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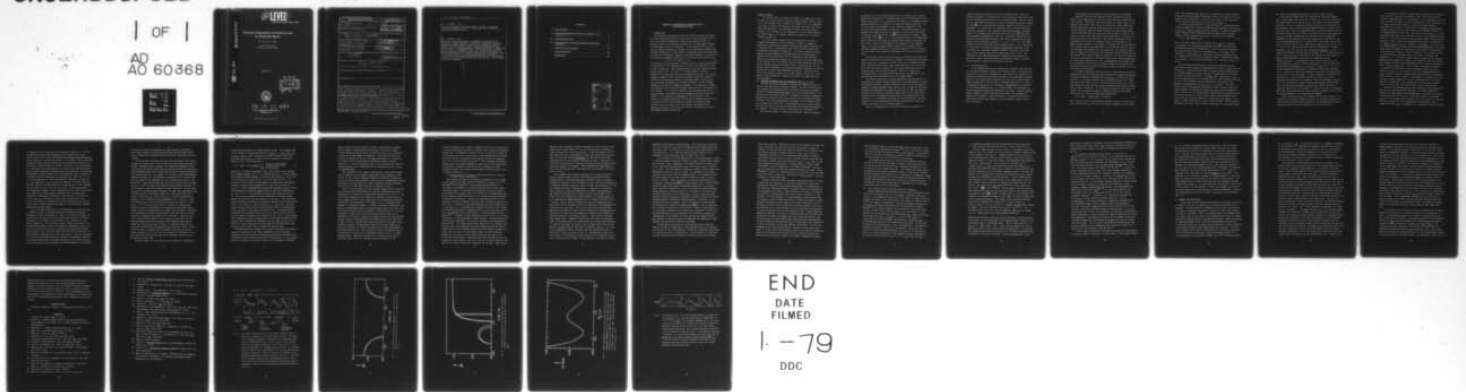
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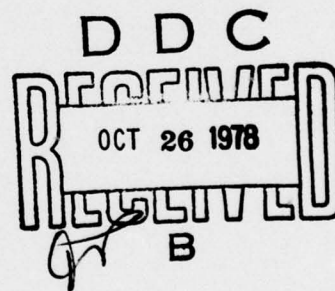
Frequency Dependence of Dielectric Loss in Condensed Matter

K.L. Ngai and C.T. White

*Semiconductors Branch
Electronics Technology Division*

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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.

CONTENTS

I. INTRODUCTION	1
II. INFRARED DIVERGENCE AND THE "UNIVERSAL" LAW $\chi(\omega) \propto \omega^{n-1}$	2
III. CORRELATED STATES	4
IV. LOW FREQUENCY INFRARED DIVERGENT DIELECTRIC RESPONSE	17
V. SUMMARY AND DISCUSSIONS	20
ACKNOWLEDGMENT	23
REFERENCES	23

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FREQUENCY DEPENDENCE OF DIELECTRIC LOSS IN CONDENSED MATTER

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 observed¹ 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 dielectric loss follows the empirical law

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

extending over several decades of frequency from low audio and sub-audio 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.

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

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present context.

The various types of dielectric response are summarized in Fig. 1. We note the virtual absence of the pure Debye response; and the validity of the universal law of dielectric response, (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 the next section 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, electrons or ions. Then in Section III we discuss several examples of low energy excitations expected in a host of systems that satisfy these elementary principles. In Section IV we derive the universal response (1) and the possible presence of a loss peak at lower frequencies. Finally, in Section V 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 experiment² of a fast charged particle. In the realm of solid state physics^{3,4} an example of infrared divergence is thought to be provided by the peculiar shape of X-ray absorption edges of metals,⁵ and the "orthogonality catastrophe" for an impurity potential inserted in a Fermi gas.⁶ 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.^{3,4}

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 response⁷⁻⁹ 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 the later sections 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. These correlated states have a smooth and continuous density of states $N(E)$, which we take as constant N . Low energy excitation of the correlated states with excitation energy E consists of removing an "occupied" state to an "unoccupied" state 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 to 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 correlated 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 satisfied. The mean number $\bar{n}$ of correlated state excitations is then $\bar{n} \propto bV^2 N^2 \int_0^{E_c} E dE/E^2$, which diverges logarithmically, where E_c is the upper "cut-off" of the correlated state excitation energy. 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 law¹ of depolarization. It is interesting to note that the infrared divergence problem when considered in the time domain as a transient response problem⁷⁻⁹ 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 Section IV, after we have discussed the correlated states in a broad classification of dielectrics in the next section.

III. Correlated States

In the preceding section 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 satisfy two rather stringent but interrelated criterion: namely (i) the characteristic response time for the correlated states is long in comparison to the switching of the Hamiltonian and (ii) these low energy excitations are not in general thermodynamically accessible at the moderate temperatures; i.e., several 100°K, since otherwise we expect significant temperature smearing of the effect. Below we discuss several examples of such correlated states which can reasonably be expected to be present in many dielectrics. One should note from the onset that although these examples are quite general, they are by no means exhaustive.

