

Theoretical derivation of possible dielectric anomalies in high-permittivity glasses

M. E. Lines

Bell Laboratories, Murray Hill, New Jersey 07974

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The theory of dielectric instabilities in high-permittivity glasses is extended to include the effects of intrinsic glass softening on approach to the crystallization temperature T_{cryst} . A number of marked dielectric features can develop via the interplay of glass softening and dipolar effects. These are described for both nonpolar and polar glass models and include anomalies both at and below T_{cryst} which closely resemble features which have been observed in high-permittivity glasses.

I. INTRODUCTION

Until very recently, materials which are ferroelectric in their crystalline form were obtainable as glasses only when the latter were prepared using an additional network-forming oxide such as SiO_2 .¹⁻³ Although these glasses can be used to study the appearance of ferroelectric properties as a function of grain size on controlled crystallization, the presence of the diluting SiO_2 network makes them of limited use in the study of possible dielectric cooperative phenomena in the glassy phase itself. However, with recent reports^{4,5} that at least some crystalline ferroelectric oxides can be directly quenched from the melt to produce a glassy form without the use of any extraneous glass-forming additive, the question of what, if any, dielectric anomalies might be anticipated for the resulting high-permittivity amorphous material is now relevant.

In an earlier paper⁶ the present author explored the concept of a ferroelectric glass and, on the assumption that basic dielectrically soft building blocks (such as BO_6 units in ABO_3 ferroelectrics, for example) remained identifiable in a randomly distorted form in the glassy matrix, examined the possible consequences of the existence of strong electric dipolar forces between these "units" on the static dielectric response of the glass. The possibility of a dielectric instability in the glassy phase was specifically examined and the character of the resulting polar phase discussed. In the absence of any experimental work the nature of the earlier contribution was necessarily rather academic. However, with the recent publication of the first dielectric measurements performed on glasses formed directly from materials which are ferroelectric in their crystalline form, we are now in a position to consider a little more closely the applicability of the theory to real systems.

In the reported experiments^{4,5} a number of dielectric features are seen both at and below the crystallization temperature with values of dielec-

tric constant ϵ in some cases exceeding 10^5 over sizable temperature regions (values far in excess of the corresponding crystalline equivalents). One obvious extension of the earlier work⁶ which is essential for any understanding of the data is for an allowance to be made for the existence of an intrinsic softening of any glassy material on approach to the crystallization instability. The earlier theory was relevant for a glassy matrix of dielectrically soft units far removed in temperature from crystallization. We shall argue below that the intrinsic glass softening on approach to crystallization at a temperature T_{cryst} is primarily a property of local (i.e., short-range) forces in the glass and thereby occurs relatively independent of the presence or nature of the long-range interactions. Thus, for example, we expect the basic microscopic character of crystallization to be largely unaffected by the presence of strong electric dipole forces at long range. In this case, the effects of intrinsic glass softening as $T \rightarrow T_{\text{cryst}}$ from below are easy to add to the earlier formalism. The details of this extension of the formal theory are reported in this paper. In Sec. II we derive the dielectric susceptibility $\chi = \epsilon/4\pi$ for a glass in an insulating nonpolar phase including the possible development of dielectric instabilities. Section III describes the equivalent calculation for a polar glassy phase. Finally, Sec. IV sketches the qualitative dielectric anomalies both at and near T_{cryst} which can develop via the interplay of intrinsic glass softening and cooperative dipolar effects. We find that these anomalies do include qualitative forms similar to those which have been reported to occur in LiNbO_3 , LiTaO_3 , and $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ glasses.^{4,5}

II. NONPOLAR PHASE

In Ref. 6 a simple microscopic model was set up describing the possible occurrence of a ferroelectric instability in an insulating glassy matrix. This model consisted of a random assembly of ar-

bitrarily distorted dielectrically soft local-atomic configurations interacting via electric dipole forces. Each configuration or unit defines a locally constrained random elementary electric dipole p_i^0 ($\sum_i p_i^0 = 0$) in the "paraelectric" phase which can be perturbed at a dielectric instability to $\vec{p}_i^0 + \vec{p}_i$, with $\sum_i \vec{p}_i \neq 0$, if the angularly averaged long-range dipole forces (which prefer a polar configuration) are sufficiently strong.

