order to develop further the idea of local distortion mediated effective electron-electron attractive interaction Anderson has employed an effective negative U Hubbard-like term $U_i\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}$ to model the effect, where $\hat{n}_{i\sigma}$ is the number operator for an electron of spin σ in a state centered at the "site" i; $|i\sigma\rangle$. One should keep in mind that i could well index the up and down spin states associated with a group of atoms and not just a single one. Let us describe a group of such centers in contact with one another as well as alternate states of the system (those with $U_i=0$) by the simplified Hamiltonian

$$H=\sum_{i\sigma}E_i\hat{n}_{i\sigma}+\sum_{ij\sigma}{}'R_{ij}a_{i\sigma}^{\dagger}a_{j\sigma}+\sum_{i}U_i\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}\ , \qquad (2)$$

where $a_{i\sigma}^{\dagger}$, $a_{i\sigma}$ create and annihilate electrons of spin σ in the state $|i\sigma\rangle$, and we take R_{ij} as R if i,j are nearest neighbors and zero otherwise. The parameters $\{E_i\}$ and $\{U_i\}$ are considered as random variables obeying the joint probability distribution $P(E_i,U_i)$ which for the time being is left unspecified. This model can be made to mimic many different situations depending on the choice of $P(E_i,U_i)$.

To obtain results from Eq. (2) we have developed[13] a generalized mean-field-like method which entails linearizing the many-body terms $U_i\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}$ as

$$U_i\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}\approx\sum_{\sigma}U_i\tilde{n}_{i-\sigma}\hat{n}_{i\sigma}-U_i\tilde{n}_{i\uparrow}\tilde{n}_{i\downarrow}\ ,$$

where $U_i\tilde{n}_{i\uparrow}\tilde{n}_{i\downarrow}$ is present to prevent double counting of the interaction. The conditionally averaged number of spin σ electrons at the site i is given by the relation

$$\tilde{n}_{i\sigma}=-\pi^{-1}\,\mathrm{Im}\int dE\,f(E)\,g_{i\sigma}(E^{+})\ , \qquad (3)$$

with f the Fermi function and E^{+} denotes the $\lim(E+is)$ as $s\rightarrow 0^{+}$. Equation (3) provides a set of generalized Hartree-Fock-like self-consistent relations determining the parameters $\tilde{n}_{i\sigma}$ since the Green functions $g_{i\sigma}$ entering these formulas are defined as $g_{i\sigma}=\langle i\sigma|(z-H_{\mathrm{el}})^{-1}|\sigma i\rangle$ where

$$H_{\mathrm{el}}=\sum_{i\sigma}(E_i+U_i\tilde{n}_{i-\sigma})\,\hat{n}_{i\sigma}+\sum_{ij\sigma}{}'R_{ij}a_{i\sigma}^{\dagger}a_{j\sigma}$$

and hence depends on $\tilde{n}_{i\sigma}$. For convenience Eq. (3) can be recast as

$$n_{i\sigma}=-\pi^{-1}\,\mathrm{Im}\int\frac{dE\,f(E)}{E^{+}-E_i-U_i\tilde{n}_{i-\sigma}-\Delta_i}\ ,$$

where Δ_i is the usual self-energy and is a function of $\{n_{j\sigma}\}$, etc.

To solve these self-consistent conditions we employ the long established coherent-potential approximation[14] (CPA) to obtain the self-energies Δ_i. This entails defining an effective medium characterized by a single potential Σ_0 which is energy dependent and can be complex, in such a way that the $G_{i\sigma}(E-\Sigma_0)=\langle\bar{g}_{i\sigma}(E)\rangle_{\mathrm{av}}$, where the brackets $\langle\ \rangle_{\mathrm{av}}$ here and henceforth denote an average over the random variables entering H_{el} and $G_{i\sigma}=\langle i\sigma|(z-H_{\mathrm{eff}})^{-1}|\sigma i\rangle$ with H_{eff} obtained by replacing the site-diagonal random potentials of H_{el} by Σ_0 at each site i and $\bar{g}_{i\sigma}=G_{i\sigma}+G_{i\sigma}t_{i\sigma}G_{i\sigma}$, where

$$t_{i\sigma}=(E_i+U_in_{i-\sigma}-\Sigma_0)/[1-(E_i+U_in_{i-\sigma}-\Sigma_0)\,G_{i\sigma}]\ .$$

The CPA is exact in both strong and weak scattering (virtual crystal) limits and hence provides an interpolation scheme for treating the intermediate cases. The use of this method greatly simplifies the computations since its functional form of Δ_i can be easily found using established techniques once the "lattice" structure is specified. For example, if we assume a simple chain then

$$\Delta=(E-\Sigma_0)-[(E-\Sigma_0)^2-4R^2]^{1/2}\ .$$

The CPA equation defining Σ_0 and hence Δ can be written explicitly for the present model as

$$\iint\frac{P(E_i,U_i)\,dE_i\,dU_i}{E^{+}-E_i-U_i\tilde{n}_{i\sigma}(E_i,U_i)-\Delta(\Sigma_0)}=\frac{1}{E^{+}-\Sigma_0-\Delta(\Sigma_0)}\ .$$