(a) Dielectrics with Electron Pairing Interactions and States

Anderson¹⁰ has recently proposed a model of amorphous semiconductors which emphasizes the role of electron pairing interactions in these systems. Anderson's ideas should apply to a large number of diamagnetic dielectrics. The concept of strong local electron pairing interactions 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 energy of this state relative to its value if it were constrained to be unoccupied. This effect can produce a self-trapping of the electron in a manner related to the formation of a small polaron; however, it also makes it favorable for the spin-mate of the occupied state to be occupied and in turn the two electrons can be more strongly self-trapped in a correlated way. The resultant quasi-particle (the two electrons and the concomitant lattice distortion) has been termed¹⁰ for obvious reasons a bipolaron. Of course the formation of such a quasi-particle is resisted by the mutual coulomb repulsion of the constituent electrons, but only in comparatively few systems, such as the transition metal oxides or impurity bands in crystalline semiconductors does this repulsive interaction dominate, giving rise to e.g. spin density fluctuations.

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 $\sum_i U_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$ 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:

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

where $a_{i\sigma}^+$, $a_{i\sigma}$ 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 other-

wise. 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 (2) we have developed¹¹ a generalized mean field-like method which entails linearizing the many-body terms $U_i n_{i\uparrow} n_{i\downarrow}$ as $U_i n_{i\uparrow} n_{i\downarrow} \rightarrow \sum_{\sigma} U_i \tilde{n}_{i-\sigma} n_{i\sigma} - U_i \tilde{n}_{i\uparrow} \tilde{n}_{i\downarrow}$ where $U_i \tilde{n}_{i\uparrow} \tilde{n}_{i\downarrow}$ is present to prevent double counting of the interaction and the conditionally averaged number of spin σ electrons at the site i is given by the relation

$$\tilde{n}_{i\sigma} = -\frac{\text{Im}}{\pi} \int dE f(E) g_{i\sigma}(E^+) \quad (3)$$

with f the fermi function and E^+ denotes the $\lim_{\epsilon \rightarrow 0^+} (E + i\epsilon)$. Equation (3) provides a set of generalized Hartree Fock-like self-consistent relations determining the parameters $\tilde{n}_{i\sigma}$ since the Green's functions $g_{i\sigma}$ entering these formulae are defined as $g_{i\sigma} = \langle i\sigma | (z - H_{e1})^{-1} | i\sigma \rangle$ where $H_{e1} = \sum_{i\sigma} (E_i + U_i \tilde{n}_{i-\sigma}) n_{i\sigma} + \sum_{ij\sigma} R_{ij} a_{i\sigma}^\dagger a_{j\sigma}$ and hence depends on $\tilde{n}_{i\sigma}$. For convenience (3) can be recast as $\tilde{n}_{i\sigma} = -(\text{Im}/\pi) \int dE f(E) / (E - E_i - U_i \tilde{n}_{i\sigma} - \Delta_i)$, where Δ_i is the usual self-energy and is a function of $\{n_{j\sigma}\}$, E and R .

To solve these self-consistent conditions we employ the long established coherent potential approximation¹² (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 $G(E - \Sigma_0) = \langle g_{i\sigma}(E) \rangle_{\text{av}}$, where the brackets $\langle \rangle_{\text{av}}$ here and henceforth denote an average over the random variables entering H_{e1} and G is the Green's function obtained by replacing the site diagonal random potentials of H_{e1} by Σ_0 at each site i . 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 $\Delta = (E - \Sigma_0) - \sqrt{(E - \Sigma_0)^2 - 4R^2}$. The CPA equation defining Σ_0 and hence Δ can be written explicitly for the present model

$$\text{as: } \iint P(E_i, U_i) dE_i dU_i / [E - E_i - U_i \hat{n}_{i0}(E_i, U_i) - \Delta(\Sigma_0)] = 1 / [E - \Sigma_0 - \Delta(\Sigma_0)].$$

We now have as inputs into the formalism some specified temperature, T , and number of electrons in the band, N_{el} , as well as particular functional forms for $G(E)$ and $P(E_i, U_i)$. The calculation then proceeds as follows: First we assume the function $\hat{n}_{i0}(E_i, U_i)$ and then solve the CPA equations using a modified Newton-Raphson technique to obtain $\Sigma_0(E)$ and hence $\Delta(\Sigma_0)$. There are presumably many $\Sigma_0(E)$ satisfying the CPA condition for a particular E ; however, the correct branch of $\Sigma_0(E)$ goes as $\langle E_i + U_i \hat{n}_{i0} \rangle$ at large energies, and this solution can be analytically extended into the region of interest (energies within the band) by use of the Newton-Raphson method. In doing this we have found it most efficient to follow a path in the complex plane slightly above the real axis ($E + i\eta$; $\eta = .05$) and then take the limit $\eta \rightarrow 0^+$ numerically. Having so determined $\Delta(\Sigma_0)$ we can then find the chemical potential μ of the system from the usual relation $N_{el} = (2/\pi) \text{Im} \int dE / \{ (e^{-\beta(E-\mu)} + 1)(E^+ - \Sigma_0 - \Delta(\Sigma_0)) \}$, where in obtaining this condition, we have employed the CPA equation. Note the CPA determined Σ_0 satisfies the important sum rule $\int dE / (E - \Sigma_0 - \Delta(\Sigma_0)) = 1$. Having $\Sigma_0(E^+)$ and μ , we then calculate a new function $\hat{n}'_{i0}(E_i, U_i)$ from (3) and this procedure is iterated until self-consistency is established, i.e. $\hat{n}_{i0}(E_i, U_i) = \hat{n}'_{i0}(E_i, U_i)$. 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 $\hat{n}_{i0}(E_i, U_i)$ can be adequately represented for intermediate values by trapezoidal interpolation. We have found for simple continuous probability distributions that this procedure converges very nicely (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 atom¹³ is $H_h = \sum_{\sigma} E_h n_{h\sigma} - \lambda_h x_h (n_{h\uparrow} + n_{h\downarrow} - 1) + c_h x_h^2/2$, where $n_{h\sigma}$ 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 back-bond stretching energy and the second is the so-called dehybridization energy.¹⁴ If we have a group of such nonbonded states interacting with one another then a simplified Hamiltonian describing the situation is $H = \sum_{i\sigma} E_i^h n_{i\sigma} - \sum_i \lambda_i x_i (n_{i\uparrow} + n_{i\downarrow} - 1) + \sum_i c_i x_i^2/2 + \sum_{ij\sigma} R_{ij} a_{i\sigma}^\dagger a_{j\sigma}$. 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 identification: $2\lambda_i^2/c_i \rightarrow U_i, E_i^h \rightarrow E_i + U_i/2$. Thus we expect the negative U model to incorporate the behavior of a simple nonbonded orbital 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 back-bonds and hence is quite general. Furthermore, in amorphous partially covalent materials because of the more localized nature of the wave function in comparison to the crystalline case one expects similar effects to arise from states with origin in the conducting band.

