approximation, only one strongly temperature-dependent optical-phonon mode. For such a system we have described many dielectrics properties quantitatively in terms of the parameters of the displacement Hamiltonian. These properties include polarization, soft-mode frequency, and linear and nonlinear static and dynamic susceptibilities, all as functions of temperature both near to and away from the Curie temperature.

A comparison of theory with experiment for some or all of these dielectric properties is sufficient to determine the relevant parameters of the displacement Hamiltonian. These parameters are microscopic and are very much more closely related to the fundamental forces of the system than are the parameters of a thermodynamic theory. In part III we actually determine them for lithium tantalate, and proceed to show how they can be used to elucidate less obvious features of detailed microscopic behavior and to support, or to reject, particular microscopic models.

The accuracy that can be achieved in any such undertaking probably depends most significantly on the validity of the "one-soft-mode" approximation for the particular ferroelectric concerned. A quantitative assessment of the number and degree of softness of the various optic modes can be made by direct measurement of the infrared or Raman spectra as a function of temperature.

The hope is that for a number of displacement ferroelectrics (and possibly even order-disorder ferroelectrics; see part II) the use of the displacement Hamiltonian and classical statistics will allow for a fairly quantitative description of nondissipative dielectric properties in terms of relatively few microscopic parameters which can themselves, as a result, be estimated with reasonable accuracy. In this way, less emphasis need be placed on thermodynamic (macroscopic) theories and explanations of experimental data can perhaps, more frequently, be given directly in terms of microscopic theory.

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Statistical Theory for Displacement Ferroelectrics. II. Specific-Heat and Soft-Mode-Frequency Calculations

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The effective field theory for displacement ferroelectrics which was developed in part I of the present series of papers is extended to include specific-heat, energy-of-ordering, and more detailed soft-mode-frequency calculations. Numerical results are computed for a simple one-soft-mode system in preparation for a test of the theory on the displacement ferroelectric $LiTaO_3$ (which is presented in the following paper). Detailed shapes of the specific-heat curves are computed and the discontinuity at the Curie temperature is displayed. The soft-mode-frequency calculations are extended beyond the small-anharmonicity region discussed in part I, thereby removing the last small-anharmonicity restriction from the method. Freed from all small-anharmonicity restrictions, it is demonstrated that the present approach is no longer confined to displacement systems, but is equally applicable for order-disorder ferroelectrics and goes over quite smoothly from one class of ferroelectric to the other.

1. INTRODUCTION

IN part I of the present series of papers,[1] an attempt was made to construct a workhorse theory for displacement ferroelectrics bearing a resemblance in spirit to the molecular-field theory (or, more closely, the cluster theories) of magnetism. In the theory, advantage is taken of the relative insensitivity of optic-mode frequencies to wave vector, in the absence of long-range electrostatic forces, to write an effective Hamiltonian for their motion in terms of a single primitive cell of the crystal lattice. The long-range dipolar interactions are then accommodated in an effective-field approximation by replacing all the other cells of the system by their thermal (ensemble) averages. The latter statistical approximation is basically a high-temperature one (neglecting short-range correlations between cells), but is one which is likely, in view of the long range of the dipolar forces, to give quite a good description of the system over the entire temperature range.

The great advantage which accrues from accepting the statistical mechanical restrictions associated with the use of an effective-field theory is the ability to describe at least some ferroelectric systems in terms of comparatively few parameters associated with an effective Hamiltonian; few enough, in particular, for these "unknowns" to be comfortably overdetermined by a comparison of theory with experiment for dielectric properties alone.

In part I, quantitative statistical calculations were performed for a particularly simple case; that of a displacement ferroelectric which has only one grossly

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[1] M. E. Lines, preceding paper, Phys. Rev. 177, 797 (1969), hereafter referred to as part I.

temperature-dependent optic lattice mode. We also used classical statistics but, because of this, we were not restricted to the use of perturbation theories or weakly anharmonic systems. Also, we used an effective Hamiltonian which is able to describe both second- and first-order phase transitions and which, as we shall point out in the present paper, is not restricted to displacement-type ferroelectrics but goes over quite naturally to allow for the description of order-disorder transitions as well.

In the following paper (part III of the present series), we test the theory for the first time on a real ferroelectric system, namely lithium tantalate $LiTaO_3$. However, in order to interpret all the relevant data now available, it is necessary to extend the theory of part I in two directions; first, to calculate the dielectric contribution to specific heat and energy of ordering and, second, to extend the earlier discussions of soft-mode frequency to cover the entire temperature range and to allow for anharmonicity which is not necessarily small. This will be done in the present paper so that, together, parts I and II will cover all the theory necessary for use in assessing the dielectric properties of $LiTaO_3$ in the effective-field approximation. Part III is then concerned solely with a comparison of theory with experiment and a related discussion of the resulting strengths and/or weaknesses of the method.

