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# Statics and dynamics of fluctuation quenching in elastic media under an ordering force: Application to light scattering in $KH_2PO_4$

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Phase transitions in elastic media, taking place under the application of the force conjugated to the order parameter (the ordering force), are discussed theoretically. The force imposes to the solid the symmetry of the new phase, and this produces a linear coupling between order parameter and scalar variables such as density and energy. If there exists a diverging susceptibility $\chi(T,\vec{q})$ in the absence of the force, it will generally become quenched by the induced coupling to density in the elastic solid. Specifically, one finds that $\chi$ acquires a discontinuity at the wave vector $q=0$, with only $\chi(T,0)$ that can diverge. This fluctuation quenching is discussed in general, and detailed calculations are given for the ferroelastic transition in $KH_2PO_4$. As light scattering is a choice investigation method in that case, particular results are given for the scattering intensity, as well as for the size and motion of the scattering cone under the applied force. The force also modifies the dynamics in an essential way, as order-parameter fluctuations become linearly coupled to entropy fluctuations. This coupling leads to a thermal central peak whose strength and width are derived.

## I. INTRODUCTION

Systems that undergo elastic transitions can be classified according to the dimension of their soft subspace in reciprocal space. A type-I instability corresponds to transitions with only soft directions, whereas type-II designates those with soft planes.[1] There exist also type-0 instabilities for which only a point, $q=0$, is soft in the Brillouin zone. Elastic transitions with symmetry breaking are always of type greater than zero.[2,3] The converse statement is generally true, namely, nonsymmetry-breaking elastic transitions are generally of type-0, except for accidental combinations of material parameters. Type-0 instabilities are known to occur in a variety of systems, for example in transitions obtained by H dissolution in certain metals,[4] or in mixed-valence compounds in which the volume compressibility exhibits an anomaly.[5] In such cases, macroscopic modes with $q \approx L^{-1}$, where $L$ is a typical sample dimension, may become important.[4] Those modes depend strongly on boundary conditions, as recently demonstrated for the Nb-H system.[6]

Type-0 second-order transitions can also be induced by application of the force conjugated to the order parameter of a symmetry-breaking transition. For example, application of the appropriate stress can transform a type-I or type-II first-order instability into a type-0 instability that terminates at a critical point (corresponding to a critical value of the external stress). A type-0 instability is also expected to occur in systems where the elastic degrees of freedom are only secondary order parameters by turning on the force conjugated to the primary order parameter, e.g., by applying a magnetic field on a compressible ferromagnet.[7] The present paper considers the statics and dynamics of such induced type-0 transitions, with special attention to the case of $KH_2PO_4$ (KDP) for which experiments have already been performed.[8] In that case, the transition is easily changed from type-I to type-0 by application of a static electric field $E$ parallel to the $z$ axis, which is the axis of the spontaneous polarization $P$ that develops at the tetragonal ($\bar{4}2m$) to orthorhombic ($2mm$) ferroelectric transition.

The absence of critical microscopic fluctuations in a type-0 transition justifies the use of a Landau expansion as will be done here.[1,8] Indeed, at such a transition one expects no diverging correlation range, no associated critical slowing down, and thus no cluster-induced nonanalycity of the free energy. Furthermore, in the case of KDP, the transition without field is type-I, which has an upper critical dimensionality of only 2.5.[1,9] Hence, a Landau approach is fully justified for $d=3$. It should be noted that the absence of critical microscopic fluctuations at a type-0 transition is purely an elastic effect. If one could ignore elastic couplings, the conclusion would be that second-order transitions induced by application of the ordering force should behave just as the liquid-gas critical point.[10] In the hypothetical case of a phase transition in a simple isotropic solid, Ginzburg and Levanyuk already pointed out that it is the presence of a nonvanishing shear modulus that prevents the divergence of microscopic fluctuations and the observation of true critical opalescence in light scattering.[11]

KDP is the model substance for H-bonded ferroelastic ferroelectrics, as well as the prototype of a rich family.[12,13] It is generally agreed that the transition is related to the ordering of protons.[14] This ordering couples to an optic mode of $B_2$ symmetry associated with cation displacement parallel to the tetragonal $c$ axis.[15] The resulting polarization couples piezoelectrically to the strain component $e_6$,[16] that is, to $xy$ shear.[13] The corresponding acoustic branches become unstable, producing the type-I transition indicated above. Brillouin scattering ideally probes that instability. The spectrum is proportional to the relevant correlation function $\langle \delta P \delta P \rangle_{\vec{q},\omega}$ where $\delta P$ designates the order-parameter fluctuations, and the subscripts $\vec{q}$, $\omega$ indicate space-time Fourier transformations. It is important to note, however, that Brillouin scattering does not give any indication as to the origin of the optic-mode softening, nor can it test tunneling theories. Conversely, the proton-ordering aspect, which could be expected to belong either to the 3D Ising or to the 3D dipolar universality classes, becomes irrelevant sufficiently close to the transition where the crossover to the type-I elastic universality class has taken place.