Indeed in an amorphous material one would expect after Anderson¹⁰ that the one electron potential E_i^h obeys a continuous probability distribution $P(E_i^h)$ 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 $W(E_i)/B = 1/2$ for $-1 \leq E_i/B \leq 1$ and zero otherwise and $U_0/B = -3$; B is unperturbed half bandwidth. Also we assumed that $T=0$, $N_{el}=1$ and employed as an unperturbed Green's function,

G, appropriate for a Cayley tree of coordination number six. In Fig. 2 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. To understand this behavior 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 ($\gtrsim \text{lev}$), excitations of the system that require only energy $E_i - E_j$ which becomes vanishingly small as $E_i \rightarrow E_j$ can be achieved by removing the electron pair from the site i to the site j . In the case $R_{ij} \rightarrow 0$, the density of pair state excitations is then $\sim P(E_i + U/2)$ which is continuous and slowly varying around E_f and as 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 temperature. 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 matrix elements V_{ij} of the potential change V abruptly switched on by the polarizing species should on the whole be independent of $E_j - E_i$, and 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. At elevated temperatures the infrared divergence will survive provided the low lying pair state excitations are thermodynamically inaccessible,

but this is a natural consequence for large enough U_i ($|U_i|/kT \gg 1$) which should produce an energy barrier between pairing states sufficient to effectively prevent thermally assisted tunneling in physical systems.

So far we have considered only pair state excitations that involve essentially transferring a pair of electrons from one pairing center to another. However, there is another (not completely orthogonal) class of low-lying excitations associated with pairing interactions that arise from breaking the pair and "placing" the electrons in states associated with non-pairing sites. For example, in the case of metal-semiconductor (Schottky) contacts one could envision transferring the electrons from pairing centers in the semiconductor (say, nonbonded orbitals) to the Fermi sea. A particular example derived from our general model is shown in Fig. 3 where we display two different self-consistent solutions to (3) obtained by using the previously detailed formalism. We have taken as inputs in calculating these examples: $T=0$, $N_{el}=3$ and G appropriate for a Cayley lattice of coordination number six. The form of $P(E_i, U_i)$ is chosen so that $P(E_i, U_i) = x\delta(U_i) \delta(E_i - E_0) + (1-x)\delta(U_i - U_0)W(E_i)$ where $W(E_i)/B = 5$ (B the unperturbed half bandwidth) for $.1 \leq E_i/B \leq .3$ and zero otherwise and x (the concentration of pairing centers) = .1 with $U_0/B = -1.6$. The solid line of Fig. 3 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 $\sim U_0/2$ below E_f as shown in Fig. 3) to the main band with the unoccupied pairing levels now appearing $\sim U_0/2$ above E_f . This is exemplified in Fig. 3 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 and a concurrent increase in the measure of the main band.

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 $H = \sum_{i\sigma} E_0 n_{i\sigma} + \sum_{ij\sigma} R_{ij} a_{i\sigma}^\dagger a_{j\sigma} + \sum_i U_j n_{j\uparrow} n_{j\downarrow} + \sum_{\sigma} E_j n_{j\sigma}$, which represents of course a special case of (2). Approximating $U_j n_{j\uparrow} n_{j\downarrow}$ as before the free energy of the system as a function of $\tilde{n}_j$ can be expressed as

$$F = K - U_j \tilde{n}_j^2 - (2/\pi) \text{Im} \int_{-\infty}^{\infty} dE f(E) \int_{-\infty}^E \frac{(U_j \tilde{n}_j + E_j)(\partial G_j(\tilde{E}^+)/\partial \tilde{E}) d\tilde{E}}{1 - (U_j \tilde{n}_j + E_j) G_j(\tilde{E}^+)} \quad (4)$$

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 $E_j + U_j/2$ lies in the vicinity of E_f and U_j/R is $\gg 1$, as is shown in Fig. 4. 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. $U_j \gtrsim .1$ 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 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 easily show that the two minima are separated for large U_j by $\sim |E_j + U_j/2 - E_f|$ 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 $(E_j + U_j/2) \gtrsim E_f$. This is of course consistent with the previously obtained results summarized in Fig. 4 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. 4) that reduces further the energy of the system (there is an orthogonality theorem⁶)

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 the next subsection where we are confronted with an analogous problem in terms of tunneling modes.