In the concept of a unit we formally separate interunit forces into two groups, those involving intraunit ions and those involving interunit ions. The former seek to stabilize the "prototype" symmetry of an undistorted unit (e.g., possibly a tetrahedron- or octahedron-based configuration in the present context) and are expressed in terms of configuration coordinates $\xi_{i,\lambda}$ to define local potential functions, while the latter are expressible as a polynomial in $\xi_{i,\lambda}$ and $\xi_{j,\lambda'}$. For an examination of dielectric properties we restrict ourselves, for simplicity, to a representation involving just those three orthogonal local displacive mode variables per unit ($\lambda = 1, 2, 3$) which are potentially soft from a dielectric standpoint and which are, in fact, degenerate in the case of a high-symmetry prototype which we shall pursue in the present paper. A representative "isolated" (i.e., in the absence of interunit forces) unit is then represented by a local Hamiltonian

$$\mathcal{H}_i = \sum_{\lambda} \left(\frac{1}{2} \pi_{i,\lambda}^2 + \frac{1}{2} \Omega^2 \xi_{i,\lambda}^2 + A \xi_{i,\lambda}^4 \right), \quad (1)$$

in which $\pi_{i,\lambda}$ is the momentum coordinate conjugate to $\xi_{i,\lambda}$, A is an anharmonicity parameter, Ω a local mode frequency, and the local potential has been assumed separable and of quasiharmonic form. Neither assumption is essential and is taken for reasons of algebraic simplicity alone.

Interunit forces are of two kinds; short-range forces which involve all local degrees of freedom and which are primarily responsible for the detailed character and degree of stability of the glassy phase; and long-range forces which are primarily of electric dipole character and which dominate the dielectric characteristics of the material. The former we represent symbolically, as far as a perturbation of Eq. (1) is concerned, by an effective strain field with components $E_{i,\lambda'}$, while the latter is readily expressed (using the dipole-energy matrix v_{ij}) as a simple bilinear coupling between unit variables $\xi_{i,\lambda}$ and $\xi_{j,\lambda'}$. The final-model Hamiltonian is then of the form

$$\mathcal{H} = \sum_{i,\lambda} \left(\frac{1}{2} \pi_{i,\lambda}^2 + \frac{1}{2} \Omega^2 \xi_{i,\lambda}^2 + A \xi_{i,\lambda}^4 - S \xi_{i,\lambda} E_{i,\lambda}^{\text{str}} \right) - \sum_{i,\lambda} \sum_{j,\lambda'} \frac{1}{2} S^2 \xi_{i,\lambda} v_{ij}^{\lambda\lambda'} \xi_{j,\lambda'}, \quad (2)$$

where S is an effective-charge parameter, and λ and λ' refer to directions which are locally orthogonal at a particular site i or j , but which vary in a random fashion with respect to coordinates fixed in space on summation over the macroscopic number of different site locations.

On the assumption that the last term in Eq. (2) is dominated by its long-range contributions, the statistical problem defined by Eq. (2) was solved in Ref. 6 in the mean-field approximation. In particular, the dielectric susceptibility was found to take the form

$$\chi = \chi_{\text{av}}^s / [1 - v_d(0) \chi_{\text{av}}^s], \quad (3)$$

in which χ_{av}^s is the isolated unit response configurationally averaged over the random local strain field, and $v_d(0) = \frac{4}{3} \pi$. Explicitly, for the local strained units defined in Eq. (2), the isolated unit response is⁶

$$\chi_{\text{av}}^s = \alpha - (12AS^2kT/\Omega^6), \quad (4)$$

to lowest order in anharmonicity A , where

$$\alpha = (S^2/\Omega^2) [1 - 12A \langle (\xi_{\lambda}^0)^2 \rangle_{\text{av}} / \Omega^2], \quad (5)$$

in which $\langle (\xi_{\lambda}^0)^2 \rangle_{\text{av}}$ is the mean-square static local coordinate displacement from prototype symmetry produced by the random strain field.

In the earlier paper, both Ω and $\langle (\xi_{\lambda}^0)^2 \rangle_{\text{av}}$ were taken to be independent of temperature T , in which case the glass susceptibility is always an increasing function of $1/T$ and may diverge, defining a ferroelectric instability within the glassy matrix if χ_{av}^s ever becomes large enough to make $v_d(0) \chi_{\text{av}}^s = 1$. We shall now argue that in a real glass, and particularly on approach to crystallization, both Ω and $\langle (\xi_{\lambda}^0)^2 \rangle_{\text{av}}$ are intrinsically temperature dependent as a result of the softening of the glass as it approaches its crystallization instability. From Eqs. (3)–(5) we see that the major perturbation of response resulting from these effects will be via the local frequency Ω and we shall concentrate on this effect alone in the present work.