The transition in KDP is known to be slightly first order.[17] Polarization measurements[18] as well as x-ray diffractometry[19] have been used to investigate the transition under hydrostatic pressure $p$, and have established that it becomes continuous above a tricritical point (TCP) about 2.5 kbar. Under application of the ordering electric field $E$, one expects two wings as sketched in Fig. 1. The present work considers the light-scattering behavior in an $ET$ plane with $p$ below the TCP value. For convenience, the value $p=0$ is selected. The transition with $p=E=0$ has already been investigated thoroughly.[20,21] Hardening of the adiabatic elastic constant under $E$ has also been observed.[20] The early experimental work was impaired by the presence of a rather strong central-peak feature,[22] which was later recognized to be static[23] and annealable.[24] It is the availability of highly perfect annealed crystals that has now allowed the observation of the reduction under $E$ of the overall scattered intensity,[8] an effect which indicates fluctuation quenching. Simultaneously, a thermal central peak occurs, whose intensity and width could also be measured.[25] This peak is produced by the coupling of thermal fluctuations to order-parameter fluctuations, and it has a similar origin to the thermal central peak of the ferroelectric phase.[26,27] That particular aspect of the present work has already been described qualitatively elsewhere.[28]

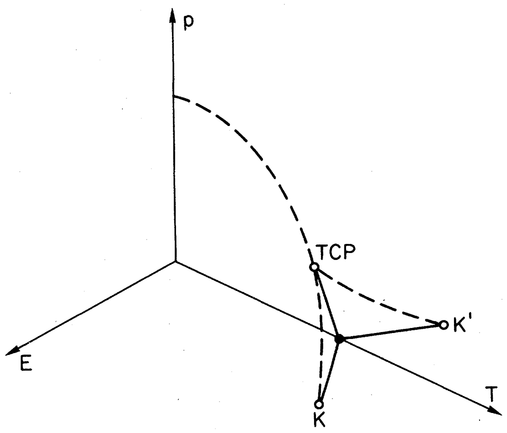


FIG. 1. KDP phase diagram. In the $E=0$ plane, the transition is of type-I, and it is continuous at pressures above the TCP. On the wings, at $E \neq 0$, the transition is of type-0, orthorhombic to orthorhombic. It becomes continuous on the lines $K$ to TCP and $K'$ to TCP.

In the following sections, the above ideas are developed in detail, first, in general terms, then, with particular application to KDP. In Sec. II, an appropriate Landau free-energy expansion is presented. In Sec. III, this expansion is used to calculate the *macroscopic* response, the shift of transition temperature with hydrostatic pressure, the $ET$ phase diagram, and the classical exponents. The relation to light scattering is discussed in Sec. IV: the scattered spectrum is related to generalized susceptibilities using the fluctuation-dissipation theorem, sum rules are presented, and expressions are derived for particular scattering geometries of interest for KDP. The *microscopic* susceptibilities needed to calculate the spectrum are then obtained using the Landau free-energy expansion; in Sec. V, only the quenching of integrated intensities, the shape of the scattering cone, and its motion with $E$, are considered. In Sec. VI, the spectral shapes are discussed: to this effect, dynamical equations are derived, and these are used to calculate the relative strength and the width of the thermal central peak.

## II. LANDAU EXPANSION IN PRESENCE OF THE ORDERING FORCE

Consider a parent phase that transforms into a lower symmetry distorted phase at some temperature $T_{tr}$. The transition is assumed to be slightly first order, so that the absolute instability of the parent phase with respect to the distortion of interest occurs at a temperature $T_a$ slightly below $T_{tr}$. Here, for convenience, we take the parent phase to be the high-temperature one. Let us assume that one can impose externally the force conjugated to the order parameter $\eta$. Under that force the symmetry is broken. However, for small enough force, a jump in $\eta$ at a temperature near $T_{tr}$ still occurs: this is a nonsymmetry-breaking transition. By varying the force, one obtains lines of first-order transition that terminate at critical points. For a one-component order parameter, the situation is as shown on the *ET* plane of Fig. 1. Invariants of the group of the parent phase can always be constructed by combining $\eta$ with those elastic degrees of freedom that transform as the identity representation of the group of the distorted phase. One such simple invariant is the product of the second-order invariant in $\eta$ with those strain combinations that transform as the identity representation of the parent group. Under the applied force, $\eta$ is nonzero; the effect of the above terms is that the nonsymmetry-breaking transition is elastically coupled. Hence, it is generally a type-0 elastic transition.

The free energy is expanded about a reference configuration of the parent phase. As the transition was assumed to be slightly first order, there is no third-order invariant in $\eta$. The susceptibilities are related to second derivatives of the free energy. Hence, to obtain the lowest-order changes of susceptibilities produced by the applied force, it is necessary that the expansion be complete up to all fourth-order invariants, including all strain couplings to the same order in $\eta$. To discuss stability limits, it would be sufficient to restrict the expansion to those strain combinations that transform as the identity representation of the distorted phase. However, in Secs. V and VI we will also be interested in waves with more general transformation properties. For this reason, it is expedient to write down a full expansion immediately. To find all terms of the expansion, it can be convenient to consider the elastic stiffness tensor of the distorted phase and to compare it to that of the parent phase. Those elements that are new in the distorted phase are polynomials odd in $\eta$, whereas those elements that are common to both tensors are even in $\eta$.