2. SPECIFIC HEAT

In part I we write an effective Hamiltonian per primitive cell (volume v) for a simple one-soft-mode displacement ferroelectric in the form

$$v\mathcal{H}_{\rm eff}=\tfrac{1}{2}(\pi^2+\omega_0^2\xi^2)+A\xi^4+B\xi^6-\eta S\xi(E+\gamma\langle P_{\rm ion}\rangle)\,, \tag{2.1}$$

where π and ξ are the conjugate momentum and displacement coordinates of the soft mode in question, E is an external (Maxwell) electric field, $\langle P_{\rm ion}\rangle$ is the ensemble averaged ionic polarization per unit volume, v is the volume of the primitive cell and ω_0, A, B, η, S, γ are temperature-independent parameters to be determined by comparing the results of theory with experiment for any particular case for which the Hamiltonian is applicable. These parameters can, of course, be simply related to fundamental force constants, polarizabilities, etc., in any specific model for the microscopic system since they are themselves (in contrast, for example, to the parameters appearing in a Devonshire free-energy expansion[2]) microscopic quantities.

The thermodynamic first law for the system can be written

$$TdS=dU-E_{\rm loc}dP_{\rm ion}\,, \tag{2.2}$$

where S is entropy and U the internal energy of the system. Differentiating with respect to temperature and using the fact that the local field $E_{\rm loc}=\eta\gamma P_{\rm ion}$ in the absence of an applied field (see part I), we find a specific heat

$$T(dS/dT)=d(U-\tfrac{1}{2}\eta\gamma P_{\rm ion}^2)/dT. \tag{2.3}$$

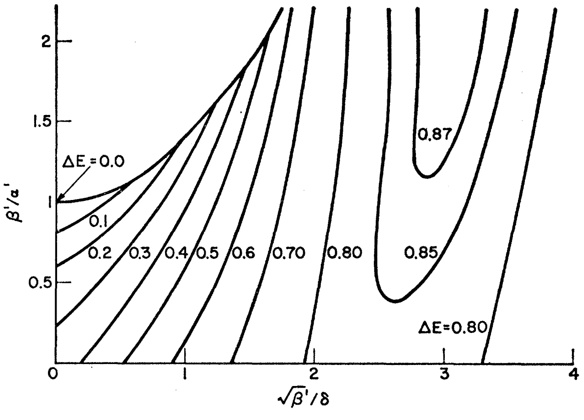

FIG. 1. The energy of ferroelectric dipole alignment ΔE (defined in Sec. 2) is plotted as a function of the dimensionless parameters β'/α' and $(\beta')^{1/2}/\delta$. The units of energy are kT_c per primitive cell. The computations cover second-order phase transitions only.

The contribution of the momentum coordinate to the specific heat per unit volume arises only from the term

$$\frac{1}{v}\frac{d}{dT}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\tfrac{1}{2}\pi^2\exp\!\left(\frac{-v\mathcal{H}_{\rm eff}}{kT}\right)d\pi d\xi/(\text{p.f.})\,, \tag{2.4}$$

where (p.f.) is the partition function. It gives a temperature-independent term $\frac{1}{2}(k/v)$, where k is the Boltzmann constant. We are, of course, concerned at present only with the dielectric contribution to specific heat (which contains the ferroelectric anomaly at the Curie point). Any temperature-independent contribution will, in practice, be indistinguishable from the very large background specific heat due to all other phonon modes of the system. Thus, the specific-heat anomaly can be described, at least classically, in terms of the displacement coordinate ξ only. Using (2.3) we write it as

$$c_{\rm anom}=\frac{1}{v}\frac{d}{dT}\left\{\int_{-\infty}^{\infty}(V+\tfrac{1}{2}\eta\gamma S\xi\langle P_{\rm ion}\rangle)\times\exp\!\left(\frac{-V}{kT}\right)d\xi\bigg/\int_{-\infty}^{\infty}\exp\!\left(\frac{-V}{kT}\right)d\xi\right\}, \tag{2.5}$$

where $\langle P_{\rm ion}\rangle=(S/v)\langle\xi\rangle$ from part I (we include pointed brackets for ensemble averages explicitly in statistical expressions; they are, of course, implied in the thermodynamic equations) and where

$$V=\tfrac{1}{2}\omega_0^2\xi^2+A\xi^4+B\xi^6-\eta S\xi(E+\gamma\langle P_{\rm ion}\rangle) \tag{2.6}$$

with external field $E=0$. Physically, the explicit $\langle P_{\rm ion}\rangle$ term in (2.5) ensures that we do not count the intercell dipolar energies twice when summing energies over cells in an effective-field approximation.

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[2] F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press, Inc., New York, 1962).

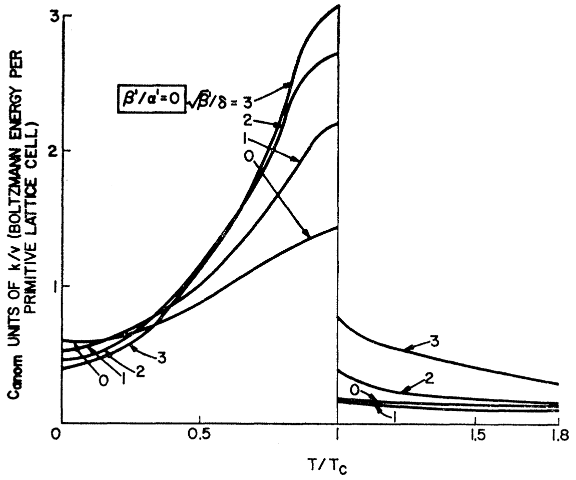

FIG. 2. The specific heat c_{anom} associated with the soft mode is plotted as a function of reduced temperature and of $(\beta')^{1/2}/\delta$ for the case $\beta'/\alpha'=0$. A temperature-independent contribution equal to $\frac{1}{2}(k/v)$ from the momentum coordinate of the effective Hamiltonian is not included.

