

Microscopic model for a ferroelectric glass

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This paper explores the concept of a ferroelectric glass and finds no fundamental objection to the concept. The essential ingredient is a dielectrically soft local atomic configuration which remains identifiable, though possibly badly distorted, in the glassy matrix. A specific model of such a glassy phase is constructed and a simple statistical theory developed to determine the necessary conditions favoring a dielectric instability. Since the essential "destabilizing" forces are of long range (the electric dipolar forces) the required averages can be performed explicitly even in ignorance of the local microscopic details of the structure. We conclude that a dielectric instability in a dielectrically soft glass can certainly not be excluded by these arguments, particularly for systems in which the basic soft unit has a high degree of symmetry in its "prototype" or undistorted form (such as the BO_6 unit in the ABO_3 crystalline ferroelectrics). The concept of a ferroelectric glass is in no way related to that of a ferroelectric ceramic, the properties of which are very closely related to those of the parent single crystal.

I. INTRODUCTION

A fundamental characteristic of the crystalline ferroelectric phase transition is the existence of a high-symmetry local crystallographic unit, or group of atoms, which distorts slightly below the Curie temperature T_C to create an elementary electric dipole configuration. Although the local high symmetry may sometimes only exist in a statistical or thermally averaged sense (as in the case of order-disorder ferroelectrics) the basic atomic displacements involved are small (typically ~ 0.1 Å) and can be switched, or reversed, by application of an external electric field. Polar materials with atomic displacements much larger than this are typically pyroelectric, not switchable by an applied field and with no disordering temperature below the melting point. The essential ingredient of crystalline ferroelectricity therefore appears to be the existence of a dielectrically "soft" local configuration of atoms (e.g., a BO_6 group in the ABO_3 perovskite and pseudo-perovskite ferroelectrics, the NO_2 group in sodium nitrite, etc.) which can become destabilized below a certain temperature, T_C , by the influence of long-range electric dipole forces which energetically prefer a polar structure.

In the microcrystallite model¹ of the glassy state it is still possible to locate identifiable local atomic configurations which are joined by irregular bonds and atom bridges to each other, but these units are randomly oriented and most importantly are in all probability badly distorted in a random manner from any prototypic "high-symmetry unit." In particular, for the case of dielectrically soft prototypic units such as octahedral BO_6 , the actual

distorted local units will in general possess spontaneous dipole moments of random magnitude and relative orientation already frozen into the glassy matrix even though their sum over the macroscopic sample vanishes. As distinct from the high-temperature phase of a crystalline order-disorder system very few if any of the local atomic configurations will undergo the thermally activated reversibility of local dipole moment characteristic of the order-disorder ferroelectric, and most of the elementary electric dipoles in the glass must remain nonzero and essentially constrained at all temperatures for which the glassy form can be maintained. Conceptually therefore any possible dielectric instability in the glassy state must take place, if at all, with respect to such a "random antipolar" configuration. It is not difficult to describe the nature of a possible ferroelectric phase which might result in this way. Thus, for example, let us imagine each basically constrained elementary electric dipole \vec{p}_i^0 to be perturbed at a dielectric instability to $\vec{p}_i^0 + \vec{p}_i$. Since $\sum_i \vec{p}_i^0 = 0$ by definition, it is only necessary to postulate a nonzero resultant for $\sum_i \vec{p}_i$ to define a spontaneously polar glassy phase. Upon switching it is only necessary that $\sum_i \vec{p}_i$ change sign, which does not require that any specific $\vec{p}_i \rightarrow -\vec{p}_i$ and certainly does not imply any changes $\vec{p}_i^0 \rightarrow -\vec{p}_i^0$.

It follows that there is no conceptual difficulty in perceiving a ferroelectric instability within a glass despite the presence of large irreversibly constrained elementary dipoles throughout the matrix at all temperatures. In this paper we shall explore the microscopic statistical mechanism which might give rise to such an instability and attempt to estimate (a) whether such an instability

can be justified statistically via a simple model calculation and (b) whether such instabilities are likely to occur in practice.

II. STATISTICAL MODEL

Consider first a representative basic distorted local unit (i.e., configuration of ions) centered at the i th coordinate site within the glass. This representative unit will be formally described later as a randomly distorted form of the prototypic unit so that the fundamental assumption of the theory is an ability to define a local prototypic unit in an unambiguous way. In glasses for which the equivalent crystalline unit cell dimensions are smaller than the distance (typically 10–15 Å) over which the local glass environment is recognizable as a moderately distorted form of the corresponding microcrystalline array (e.g., perovskite glasses) the prototypic unit can be taken equal to the equivalent crystalline unit cell. For other cases; we take to be potentially ferroelectric only those for which a small group of atoms within the equivalent crystalline unit cell is physically recognizable as the origin an actually or potentially reversible local electric dipole and is still identifiable as a unit in the glass.

With this definition of a “unit” we formally separate interior forces into two groups; those involving intraunit ions and those involving interunit ions. The former, which basically stabilize the prototype symmetry of the undistorted unit, are expressed in terms of configurational coordinates to define local potential functions, and we retain interest only in those local modes $\xi_{i,\lambda}$ (see Sec. III) which are optically active and which therefore contribute directly to the local electric dipole moment. Of the interunit forces, which in principle can now be formally expressed as polynomials in the interunit configurational coordinates, we retain only terms bilinear in $\xi_{i,\lambda}\xi_{j,\mu}$. These are made up in general of short-range repulsive forces and of electric dipolar contributions which are of both short and long range. Since ferroelectric transitions almost invariably exhibit mean-field critical properties, and the latter demonstrate a dominance of long-range forces in creating the associated dielectric instability, we shall throughout this paper approximate the interunit interactions by electric dipolar forces alone.