We now have as inputs into the formalism some specified temperature, T, and number of electrons per site in the band, N_{el}, as well as particular functional forms for $G_{i\sigma}(E)$ and $P(E_i,U_i)$. The calculation then proceeds as follows: First we assume the function $\tilde{n}_{i\sigma}(E_i,U_i)$ and then solve[13] the CPA equations using a modified Newton-Raphson technique to obtain $\Sigma_0(E)$ and hence $\Delta(\Sigma_0)$. Having determined $\Delta(\Sigma_0)$ we can then find the chemical potential μ of the system from the usual relation

$$N_{\mathrm{el}}=-\left(\frac{2}{\pi}\right)\mathrm{Im}\int dE/\{(e^{-\beta(E-\mu)}+1)[E^{+}-\Sigma_0-\Delta(\Sigma_0)]\}\ ,$$

where in obtaining this condition, we have employed the CPA equation. Note the CPA determined Σ_0 satisfies the important sum rule $-\pi^{-1}\,\mathrm{Im}\int dE/[E^{+}-\Sigma_0-\Delta(\Sigma_0)]=1$. Having $\Sigma_0(E^{+})$ and μ, we than calculate a new function $\tilde{n}'_{i\sigma}(E_i;U_i)$ from Eq. (3) and this procedure is iterated until self-consistency is established, i.e., $\tilde{n}'_{i\sigma}(E_i,U_i)=\tilde{n}_{i\sigma}(E_i,U_i)$. If a continuous probability distribution is assumed for the random variables, it is of course not numerically feasible to establish self-consistency at each point in (E_i,U_i) space. In these instances we establish self-consistency at a grid of points assuming that $\tilde{n}_{i\sigma}(E_i,U_i)$ can be adequately represented for intermediate values by trapezoidal interpolation. We have found for simple continuous probability distributions that this procedure converges very nicely[13] (well within the realm of numerical feasibility) as the number of points in the grid is increased. Note that usually more than one self-consistent solution exists and this will prove important to our subsequent development.

Before detailing some of the examples that we have treated, it is convenient to backtrack somewhat and draw a relationship between electron pairing interactions and covalency and in so doing motivate these cases and further stress the generality of the pairing ideas.

As a prototype consider a simple dangling bond such as one associated with an Si atom which is bonded to three neighboring silicons leaving a dangling hybrid. If we denote by x_h the displacement of this atom from where it would sit if the dangling hybrid were constrained to be singly occupied with energy E_h then a "Hamiltonian" partially describing the energetics of this atom[11] is

$$H_h = \Sigma_0 E_h \hat{n}_{h\sigma} - \lambda_h x_h(\hat{n}_{h\uparrow} + \hat{n}_{h\downarrow} - 1) + \tfrac{1}{2} c_h x_h^2 ,$$

where $\hat{n}_{h\sigma}$ is the number operator for electrons of spin σ in the dangling hybrid orbital $|h\sigma\rangle$. The last term entering H_h is a backbond stretching energy and the second is the so-called dehybridization energy.[10,11] If we have a group of such nonbonded states interacting with one another then a simplified Hamiltonian describing the situation is

$$H = \sum_{i\sigma} E_i^h n_{i\sigma} - \sum_i \lambda_i x_i (\hat{n}_{i\uparrow} + \hat{n}_{i\downarrow} - 1) + \sum_i \tfrac{1}{2} c_i x_i^2 + \sum_{ij\sigma} R_{ij} a_{i\sigma}^\dagger a_{j\sigma} .$$

We can now view the displacements x_i as parameters entering the Hamiltonian to be determined self-consistently by requiring the free energy of the system to be stationary with respect to their variations. This results in a set of self-consistent conditions which can be used to eliminate the parameters x_i. It is then a simple matter to show that the resultant Hamiltonian is essentially similar to the negative U model (2) within the context of our mean-field approximation if we make the identifications: $-2\lambda_i^2/c_i \equiv U_i$, $E_i^h \equiv E_i + \frac{1}{2} U_i$. Thus we expect the negative U model to incorporate the behavior of a simple nonbonded orbital whenever $\lambda_i^2/c_i >> U_{\text{Coulb}}$ since the analysis of course is not limited to only the Si dangling hybrid but applies whenever one has a dangling bond associated with covalent backbonds and hence is quite general.

Consider now as a first example of electron self-trapping states with the desired properties those pairing states associated with breaking the pair and "placing" the electrons in states associated with nonpairing sites. Such a case could be physically realized, e.g., with metal-semiconductor (Schottky) contacts where one could envision transferring the electrons from pairing centers in the semiconductor (say, nonbonded orbitals) to the Fermi sea. A particular example derived from the general model (2) is shown in Fig. 2 where we display two different self-consistent solutions to Eq. (3) obtained by using the previously detailed formalism. We have taken as inputs in calculating these examples: $T=0$, $N_{\text{el}}=0.3$, and $G_{i\sigma}$ appropriate for a Cayley lattice with each atom having six nearest neighbors. The form of $P(E_i, U_i)$ is chosen so that

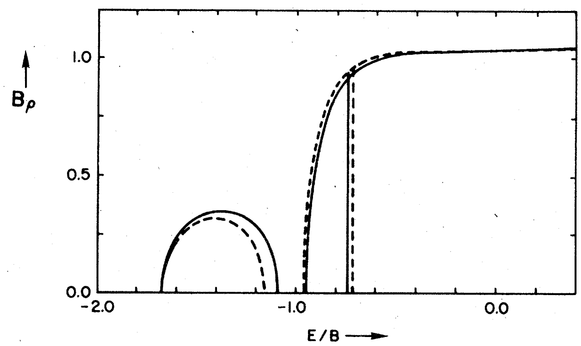

FIG. 2. Illustrates the effects on the electronic spectrum due to transfer of electrons from pairing centers to a nonpairing band. Note the vertical lines represent the position of the highest occupied state at zero temperature.

$$P(E_i, U_i) = (1-x)\delta(U_i)\delta(E_i - E_0) + x\,\delta(U_i - U_0)\,W(E_i) ,$$

where $W(E_i)/B = 5$ (B is the unperturbed half-bandwidth) for $0.1 \leq E_i/B \leq 0.3$ and zero otherwise and x (the concentration of pairing centers) $=0.1$ with $U_0/B = -1.6$. The solid line of Fig. 2 is within our formalism the density of states corresponding to the numerically determined lowest energy state of the system while the dashed line represents a low-lying self-consistently obtained excited state; a fact that we have verified directly by comparing the energies of the two cases. These two solutions differ from one another by the transfer of electrons from the pairing centers (which when occupied in this example form a band of states $\sim \frac{1}{2} U_0$ below E_F, the "Fermi-level," as shown in Fig. 2) to the main band with the unoccupied pairing levels now appearing $\sim \frac{1}{2} U_0$ above E_F. This is exemplified in Fig. 2 in going from the ground to excited state by the slight increase in "E_F", as well as the decrease in the measure of the pair band below the main band edge.