Now, $\langle P_{\text{ion}}\rangle$ as a function of temperature has already been computed in part I for a range of values of the effective Hamiltonian parameters. It follows that c_{anom} can now be computed directly from (2.5). This is most conveniently done in terms of the dimensionless parameters $\beta'/\alpha'=\omega_0^2/(\eta\gamma S^2/v)$ and $(\beta')^{1/2}/\delta=-A/(B\eta\gamma S^2/v)^{1/2}$ which were used in part I. We have computed numerically for the case where A is negative, which is appropriate for $LiTaO_3$ and, we suspect, for most other ferroelectric systems of interest, e.g., order-disorder systems and those exhibiting a first-order phase transition.

In Fig. 1, we show the computed values of $\Delta E=E(T_c)-E(0)$, the energy associated with the ferroelectric ordering, where

$$vE(T)=\langle V+\tfrac{1}{2}\eta\gamma P_{\text{ion}}^2\rangle_T-\tfrac{1}{2}kT\,, \tag{2.7}$$

the difference in energy between the harmonic and anharmonic cases. Computations are carried out only over that area of β'/α', $(\beta')^{1/2}/\delta$ space corresponding to a second-order phase transition (see part I) and results are given in units of kT_c/v, where T_c is the Curie temperature.

In Figs. 2 and 3, the specific heat c_{anom} is plotted as a function of T/T_c for various values of β'/α' and $(\beta')^{1/2}/\delta$. The curve shapes show a discontinuity at the Curie temperature but retain a high-temperature tail indicative of short-range interaction effects (effects which, in our effective-field approximation, result solely from interactions within each primitive cell). In the small anharmonicity limit $\beta'/\alpha'\rightarrow 1$, $(\beta')^{1/2}/\delta\rightarrow 0$, we see that $c_{\text{anom}}\rightarrow\frac{1}{2}k/v$ and becomes temperature-independent and equal to the momentum contribution.

The calculations are all classical and so we are not surprised to find a violation of the thermodynamic third law as $T\rightarrow 0$. In any real system, quantum effects must eventually dominate at low temperatures and reduce c_{anom} to zero in this limit. This shortcoming of the present computations is not serious in practice for systems which are essentially classical (as far as dielectric properties are concerned) for temperatures $\sim T_c$, since only in this latter temperature range can the dielectric anomaly in the specific heat be experimentally separated from the phonon background. For the particular case of $LiTaO_3$, the soft-mode frequency at low temperatures is $\sim$200 cm^{-1} which is about 300°K in temperature units. For an oscillator of frequency ν, quantum "freezing out" effects for specific heat begin when $kT/h\nu\approx 1$, and the specific heat is half quenched when $kT/h\nu\approx 0.3$ (see for example Rushbrooke[3]). Thus, for $LiTaO_3$, quantum effects begin to appear when $T\sim 300$°K and c_{anom} is half quenched when $T\sim 100$°K. The Curie temperature is 890°K. It is quite likely, however, that quantum effects in the background specific heat will be felt at a much higher temperature since the mean or "Einstein" frequency of all phonons in the lattice is considerably higher than that of the zero-wave-vector soft mode.

3. DISPLACEMENT AND ORDER-DISORDER FERROELECTRICS

The present theory, as developed in part I, was designed to describe displacement ferroelectrics. Such systems are usually thought of as those for which each and every elementary cell of the crystal loses its dipole moment for temperatures greater than T_c; that is, becomes centrosymmetric. Other ferroelectrics retain elementary dipole moments in each cell even in the nonpolar state, the macroscopic polarization being statistically zero when $T>T_c$ because of a randomness in distribution of the elementary dipoles. These are referred to as order-disorder systems.

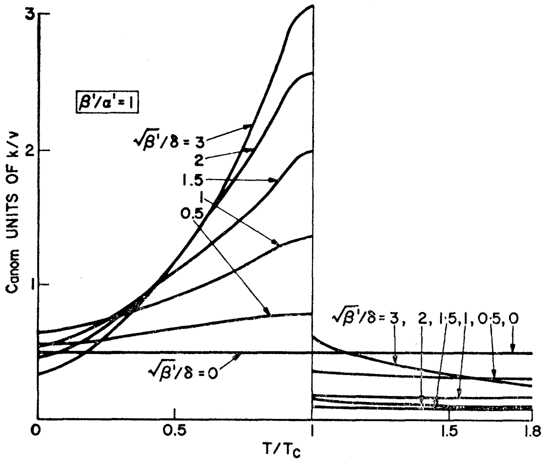

FIG. 3. As Fig. 2, but for $\beta'/\alpha'=1$.