The formal statistical approximation to be used will be a neglect of interunit dipole correlations. However, the effective field formalism to be set out is actually able to account for possible regions of correlated motion larger than one unit as defined above. To the extent that the theory is able to interpret experimental data for any particular

case, the “best fit” values of the relevant effective Hamiltonian parameters can be calculated. One can then estimate at least in principle what fraction of the dipolar energy is contained in the random-phase (effective field) term and what fraction should therefore be attributed to the correlated atoms. In this manner a “correlation volume” can be deduced which may include several units as defined above. In this paper, however, we shall not dwell on such parameter interpretational matters or on the physically most accurate interpretation of the displacement coordination $\xi_{i,\lambda}$ for any supposed specific microscopic structural situation. We shall simply assume a prototypic unit as defined above and formally define a statistical (mean-field) approximation which replaces interunit bilinear interactions by a mean-field.

We suppose initially that we are in a macroscopically nonpolar phase. Let us describe the static dielectric response of the representative i th unit to a small uniform perturbing electric field \vec{E} in two separate circumstances; firstly in the supposed absence of any electric dipolar forces between the constituent units and second in the actual physical situation with the dipolar forces present. In the first case we define a so-called “single-unit” response,² denoted by superscripts s , in the form

$$\vec{p}_i^s = \vec{\chi}_i^s \cdot \vec{E}, \quad (2.1)$$

where the single-unit zero-field dielectric susceptibility $\vec{\chi}_i^s$ describes the static response of the equilibrium constrained dipole moment \vec{p}_i^0 to the field. We shall take \vec{E} to be an internal Maxwell field rather than an external applied field thereby setting aside any questions relating to macroscopic boundary conditions. In the second case, with dipolar forces included, we define the actual physical i th-unit response in the analogous form

$$\vec{p}_i = \vec{\chi}_i \cdot \vec{E}. \quad (2.2)$$

The simplest statistical approximation we can make is the mean-field approximation in which we now replace all local unit ionic configurations j by their thermal averages. In this approximation the dipole-dipole interactions between unit i and all the others can be replaced by an effective internal field \vec{E}_i^{eff} so that the actual response \vec{p}_i to applied (uniform) field \vec{E} becomes equivalent to the single-unit response \vec{p}_i^s to the effective field, i.e.,

$$\vec{p}_i = \vec{\chi}_i^s \cdot \vec{E}_i^{\text{eff}}. \quad (2.3)$$

We now consider a thermally averaged local unit configuration of ions centered at site $j \neq i$ in the presence of an applied Maxwell field \vec{E} in the di-

rection Z . The local unperturbed dipole moment at j is, by definition, \vec{p}_j^0 , and the local dielectric susceptibility $\vec{\chi}_j$. It follows that the resultant dipole moment at j is $\vec{p}_j^0 + \vec{\chi}_j \cdot \vec{E}$. Now the local zero-field susceptibility $\vec{\chi}_j$ can quite generally be diagonalized with respect to local coordinate axes x_j, y_j, z_j which are peculiar to the j th site. Let the local axes x_j, y_j, z_j make polar angles θ_j, ϕ_j with field direction Z : the induced dipole moment can then be expressed in the form

$$\vec{p}_j = (\chi_j^{xj} \sin \theta_j \cos \phi_j, \chi_j^{yj} \sin \theta_j \sin \phi_j, \chi_j^{zj} \cos \theta_j) E, \quad (2.4)$$

where χ_j^{xj} , χ_j^{yj} , and χ_j^{zj} are the principle zero-field local susceptibility tensor elements.

Now the important property of dipole forces in the static mean-field approximation is that they are of long range. In particular, for lattices of sufficiently high symmetry (e.g., simple cubic) the short-range contributions cancel exactly and the resulting effective field consists only of contributions of essentially infinite range. Within a glassy matrix local correlations are typically maintained over only a few nanometers, so that a very efficient, while not perfect, cancellation of short-range contributions will hold for this case also. It is therefore valid, within the mean-field scheme, to assume the dipolar interactions to be dominated by the long-range contributions. Let us write the dipolar interaction between the i th and j th units, now taken to be very remote from one another, as $\vec{p}_i' \cdot \vec{v}_{ij} \cdot \vec{p}_j'$ where $\vec{p}_j' = p_j^0 + p_j$ is the total electric dipole moment at site j , and where \vec{v}_{ij} defines a dipole energy matrix. Because of the long-range condition it is a good approximation to replace each of the dipoles \vec{p}_j' by its configurational average value $\langle \vec{p}_j' \rangle_{av} = \langle \vec{p}_j \rangle_{av}$. Since the local principal susceptibility components and the local angular coordinates are independent random variables (at least in the zero-field limit) the configurationally averaged moment at the j th site is in the direction Z of the applied field and of magnitude given by

$$\begin{aligned} \langle \vec{p}_j' \rangle_{av} &= \langle (\chi_j^{xj})_{av} \langle \sin^2 \theta_j \cos^2 \phi_j \rangle_{av} \\ &\quad + \langle (\chi_j^{yj})_{av} \langle \sin^2 \theta_j \sin^2 \phi_j \rangle_{av} + \langle (\chi_j^{zj})_{av} \langle \cos^2 \theta_j \rangle_{av} \rangle_{av} \vec{E} \\ &= \frac{1}{3} \langle (\chi_j^{xj})_{av} + \langle (\chi_j^{yj})_{av} + \langle (\chi_j^{zj})_{av} \rangle_{av} \rangle_{av} \vec{E} \\ &= \chi_{av} \vec{E}, \end{aligned} \quad (2.5)$$

where

$$\chi_{av} = \langle (\chi_j^{xj})_{av} = \langle (\chi_j^{yj})_{av} = \langle (\chi_j^{zj})_{av} \rangle_{av}, \quad (2.6)$$

the equality of the configurationally averaged susceptibility components following since we have implied no systematic scheme for differentiating

between them (such could, of course, be easily given, e.g., by defining $\chi_j^{xj} \geq \chi_j^{yj} \geq \chi_j^{zj}$, but only complicates the formalism).