Physically, the point in question is to what extent is the local strain field $E_{i,\lambda}^{\text{str}}$ perturbed by the dynamic motion of the i th unit itself. The strain field is produced by the near-neighbor units which are in local equilibrium under the influence of all near-neighbor forces. In particular, since the latter couple to some degree with the polar mode ξ_{λ} at each site, the local environment of the i th unit will respond to a change in the value of displacement $\xi_{i,\lambda}$. In other words, $E_{i,\lambda}^{\text{str}}$ is a function of $\xi_{i,\lambda}$ and may therefore, in lowest order, be expressed in the form

$$E_{i,\lambda}^{\text{str}} = E_{i,\lambda}^0 + E_{i,\lambda}^{\text{str}} \xi_{i,\lambda}. \quad (6)$$

We neglect correlations between $E_{i,\lambda}^{\text{str}}$ and $\xi_{i,\lambda'}$, ($\lambda' \neq \lambda$) for simplicity only. We propose that the local environment adjusts to the i th cell motion to an increasing degree as the crystallization instability at T_{cryst} is approached from below (i.e., $E_{i,\lambda}^{\text{str}}$ is temperature dependent) and it is in this sense we refer to the glass as becoming "soft" as $T \rightarrow T_{\text{cryst}}^-$.

If we use the relation Eq. (6) in the equation of motion for the mode $\xi_{i,\lambda}$ we obtain

$$\pi_{i,\lambda} = -\Omega^2 \xi_{i,\lambda} - 4A \xi_{i,\lambda}^3 + S(E_{i,\lambda}^{\text{str}} + E_{i,\lambda}^{\text{str}*} \xi_{i,\lambda}) + \sum_{j,\lambda'} S^2 v_{ij}^{\lambda\lambda'} \xi_{j,\lambda'}. \quad (7)$$

Using Hamilton's equations of motion, this form, Eq. (7), results directly from the effective Hamiltonian

$$\mathcal{H}^{\text{eff}} = \sum_{i,\lambda} \left(\frac{1}{2} \pi_{i,\lambda}^2 + \frac{1}{2} \Omega_{i,\lambda}^2(T) \xi_{i,\lambda}^2 + A \xi_{i,\lambda}^4 - S \xi_{i,\lambda} E_{i,\lambda}^{\text{str}} \right) - \sum_{i,\lambda} \sum_{j,\lambda'} \frac{1}{2} S^2 \xi_{i,\lambda} v_{ij}^{\lambda\lambda'} \xi_{j,\lambda'}, \quad (8)$$

in which the "effective" local frequency $\Omega(T)$ is given by

$$\Omega_{i,\lambda}^2(T) = \Omega^2 - S E_{i,\lambda}^{\text{str}}, \quad (9)$$

the only changes from the Hamiltonian, Eq. (2), solved in Ref. 6 to the new Hamiltonian, Eq. (8), being the purely symbolic one $E_{i,\lambda}^{\text{str}} \rightarrow E_{i,\lambda}^{\text{str}} + S \xi_{i,\lambda} E_{i,\lambda}^{\text{str}}$ and the recognition of the temperature-dependent local harmonic frequency defined by Eq. (9), where for the high-symmetry prototype the subscript λ can now be dropped.

The softening of local frequency $\Omega(T)$ is a near-neighbor force phenomenon and is therefore, in the long-range mean-field v_{ij} approximation used to solve the dielectric many-body problem in Ref. 6, completely independent of the cooperative dipolar aspects of the problem. We may therefore obtain the solutions for mean-field dielectric response on approach to crystallization in a glass by simply substituting the temperature-dependent $\Omega(T)$ for Ω in the earlier solutions Eqs. (3)–(5). First, however, we must ascertain the anticipated form for $\Omega(T)$ as a function of T . From the correlated effective-field theory of structural or magnetic phase transitions the general behavior of a local correlated field parameter such as $E_{i,\lambda}^{\text{str}}$ is known.^{7,8} Starting from small values at temperatures remote from the relevant instability (e.g., T_{cryst}) it increases at a steadily increasing rate as $T \rightarrow T_{\text{cryst}}$ to approach a finite value with finite slope at $T = T_{\text{cryst}}$. The detailed form of this temperature dependence is a function of the nature of the driving forces producing the instability and

very little is known at this time about the molecular dynamics of the glass-crystal transition. We have therefore chosen to use for the temperature dependence of the local frequency $\Omega(T)$ a simple empirical two-parameter form which satisfies all the qualitative criteria set out above, but which, of course, we do not expect to be particularly quantitatively valid over a wide temperature range; it is

$$\Omega^2(t) = \Omega^2(1 - \Delta e^{-\rho(1-t)}), \quad (10)$$

in which $t = T/T_{\text{cryst}}$. The alternative procedure of expanding $\Omega(t)$ as a Taylor series in t could, of course, be used, but would necessarily involve more parameters.