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[3] G. S. Rushbrooke, *Introduction to Statistical Mechanics* (Clarendon Press, Oxford, England, 1949), p. 33.

In reality, the situation can never be quite as clear cut as this. Since we are concerned with the state of the system for $T>T_c$, we must always be concerned with thermally averaged quantities in attempting to differentiate between the two types of ferroelectric. Thus, order-disorder systems will, in general, be those for which the most probable distribution of ions within a primitive cell when $T>T_c$ is not centrosymmetric.

To simplify lattice dynamical calculations for ferroelectric systems it is often convenient to represent the nonpolar state by a centrosymmetric effective ion potential function, in which only even terms in the optic-mode expansion need be retained (see part I). However, it is not generally recognized that the use of such a potential function does not restrict the method to displacement-type systems, except when a subsequent use of perturbation methods restricts the theory further to cases of small anharmonicity. In the present theory, the small-anharmonicity restriction is lifted and we may readily demonstrate how it is possible to progress smoothly from displacement to order-disorder systems by a continuous variation of the relevant parameters in the effective Hamiltonian (2.1).

Consider the case when the coefficient A is negative. For temperatures $T>T_c$, and with zero external field, the effective Hamiltonian per cell reduces to

$$v\mathcal{H}_{\mathrm{eff}}=\tfrac{1}{2}(\pi^2+\omega_0^2\xi^2)+A\xi^4+B\xi^6\,,\quad T\geq T_c\,. \tag{3.1}$$

The displacement coordinate contribution $U(\xi)$ to (3.1) is roughly sketched in Fig. 4 for increasing values of negative quartic anharmonicity. It is evident that there is a limiting value of A above which the potential U develops side minima for which $U(\xi_{\mathrm{min}})\leq U(0)$. In this region ξ is statistically located with equal probability near each of these side minima and is more likely to be found there than near what is now a subsidiary minimum at $\xi=0$ (the centrosymmetric position). Thus, the condition $U(\xi_{\mathrm{min}})=U(0)$ marks the boundary between what are normally thought of as displacement and order-disorder ferroelectrics. In detail, the required boundary is obtained from the simultaneous nonzero solution of the equations

$$\begin{aligned} U(\xi)&=\tfrac{1}{2}\omega_0^2\xi^2+A\xi^4+B\xi^6=0\,,\\ (d/d\xi)U(\xi)&=\omega_0^2\xi+4A\xi^3+6B\xi^5=0\,. \end{aligned} \tag{3.2}$$

Solving, we find

$$\xi_{\mathrm{min}}^4=\omega_0^2/2B=(-A/2B)^2\,. \tag{3.3}$$

It follows that the system represents an order-disorder situation if $A^2>2B\omega_0^2$ which, in terms of the dimensionless parameters used in Fig. 1, becomes

$$\beta'/\alpha'<\tfrac{1}{2}(\beta'^{1/2}/\delta)^2\,,\quad \text{order-disorder}. \tag{3.4}$$

It is of interest to compare this inequality with two others derived in part I. In the present notation, a system will exhibit ferroelectric ordering only if $\beta'/\alpha'<1+\frac{2}{3}(\beta'^{1/2}/\delta)^2$, and the phase transition will be of second order if $\beta'/\alpha'<1+\frac{2}{5}(\beta'^{1/2}/\delta)^2$. Thus, it follows that all order-disorder systems will become ferroelectric (within the effective field and one-soft-mode approximations) at a low enough temperature, and that displacement and order-disorder ferroelectrics can both exhibit either first- or second-order phase transitions. However, we ought still to retain some reservations about the proof of the latter statement since the coefficient $\frac{2}{5}$ in the above inequality for second-order transitions was obtained rigorously only in the small-anharmonicity limit (part I).

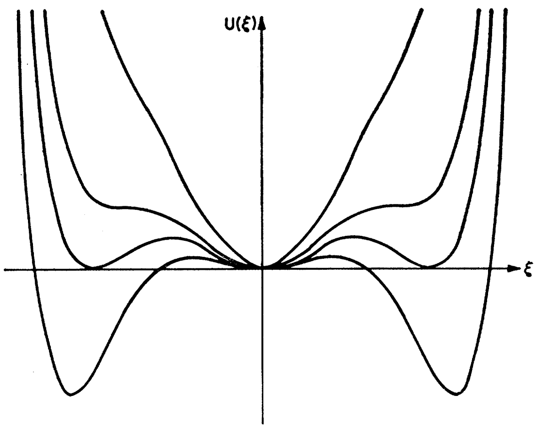

FIG. 4. A rough sketch of the variation in shape of the potential $U(\xi)$ [Eq. (4.12)] as the negative quartic contribution to anharmonicity is increased.