It follows immediately from (2.5) that the effective field \vec{E}_i^{eff} of (2.3) can now be expressed in the form

$$\vec{E}_i^{\text{eff}} = \sum_j \vec{v}_{ij} \chi_{av} \cdot \vec{E} + \vec{E}. \quad (2.7)$$

Expanding the local effective field into its components along the local axes x_i, y_i, z_i which diagonalize the isolated unit response $\vec{\chi}_i^0$ we have

$$\begin{aligned} E_i^{\text{eff}, x_i} &= \sum_j [(v_{ij}^{11}) s_i c_i' + (v_{ij}^{12}) s_i s_i' + (v_{ij}^{13}) c_i] \chi_{av} E + s_i c_i' E, \\ E_i^{\text{eff}, y_i} &= \sum_j [(v_{ij}^{21}) s_i c_i' + (v_{ij}^{22}) s_i s_i' + (v_{ij}^{23}) c_i] \chi_{av} E + s_i s_i' E, \\ E_i^{\text{eff}, z_i} &= \sum_j [(v_{ij}^{31}) (s_i c_i' + (v_{ij}^{32}) s_i s_i' + (v_{ij}^{33}) c_i] \chi_{av} E + c_i E, \end{aligned} \quad (2.8)$$

in which

$$\begin{aligned} s_i &= \sin \theta_i, \quad c_i = \cos \theta_i, \\ s_i' &= \sin \phi_i, \quad c_i' = \cos \phi_i, \end{aligned} \quad (2.9)$$

with θ_i, ϕ_i defining the polar orientation of the field direction Z with respect to the local axes x_i, y_i, z_i , and where the v_{ij} superscripts label the tensor components of dipole energy also in the local coordinate reference frame. The resulting i th unit response, from (2.3), follows immediately as

$$\vec{p}_i = (\chi_i^{s_x i} E_i^{\text{eff}, x_i}, \chi_i^{s_y i} E_i^{\text{eff}, y_i}, \chi_i^{s_z i} E_i^{\text{eff}, z_i}). \quad (2.10)$$

Finally, we configurationally average over the possible sites i noting again that for infinitesimal fields \vec{E} and \vec{E}_i^{eff} the local principal susceptibility components and local angular coordinates are independent random variables. It follows that $\langle \vec{p}_i' \rangle_{av} = \langle \vec{p}_i \rangle_{av}$ where

$$\begin{aligned} \langle \vec{p}_i' \rangle_{av} &= \frac{1}{3} [v^{11}(0) \langle \chi_i^{s_x i} \rangle_{av} + v^{22}(0) \langle \chi_i^{s_y i} \rangle_{av} \\ &\quad + v^{33}(0) \langle \chi_i^{s_z i} \rangle_{av}] \chi_{av} \vec{E} \\ &\quad + \frac{1}{3} [\langle \chi_i^{s_x i} \rangle_{av} + \langle \chi_i^{s_y i} \rangle_{av} + \langle \chi_i^{s_z i} \rangle_{av}] \vec{E}, \end{aligned} \quad (2.11)$$

in which

$$v(0) = \sum_j v_{ij}, \quad (2.12)$$

and we have recognized the fact that for long-range dominated forces with a glass $v^{11}(0)$, $v^{22}(0)$, and $v^{33}(0)$ are independent of local reference frame. They must, therefore, also be equal [say = $v_{\text{diag}}(0)$] so that (2.11) can be contracted to

$$\langle \vec{p}_i \rangle_{\text{av}} = \frac{1}{3} \vec{E} [\langle \chi_i^{s_x x_i} \rangle_{\text{av}} + \langle \chi_i^{s_y y_i} \rangle_{\text{av}} + \langle \chi_i^{s_z z_i} \rangle_{\text{av}}] \times [v_{\text{diag}}(0)\chi_{\text{av}} + 1]. \quad (2.13)$$

Defining

$$\langle \chi_i^{s_x x_i} \rangle_{\text{av}} = \langle \chi_i^{s_y y_i} \rangle_{\text{av}} = \langle \chi_i^{s_z z_i} \rangle_{\text{av}} = \chi_{\text{av}}^s$$

and using (2.2) we are now able to define the configurationally averaged (i.e., bulk) dielectric susceptibility per unit in the form

$$\chi_{\text{av}} = \langle p_i \rangle_{\text{av}} / E = \chi_{\text{av}}^s [1 + v_{\text{diag}}(0)\chi_{\text{av}}], \quad (2.14)$$

from which we find the explicit form

$$\chi_{\text{av}} = \chi_{\text{av}}^s / [1 - v_{\text{diag}}(0)\chi_{\text{av}}^s]. \quad (2.15)$$

It is clear that a divergence, representing a ferroelectric instability, will occur when

$$v_{\text{diag}}(0)\chi_{\text{av}}^s = 1. \quad (2.16)$$

In order to examine the detailed temperature dependence of χ_{av} and to discuss the possibility of achieving the condition (2.16) it is necessary to consider more explicitly the form, and particularly the temperature dependence, of χ_{av}^s .