Substituting $\Omega(t)$ of Eq. (10) in Eqs. (4) and (5), and expanding to first order of smallness in Δ and A , we obtain

$$\chi_{\text{av}}^s = \alpha(1 + a e^{-\rho(1-t)} - bt), \quad (11)$$

where

$$a = S^2 \Delta / \Omega^2 \alpha, \quad b = 12 A S^2 k T_{\text{cryst}} / \Omega^6 \alpha, \quad (12)$$

with a , and b positive and small compared with unity. The zero-field glass susceptibility follows immediately from Eq. (3) in the form

$$\chi = \frac{(1 + a e^{-\rho(1-t)} - bt) \alpha}{1 - v_d(0) \alpha (1 + a e^{-\rho(1-t)} - bt)}. \quad (13)$$

III. POLAR PHASE

Equation (13) is valid only in a nonpolar phase (for which the denominator is positive). If for any t this denominator goes to zero, then a polar instability is precipitated within the model. In the polar phase, the general character of which was discussed in Ref. 6, the glass susceptibility is still given by the form of Eq. (3), but where now the single-unit response χ_{av}^s must be interpreted as the differential susceptibility at the finite local dipolar field E_0 produced by the long-range dipolar order. It is therefore necessary to work with the finite-field single-unit response function

$$\chi_{\lambda, \text{av}}^s(E_\lambda) = \alpha - 12 A S^2 k T / \Omega^6 - 12 A S^4 E_\lambda^2 / \Omega^8, \quad (14)$$

taken from Eq. (6.1) of Ref. 6. Substituting the temperature-dependent local frequency $\Omega(t)$ of Eq. (10) in place of Ω in Eq. (14), and expanding to the first order of smallness in Δ and A , gives

$$\chi_{\lambda, \text{av}}^s(E_\lambda) = \alpha(1 + a e^{-\rho(1-t)} - bt - c E_\lambda^2), \quad (15)$$

in which a and b are again given by Eqs. (12), and

$$c = 12 A S^4 / \Omega^8 \alpha. \quad (16)$$

The two basic equations required from the for-

mal theory of Ref. 6 for the polar glassy phase are those for the isolated unit glass response $\chi_{av}^s(E)$ and for the equilibrium value of local dipolar field E_0 in the absence of applied field [Eqs. (4.3) and (4.6) of that paper, respectively]. For the high-symmetry prototype case these are

$$\chi_{av}^s(E) = 3\alpha \langle (1 + ae^{-\rho(1-t)} - bt) \cos^2\theta - cE^2 \cos^4\theta \rangle_\theta \quad (17)$$

and

$$\chi_{av}^s(E_0) = 1/v_d(0), \quad (18)$$

where the average $\langle \dots \rangle_\theta$ is a spherical average over the polar angle θ . Using the spherical averages $\langle \cos^2\theta \rangle_\theta = \frac{1}{3}$, $\langle \cos^4\theta \rangle_\theta = \frac{1}{5}$, Eq. (17) reduces to

$$\chi_{av}^s(E) = \alpha \left[1 + ae^{-\rho(1-t)} - bt - \left(\frac{3}{5}\right) cE^2 \right]. \quad (19)$$

Let us now consider the glass polarization in the absence of an applied field but in the presence of an infinitesimal *local* perturbing field dE . In the unperturbed case the spontaneous polarization P_0 is

$$P_0 = \chi_{av}^s(E_0)E_0, \quad (20)$$

while in the presence of the perturbing field it becomes

$$P_0 + dP = \left[\chi_{av}^s(E_0) + \left(\frac{\partial \chi_{av}^s(E)}{\partial E} \right)_{E_0} dE \right] (E_0 + dE). \quad (21)$$

Substituting Eq. (19) in Eqs. (20) and (21) we can now explicitly relate dP to dE to define the differential susceptibility $\chi_{av,d}^s = dP/dE$ in the form

$$\chi_{av,d}^s = \alpha \left(1 + ae^{-\rho(1-t)} - bt - \frac{6}{5} cE_0^2 \right). \quad (22)$$

However, E_0 as a function of t is known from Eq. (18), viz.,

$$\frac{3}{5} \alpha c E_0^2 = \alpha (1 + ae^{-\rho(1-t)} - bt) - 1/v_d(0). \quad (23)$$

Substituting into Eq. (22) gives the final form

$$\chi_{av,d}^s = 3/v_d(0) - 2\alpha(1 + ae^{-\rho(1-t)} - bt). \quad (24)$$

Using this in place of χ_{av}^s in Eq. (3) gives us, finally, the response of the polar glass to an infinitesimal applied uniform Maxwell field. It is

$$\chi = \frac{3/v_d(0) - 2\alpha(1 + ae^{-\rho(1-t)} - bt)}{2\alpha v_d(0)(1 + ae^{-\rho(1-t)} - bt) - 2}. \quad (25)$$