One remaining inequality which will be discussed in the following section can also be mentioned here. We shall find below that, in a classical system, the soft mode of the lattice has a frequency which tends to zero at the Curie temperature only if the potential function $U(\xi)$ has a single local minimum (i.e., at $\xi=0$). The limiting condition occurs when the first and second derivatives of $U(\xi)$ with respect to ξ are simultaneously equal to zero. That is, when

$$\begin{aligned} (d/d\xi)U(\xi)&=\omega_0^2\xi+4A\xi^3+6B\xi^5=0\,,\\ (d^2/d\xi^2)U(\xi)&=\omega_0^2+12A\xi^2+30B\xi^4=0\,. \end{aligned} \tag{3.5}$$

Solving, we find a zero-frequency soft mode at T_c only if $A^2<3B\omega_0^2/2$, which, in dimensionless parameters, is $\beta'/\alpha'>\frac{2}{3}(\beta'^{1/2}/\delta)^2$. We should emphasize that this is a classical result and does not allow for any possibility of tunnelling through a potential barrier. It seems clear (see, for example, Vaks *et al.*[4]) that for cases where barrier penetrability is not small, a quantum description of critical vibrations for $T\rightarrow T_c$ will allow for a soft-mode frequency going to zero somewhat beyond the classical boundary. The various regions of interest within the β'/α', $(\beta')^{1/2}/\delta$ parameter space are shown in Fig. 5.

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[4] V. G. Vaks, V. M. Galitskii, and A. I. Larkin, Zh. Eksperim. i Teor. Fiz. **51**, 1592 (1966) [English transl.: Soviet Phys.—JETP **24**, 1071 (1967)].

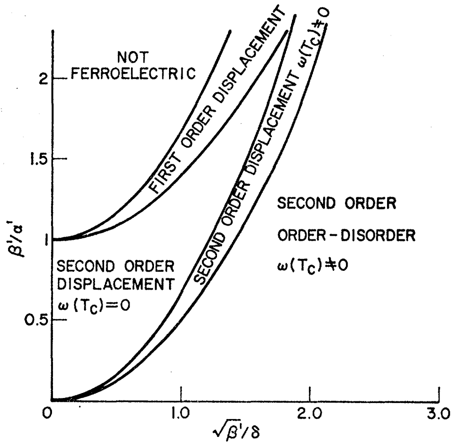

FIG. 5. In the nomenclature of the present series of papers, the qualitative features of the ferroelectric behavior are governed by the parameters β'/α' and $(\beta')^{1/2}/\delta$. The different types of phase transition describable in terms of these parameters are shown, where $\omega(T_c)$ refers to the soft-mode frequency at the Curie temperature. We have defined a displacement ferroelectric as one for which the most probable distribution of ions when $T>T_c$ is centrosymmetric. The results for $\omega(T_c)$ are obtained from a classical calculation and no allowance has been made for quantum-mechanical tunnelling.

4. SOFT-MODE FREQUENCY

In part I, we calculated the temperature dependence of soft-mode frequency only for temperatures close to the Curie point referring, for details, to an earlier description of nonequilibrium properties for a similar model given by Aizu.[5] However, as stressed in part I, these results are limited also to the small-anharmonicity approximation even though Aizu overlooks this and applies them outside this very limited domain. In order to interpret the soft-mode data for $LiTaO_3$ in part III, we require theoretical results for the entire temperature range and results which are also valid far outside the small-anharmonicity region. We proceed as follows.

From the assembly of primitive cells making up the lattice, we single out one to be the "system," the rest acting as a "reservoir." We write the total Hamiltonian $\mathcal{H}$ as the sum of a system Hamiltonian $\mathcal{H}_s$, a reservoir Hamiltonian $\mathcal{H}_r$, and an interaction Hamiltonian $\mathcal{H}_{\text{int}}$. The density matrix (or distribution function in the classical case) for the combined system reservoir complex we label ρ. It has an equation of motion

$$\partial\rho/\partial t=(\mathcal{H},\rho)\,, \tag{4.1}$$

where $(\mathcal{H},\rho)$ represents the commutator divided by $i\hbar$ (or the Poisson bracket[6] for the classical case). The density matrix f_s for the system is the trace over reservoir variables of ρ, that is

$$f_s=\text{tr}_r\rho\,. \tag{4.2}$$

It follows that the equation of motion for f_s is

$$\partial f_s/\partial t=\text{tr}_r(\partial\rho/\partial t)=\text{tr}_r(\mathcal{H}_s+\mathcal{H}_{\text{int}},\rho)\,, \tag{4.3}$$

where we have used the fact that the trace over the reservoir of a commutator of two operators vanishes if one of the operators depends only on the reservoir variables. Equation (4.3) now reduces to

$$\partial f_s/\partial t=(\mathcal{H}_s,f_s)+\text{tr}_r(\mathcal{H}_{\text{int}},\rho)\,. \tag{4.4}$$

In the Hartree or self-consistent-field approximation, we write $\rho=f_sf_r$. Then, noting that

$$(\mathcal{H}_{\text{int}},f_sf_r)=f_s(\mathcal{H}_{\text{int}},f_r)+(f_r\mathcal{H}_{\text{int}},f_s)\,, \tag{4.5}$$

the equation of motion for the system density matrix (distribution function) reduces to

$$\partial f_s/\partial t=(\mathcal{H}_s+\langle\mathcal{H}_{\text{int}}\rangle_r,f_s)\,, \tag{4.6}$$

where

$$\langle\mathcal{H}_{\text{int}}\rangle_r=\text{tr}_r(f_r\mathcal{H}_{\text{int}})\,. \tag{4.7}$$

Thus, in this approximation, the system behaves as if it were subject to an effective Hamiltonian $\mathcal{H}_s+\langle\mathcal{H}_{\text{int}}\rangle_r$.