III. "SINGLE-UNIT" RESPONSE

We shall consider the representative "isolated" local configurational unit of ions at site i to be a prototype high-symmetry cluster distorted, possibly very significantly, by a random *local strain field* \vec{E}_i^{str} . Suppose, for simplicity, that the *prototype* unit has just three orthogonal local displacive modes of vibration ξ_λ , $\lambda = 1, 2, 3$ governed by a local potential $V(\vec{\xi})$ which is separable in the form

$$V(\vec{\xi}) = \sum_\lambda V_\lambda(\xi_\lambda). \quad (3.1)$$

Representing each component potential V_λ of the prototype unit by an even-order anharmonic oscillator form, the representative local configurational unit has a motion described by the local Hamiltonian

$$\mathcal{H}_{i,\lambda}(\xi_\lambda) = \frac{1}{2}\pi_\lambda^2 + \frac{1}{2}\Omega_\lambda^2 \xi_\lambda^2 + A_\lambda \xi_\lambda^4 - S_\lambda \xi_\lambda E_{i,\lambda}^{\text{str}}, \quad (3.2)$$

in which $E_{i,\lambda}^{\text{str}}$ is the component of local strain field in the direction λ , S_λ is an effective charge parameter for the λ th local vibrational mode, and π_λ is the momentum coordinate conjugate to ξ_λ . The equilibrium value of ξ_λ , given by $\partial \mathcal{H}_{i,\lambda} / \partial \xi_\lambda = 0$, is therefore $\xi_{i,\lambda}^0$ where

$$\Omega_\lambda^2 \xi_{i,\lambda}^0 + 4A_\lambda (\xi_{i,\lambda}^0)^3 = S_\lambda E_{i,\lambda}^{\text{str}}. \quad (3.3)$$

Writing $\xi_\lambda = \xi_{i,\lambda}^0 + \Delta_\lambda$ and substituting into (3.2) gives

$$\mathcal{H}_{i,\lambda}(\xi_\lambda) - \mathcal{H}_{i,\lambda}(\xi_{i,\lambda}^0) = \sum_n s_{n,\lambda}^{(i)} \Delta_\lambda^n, \quad (3.4)$$

where, using (3.3),

$$\begin{aligned} s_{1,\lambda}^{(i)} &= 0, \\ s_{2,\lambda}^{(i)} &= \frac{1}{2}\Omega_\lambda^2 + 6A_\lambda (\xi_{i,\lambda}^0)^2 = \frac{1}{2}\Omega_{i,\lambda}^2 \text{ (say)}, \\ s_{3,\lambda}^{(i)} &= 4A_\lambda \xi_{i,\lambda}^0, \\ s_{4,\lambda}^{(i)} &= A_\lambda, \\ s_{n,\lambda}^{(i)} &= 0; \quad n > 4. \end{aligned} \quad (3.5)$$

Thus, expanding each potential function about its minimum value, we may now consider the response to an applied field \vec{E} (components E_λ) by examining the Hamiltonian

$$\mathcal{H}_{i,\lambda}(\Delta_\lambda) = \frac{1}{2}\pi_\lambda^2 + \frac{1}{2}\Omega_{i,\lambda}^2 \Delta_\lambda^2 + s_{3,\lambda}^{(i)} \Delta_\lambda^3 + s_{4,\lambda}^{(i)} \Delta_\lambda^4 - S_\lambda E_\lambda \Delta_\lambda. \quad (3.6)$$

Contracting the notation we rewrite this in the form

$$\mathcal{H}_i / kT = \frac{1}{2}\pi^2 / kT + \frac{1}{2}w_i^2 + a_3^{(i)} w_i^3 + a_4^{(i)} w_i^4 - g_i w_i, \quad (3.7)$$

where

$$\begin{aligned} w_i &= \Omega_{i,\lambda} \Delta_\lambda (kT)^{-1/2}, \quad a_3^{(i)} = s_{3,\lambda}^{(i)} (kT)^{1/2} / \Omega_{i,\lambda}^3, \\ a_4^{(i)} &= s_{4,\lambda}^{(i)} kT / \Omega_{i,\lambda}^4, \quad g_i = S_\lambda E_\lambda (kT)^{-1/2} / \Omega_{i,\lambda}. \end{aligned} \quad (3.8)$$

The free-energy per mode λ of the ensemble of systems i can now be expressed classically as

$$F_i = -kT \ln \left(\frac{1}{h} \int \int e^{-\mathcal{H}_i / kT} (kT)^{1/2} \Omega_{i,\lambda}^{-1} d\pi dw_i \right), \quad (3.9)$$

and evaluated analytically to give

$$F_i = -kT \left[\ln(kT / \hbar \Omega_{i,\lambda}) + \frac{1}{2}g_i^2 - a_4^{(i)} (3 + 6g_i^2 + g_i^4) - a_3^{(i)} (3g_i + g_i^3) \right], \quad (3.10)$$

correct to first order in a_3 and a_4 . The "single-unit" response $\chi_{i,\lambda}^s$ now follows directly as

$$\frac{-\partial^2 F_i}{\partial E_\lambda^2} = -S_\lambda^2 (\Omega_{i,\lambda}^2 / kT)^{-1} \frac{\partial^2 F}{\partial g_i^2},$$

in the form

$$\chi_{i,\lambda}^s = (S_\lambda^2 / \Omega_{i,\lambda}^2) [1 - 6a_3^{(i)} g_i - 12a_4^{(i)} (1 + g_i^2)]. \quad (3.11)$$