More succinctly, the responses Eqs. (13) and (25) for the nonpolar and polar phases, respectively, may therefore be written

$$\chi/\alpha = \Theta / (1 - \alpha v_d(0)\Theta), \quad \text{nonpolar}, \quad (26)$$

and

$$\chi/\alpha = [1.5/\alpha v_d(0) - \Theta] / [\alpha v_d(0)\Theta - 1], \quad \text{polar}, \quad (27)$$

in which

$$\Theta = 1 + ae^{-\rho(1-t)} - bt. \quad (28)$$

The phase transition occurs if ever the condition $\alpha v_d(0)\Theta = 1$ is reached; otherwise the glass can exist throughout its range of metastability in either the polar or nonpolar configuration. Writing $t = t_C$ at the ferroelectric Curie point and considering small deviations $dt = t - t_C$ of temperature from the instability, we find from Eqs. (26) and (27)

$$\alpha\chi^{-1} = -q dt/\Theta_C^2, \quad \text{nonpolar}, \quad (29)$$

$$\alpha\chi^{-1} = 2q dt/\Theta_C^2, \quad \text{polar}, \quad (30)$$

in which Θ_C is the value of Θ at the Curie point $t = t_C$, and

$$q = a\rho e^{-\rho(1-t_C)} - b. \quad (31)$$

We regain the familiar mean-field Curie-Weiss finding for second-order transitions with the slope of the reciprocal susceptibility in the "ordered" phase being minus two times the equivalent property in the "disordered" phase. However, the sign of q is now no longer necessarily negative as in conventional theories (the condition which requires the disordered phase to be higher in temperature than the ordered phase). If the glass-softening contribution $a\rho \exp[-\rho(1-t_C)]$ outweighs the anharmonicity contribution b in Eq. (31), then the polar phase can, at least within the model, occur at the higher temperature. In fact, as we shall see below, the equation for the existence of a dielectric instability $\alpha v_d(0)\Theta = 1$ can have more than one solution $t = t_C$ so that the range of possible types of dielectric phenomena predicted by the model is quite varied. We shall examine these in more detail in Sec. IV.

IV. POSSIBLE TYPES OF DIELECTRIC ANOMALY IN GLASSES NEAR CRYSTALLIZATION

Far from crystallization, where glass-softening effects are small, the present theory reduces to that discussed in Ref. 6. In the present paper we therefore focus on anomalies which can occur at or near the crystallization temperature $t = 1$ and for which a of Eq. (12) is at least of the same order of magnitude as b . Perhaps the most common situation will be that of a glass which never becomes critically soft and remains nonpolar throughout. Consider, for simplicity, the case $a \gg b$ in Eq. (13). Putting $b = 0$ and setting

$$1 - (1 + a)v_d(0)\alpha > 0, \quad \text{nonpolar}, \quad (32)$$

we generate susceptibility curves of the kind shown in Fig. 1. The common feature is a cusp at T_{cryst} with a positive curvature as $t \rightarrow 1$. The "soft unit" polarizability α is directly determined by the value of the static susceptibility χ far from T_{cryst}

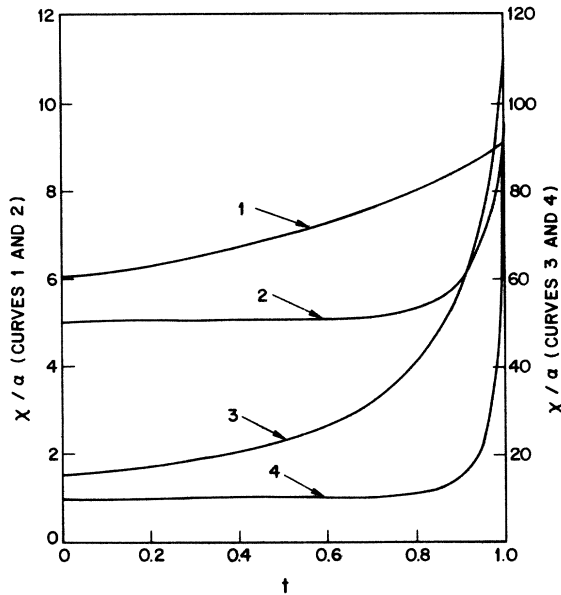


FIG. 1. Dielectric susceptibility as a function of reduced temperature $t = T/T_{\text{cryst}}$ for a dielectrically soft nonpolar glass, as calculated from Eq. (13) using parameters $b = 0$, $a = 0.1$, and (curve 1) $v_d(0)\alpha = 0.8$, $\rho = 1$; (curve 2) $v_d(0)\alpha = 0.8$, $\rho = 10$; (curve 3) $v_d(0)\alpha = 0.9$, $\rho = 1$; (curve 4) $v_d(0)\alpha = 0.9$, $\rho = 10$.