Considering the one-soft-mode ferroelectric problem and, in particular, Hamiltonian (2.1), it is now clear how we can cast this particular problem in the above formalism by writing

$$\mathcal{H}_s=\tfrac{1}{2}(\pi^2+\omega_0{}^2\xi^2)+A\xi^4+B\xi^6-\eta S\xi E\,, \tag{4.8}$$

$$\langle\mathcal{H}_{\text{int}}\rangle_r=-\eta S\xi\gamma\langle P_{\text{ion}}\rangle_r\,. \tag{4.9}$$

Moreover, since we shall only be directly concerned with the zero-wave-vector mode, we can write

$$\langle P_{\text{ion}}\rangle=\langle P_{\text{ion}}\rangle_r=\langle P_{\text{ion}}\rangle_s=(1/v)\ \text{tr}_s(Sf_s\xi)\,. \tag{4.10}$$

Now, working classically, and therefore defining (a,b) to be the Poisson bracket $(\partial a/\partial\xi)(\partial b/\partial\pi)-(\partial a/\partial\pi)(\partial b/\partial\xi)$, Eq. (4.6) becomes

$$\frac{\partial f_s}{\partial t}=\frac{\partial f_s}{\partial\pi}\left[\frac{\partial U}{\partial\xi}-\eta S(E+\gamma\langle P_{\text{ion}}\rangle)\right]-\pi\frac{\partial f_s}{\partial\xi}\,, \tag{4.11}$$

where

$$U=\tfrac{1}{2}\omega_0{}^2\xi^2+A\xi^4+B\xi^6\,. \tag{4.12}$$

One easily verifies that the equilibrium value of f_s is

$$f_{\text{eq}}=\exp\left(\frac{-\mathcal{H}_{\text{eq}}}{kT}\right)\bigg/\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp\left(\frac{-\mathcal{H}_{\text{eq}}}{kT}\right)d\pi d\xi\,, \tag{4.13}$$

where

$$\mathcal{H}_{\text{eq}}=\mathcal{H}_s+\langle\mathcal{H}_{\text{int}}\rangle_{s,\text{eq}}\,. \tag{4.14}$$

Care is taken to distinguish between $\langle\mathcal{H}_{\text{int}}\rangle$ and $\langle\mathcal{H}_{\text{int}}\rangle_{\text{eq}}$ (we may now drop the subscript s), the subscript eq denoting the situation in the limit $f\rightarrow f_{\text{eq}}$ of Eq. (4.13).

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[5] K. Aizu, J. Phys. Soc. Japan **21**, 1240 (1966).

[6] D. ter Haar, *Elements of Hamiltonian Mechanics* (North-Holland Publishing Co., Amsterdam, 1961).

We now wish to describe small oscillations of the system about the equilibrium state, i.e., to describe small deviations of f from f_{eq}. We write

$$f(\xi,\pi,t)=f_{\text{eq}}(\xi,\pi)+\sigma(\xi,\pi)e^{-i\omega t}. \tag{4.15}$$

Substituting (4.15) into (4.11) we find the equation of motion for σ in the form

$$-i\omega\sigma+\pi\frac{\partial\sigma}{\partial\xi}+\frac{\partial\sigma}{\partial\pi}\left[\eta S(E+\gamma\langle P_{\text{ion}}\rangle)-\frac{\partial U}{\partial\xi}\right]+\frac{\eta\gamma S^2}{v}\frac{\partial f_{\text{eq}}}{\partial\pi}\operatorname{tr}(\xi\sigma)=0, \tag{4.16}$$

where

$$\operatorname{tr}(\xi\sigma)=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\xi\sigma(\xi,\pi)d\xi d\pi. \tag{4.17}$$

This equation of motion takes on a much simplified form when expressed in terms of new canonical variables $\mathcal{H}$ and θ, where $\mathcal{H}$ is the total effective Hamiltonian per cell (system) as given in (2.1) and θ is an angle variable[7] denoting time along the trajectory, and defined by

$$d\theta=d\xi/\pi(\mathcal{H},\xi). \tag{4.18}$$

In terms of the new variables, the equation of motion for $\sigma(\theta,\mathcal{H})$ is

$$-i\omega\sigma+\frac{\partial\sigma}{\partial\theta}=\frac{\pi(\theta,\mathcal{H})}{kT}f_{\text{eq}}(\mathcal{H})Q, \tag{4.19}$$

where

$$Q=\frac{\eta\gamma S^2}{v}\int\int\xi(\theta,\mathcal{H})\sigma(\theta,\mathcal{H})d\theta d\mathcal{H}. \tag{4.20}$$