Using (3.5) we can now express (3.11) explicitly to first order in small quantities in the form

$$\chi_{i,\lambda}^s = (S_\lambda^2 / \Omega_\lambda^2) [1 - 12a_4 (1 + g^2 + y_{i,\lambda}^2) - 6a_3^{(i)} g], \quad (3.12)$$

in which

$$a_4 = A_\lambda kT / \Omega_\lambda^4, \quad g = S_\lambda E_\lambda (kT)^{-1/2} / \Omega_\lambda, \quad (3.13)$$

$$y_{i,\lambda}^2 = \Omega_\lambda^2 (\xi_{i,\lambda}^0)^2 / kT.$$

Thus, χ_i^s involves deviations from the prototype configuration only in the $a_4 y^2$ and $a_3 g$ terms. However, in forming a configurational average over the random local strain field (i.e., over $\xi_{i,\lambda}^0$) the final term in (3.12) vanishes and we are left with

$$\chi_{\lambda,av}^s \equiv \langle \chi_{\lambda}^s \rangle_{av} \quad (3.14)$$

$$= (\Omega_{\lambda}^2 / \Omega_{\lambda}^2) [1 - 12a_4(1 + g^2 + \langle y_{\lambda}^2 \rangle_{av})],$$

where

$$\langle y_{\lambda}^2 \rangle_{av} = (\Omega_{\lambda}^2 / kT) \langle (\xi_{\lambda}^0)^2 \rangle_{av}, \quad (3.15)$$

provides the only remaining measure of contributions from local deformations in this approximation. Written explicitly in terms of the original parameters of (3.2), this result is

$$\chi_{\lambda,av}^s = \frac{S_{\lambda}^2}{\Omega_{\lambda}^2} \left(1 - \frac{12A_{\lambda}kT}{\Omega_{\lambda}^4} - \frac{12A_{\lambda}S_{\lambda}^2E_{\lambda}^2}{\Omega_{\lambda}^6} - \frac{12A_{\lambda}\langle (\xi_{\lambda}^0)^2 \rangle_{av}}{\Omega_{\lambda}^2} \right). \quad (3.16)$$

The average χ_{av}^s of Eq. (2.16) is now defined as

$$\chi_{av}^s = \frac{1}{3} \sum_{\lambda} \chi_{\lambda,av}^s, \quad (3.17)$$

or more specifically its zero-field value.

We shall consider below some interesting special cases but, for the moment, we note a particular simplification which has resulted from the assumption that $V(\xi)$ is separable as shown in (3.1). For this situation (but not in general) the principal axis directions are not perturbed by the strain field or by any other finite effective field. In such a case it is very simple to extend the statistical theory of Sec. II into the "ordered" polar phase.

IV. POLAR PHASE

Below a ferroelectric instability, the effective field \vec{E}^{eff} of (2.3) takes on finite values. In the absence of an applied field we shall write below T_c a finite response at the representative site i in the form

$$\vec{p}_i = \vec{\chi}_i^s(\vec{E}^{\text{eff}}) \cdot \vec{E}^{\text{eff}}, \quad (4.1)$$

defining a "single-unit" field dependent response $\vec{\chi}_i^s(\vec{E})$, the principal diagonal components of which, for our model, are given by (3.12). In analogy with (2.4) a finite response at site j can be written

$$\vec{p}_j = (\chi_j^{s,xj}(E_{\text{eff}}^{xj})s_jc_j', \chi_j^{s,yj}(E_{\text{eff}}^{yj})s_jc_j', \chi_j^{s,zj}(E_{\text{eff}}^{zj})c_j)E^{\text{eff}}, \quad (4.2)$$

where E_{eff}^{xj} signifies the component of \vec{E}^{eff} in the direction of the x_j th principal axis of the field-dependent susceptibility tensor at the site j , etc. Since, with the restriction (3.1), these principal axes are not field dependent, the local angular coordinates and susceptibility components can again be taken as independent random variables in estimating the configurationally averaged moment at the j th site. In analogy with (2.5) we find $\langle \vec{p}_j \rangle_{av}$

$= \langle \vec{p}_j \rangle_{av} = \chi_{av}^s(\vec{E}^{\text{eff}})\vec{E}^{\text{eff}}$, defining the field-dependent response

$$\chi_{av}^s(E^{\text{eff}}) = [\langle \chi_{av}^{s,xj}(E^{\text{eff}}s_jc_j')s_j^2c_j'^2 \rangle_{av} + \langle \chi_{av}^{s,yj}(E^{\text{eff}}s_jc_j')s_j^2c_j'^2 \rangle_{av} + \langle \chi_{av}^{s,zj}(E^{\text{eff}}c_j)c_j^2 \rangle_{av}], \quad (4.3)$$

in which $\chi_{av}^{s,xj}$ denotes a configurational average of $\chi_j^{s,xj}$ with θ_j and ϕ_j fixed, and $\langle \dots \rangle_{av}$ is an dependent average over θ_j and ϕ_j . It is these averages which, for a more general prototype potential, can be coupled and field dependent even in the absence (which we assume throughout) of any physical rotation of the basic units in the field.