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 $F(\hat{n}_i)$ and the corresponding low-lying excitations, and once again for large U_i thermally assisted tunneling from one state to the other would not be expected to occur.

Thus, we have detailed two rather general examples which illustrate how electron pairing interactions can provide correlated states with characteristics sufficient to produce the "universal law"; Eq. (1). Of course these examples are not completely unrelated, and one expects in many systems that both types of excitations are simultaneously present and operative in producing an ω^{n-1} behavior of χ ". Although we have phrased our discussion primarily 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 gapless correlated 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 pairing 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 pairing states in 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 MOSFETs¹² where one is dealing with an oxide-semiconductor interface in contact with a quasi-two dimensional electron gas. Furthermore, recently¹⁵ 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.¹⁶ 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,¹⁷ Phillips¹⁸ and by Anderson.¹⁹ 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 $E(x)$ as a function of its generalized position coordinate 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^{17,19} 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 non-zero, smooth and continuous for $\Delta E \lesssim kT$. Those tunnel-

ing modes that contribute to the low temperature linear specific heat compose only a small subset^{17,19} of the total density of alternate states or modes with level splitting ΔE . It has been pointed out^{17,19} that there are also a large number of 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 silica²⁰ and glycerol²¹ has shown that the zero-point entropy is finite for both.

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 thermodynamically accessible can be eliminated at the outset for consideration of infrared divergent response at $\omega/2\pi < 10$ GHz. Our interest is in the low frequency dielectric response where ω is smaller or much smaller than 10 GHz and the ambient temperature is usually room temperature. Any infrared divergence had it existed would be obliterated by the effects of finite temperature T which replaces the characteristic t^{-n} by an exponentially damped dependence in the response function^{9,22} for $t \gg \hbar/kT$. Thus we need to consider only very low energy tunneling modes where the two alternate levels of a mode must be thermodynamically inaccessible to each other. The very low ΔE of the tunneling modes guarantees contribution to the dielectric response at corresponding low frequencies $\omega \lesssim \Delta E/\hbar$, and thermodynamical inaccessibility enables the infrared divergence to survive at finite T . This class of tunneling modes should exist. Anderson¹⁹ pointed out that since the configurations of the atoms (spins) is random, there must 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 for thermo-

dynamically inaccessible tunneling modes. 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 $\Delta E = |T_{12}|$.

Let us confine our further discussions to only spin glasses. There, it has been argued by Anderson,¹⁹ 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 lie in the interval $|T|$ and $|T| + d|T|$ is proportional to $|T|d|T|$. Hence the density of states of inaccessible, 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 . Here we envisage the sudden potential change inducing a virtual transition of one level to an excited state which has easy access to the other level. In other words the sudden potential change introduces an additional transition channel that allows thermodynamically inaccessible tunneling modes to contribute to low frequency dielectric response. Within this class of tunneling modes, the condition for infrared divergence $|v_{12}|^2 N(\Delta E) = n\Delta E$ is satisfied. The universal law follows for spin-glasses. A model of spin glasses in the Ising model formulation has recently been analyzed,²³ in which the exchange interactions J_{ij} are assumed to be distributed randomly and independently of one another over both positive and negative values. Many features of the spin glasses including the low temperature linear specific heat have been derived from the model.

The spin-glass system and the resultant spin-spin interaction models can often be transcribed to other physical models with non-spin interactions.²⁴ 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 $v(|\mathbf{r}_i - \mathbf{r}_j|)$. The correspondence between the lattice gas and the Ising model is seen by identifying occupied sites to up spin and empty sites to down spin and the nearest neighbor atom-atom interaction ϵ_{AA} to $-4 J_{ij}$, with J_{ij} 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} , 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 $(2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB})/4$ then correspond 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 modelling 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 which can be either accessible or inaccessible. 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 which are only accessible when a sudden potential change has occurred. This class of tunneling modes again satisfies 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 conductor²⁵ 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.²⁶ 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^{27,28} 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 heat²⁸ contribution which is nearly linear in T as in the case of spin glasses.

To conclude this Section, we note that the apparent arbitrary division of dielectrics according to whether electron pairing interactions or ion-ion interactions, etc., dominate the behavior of the dielectrics is very natural after all. Ions have closed atomic shells and molecules are usually covalently bonded. In both cases electron pairing interaction has already gone to completion, although the origins of the pairing interaction 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. Low Frequency Infrared Divergent Dielectric Response

Having demonstrated that dielectrics with diverse interaction types should have invariably some very low frequency excitations that 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 function²⁹ and examine its properties. The total dielectric polarization P induced by an electric field $E(t)$ can be calculated by standard methods^{30,31} of linear response. The interaction of the polarization with the electric field is given by $H_{int} = -P \cdot E(t)$ where P is the operator of the polarization. The perturbation H_{int} induces a polarization density $\langle P \rangle = \langle P \rangle_0 + \int_{-\infty}^t \psi(t-t') \cdot E(t') dt'$ where $\psi(t-t') = -\langle P(t) P(t') \rangle$ is the dielectric polarizability tensor, and $\langle P \rangle_0$ is the polarization density in the equilibrium state as $E \rightarrow 0$, which can be nonzero for some dielectrics such as ferroelectrics. For simplicity consider the dielectric tensor ψ 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 $\psi_{ii}(t-t') = \beta \langle P_i(t) \dot{P}_i(t') \rangle_0$ where