Taking ξ, π, and σ to be periodic with period $T(\mathcal{H})$, we can expand them

$$\begin{aligned}\xi&=\sum_n \xi_n\exp(-in\omega_H\theta),\\ \pi&=\sum_n \pi_n\exp(-in\omega_H\theta),\\ \sigma&=\sum_n \sigma_n\exp(-in\omega_H\theta),\end{aligned} \tag{4.21}$$

where $\omega_H=2\pi/T(\mathcal{H})$. Using the Hamilton equation of motion $\pi_n=-in\omega_H\xi_n$, a solution of (4.19) is now readily found in the form

$$\sigma_n=\frac{n\omega_H Q f_{\text{eq}}\xi_n}{(\omega+n\omega_H)kT}. \tag{4.22}$$

Putting this solution in (4.20) we obtain, finally, the temperature dependence of the frequency ω in the implicit form

$$kT=\frac{\eta\gamma S^2}{v}\int\sum_{n=-\infty}^{+\infty}\left[1+\frac{\omega^2}{n^2\omega_H{}^2-\omega^2}\right]f_{\text{eq}}|\xi_n|^2d\mathcal{H}, \tag{4.23}$$

where $|\xi_n|^2$ is written for $\xi_n\xi_{-n}$. Noting that

$$\langle\xi^2\rangle_{\text{eq}}=\sum_{n=-\infty}^{+\infty}f_{\text{eq}}|\xi_n|^2d\mathcal{H}, \tag{4.24}$$

and that the $n=0$ term from the sum in (4.23) vanishes, we can rewrite the frequency equation as

$$kT/(\eta\gamma S^2/v)-\langle\xi^2\rangle_{\text{eq}}=-\int f_{\text{eq}}|\xi_0|^2d\mathcal{H}+\int\sum_{n=1}^{\infty}\frac{2\omega^2}{n^2\omega_H{}^2-\omega^2}f_{\text{eq}}|\xi_n|^2d\mathcal{H}. \tag{4.25}$$

As far as statistical mechanics is concerned the job is now done but, to put (4.25) into a useful form (i.e., to express ω directly as a function of temperature and the parameters of the effective Hamiltonian), it is still necessary to solve (2.1) for the classical motion of a single system and this, in general, requires numerical computation. However, the problem does simplify enormously in a few special cases. Consider, first, the situation when $T\to 0$.

A. Low-Temperature Limit

At very low temperatures $\xi\to\xi_0$ where, by minimizing the Hamiltonian (2.1) with respect to ξ and writing $\langle P_{\text{ion}}\rangle=(S/v)\xi_0$, we have, for $E=0$,

$$\xi_0=(1/6B)^{1/2}(-2A+\{4A^2+6B[(\eta\gamma S^2/v)-\omega_0{}^2]\}^{1/2})^{1/2}. \tag{4.26}$$

Also, in this limit, the motion of the system will be very closely harmonic about ξ_0. Expanding the effective ionic potential about $\xi=\xi_0$, we find

$$v\mathcal{H}_{\text{eff}}=\mathcal{H}=\tfrac{1}{2}\pi^2+\text{const}+\tfrac{1}{2}\Omega_0{}^2(\xi-\xi_0)^2+\cdots, \tag{4.27}$$

where

$$\Omega_0{}^2=\omega_0{}^2+12A\xi_0{}^2+30B\xi_0{}^4. \tag{4.28}$$

In this quasiharmonic state, all ξ_n are zero except for $n=0$, 1. Writing $\xi-\xi_0=\xi_1\exp(-i\Omega_0\theta)+\xi_{-1}\exp(i\Omega_0\theta)$, and using the fact that

$$|\xi_1|^2+|\xi_{-1}|^2=\mathcal{H}/\Omega_0{}^2, \tag{4.29}$$

Eq. (4.23) [or Eq. (4.25)] now reduces to

$$\Omega_0{}^2-\omega^2=\frac{\eta\gamma S^2}{v}\int_0^{\infty}ze^{-z}dz\bigg/\int_0^{\infty}e^{-z}dz=\frac{\eta\gamma S^2}{v}. \tag{4.30}$$

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[7] L. D. Landau and E. M. Lifshitz, *Mechanics* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1960).

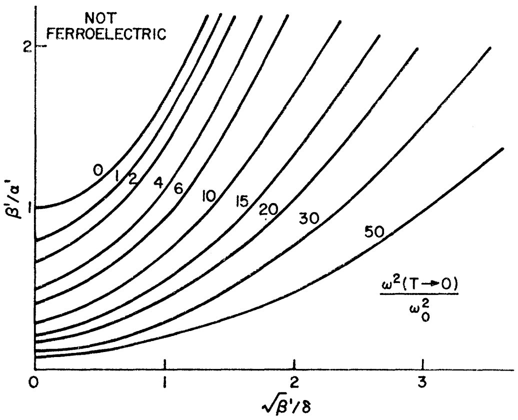

FIG. 6. The soft-mode frequency $\omega(T \to 0)$ is shown in the form $\omega^2(T \to 0)/\omega_0^2$ as a function of β'/α' and $(\beta')^{1/2}/\delta$. The calculation has been carried out by a method which is valid both for displacement and order-disorder systems, and also for ferroelectrics exhibiting either a first- or second-order phase transition at T_c.