Proceeding as in Sec. II we now calculate the effective field at site i , the associated response from (4.1), and finally the configurationally averaged response

$$\langle \vec{p}_i \rangle_{av} = [v^{11}(0)\langle \chi_{av}^{s,xi}(E^{\text{eff}}s_i c_i')s_i^2 c_i'^2 \rangle_{av} + v^{22}(0)\langle \chi_{av}^{s,yi}(E^{\text{eff}}s_i c_i')s_i^2 c_i'^2 \rangle_{av} + v^{33}(0)\langle \chi_{av}^{s,zi}(E^{\text{eff}}c_i)c_i^2 \rangle_{av}] \chi_{av}^s(E^{\text{eff}})\vec{E}^{\text{eff}}. \quad (4.4)$$

But since $\langle \vec{p}_i \rangle_{av} = \chi_{av}^s(E^{\text{eff}})\vec{E}^{\text{eff}}$ by definition, it follows that E^{eff} in the polar phase is determined by the equation

$$\langle \chi_{av}^{s,xi}(E^{\text{eff}}s_i c_i')s_i^2 c_i'^2 \rangle_{av} + \langle \chi_{av}^{s,yi}(E^{\text{eff}}s_i c_i')s_i^2 c_i'^2 \rangle_{av} + \langle \chi_{av}^{s,zi}(E^{\text{eff}}c_i)c_i^2 \rangle_{av} = 1/v_{\text{diag}}(0), \quad (4.5)$$

where we have again used the relation $v^{11}(0) = v^{22}(0) = v^{33}(0) = v_{\text{diag}}(0)$ for the bulk spherical symmetry of the glass structure. This may be written more succinctly using (4.3) in the form $\chi_{av}^s(E^{\text{eff}})v_{\text{diag}}(0) = 1$, or as

$$\sum_{\lambda} \langle \chi_{\lambda,av}^s(E^{\text{eff}} \cos \theta) \cos^2 \theta \rangle_{\theta} = 1/v_{\text{diag}}(0), \quad (4.6)$$

where $\langle \dots \rangle_{\theta}$ implies a spherical average over the polar angle θ . The susceptibility $\chi_{\lambda,av}^s$ within our model is given by (3.16), and the spontaneous polarization P follows as $N\langle p_i \rangle_{av}$, where

$$\langle p_i \rangle_{av} = \chi_{av}^s(E^{\text{eff}})E^{\text{eff}} = E^{\text{eff}}/v_{\text{diag}}(0), \quad (4.7)$$

and N is the number of elementary cluster units per unit volume. We see that $P \rightarrow 0$ when $E^{\text{eff}} \rightarrow 0$ which, from (4.6), is when

$$\sum_{\lambda} \frac{1}{3} \chi_{\lambda,av}^s(0) = \chi_{av}^s = 1/v_{\text{diag}}(0),$$

in agreement with (2.16). The model therefore indicates a second-order instability.

V. STRONGLY UNIAXIAL PROTOTYPE UNIT

We consider as our first specific example the case for which the prototype unit in the glass is strongly uniaxial such that $\chi_{x,av}^s \approx \chi_{y,av}^s \ll \chi_{z,av}^s$. If we take the x and y susceptibilities to be of the first order of smallness then we may define, from (3.16),

$$\begin{aligned}\alpha_x &= \chi_{x,av}^s \approx S_x^2/\Omega_x^2, \\ \alpha_y &= \chi_{y,av}^s \approx S_y^2/\Omega_y^2.\end{aligned}\quad (5.1)$$

The local "soft" axis is therefore the z axis for which we have

$$\chi_{z,av}^s(E_z) = \alpha_z - 12A_z S_z^2 k T / \Omega_z^6 - 12A_z S_z^4 E_z^2 / \Omega_z^8, \quad (5.2)$$

in which

$$\alpha_z = (S_z^2/\Omega_z^2)(1 - 12A_z \langle (\xi_z^0)^2 \rangle_{av} / \Omega_z^2). \quad (5.3)$$

It follows, from (3.17), that

$$\chi_{av}^s = \frac{1}{3} \sum_{\lambda} \chi_{\lambda,av}^s(E=0) = (\alpha^*/3) - 4A_z S_z^2 k T / \Omega_z^6, \quad (5.4)$$

where $\alpha^* = \alpha_x + \alpha_y + \alpha_z$, from which, using (2.16), we calculate a Curie temperature

$$kT_C^{\text{glass}} = (\Omega_z^6/12A_z S_z^2) [\alpha^* - 3/v_{\text{diag}}(0)]. \quad (5.5)$$

Our model will therefore exhibit a glassy ferroelectric phase provided that $\alpha^* > 3/v_{\text{diag}}(0)$. In this case, using (2.15), we find a divergence of uniform static susceptibility as $T \rightarrow T_C$ of the form

$$\chi_{av}^{\text{glass}} = [\Omega_z^6/4v_{\text{diag}}^2(0)A_z S_z^2 k] (T - T_C)^{-1}, \quad T \rightarrow T_C^+, \quad (5.6)$$

i.e., a Curie-Weiss law.

Below the Curie point, when one exists, the polar phase develops with a spontaneous local effective field given by (4.6). Substituting (5.1) and (5.2) into (4.6) we find the explicit form for the uniaxial prototype unit

$$\begin{aligned}(\alpha^* - 12A_z S_z^2 k T \Omega_z^{-6}) \langle \cos^2 \theta \rangle_{\theta} \\ - 12A_z S_z^4 E_{\text{eff}}^2 \Omega_z^{-8} \langle \cos^4 \theta \rangle_{\theta} = 1/v_{\text{diag}}(0).\end{aligned}\quad (5.7)$$

Evaluating the spherical averages $\langle \cos^2 \theta \rangle_{\theta} = \frac{1}{3}$ and $\langle \cos^4 \theta \rangle_{\theta} = \frac{1}{5}$, and using (5.5), this equation simplifies to

$$E_{\text{eff}}^2 = 5\Omega_z^2 k (T_C - T) / 3S_z^2, \quad (5.8)$$

from which the spontaneous polarization follows as $P = NE_{\text{eff}}/v_{\text{diag}}(0)$, viz.,

$$P(T) = N[5\Omega_z^2 k (T_C - T) / 3S_z^2 v_{\text{diag}}^2(0)]^{1/2}. \quad (5.9)$$

We note in particular that

$$P(T)/P(0) = [(T_C - T)/T_C]^{1/2}, \quad (5.10)$$

although such a simple form is expected to be valid only for the model (3.2) of a quasiharmonic displacive unit stabilized by quartic anharmonicity.