$\langle \dots \rangle_0$ denotes averaging with the equilibrium distribution function, $\beta = 1/k_B T$ and $P_i(t')$ the derivative of $P_i(t')$ with respect²⁸ 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 method³¹ to take into account a time dependent jump transition rate $W(\tau)$. Rewriting $t-t'$ as τ , we wish to calculate $\psi_{ii}(\tau) = -\beta \langle P_i(t) \dot{P}_i(t-\tau) \rangle_0$, where the derivative is now with respect to τ . Doing this we obtain the result $\psi_{ii}(\tau) = 2\beta p_0^2 W(\tau) \exp(-2 \int_0^\tau W(\tau) d\tau)$ 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 with probability per unit time W_0 . The form of $\phi(\tau)$ has been given^{3,4} and in our notation is $\phi(\tau) = \int_0^{E_c} v_0^2 N(E) (1 - e^{-iEt}) dE/E^2$. We have seen in the last section that there exists some class of correlated states in the dielectrics we considered so that $v_0^2 N(E) \equiv b v_0^2 E$ is proportional to E and satisfies the condition for infrared divergence in the number of these low energy correlated states excitations. The integral, $\phi(\tau)$, has been evaluated under this circumstance⁴ and yields $\phi(\tau) = b v_0^2 \{ \gamma + \ln(iE_c \tau) + E_1(iE_c \tau) \}$ where $\gamma = 0.5722$, $E_1(ix)$ is a standard integral which vanishes at large x . The jump transition rate is $W(\tau) = W_0 |e^{-\phi(\tau)}|$. On defining a time τ_0 by $1/\tau_0 = 2W_0$ and combining equations, we obtain

$$\psi_{ii}(\tau) = (\beta p_0^2 / \tau_0) | \exp(-\phi(\tau)) | \exp(-\int_0^\tau | \exp(-\phi(\tau)) | d\tau / \tau_0) \quad (5)$$

Consider the case when either the infrared divergent correlated states do not exist or the coupling v_0^2 of the hopping charges (dipoles) 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 $\chi_{ii}(\omega) = \beta p_0^2 (1 + i\omega\tau_0)$ 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 $E_c t \gg 1$ is $\psi_{ii}(\tau) = (\beta p_o^2 / \tau_o) e^{-n\gamma} (E_c \tau)^{-n} \exp(-e^{-n\gamma} \tau^{1-n} / (1-n) \tau_o E_c^n)$ where we have put $n \equiv bV_o^2$ 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} be dominated by the exponential function. This occurs roughly at $\tau_p \approx \left[(1-n) e^{n\gamma} E_c^n \tau_o \right]^{1/(1-n)}$. $\chi_{ii}(\omega)$, the Fourier transform of $\psi_{ii}(\tau)$ of Eq. (5) can be obtained numerically. Several representative results for reasonable choices of the parameters n , E_c and τ_o are shown in Fig. 5. A peak in $\chi''(\omega)$ exists and its location is close to the value of $\omega_p = 1/\tau_p$. 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 $\omega_p = \left[(1-n) e^{n\gamma} \tau_o E_c^n \right]^{1/(n-1)}$ is a decreasing function of increasing τ_o and E_c and depends sensitively also on the infrared divergence exponent n . In general τ_o is temperature dependent and usually has a clearly defined activation energy E_A : $\tau_o(T) = \tau_\infty \exp(E_A/k_B T)$. This alone introduces a temperature dependence into $\omega_p \propto \exp(-E_A/(1-n)k_B T)$, with an apparent activation energy 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. If a post-peak either occurs at too low a frequency to be measured or obscured by another mechanism, it can be revealed at higher frequencies by raising the temperature. This behavior has been seen for example in the ionic conductor Hollandite of the composition $K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$ as T ranges from 77K to 230K. If n is close to unity, E_A can be much larger than E_A and corresponds to an unreasonably high "activation energy" as is found for the α loss peaks of many materials.¹

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 excitation 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 preceding paragraphs, $\chi''(\omega) \propto \int_{-\infty}^{\infty} dt \exp(i\omega\tau) \exp(-\phi(\tau))$. For $E_c \tau$ large, $\phi(\tau)$ can be approximated by $n\gamma + n \ln(iE_c \tau)$. The approximate dielectric loss $\chi''(\omega)$ is then proportional to $1/\omega^{1-n}$ which is identical to the universal law¹ 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).

V. 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 after all. 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. These include the thermodynamical inaccessibility of these states from one to another, and yet the possibility of excitation when a sudden change in potential occurs. 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 implies 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 Cerenkov (or Bremsstrahlung) radiation or the X-ray edge singularity problem, since energies in the present regime of interest are so low that for these cases, the spontaneous photons or electron-hole pairs 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 are thermodynamically inaccessible from one to another. The infrared divergence is retained at finite temperatures even 10 GHz. In all infrared divergence problems, an upper cut off E_c of the excitation energies E is needed either to insure convergence at large E or simply that we run out of these excitations as E increases. In the specific examples we discussed here, the upper cut-off energies are deduced by examining the nature of these excitations. 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 cut-off of the correlated state excitations, and the value of n . The occurrence of a post-peak in some classes of dielectrics and the non-occurrence 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. An interesting example is the thermal oxidized Si-SiO₂ interface in MOS device structures. The present authors¹³ have investigated the local electron pairing interaction on dangling bonds and weaker/stronger bonds³² (a concept also introduced by Anderson¹⁰) and the resultant electronic structure of the Si-SiO₂ interface.³² Both the dangling bonds and the weaker/stronger bonds give rise to pair states which are strongly self-trapped and have the interesting dynamic character when electrons are excited in pairs. Correlated pair states at the