Further insight into this behavior can be gained by considering a single pairing impurity in a tight-binding lattice. The situation can be described by the model Hamiltonian

$$H = \sum_{i\sigma}{}' E_0 \hat{n}_{i\sigma} + \sum_{ij\sigma}{}' R_{ij} a_{i\sigma}^\dagger a_{j\sigma} + U_j \hat{n}_{j\uparrow}\hat{n}_{j\downarrow} + \sum_\sigma E_j \hat{n}_{j\sigma} ,$$

which represents of course a special case of Eq. (2). Approximating $U_j \hat{n}_{j\uparrow}\hat{n}_{j\downarrow}$ as before the free energy of the system as a function of $\tilde{n}_j$ can be expressed as

$$F = K - U\tilde{n}_j^2 - \left(\frac{2}{\pi}\right)\mathrm{Im}\int_{-\infty}^{\infty} dE\, f(E) \times \int_{-\infty}^{E} \frac{(U\tilde{n}_j + E_j)[\partial G_j(\tilde{E}^+)/\partial\tilde{E}]\, d\tilde{E}}{1-(U\tilde{n}_j + E_j)G_j(\tilde{E}^+)}, \quad (4)$$

where K is a constant independent of $\tilde{n}_j$ and we have used the up-down spin symmetry present for $U_j < 0$ to replace $\tilde{n}_{j\sigma}$ by $\tilde{n}_j$. The free energy F possesses a double minimum as a function of $\tilde{n}_j$ when $E_j + \frac{1}{2}U_j$ lies in the vicinity of E_F and U_j/R is $>>1$, as is shown in Fig. 3. In arriving at these results we have chosen for simplicity a rectangular density of states of half-bandwidth B to model the main band, i.e.,

$$G_{i\sigma}(Z) = -(1/2B)\ln[(Z-B)/(Z+B)],$$

and neglected temperature effects which are unimportant at moderate temperatures for physically expected U_j; i.e., $|U_j| \gtrsim 0.1$ eV. At the minima $\tilde{n}_j$ satisfies the appropriate form of Eq. (3) and hence represents the self-consistently obtained average number of electrons of one-spin species at the site j. The two minima hence correspond to distinctly different occupancy of the pairing center since in one case $\tilde{n}_j \sim 0$ and the other $\tilde{n}_j \sim 1$. That is, on one hand, on the average almost two electrons occupy the pairing levels which lie approximately at $E_j - U_j$, while on the other, the pairing center is effectively unoccupied and its associated states lie at $\sim E_j$. One can show that the two minima are separated for large U_j by $\sim |E_j + \frac{1}{2}U_j - E_F|$ and hence such a negative U center can give rise to a low-lying excitation of the system if its characteristic parameters are such that

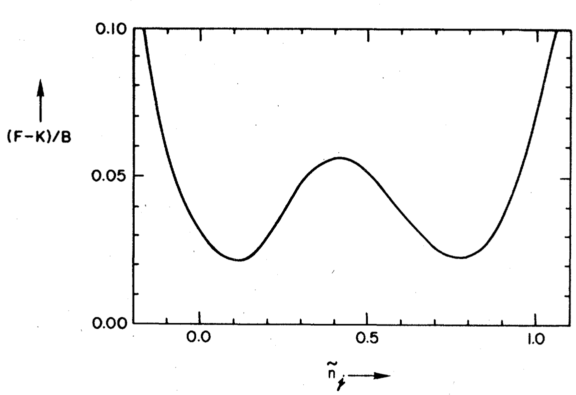

FIG. 3. Shows the dependence of the free energy $(F-K)/B$, on the average electronic occupancy, $\tilde{n}_j$, of a single pairing center in a tight-binding lattice when $|U_j|/B \gtrsim 1$ and $E_j + \frac{1}{2}U_j \approx E_F$. The zero of energy is taken at the center of the unperturbed band and $U/B = -1.6$. $E_F/B = -0.794$, $E_j/B = 0.2$.

$E_j + \frac{1}{2}U_j \approx E_F$. This is of course consistent with the previously obtained results summarized in Fig. 2 and is just a rather more specific case.

Although within the context of the present mean-field-like approximation we cannot make a new linear combination of the two states represented by the essentially degenerate generalized Hartree-Fock self-consistent solutions (associated with the minima of Fig. 3) that reduces further the energy of the system (there is an orthogonality theorem[15]) such an effect of course physically exists. The resultant intrinsic matrix element connecting these states should itself be a random variable because of the different allowed choices of E_i, U_i sufficient to produce the same degree of degeneracy. Such being the case, one expects the density of the very-low-lying excitations at a particular E to behave as E and contribute an infrared divergent dielectric response (1). We will postpone details of this argument until Sec. III B.

The essentials of the present low-lying pair-state picture should not be smeared out at reasonable temperatures since although, e.g., the details of Fig. 3 may be somewhat different at different temperatures one still finds a double minimum in $F(\tilde{n}_i)$ and the corresponding low-lying excitations.

Another not completely orthogonal class of electron pairing states with the desired properties would be expected to exist in systems where these are a number of essentially equivalent pairing centers the number of which exceeds the number of available electrons. In these instances one can envision very low-energy tunneling-mode-like excitations corresponding to different arrangements of the electrons over these pairing centers and correlated states of this type as we shall see in Sec. III B should exhibit the correct infrared divergent behavior.