Within this simple model, however, it is now interesting to compare the equivalent findings for a crystalline lattice made up from these same strongly uniaxial constituent units. In the crystal all the units are relatively aligned and dielectric instability will occur, if at all, along the local z axis of each unit, which is now the z axis of the crystal. The defining equations for crystalline ferroelectricity corresponding to (2.15) and (4.6) are $\chi_i = \alpha_i/[1 - v_{ii}(0)\alpha_i]$, $i = x, y$,

$$\chi_z = \chi_z^s/[1 - v_{zz}(0)\chi_z^s], \quad T > T_C \quad (5.11)$$

and

$$\chi_z^s(E^{\text{eff}}) = 1/v_{zz}(0), \quad T < T_C \quad (5.12)$$

where $v_{zz}(0)$ is the diagonal component of the dipolar interaction tensor for displacements along the crystalline z axis and will depend on the detailed crystal structure and, in particular, will differ in general from $v_{\text{diag}}(0)$. The susceptibility χ_z^s in these equations differs from $\chi_{z,av}^s$ of (5.2) only in having α_z replaced by $\alpha_z^0 = S_z^2/\Omega_z^2$. The crystalline equations for Curie temperature, susceptibility, and spontaneous polarization, now follow immediately as

$$kT_C^{\text{cryst}} = (\Omega_z^6/12A_z S_z^2) [\alpha_z^0 - (1/v_{zz}(0))], \quad (5.13)$$

$$\chi_z^{\text{cryst}} = [\Omega_z^6/12v_{zz}^2(0)A_z S_z^2 k] (T - T_C)^{-1}, \quad T \rightarrow T_C^+, \quad (5.14)$$

$$P(T) = N[\Omega_z^2 k (T_C - T) / S_z^2 v_{zz}^2(0)]^{1/2}, \quad (5.15)$$

and

$$P(T)/P(0) = [(T_C - T)/T_C]^{1/2}. \quad (5.16)$$

Comparing T_C^{glass} of (5.5) and T_C^{cryst} of (5.13) we see that unless $v_{zz}(0)$ is much less than $v_{\text{diag}}(0)$ then T_C^{glass} is likely to be very much smaller than T_C^{cryst} for the case of strongly uniaxial units. It suggests that displacive crystalline ferroelectrics with a strongly uniaxial basic unit will probably not give rise to any ferroelectric instability in the glassy matrix (i.e., $T_C^{\text{glass}} < 0$). On the other hand it also suggest that a dielectrically unstable glass might be found in systems for which the equivalent crystalline phase is pyroelectric (T_C^{cryst} higher than the melting point).

One should not confuse the idea of a glassy ferroelectric with the well established concepts of ferroelectric ceramics. The latter are aggregates of crystallites with sharp boundaries and with dimensions measured in microns (which is typically several orders of magnitude larger than the possible local structural integrity of the glass). Ex-

cept for problems concerning domain clamping by spontaneous anisotropic strains at the grain boundaries and a broadening of the phase transition region by the inhomogeneous distribution of stresses and electric fields, most ceramics approach a powder averaged bulk ferroelectric behavior. Thus, for example, we would anticipate a bulk ceramic susceptibility

$$\chi^{\text{ceram}} = \frac{1}{3}(\chi_x^{\text{cryst}} + \chi_y^{\text{cryst}} + \chi_z^{\text{cryst}}) \quad (5.17)$$

in which

$$\begin{aligned} \chi_x^{\text{cryst}} &= \alpha_x / [1 - v_{xx}(0)\alpha_x], \\ \alpha_y^{\text{cryst}} &= \alpha_y / [1 - v_{yy}(0)\alpha_y], \end{aligned} \quad (5.18)$$

and χ_z^{cryst} is given by (5.14) on approach to the Curie temperature. Thus, the ceramic susceptibility diverges at T_C^{cryst} in the simplest model and is quite different from the concept of the glassy instability. The extent to which the glass transition might also be expected to be broadened by inhomogeneity depends upon the characteristic dimensions of these inhomogeneities within the glass. It is certainly not the case that a "frozen-in" random disorder necessarily precipitates a diffuse phase transition.³

VI. HIGHLY SYMMETRIC PROTOTYPE UNIT

The analogous equations for the case of symmetric prototype units can be obtained in an exactly equivalent manner and will be given here without detailed discussion. If we define the high-symmetry unit by

$$\begin{aligned} \chi_{x,\text{av}}^s &= \chi_{y,\text{av}}^s = \chi_{z,\text{av}}^s \\ &= \alpha - 12AS^2kT/\Omega^6 - 12AS^4E^2/\Omega^8, \end{aligned} \quad (6.1)$$

where

$$\alpha = (S^2/\Omega^2)[1 - 12A\langle(\xi^0)^2\rangle_{\text{av}}/\Omega^2], \quad (6.2)$$

then we find for the glass

$$kT_C^{\text{glass}} = (\Omega^6/12AS^2)[\alpha - 1/v_{\text{diag}}(0)], \quad (6.3)$$