interface give rise to electron pair excitations with arbitrary low energies and should give rise to 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 characterization 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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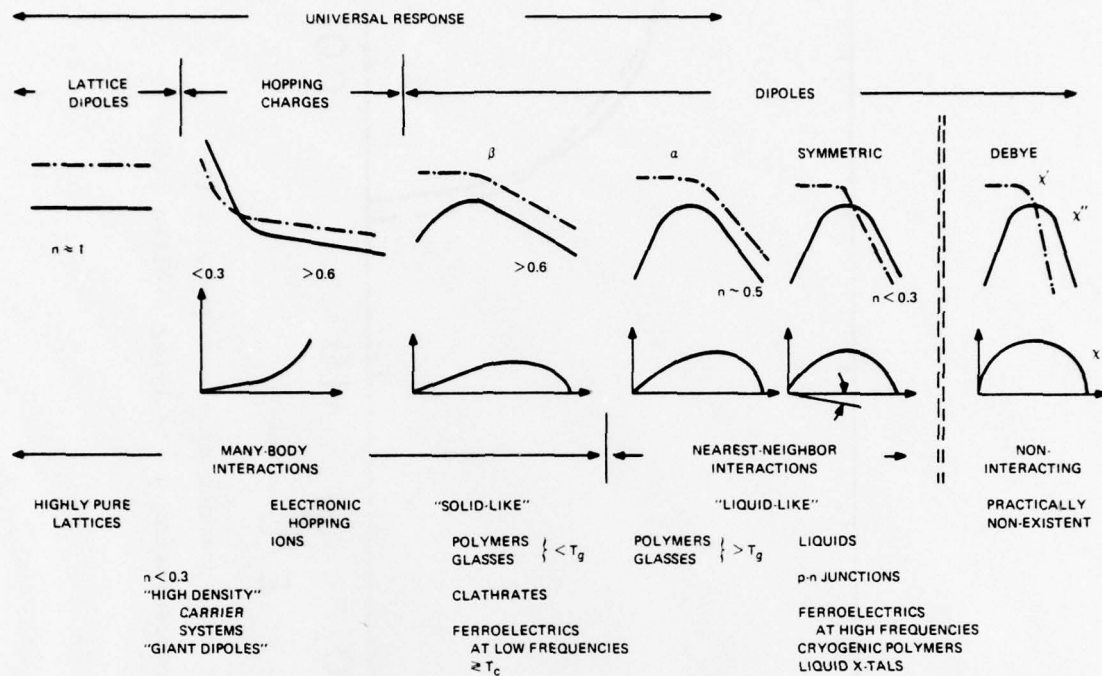


Fig. 1. A schematic representation of the various observed types of dielectric response in the entire range of solids. The upper set of diagrams represent the shapes of the logarithmic plots of $\chi'(\omega)$ -chain-dotted lines, and $\chi''(\omega)$ -solid lines, ranging from the ideal Debye through the α and β peaks and on to the universal dependence for charged carrier systems. The limiting forms of behaviour 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 corresponding complex χ plots. The various types of materials obeying the respective types of response are shown and the presumed polarization mechanisms are indicated.