Next consider a situation, that may obtain in certain amorphous glasses,[12] where the one-electron potentials of Eq. (2), E_i, obey a continuous probability distribution $P(E_i)$ spanning the forbidden gap. To model the resultant situation we have solved the self-consistent equation (3) assuming $P(E_i, U_i) = \delta(U_i - U_0)\, W(E_i)$ where $W(E_i)/B = \frac{1}{2}$ for $-1 \le E_i/B \le 1$ and zero otherwise and $U_0/B - 3$; B is unperturbed half-bandwidth. Also we assumed that $T = 0$, $N_{\mathrm{el}} = 1$ and employed as an unperturbed Green function, G, appropriate for a Cayley tree with each atom having six nearest neighbors. In Fig. 4 we exhibit the numerically determined lowest energy state of the system (solid line), as well as another self-consistent solution (dashed line) which represents a low-lying excitation of the system. The two solutions essentially differ from one another by the transfer of electrons from one group of pairing centers to another, and in this way, although there is a large gap in the one-electron spectrum very-low-lying excitations can be achieved leading to a gapless pair-state spectrum.[12] To understand this behavior

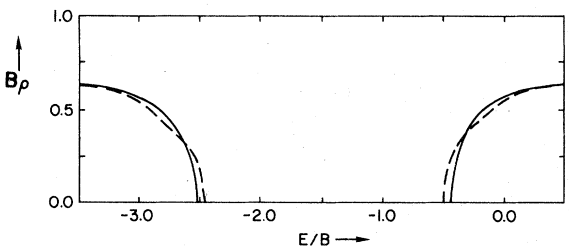

FIG. 4. Illustrates two different arrangements of electrons over the pairing states with the dashed line representing a low-lying excited state of the lowest-energy state (solid line).

further consider two isolated pairing centers labeled i,j in competition with one another for two electrons. Then if $U_i = U_j$ it is not the magnitude of U that determines the occupancy but rather E_i, E_j. For example if $E_i < E_j$ then the site labeled i is doubly occupied and that labeled j is doubly empty in the ground state. Thus, although the one electron states lie at $E_i + U_i$ and E_j, and are hence usually well separated in energy ($\gtrsim 0.1$ eV), excitations of the system that require only energy $|E_i - E_j|$ which becomes vanishingly small as $E_i \to E_j$ can be achieved by removing the electron pair from the site i to the site j. In the case $R_{ij} \to 0$, the density of pair-state excitations is then $\sim P(E_i + \frac{1}{2} U_i)$ which is continuous and slowly varying around E_F and we have seen a similar picture also applies if we assume some coupling between the pairing centers.

Such a smooth distribution of self-trapped pair-state excitations is expected to have a character sufficient to produce an infrared divergence at very low temperautres if we suppose that a *field induced* hop introduces a coupling between these states largely independent of energy. This is so because the density of states of low-energy pair-state excitations with energy E is $\sim N^2(E_F)E$, where $N(E_F)$ is the density of pair states at E_F. Furthermore, the fact that the pair states are strongly self-trapped implies that their response time can be much longer than the time characteristic of the hopping or reorientation of the charge species. Thus all conditions for an infrared divergent dielectric response are apparently satisfied. This behavior, however, will be completely smeared out at experimental temperatures unless we suppose that the energy barriers between pairing states is sufficient to prevent thermally assisted tunneling. Thus the system at finite temperature is presumed locked into a metastable state and this could happen for large enough negative U. We mention this case only for completeness and because it is complementary to our previous examples where it is supposed that each tunneling mode (TM) has equal probability of being in either of its two states. Note that the possibility of low-lying excitations which are thermodynamically inaccessible over at least the time of a specific-heat measurement has already been pointed out[16] and in amorphous materials metastable states may persist almost indefinitely. Further note though that in this metastable regime the response of the system should depend on its history.

Thus, we have detailed several rather general examples which illustrate how electron self-trapping can provide correlated pair states with characteristics sufficient to produce the universal law; Eq. (1). Further examples can be found in those instances where the Coulomb repulsion dominates, favoring single self-trapping of the electron. In these cases, various subgroups of correlated states can be identified completely analogous to the bipolaron ones outlined above. Intermediate subgroups can also be defined where, e.g., one envisions very-low-energy excitations which entail disassociation of a bipolaron into two singly self-trapped electrons or vice versa. Although we have phrased our discussion implicitly in terms of amorphous systems where one expects an appreciable number of weaker (stronger) bonds, lone pairs, etc., to be present giving rise to the self-trapping states, it is also reasonable to expect that such low-lying excitations occur and are important in more nearly crystalline covalent solids since the remaining self-trapping centers in these materials could partially pin the Fermi level in their vicinity. Another point that should not be overlooked is the probable presence of an appreciable density of self-trapping centers effective in determining the electronic structure of various interfaces such as oxide-semiconductor, metal-semiconductor, etc. This follows since these interfacial regions are expected on the whole to be disordered giving rise, e.g., to weaker (stronger) bonds. Indeed the presence of such centers can be used to understand some of the more puzzling electronic behavior of the localized inversion layer regime of metal-oxide-semiconductor field-effect transitors (MOSFET's)[17] where one is dealing with an oxide-semiconductor interface in contact with a quasi-two-dimensional electron gas. Furthermore, recently[18] we have carried out an analysis of the origin and role of such states at metal-semiconductor (Schottky) interfaces and the resultant picture has been found to be consistent with the so-called covalent-ionic trend.[19] Thus, although interface or contact effects are usually ignored we expect that such systems should also exhibit a dielectric loss obeying the universal law and a systematic study of the details could provide a powerful probe of the interfacial structure.