Thus, as $T \to 0$, we find $\omega \to \omega(0)$, where

$$\omega^2(0)=\omega_0^2+12A\xi_0^2+30B\xi_0^4-(\eta\gamma S^2/v). \quad (4.31)$$

Using (4.26), we can easily express $\omega(0)$ in terms of the parameters of the effective Hamiltonian. It is most easily cast in terms of the dimensionless parameters β'/α' and $(\beta')^{1/2}/\delta$ and we show the final result in Fig. 6 where we plot $\omega^2(0)/\omega_0^2$ as a function of these dimensionless parameters, the calculations being valid for displacement and order-disorder regions as well as for both second- and first-order systems. In particular, we note that $\omega(0) \to 0$ as we approach the ferroelectric-nonferroelectric boundary.

B. Near the Curie Temperature

For temperatures $T \to T_c$ we are also able to effect some simplification of (4.25). Let us first consider the term $\int f_{\text{eq}}|\xi_0|^2 d\mathcal{H}$. The function ξ_0 is the value of ξ averaged over a period of oscillation (i.e., averaged over θ for a particular value of $\mathcal{H}$). For temperatures $T > T_c$, where the effective potential U from (4.12) is symmetric in ξ, $|\xi_0|^2$ is zero for all $\mathcal{H}$ unless $U(\xi)$ has subsidiary minima for some nonzero values of ξ. In Sec. 3, we showed this to occur when $\beta'/\alpha' < \frac{3}{4}(\beta'^{1/2}/\delta)^2$. In general, the integral $\int f_{\text{eq}}|\xi_0|^2 d\mathcal{H}$ is made up of two parts; one which is temperature-independent and, in particular, is zero for the case of a single minimum $U(\xi)$, and one which is temperature-dependent and is very closely, though not exactly, equal to $\langle\xi\rangle_{\text{eq}}^2$.

Using the values for $\langle\xi^2\rangle_{\text{eq}}-\langle\xi\rangle_{\text{eq}}^2$ computed in part I, Eq. (4.25) becomes, for $T \to T_c$,

$$\frac{k(T-T_c)\Phi}{(\eta\gamma S^2/v)} \approx -\Delta+\int \sum_{n=1}^{\infty} \frac{2\omega^2}{n^2\omega_H^2-\omega^2} f_{\text{eq}}|\xi_n|^2 d\mathcal{H}, \quad (4.32)$$

where Φ takes on values $\frac{2}{3}-\mu'$ and $-2(\frac{2}{3}-\mu')$ in the paraelectric and ferroelectric states, respectively, (where μ' is computed in Fig. 12 of part I), and where Δ is the paraelectric value of $\int f_{\text{eq}}|\xi_0|^2 d\mathcal{H}$.

For systems with single minimum $U(\xi)$ we have $\Delta=0$, and it follows immediately that $\omega^2 \propto T-T_c$ as $T \to T_c$ from both the polar and nonpolar phases for such a case. We can now make contact with Aizu[5] by considering the case for small anharmonicity. In this limit, $\omega_H \to \omega_0$ and the motion is again quasiharmonic (i.e., all ξ_n zero except for $n=0, 1$). Thus, for $T \to T_c$, Eq. (4.32) reduces to

$$\frac{k(T-T_c)\Phi}{\eta\gamma S^2/v} \approx \frac{\omega^2}{\omega_0^2}\langle\xi^2\rangle_{\text{eq}} = \frac{\omega^2 kT_c}{\omega_0^2(\eta\gamma S^2/v)}, \quad (4.33)$$

where we have used the Eq. (5.2) from part I to relate $\langle\xi^2\rangle_{\text{eq}}$ at the Curie temperature to kT_c. From (4.33) we find

$$\begin{aligned} \omega_p^2(T \to T_c) &= \omega_0^2\Phi_p(T-T_c)/T_c, \\ \omega_f^2(T \to T_c) &= \omega_0^2\Phi_f(T-T_c)/T_c, \end{aligned} \quad (4.34)$$

where the subscripts p and f refer to the paraelectric and ferroelectric phases, respectively. Aizu, however, uses these equations for the limit $(\beta')^{1/2}/\delta \to 0$, $(\beta'/\alpha') \propto \omega_0^2 \to 0$ (for which case $\Phi_p=1$ and $\Phi_f=-2$), and this is certainly far outside the small anharmonicity range for which they are valid.

For larger anharmonicity systems, frequencies must be computed numerically using (4.32). For most cases within the displacement phase of β'/α', $(\beta')^{1/2}/\delta$ space, the error incurred by neglecting all values of n larger than one is quite small. With this approximation, the soft-mode problem reduces to a determination of ω_H and $\xi_1(\mathcal{H})$ by solving the classical mechanical problem of motion in a potential $U(\xi)$ [Eq. (4.12)] followed by a numerical evaluation of

$$\int_0^{\infty} |\xi_1|^2 \left(\frac{1}{\omega_H}\right)^2 \exp\left(\frac{-\mathcal{H}}{kT}\right) d\mathcal{H},$$

making use of the fact that $\omega_H^2 \gg \omega^2$ for all $\mathcal{H}$ when $T \to T_c$.