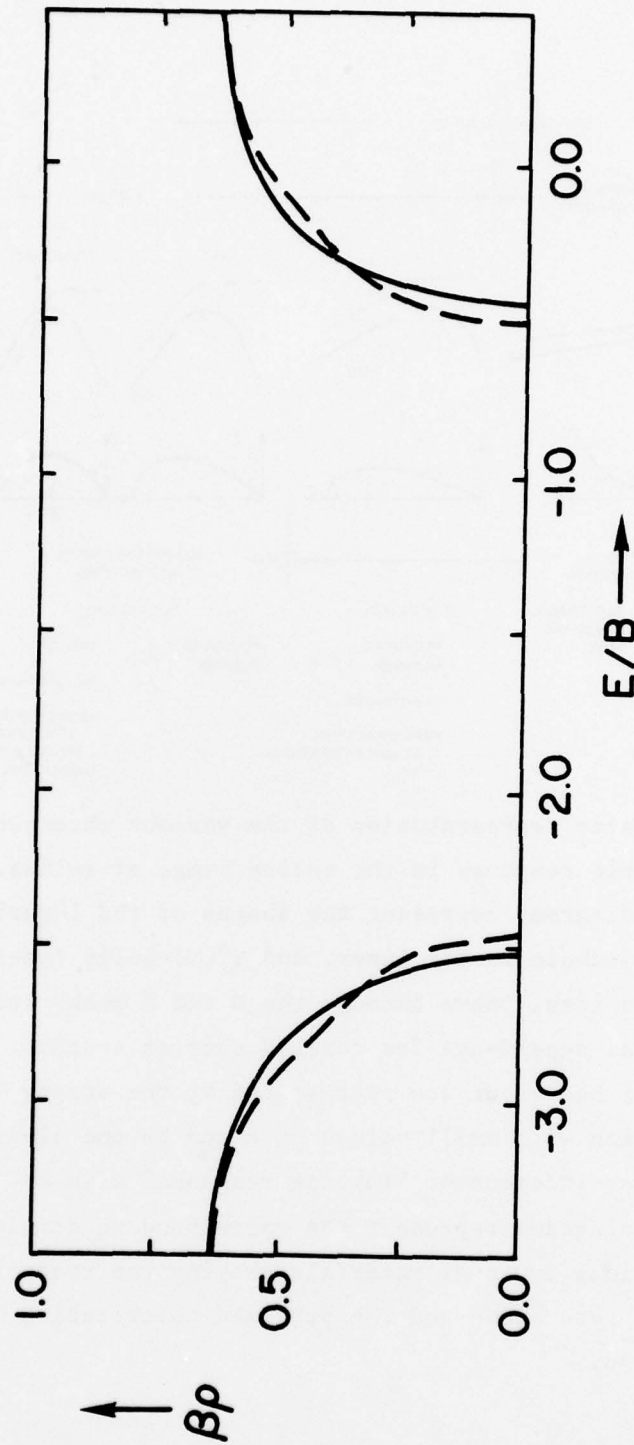


Fig. 2. Illustrates two different arrangements of electrons over the pairing states with (b) representing a low lying excited state of (a).

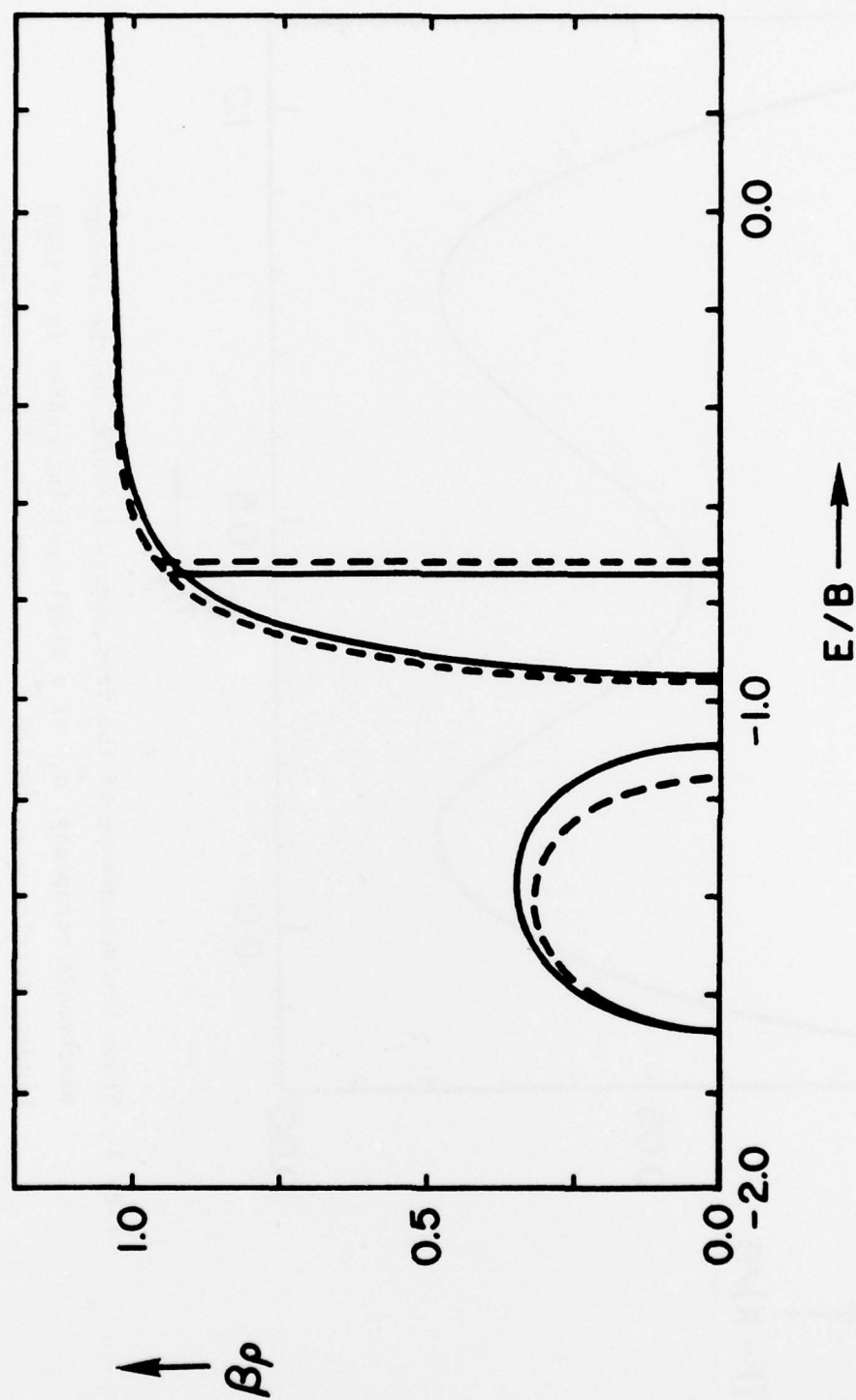


Fig. 3. Illustrates the effects on the electronic spectrum due to transfer of electrons from pairing centers to a non-pairing band.