B. Dielectrics with atom-atom or molecule-molecule or ion-ion or dipole-dipole interactions

New concepts and ideas on low-energy excitations in real glasses and spin glasses have been recently introduced by Anderson *et al.*,[20] Phillips,[21] and by

Anderson.[16] They propose the existence of a statistical distribution of localized tunneling levels and/or modes. A tunneling mode in a real glass is realized by an atom (or group of atoms) which has an energy $E(\vec{x})$ as a function of its generalized position coordinate $\vec{x}$ which exhibits two local minima of energy difference ΔE separated by a barrier. Similarly in spin-glasses spins are considered as classical dynamical quantities with a potential energy surface that is a function of the simultaneously specified orientations of all the spins (i.e., a N-dimensional configuration space); local minima in the energy correspond to metastable states of the spin glass associated with different spin configurations. A tunneling mode for spin-glasses[16,20] is defined in spin-configuration space as two local minima separated by a quantum-mechanical energy barrier. Tunneling between one local minimum and another, if it occurs, involves the rearrangement of several spins. The linear specific heat observed in real glasses (spin glasses) comes from tunneling modes whose energy barriers are sufficiently great so that resonant tunneling of atoms (spins) between local minima does not occur, but sufficiently small such that tunneling between the two levels can take place during the time span of the specific-heat measurement. Tunneling modes that contribute to the low-temperature linear specific heat have a density of levels $N(\Delta E)$ per unit ΔE which is nonzero, smooth, and continuous for $\Delta E \lesssim kT$. Those tunneling modes that contribute to the low-temperature linear specific heat compose only a small subset[16,20] of the total density of alternate states or modes with level splitting ΔE.

The spin-glass system and the resultant spin-spin interaction models can often be transcribed to another physical models with nonspin interactions.[22] Well-known examples include the Ising model equivalence to a lattice gas and to a binary alloy. A lattice gas is a collection of atoms (molecules) whose positions can take on only discrete values which form a lattice. Each lattice site can be occupied by at most one atom. In general the potential energy of the system of atoms corresponds to a gas in which the atoms are located only on lattice sites and interact through a two-body potential $v(|\vec{r}_i - \vec{r}_j|)$. The correspondence between the lattice gas and the Ising model is seen by identifying occupied sites with up spin and empty sites with down spin and the nearest-neighbor atom-atom interaction ϵ_{AA} with $-4J_{ij}$, where J_{ij} is the Ising interaction between spins. A binary alloy in a lattice model corresponds to sites occupied by A or B atoms (molecules). Let ϵ_{AA}, ϵ_{AB}, and ϵ_{BB} represent the interaction energies between the atoms. A site occupied by an atom A is identified with an up spin and a site occupied by an atom B with a down spin. The quantity $\frac{1}{4}(2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB})$ then corresponds to J in the Ising model.

Consider dielectrics where atom-atom, molecule-molecule or ion-ion interactions are important. In the lattice gas and/or binary alloy modeling of dielectrics with random interactions, the equivalence to the spin-glass Ising model implies a dielectric state corresponding to the spin-glass state exists. Such dielectrics will have, in analogy to spin-glasses, tunneling modes. In direct analogy to a tunneling mode in spin-glasses which corresponds to several spins turned over, in these dielectrics a tunneling mode corresponds to the change of the atomic (molecular or ionic) occupancy of several sites to get from one energy minimum to the other. The essential point is the existence of very-low-energy tunneling modes in these dielectrics. This class of tunneling modes will be shown in Sec. IV to again satisfy the criterion for infrared divergence and hence yields the universal law. The lattice-gas and binary-alloy model should be good representations of many dielectrics including the class of solid-state ionic conductors[23] or solid electrolytes such as AgI, CaF, and Na β alumina. In fact ionic conductivity for these solids has been calculated in the lattice-gas model.[24] In the case of Na β alumina, there is the repulsive interaction among the diffusing sodium ions and also the attractive interactions between the ions and their randomly distributed, compensating defects. These properties imply a lattice gas with random interactions. There is indeed ample experimental evidence[25,26] for the existence of tunneling modes in alkali β alumina as well as Ag β alumina. In particular there is an excess low-temperature specific-heat[26] contribution which is nearly linear in T as in the case of spin-glasses.

For completeness, we mention again that it has been pointed out[16] that there are also a large number of tunneling modes having small ΔE which have their two alternate states inaccessible to each other because their energy barriers are too large for tunneling to occur. Those pairs of levels are practically not connected, and some of them contribute to the zero-point entropy of the glass. Indeed experimental measurements of fused silica[27] and glycerol[28] has shown that the zero-point entropy is finite for both. Such tunneling modes can also produce an infrared divergent response although considerations of thermal histories become important.

To conclude this section, we note that the apparent arbitrary division of dielectrics (implicit in this section) according to whether electron self-trapping interactions or ion-ion interactions, etc., dominate the behavior of the dielectrics is quite natural. Ions have closed atomic shells and molecules are usually covalently bonded. In both cases electron self-trapping interactions have already gone to completion, although the origins of the pairing interactions in the two cases are entirely different. The residual interactions are then the ion-ion or the molecule-molecule interactions, which then should play the important role in providing correlated states and their excitations.

IV. INFRARED-DIVERGENT RESPONSE OF CORRELATED STATES

Let us examine the transient response of the tunneling modes to sudden potential change caused by fast quantum transition of some charged species. Tunneling modes whose alternate states are such that $\omega/2\pi > 10$ GHz can be eliminated from the outset for consideration of infrared divergent response. Our interest is in the low-frequency dielectric response where ω is smaller or much smaller than 10 GHz. It may already be noted by the reader that many of the examples of correlated states presented in Sec. III have some common characteristics although the identity of the correlated states can differ drastically from one example to another. Correlated states can be electronic in origin, paired electron states in bonds, lone pairs, or arise from defects and impurities; or single-electron self-trapping states; or even be associated with extended electronic states. Correlated states of atomic or molecular origin can be the atomic (or molecular) configuration state of a set of atoms (molecules); or spin-configuration state of a set of spins; or the configuration state of a cluster of ions or a group of dipoles. Excitation (de-excitation) of correlated states consists of the transfer of occupancy of state of lower (higher) energy to another of higher (lower) energy. For succinct discussion we shall focus on the case of an atomic-configuration state and spin-configuration state where excitations are the conventionally called tunneling modes. However, we emphasize again that the discussions in the remainder of this section hold as well for the electron self-trapping tunnelinglike modes detailed in Sec. III.