$$\chi_{\text{av}}^{\text{glass}} = [\Omega^6/12v_{\text{diag}}^2(0)AS^2k](T - T_C^*)^{-1}, \quad T - T_C^*, \quad (6.4)$$

$$P(T) = N[5\Omega^2k(T_C - T)/3S^2v_{\text{diag}}^2(0)]^{1/2}. \quad (6.5)$$

The equivalent findings for the crystalline form are

$$kT_C^{\text{cryst}} = (\Omega^6/12AS^2)[\alpha^0 - 1/v_{rr}(0)], \quad (6.6)$$

$$\chi_r^{\text{cryst}} = [\Omega^6/12v_{rr}^2(0)AS^2k](T - T_C^*)^{-1}, \quad T - T_C^*, \quad (6.7)$$

with $\alpha^0 = S^2/\Omega^2$. In the latter two equations, r denotes the crystalline direction for which the dielectric instability occurs—it will be decided by the symmetry of the crystalline lattice. We have not

given results for the ordered phase since these will depend in a more intricate manner on the particular parameters of the crystalline model; in fact there might possibly be more than one ordered phase with a suitable choice of model parameters.

In the simplest effective field scheme, neglecting all correlation effects, one would expect $v_{\text{diag}}(0)$ in the glassy matrix to have essentially the Lorentz value $4\pi/3$. On the other hand, the crystalline structure will take advantage of any anisotropy in v to polarize along a direction for which $v_{rr}(0)$ is a maximum; it follows that $v_{rr}(0) \geq 4\pi/3$. Also, since

$$\alpha = \alpha^0 - 12AS^2\langle(\xi^0)^2\rangle_{\text{av}}/\Omega^4, \quad (6.8)$$

we know that, within the present model at least, α is less than α^0 . It now follows from a comparison of (6.3) and (6.6) that, once again, we anticipate T_C^{glass} to be less than T_C^{cryst} , though perhaps not so dramatically so as for the case with strongly uniaxial prototype units.

Even such qualitative predictions as these, however, must be tempered with some caution. For example, it is possible (though not necessary) to have $\alpha > \alpha^0$ if the local Hamiltonian (3.2) has a negative quartic anharmonicity, the local motion being stabilized by higher-order terms. The negative sign of A_λ has been well established for some ABO_3 ferroelectrics^{4,5} and is suspected for many others. More particularly, our model is so far restricted to a quasiharmonic prototype potential and we have used a simple statistical approximation neglecting all effects from correlated neighbor motion, effects which are known to be very important in crystalline ferroelectrics⁶⁻⁸ and which may well be changed in a rather drastic manner in passing to the glassy form. Finally, since α and $1/v(0)$ in the equations for T_C may well be large compared to their difference, relatively small percentage changes in either can result in a large variation of Curie temperature, even to completely removing the dielectric instability from that temperature range $0 < T_C < T_0$ (where T_0 is the melting temperature for a crystal or the crystallization temperature for a glass) of experimental significance.

VII. SUMMARY

We have established that there is no conceptual difficulty in perceiving a state of matter which is both glassy and ferroelectric and we have constructed a simple model of such a system. Using the effective-field theory of statistical mechanics we have also described the physical mechanism whereby a dielectric instability might be produced in a glass. The essential ingredient is a high-

symmetry dielectrically soft "prototype" local atomic configuration which remains identifiable, though in a randomly distorted form, in the glassy matrix. Essentially all the actual local units then possess "frozen-in" electric dipoles of random magnitude and orientation but which cancel when summed over the macroscopic sample. The polar phase is then defined as a small "polar" perturbation from this frozen random configuration of dipoles and is therefore really no more than an extension of the concept of the "dirty ferroelectric"⁹ to the stage where even an average translational invariance is lost.

A detailed local field theory has been set out for a displacive prototype unit and shows that a dielectric instability will occur, if at all, from a cancellation of the short-range forces which "stabilize" (in the metastable glassy sense) the frozen-in antipolar configuration and the long-range electric dipole forces which prefer a configuration with a macroscopic dipole moment. An enormous simplification of theory results from the fact that the temperature-dependent "destabilizing" part of the local field is dominated in the effective field approximation by the long-range dipolar contribution for which "glass" averages can be carried out explicitly even in complete ignorance of the detailed structure of the glass on a microscopic scale. The theory suggests that ferroelectric crystals with a strongly uniaxial prototype unit will prob-

ably not be ferroelectric in the glassy form because the dipolar effective field is drastically reduced for this case by the orientational averaging. Strongly pyroelectric crystals may therefore be better candidates for glassy ferroelectrics in this category.

For ferroelectric crystals with a highly symmetric prototypic unit (e.g., the BO_6 octahedral unit in many ABO_3 ferroelectrics) the "isolated unit" susceptibility is quasi-isotropic so that the effective field at one unit due to an induced polarization in a second unit is little affected by the relative orientation of the two. In this case the long-range dipolar properties are accordingly less affected by the configurational averaging procedure and the chances of finding a ferroelectric crystal of this type which remains ferroelectric in the glassy form seems higher. Nevertheless even here the dielectric changes wrought by forming the glass may still be very large, reflecting the change of "lattice symmetry" (i.e., Lorentz parameter), the effects of averaged local distortions from the prototype, and the change in the nature of the dynamics. Finally we note that in view of the ubiquitous presence of the frozen-in dipoles, these dielectrically soft glasses, whether ferroelectric or not, will show a strong dielectric anomaly at the crystallization temperature due to the decreasingly "frozen" character of the local dipoles as the crystallization instability is approached from below.

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