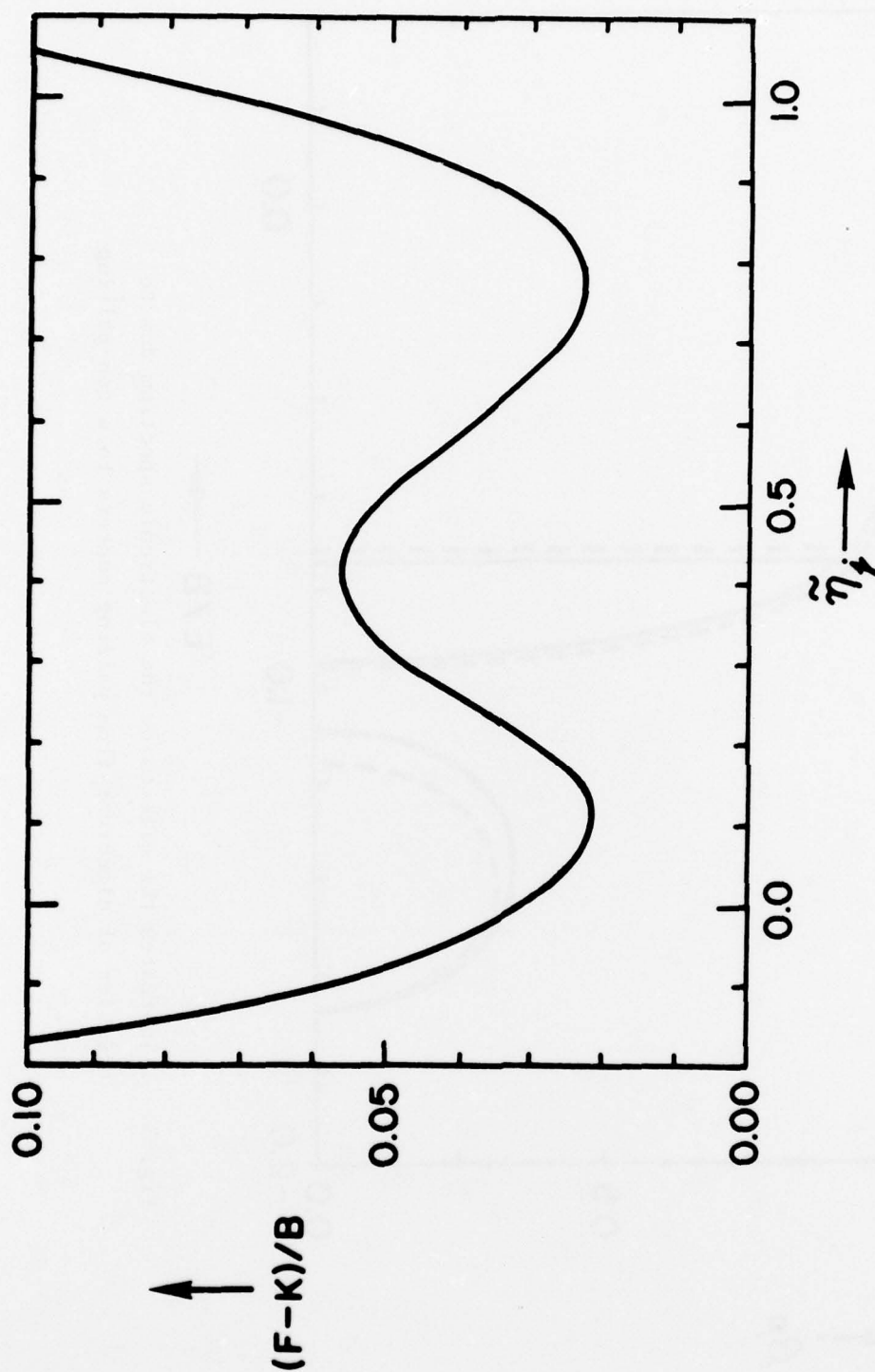


Fig. 4. Shows the dependence of the free energy $(F-K)/\beta$, on the average electronic occupancy, $\bar{n}_j$, of a single pairing center in a tight binding lattice when $|\omega_j|/\beta \hat{=} 1$ and $E_j + U_j/2 \hat{=} E_f$. The zero of energy is taken at the center of the unperturbed band and $U/\beta = 1.6$, $E_f/\beta = -.794$.

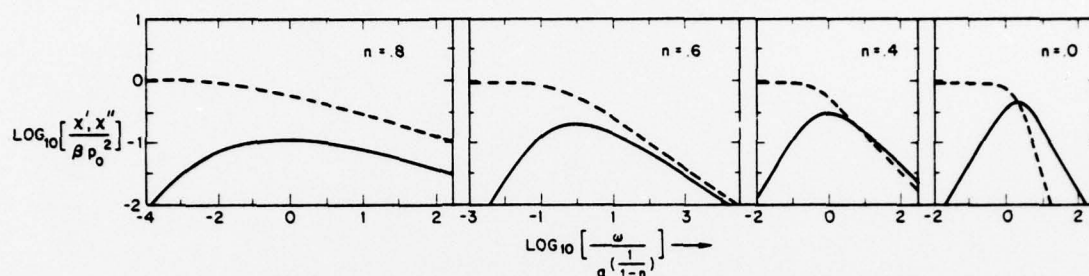


Fig. 5. The behavior of χ' , χ'' in the present theory for several different values of n . Note the peak shape is independent of $a \equiv e^{-n\gamma} / (1-n)\tau_0 E_c^n$ but strongly dependent on n . The slope m of each of these $\log(\chi')$ versus $\log(\omega)$ plots varies continuously from zero 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.