The very low ΔE of the tunneling modes guarantees contribution to the dielectric response at corresponding low frequencies $\omega \approx \Delta E/h$. This class of tunneling modes should exist. Since the configurations of the atoms (spins) is random, there must[16] be very many locations (of order N, the number of atoms or sets of atoms) where there are two possible configurations of very similar energies E_1 and E_2. If E_1 and E_2 are independent random variables, then the probability $p(\Delta E)$ of finding $\Delta E = |E_2 - E_1|$ is finite as $\Delta E \rightarrow 0$. But physically this is not true because it is possible to tunnel between the two alternate levels with a tunneling matrix element T_{12} even though it is small. The energy-level separation will be at least $\Delta E > |T_{12}|$, the off-diagonal matrix element between the alternate levels. For this class of very-low-energy inaccessible tunneling modes (i.e., <10 GHz) the physical energy difference ΔE is determined by the off-diagonal matrix element $\Delta E = |T_{12}|$.

It has been argued by Anderson,[16] that T_{12} being a complex matrix element acts like the x and y components of the random field that prevents the actual level splitting ΔE going to zero even though $|E_1 - E_2| \rightarrow 0$ unless $T_{12} \rightarrow 0$ also. For low-frequency dielectric response, we are particularly interested in the $\Delta E = |T_{12}| \rightarrow 0$ limit. T_{12} consists of two random variables since it has real and imaginary parts. The probability that the mode energy ΔE lies in the interval $|T|$ and $|T| + d|T|$ is proportional to $|T| d |T|$. Hence the density of states of very-low-energy, tunneling modes $N(\Delta E)$ is proportional to ΔE. Now the sudden potential change that induces transitions between the two alternate levels should not depend on ΔE. Hence, for atomic- and spin-configuration states the condition $|V_{12}|^2 N(\Delta E) = nE$ for infrared divergence of the response through correlated state excitations (i.e., tunneling modes here) is satisfied. This statement applies also to cases in which other types of correlated states are concerned. This will lead to the desired functional dependence in χ'' of Eq. (1) as well as the loss peaks, as will be disucssed in Sec. V.

V. LOW-FREQUENCY INFRARED-DIVERGENT DIELECTRIC RESPONSE

Having argued that dielectrics with diverse interaction types should have invariably some very low-frequency excitations that respond in an infrared divergent manner to fast transitions of polarizing species and contribute a time dependence of the form t^{-n} at large t to some correlation function, we embark on the derivation of the dielectric response function and examine its properties. The total dielectric polarization $\vec{P}$ induced by an electric field $\vec{E}(t)$ can be calculated by standard methods[29,30] of linear response. The interaction of the polarization with the electric field is given by

$$H_{\text{int}} = -\vec{P} \cdot \vec{E}(t) , \tag{5}$$

where $\vec{P}$ is the operator of the polarization. The perturbation H_{int} induces a polarization density

$$\langle \vec{P} \rangle = \langle \vec{P} \rangle_0 + \int_{-\infty}^{t} \vec{\psi}(t-t') \cdot \vec{E}(t')\, dt , \tag{6}$$

where $\vec{\psi}(t-t') = -\langle\langle \vec{P}(t)\vec{P}(t') \rangle\rangle$ is the dielectric polarizability tensor, and $\langle \vec{P} \rangle_0$ is the polarization density in the equilibrium states as $\vec{E} \rightarrow 0$, which can be nonzero for some dielectrics such as ferroelectrics. For simplicity consider the dielectric tensor $\vec{\psi}$ to be diagonal. In the case when classical statistical mechanics suffice (as often is the case for dielectrics at finite temperatures), the response function simplifies to the time correlation function

$$\psi_{ii}(t-t') = \beta \langle P_i(t) \dot{P}_i(t') \rangle_0 , \tag{7}$$

where $\langle \cdots \rangle_0$ denotes averaging with the equilibrium distribution function, $\beta = 1/k_B T$, and $\dot{P}_i(t')$ is the derivative of $P_i(t')$ with respect to t'.

If $P_i(t)$ takes on either of two values $\pm p_0$ and makes transitions from one value to the other, as in the case of a system of particles with a dipole moment or the case of a charged particle that can occupy one of two alternate sites, then ψ_{ii} can be readily calculated by generalizing the method[30] to take into account a time-dependent jump transition rate $W(\tau)$. Rewriting $t-t'$ as τ, we wish to calculate $\psi_{ii}(\tau)=-\beta\langle\vec{P}_i(t)\dot{\vec{P}}_i(t-\tau)\rangle_0$, where the derivative is now with respect to τ. Doing this we obtain the result

$$\psi_{ii}(\tau)=2\beta p_0^2 W(\tau)\exp\left[-2\int_0^\tau W(\tau)\,d\tau\right], \qquad (8)$$

for the time dependence of the dielectric response function. The task that remains is to calculate $W(\tau)$ including the possibility of an infrared divergence of correlated states excitations. Let $\phi(\tau)$ describe the time response of the correlated states to the sudden jump of the electron (dipole) from one position to another.