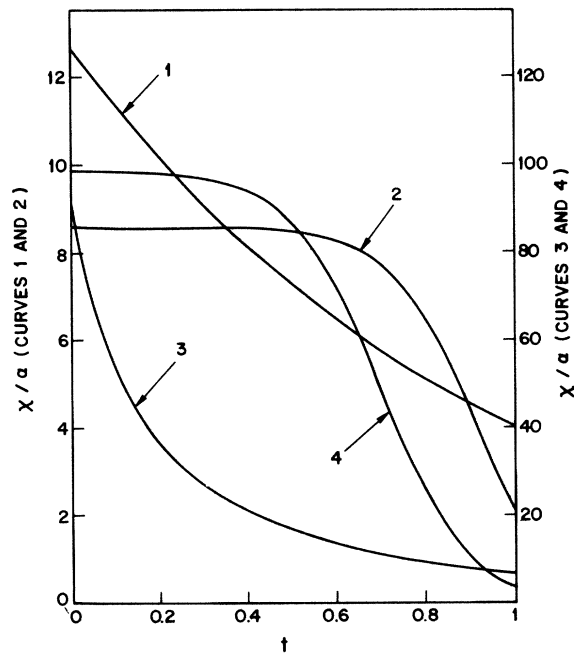


FIG. 2. Dielectric susceptibility as a function of reduced temperature $t = T/T_{\text{cryst}}$ for a dielectrically soft polar glass, as calculated from Eq. (25) using parameters $b = 0$, $a = 0.1$, and (curve 1) $v_d(0)\alpha = 1$, $\rho = 1$; (curve 2) $v_d(0)\alpha = 1.05$, $\rho = 10$; (curve 3) $v_d(0)\alpha = 0.97$, $\rho = 1$; (curve 4) $v_d(0)\alpha = 1.005$, $\rho = 10$.

(e.g., as $t \rightarrow 0$), where the response is approximately temperature independent. In this region $\Theta \approx 1$ and

$$\chi \approx \chi_0 = \alpha / (1 - \frac{4}{3}\pi\alpha). \quad (33)$$

The detailed nature of the cusp determines, within the model, the parameters a and ρ which characterize the glass softening.

The opposite extreme of having a polar phase throughout is described by Eq. (25) when

$$1 - (1 + ae^{-\rho})v_d(0)\alpha < 0, \text{ polar}. \quad (34)$$

For this case the model assumes the existence of a single polar domain oriented parallel to the applied field and neglects all the complexities con-

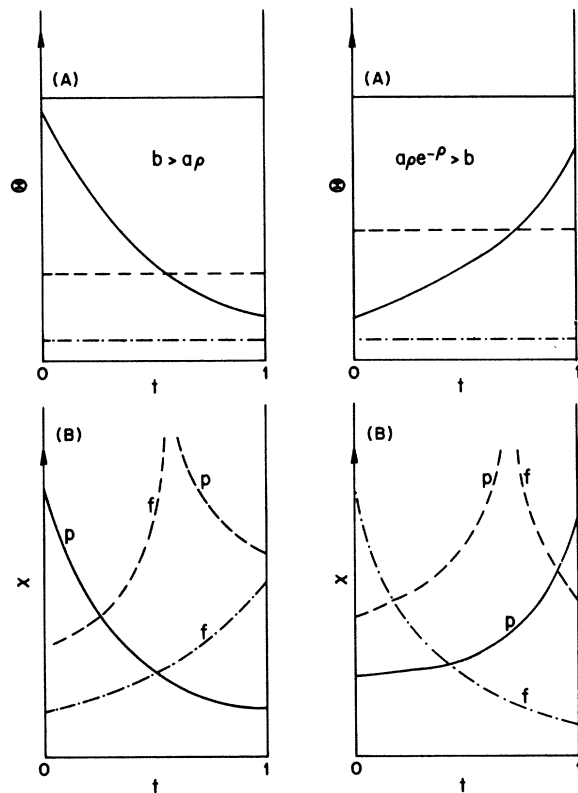


FIG. 3. (A) Two qualitatively different monotonic forms which the function Θ of Eq. (28) can adopt as a function of reduced temperature t (occurring when $b > a\rho$ and $a\rho e^{-\rho} > b$, respectively). Also shown in (A) are three separate horizontal lines denoting different constant values $1/[v_d(0)\alpha]$, the intersection of Θ with which produces a dielectric instability. The (full, dashed, and dot-dashed) curves (B) indicate the qualitative forms of static dielectric response χ [from Eqs. (26) and (27)] resulting for each of the correspondingly marked $1/[v_d(0)\alpha]$ lines in the associated (A) diagram above it. In (B), p denotes a paraelectric phase, and the symbol f a ferroelectric (or polar) phase.

cerning possible domain formation and growth strain anisotropy which would likely be important in unpoled samples. Typical susceptibility curves for the $b=0$ polar situation are shown in Fig. 2. As can be seen from the figure, the trend in this case is for χ to be a decreasing function of t .