The form of $\phi(\tau)$ in our notation is

$$\phi(\tau)=\int_0^{E_c} V_0^2\, N(E)[1-\cos(E\tau)]\,dE/E^2 ,$$

and is different from the form normally given.[4,5] The difference is the appearance of the cosine term instead of $\exp(-iEt)$, and is due to both excitation and de-excitation of correlated states that now must be taken into consideration. We have seen in Sec. IV that there exists some class of correlated states in the dielectrics we considered so that $V_0^2N(E)\equiv bV_0^2E$ is proportional to E and satisfies the condition for infrared divergence in the number of these low-energy correlated-states excitations. The integral, $\phi(\tau)$, can be evaluated and yields

$$\phi(\tau)=bV_0^2\,\mathrm{Re}[\gamma+\ln(iE_c\tau)+E_1(iE_c\tau)] , \qquad (9)$$

where $\gamma=0.5722$, and $E_1(ix)$ is a standard integral which vanishes at large x. The jump transition rate is $W(\tau)=W_0e^{-\phi(\tau)}$ where W_0 is time independent. On defining a time τ_0 by $1/\tau_0=2W_0$ and combining equations, we obtain

$$\psi_{ii}(\tau)=(\beta p_0^2/\tau_0)e^{-\phi(\tau)}\exp\left[-\int_0^\tau e^{-\phi(\tau)}\,d\tau/\tau_0\right] . \qquad (10)$$

Consider the case when either the infrared divergent correlated states do not exist or the coupling V_0^2 of the hopping charges (dipole) to the correlated states is vanishingly small. Then in either case $\phi(\tau)\rightarrow 0$ and

$$\psi_{ii}(\tau)=(\beta p_0^2/\tau_0)\exp(-\tau/\tau_0) ,$$

whose Fourier transform is $\chi_{ii}(\omega)=\beta p_0^2(1+i\omega\tau_0)^{-1}$, which is the classical Debye susceptibility. Recapturing the classical Debye laws by turning off the low-energy correlated-state excitation is of course no surprise. The interesting point is that dielectrics or dielectric interfaces in nature seldom obey the Debye law which implies there should exist some low-energy correlated-states excitations which are coupled to the carriers (charges, dipoles) of the dielectric.

The dielectric response function for $E_c\tau \gg 1$ is

$$\psi_{ii}(\tau)=(\beta p_0^2/\tau_0)e^{-n\gamma}(E_c\tau)^{-n} \times\exp[-e^{-n\gamma}\tau^{1-n}/(1-n)\tau_0E_c^n] , \qquad (11)$$

where we have put $n\equiv bV_0^2$ and assumed $n<1$. By inspection one can observe that although the $(E_c\tau)^{-n}$ term may initially determine the τ dependence of ψ_{ii}, for sufficiently large values of τ, ψ_{ii} will be dominated by the exponential function. This occurs roughly at

$$\tau_p\approx[(1-n)e^{n\gamma}E_c^n\tau_0]^{1/(1-n)} . \qquad (12)$$

The Fourier transform of $\psi_{ii}(\tau)$ of Eq. (11), $\chi_{ii}(\omega)$, can be obtained numerically. Several representative results for representative values of n are shown in Fig. 5. A peak in $\chi''(\omega)$ exists and its location is

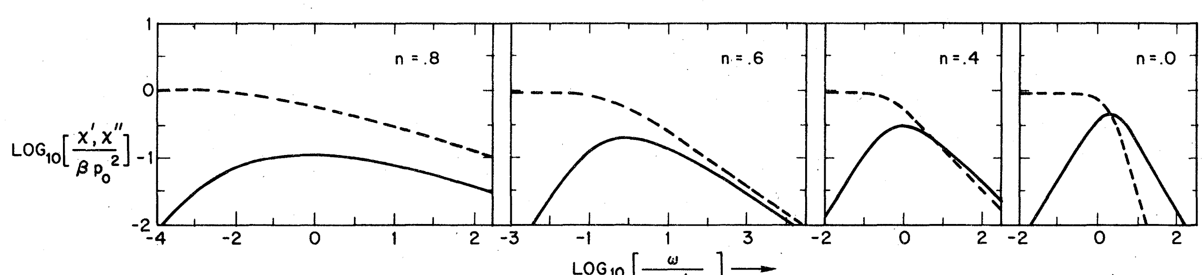

FIG. 5. Behavior of χ', χ'' in the present theory for several different values of n. Note the peak shape is independent of $a\equiv e^{-n\gamma}/(1-n)\tau_0E_c^n$ but strongly dependent on n. The slope m of each of these $\log(\chi'')$ vs $\log(\omega)$ plots varies continuously from zero to one for $\log(\omega)<\log(\omega_p)$, where ω_p is the post-peak position. m for a fixed decrement of $\log(\omega)$, i.e, at a value of ω with $\log(\omega/\omega_p)<0$ and fixed, decreases as n increases. In view of this property one should *not* take the asymptote of the lowest available frequency measurements of $\chi''(\omega)$ and attach a universal meaning to the slope of that asymptote but rather analyze the local slope m at a fixed decrement below the post peak.

close to the value of $\tilde{\omega}_p = 1/\tau_p$. This post $1/\omega^{1-n}$ peak may be identified with the α or the β peaks commonly observed in dipole systems such as polymers, liquids, p-n junctions, ferroelectrics, liquid crystals, cryogenic polymers, and some glasses. The approximate peak position

$$\tilde{\omega}_p = [(1-n)e^{n\gamma}\tau_0 E_c^n]^{1/(n-1)} \tag{13}$$

is a decreasing function of increasing τ_0 and E_c and depends sensitively also on the infrared divergence exponent n. In general τ_0 is temperature dependent and usually has a clearly defined activation energy E_A: $\tau_0(T) = \tau_\infty \exp(E_A/k_B T)$. This alone introduces a temperature dependence into

$$\tilde{\omega}_p \propto \exp[-E_A/(1-n)k_B T] \tag{14}$$

with an apparent activation energy $\tilde{E}_A$ of $E_A/(1-n)$. Increase in temperature will cause a lateral shift of the universal law and its post peak along the frequency axis.

A wide range of dielectrics have associated with them the presence of charge carriers of electronic or ionic nature. These charge carriers are also evidently responsible for dc conductivity. Thus one expects that charge carrier hopping transitions, under excitaiton by a time-varying electric field, do not necessarily involve only two preferred sites. Consider the charge carriers that do not jump randomly between two states/sites, then the dielectric loss is simply proportional to the probability of exciting low-energy correlated-state excitations. With the same time response function of the correlated states $\phi(\tau)$ as displayed in the preceding paragraphs,

$$\chi''(\omega) \propto \int_{-\infty}^{\infty} dt(i\tau\omega)\exp[-\phi(\tau)] \; .$$

For $E_c\tau$ large, $\phi(\tau)$ can be approximated by $n\gamma + n\ln(E_c\tau)$. The approximate dielectric loss $\chi''(\omega)$ is then proportional to $1/\omega^{1-n}$ which is identical to the universal law[1] and the absence of a loss peak. This predicted type of dielectric response is indeed observed in a very wide range of dielectrics of all physical and chemical characteristics, and interestingly they are always associated with the presence of hopping charge carriers (Fig. 1). A second universal law $(\omega/\omega_c)^{n_2-1}$ will follow a first $(\omega/\omega_c)^{n_1-1}$ on decreasing ω if there are available two types of correlated states that can contribute to infrared divergences. From sum rule considerations on $\chi''(\omega)$, we expect $n_2 < n_1$ which is also observed (Fig. 1).

VI. SUMMARY AND DISCUSSIONS

In this work we have broadly and arbitrarily classified dielectrics according to the type of interaction or correlations inherent in all materials. We have found that independent of the type of correlations, a dielectric in general has gapless "correlated states" whose density of states is continuous. These correlated states have response times much longer than the time taken by the hopping between sites of charged particles or jumping between orientations of dipoles. Hence the hopping or jumping movements can be considered instantaneous as far as the correlated states are concerned and they experience a sudden change of the potential induced by the charged particles or dipoles. The transient response of the system is the emission of low-energy excitations of the correlated states which cause the response to have a t^{-n} time dependence or an infrared-divergent-like $1/\omega^{1-n}$ frequency response of the dielectric loss. We have thus arrived at a fundamental mechanism for the empirical ω^{n-1} dependence (accompanied sometimes by a peak at low enough ω) of the dielectric loss obeyed by nearly all dielectrics and the mechanism is operative independent of the type of physical structure and chemical bonding in the materials, and whether the polarization is associated with permanent dipoles or hopping charge carriers of electronic or ionic nature.

This arbitrary classification of dielectrics according to the present scheme is quite general. The classification is based on the type of dominant correlations and the correlated states they render. Detailed developments of the electron pairing correlations and of the ion-ion correlations have been given. Correlated states are identified in both cases. Types of correlations other than those between electrons or between ions could conceivably lead to some sort of correlated states as has been demonstrated explicitly for the cases of electron pairing correlations and the ion-ion correlation. These correlated states although they may have very different physical origin and interpretations dependent on which class of dielectrics share some common important properties. The very low-energy excitations of these correlated states have an infrared divergent behavior, and lead to the low-frequency dielectric response obeying a universal law, $\chi''(\omega) \propto 1/\omega^{1-n}$, with sometimes the appearance of a post peak at low enough ω. The Debye law holds only in the probably seldom realized cases where the correlated-state excitations are either nonexistent or ineffective because of weak coupling to the hopping charges (dipoles) that contribute to the Debye susceptibility. The invariable deviation from the Debye laws in most dielectrics is taken to imply that the existence of very-low-energy correlated-state excitations are often the rule rather than the exception. We emphasize the importance here of not only the recognition of the Curie–von Schweidler law as an infrared divergence phenomenon but also the subtle task of identifying the (correlated state) excitations that are responsible for it. There is an important difference between the present case and the Cherenkov (or bremsstrahlung) radiation on the x-ray edge singularity problem, since energies in the present regime of interest are so low that for these cases, the spontaneous photon or electron-hole pair produced infrared divergence is entirely smeared out at finite temperatures. This is not the case here for the particular correlated states responsible for such low-energy dielectric response singularities. The infrared divergence is retained at finite temperatues even 10 GHz. In all infrared divergence problems, an upper cutoff E_c of the excitation energies E is needed either to insure convergence at large E or simply because we run out of these excitations as E increases, or $|V|^2N(E) \propto E$ no longer holds for $E > E_c$. The universal law $\chi''(\omega) \propto 1/\omega^{1-n}$ may be modified at low enough frequencies in dipolar dielectrics by the introduction of a peak, and this may or may not occur within the frequency spectrum scanned, dependent on the magnitude of E_c, the upper cutoff of the correlated-state excitations, and the value of n. The occurrence of a post peak in some classes of dielectrics and the nonoccurrence in other classes can be correlated. Order of magnitude estimates of E_c are possible for certain classes of dielectrics and the post-peak frequency predicted seems to be consistent with experimental data. The temperature dependence of the post-peak position is also consistent with experimental data.

In addition to bulk dielectrics we have considered also the interfaces of a dielectric with another dielectric or a semiconductor or a metal. Another interesting example of these interfacial systems is the thermal oxidized Si-SiO_2 interface in metal-oxide-semiconductor (MOS) device structures. The present authors have investigated the local electron pairing interaction at dangling bonds and weaker (stronger) bonds[31] (a concept also introduced by Anderson[11]) and the resultant electronic structure of the Si-SiO_2 interface.[31] Both dangling bonds and the weaker (stronger) bonds can give rise to pair states which are strongly self-trapped and have the interesting dynamic character when, e.g., electrons are excited in pairs. In particular, correlated states of this type at the interface give rise to electron pair excitations with arbitrary low energies and hence should produce an infrared divergent dielectric response. We wish to point out that low-frequency dielectric response measurements of the interfacial region could be a powerful and novel tool for the charcterization of devices. These measurements may have the potential of yielding more in-depth understanding of interfaces when coupled with conventional measurements such as capacitance versus gate voltage.

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