More generally, of course, we must consider situations for which the parameter b is nonzero, e.g., $a \sim b \ll 1$. The qualitative possibilities resulting from this situation are readily understood by putting $\alpha v_d(0) \approx 1$ and $\Theta \approx 1$ in the numerators of Eqs. (26) and (27), viz.,

$$\chi \approx \frac{1/v_d(0)}{[v_d(0)\alpha]^{-1} - \Theta}, \text{ nonpolar,} \quad (35)$$

$$\chi \approx \frac{0.5/v_d(0)}{\Theta - [v_d(0)\alpha]^{-1}}, \text{ polar,} \quad (36)$$

and considering graphically the function $\Theta - [v_d(0)\alpha]^{-1}$, where the last term is just a constant, as a function of reduced temperature t . From Eq. (28) which defines Θ we see that $\partial^2\Theta/\partial t^2 = a\rho^2 \exp[-\rho(1-t)]$ is always positive. The qualitatively different forms which the function $\Theta(t)$ can have, therefore, are shown in Figs. 3 and 4. By

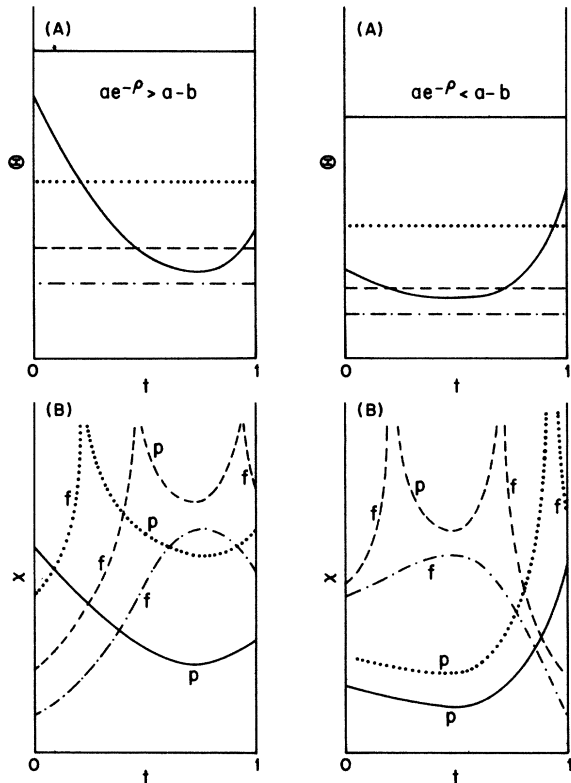


FIG. 4. Same as Fig. 3 but for parameter values $a\rho > b > a\rho e^{-\rho}$ which allow Θ of Eq. (28) to be double valued as a function of reduced temperature $t = T/T_{\text{cryst}}$.

considering the possible intersections of these curves with the constant $1/v_d(0)\alpha$ (i.e., the possible dielectric instabilities) the qualitative forms of the possible susceptibility curves are immediately evident from Eqs. (35) and (36). They are also shown in Figs. 3 and 4 below the corresponding Θ curves. Wherever $\Theta > [v_d(0)\alpha]^{-1}$, the polar phase is stable; wherever $\Theta < [v_d(0)\alpha]^{-1}$, the nonpolar phase is stable.

Most intriguing are the situations for which two instabilities arise, with a nonpolar phase sandwiched between two polar phases. This can arise

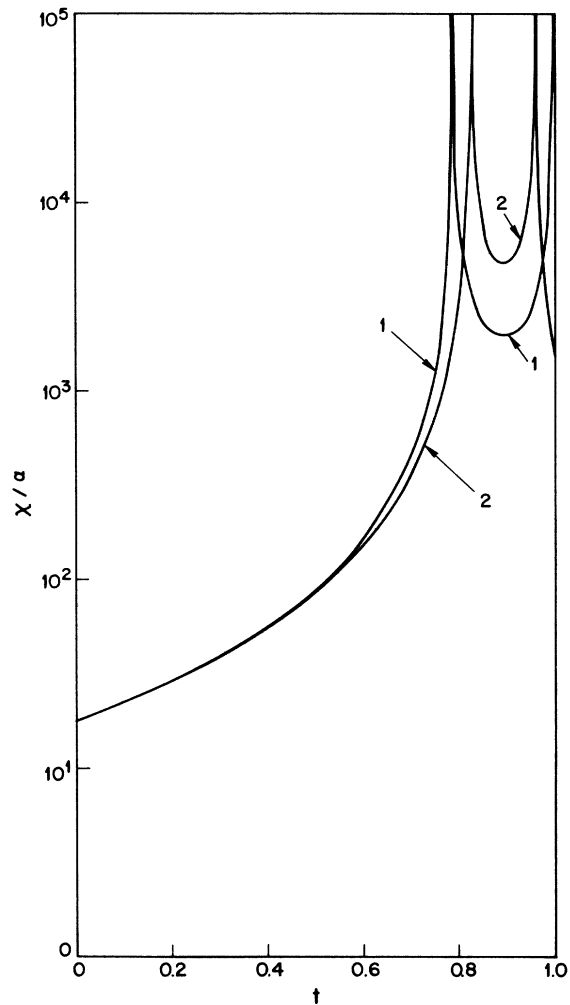


FIG. 5. Dielectric susceptibility as a function of reduced temperature $t = T/T_{\text{cryst}}$ as calculated from Eqs. (13) and (25) for two cases which show a double susceptibility divergence. The curves are both for parameter values $a = 0.1$, $b = 0.09$, $\rho = 1$, but with curve 1 having $v_d(0)\alpha = (1+a-b)^{-1}$, the condition which produces a dielectric divergence at the crystallization temperature itself, and curve 2 having the slightly larger value $v_d(0)\alpha = (1+a-b)^{-1} + 0.0003$.

when $a\rho > b > a\rho e^{-\rho} > \rho(a-b)$ for suitable $v_d(0)\alpha$ values and we examine this situation more quantitatively in Fig. 5. We note that a dielectric instability can even result at T_{cryst} itself if

$$v_d(0)\alpha = \Theta_{\text{cryst}}^{-1} = (1+a-b)^{-1}, \quad (37)$$

where Θ_{cryst} is the value of Θ at the crystallization temperature. In this instance the location of the second singularity is particularly simple to evaluate analytically. Substituting Eq. (37) in Eq. (26) we find

$$\chi/\alpha = \Theta \Theta_{\text{cryst}} / (\Theta_{\text{cryst}} - \Theta), \quad (38)$$

which diverges when $\Theta = \Theta_{\text{cryst}}$, viz., when

$$ae^{-\rho(1-t)} - bt = a - b. \quad (39)$$

For small values of $1-t$ we can expand the exponential to obtain, in second order,

$$(1-t)[a\rho - \frac{1}{2}a\rho^2(1-t) - b] = 0, \quad (40)$$

with solutions

$$t = t_C^{(1)} = 1, \quad t = t_C^{(2)} = 1 - 2(a\rho - b)/a\rho^2. \quad (41)$$

However, since these findings are based only upon the empirical form assumed for local-mode glass softening, i.e., Eq. (10), too much significance should perhaps not be attached to the precise analytic forms at this time.

V. DISCUSSION

The important conclusions from the above analysis are the qualitative predictions of Figs. 3 and 4 namely, that a cooperative dipolar mechanism, coupled with a local lattice vibrational softening on approach to a glass to crystalline instability, can give rise to possible dielectric anomalies of varied forms both at and below the crystallization temperature itself.

Experimentally, the three dielectrically soft glasses $\text{Pb}_5\text{Ge}_3\text{O}_{11}$, LiTaO_3 , and LiNbO_3 for which we already have susceptibility data each exhibit qualitatively different behavior on approaching to T_{cryst} . The first ($\text{Pb}_5\text{Ge}_3\text{O}_{11}$) appears to be para-

electric throughout and the susceptibility rises monotonically with increasing T to exhibit a sharp cusp⁴ at T_{cryst} of the form shown in Fig. 3(B) for $a\rho e^{-\rho} > b$. LiTaO_3 has a similar response as a function of T except that the magnitude of the dielectric constant is much larger and the anomaly at T_{cryst} is more rounded⁵ and may peak below the crystallization instability. If so, this could indicate the existence of a polar glassy phase (i.e., the f curve of Fig. 4(B) for $ae^{-\rho} > (a-b)$). Finally, and most intriguingly, LiNbO_3 glass exhibits a double-peaked anomaly⁵ like curve 1 of Fig. 5, again with extremely high values ($>10^5$) for the dielectric constant. This implies, within the present model not only the existence of a polar glassy phase but actually of a polar glassy phase transition.

In each of the above three cases, good quantitative fits to the susceptibility data can be obtained using Eqs. (26) and (27) with appropriate parameters. However, no great significance should be attached to this at the present time since there is evidence⁵ that at least a significant (and perhaps dominant) contribution to the dielectric constant close to crystallization may be due to interfacial polarization caused by Li^+ -ion motion in the lithium-containing glasses. This facet of the problem has not been included in the model of this paper. However, an increasing ionic conductivity on approaching T_{cryst} would not seem to account for the double-peaked character of the LiNbO_3 response, and the possibility that the lower-temperature peak does indeed mark a ferroelectric Curie temperature T_C remains an intriguing possibility. The glass can be poled⁵ and shows quite a strong pyroelectric effect at room temperature after poling. This response persists at least for several days but is lost on heating above T_C . This is consistent with the existence of a spontaneously polarized glassy phase below T_C but is not conclusive because the "transition" at T_C is not sharp and the polar nature could result merely from electret formation on poling due to the extremely large values of dielectric constant at the poling temperature.

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