The above ideas are now applied to the particular case of KDP. Here, two additional circumstances have to be considered: (i) $P$ and $e_6$ are linearly coupled in the parent phase. Hence, either one, or a linear combination, could be taken as suitable order parameter. We select $P$ as primary order parameter, as the applied force is the electric field $E$ conjugated to $P$. However, in the distorted phase, $e_6$ is an odd polynomial in $P$, and this generates additional terms in the Landau expansion. (ii) The orthorhombic $x,y$ axes of the distorted phase are rotated by $\pi/4$ around $\hat{z}$ with respect to the tetragonal $x,y$ axes. This means that the three orthorhombic strains $e_i^0$ ($i=1$ to 3) that transforms as the identity representations of the distorted phase are related to strains $e_i$ in the tetragonal axes by $e_1=e_2=\frac{1}{2}(e_1^0+e_2^0)$, $e_6=e_1^0-e_2^0$, $e_3=e_3^0$. In the following, only tetragonal axes of the parent phase will be used. However, as mentioned more generally above, the expansion will not be restricted to $e_1=e_2$ as we will later be interested in waves propagating along $\hat{x}$.

To describe the isothermal macroscopic response under constant external forces (constant stress $\vec{\sigma}$ and electric field $\vec{E}$), it is appropriate to use the Gibbs free-energy density $G(\vec{\sigma},\vec{E},T)$. To describe wave properties, it is more convenient to use an expansion in terms of strain and polarization (Helmoltz free energy $F$). The relation between $G$ and $F$ is simply

$$G(\vec{\sigma},\vec{E},T)=F(\vec{e},\vec{P},T)-\vec{e}\cdot\vec{\sigma}-\vec{P}\cdot\vec{E}\ ,$$

from which $\vec{e}$ and $\vec{P}$ are eliminated using the equilibrium conditions $\partial F/\partial e_i=\sigma_i$ and $\partial F/\partial P_j=E_j$. Here, we proceed to a Helmoltz expansion and subtract the products $e_i\sigma_i$ and $EP$ (only the ordering field $E_3\equiv E$ is considered). Although the canonical transformation will not be completed immediately, we call the result the Gibbs free-energy density. It is written

$$G=F_0+G_P+G_E+G_{PE}+G_{TE}\ . \tag{2.1}$$

The reference configuration is for the moment taken to be the paraelectric phase at $T=T_a$ (free Curie temperature), assuming that point could be reached, and with no applied forces ($E=\vec{\sigma}=0$). In Eq. (2.1):

(1) $F_0$ is the background lattice free-energy density, related to the background specific heat $C_{P,e}$ by

$$\left(\frac{\partial^2 F_0}{\partial T^2}\right)_{P,e}=-\frac{\rho C_{P,e}}{T}\ , \tag{2.2}$$

where the subscripts designate constant polarization and strain, and where $\rho$ is the density.

(2) $G_P$ is the polarization contribution, where only $P_3\equiv P$ will be considered, since only the ordering field is applied

$$G_P=\tfrac{1}{2}a(T-T_c)P^2+\tfrac{1}{4}BP^4+\cdots-PE\ . \tag{2.3}$$

Here, $T_c$ is the "clamped" Curie temperature, which is the instability point in the absence of coupling to the elastic degrees of freedom. Note that $B$ is *not* the macroscopically measured "Landau $B$ coefficient." The latter will be designated by $B_M$ and it is derived in the following section. The dots represent sixth order and higher terms necessary to stabilize the system. A full expansion to sixth order in $P$ would contain a large number of unknown coefficients and would hardly be useful. Hence, a term $\frac{1}{6}CP^6$ will be added simply to the macroscopic free energy in the next section [Eq. (3.16)] in order to discuss the phase digram. The coefficient $C$ is then equal to the macroscopic value that can be derived from polarization measurements.[18]

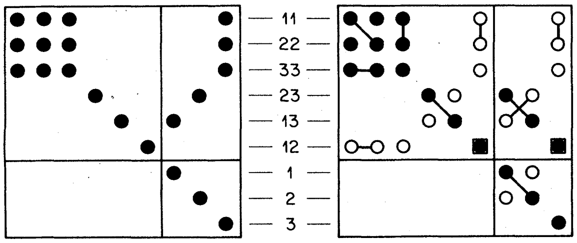
(3) $G_E$ is the pure elastic contribution to fourth order in $P$, remembering that $e_6$ is linear, and that $e_1$, $e_2$, and $e_3$ are quadratic in $P$:

$$G_E=\tfrac{1}{2}C_{11}E_1^2+\tfrac{1}{2}C_{11}e_2^2+C_{12}e_1e_2+\tfrac{1}{2}C_{33}e_3^2+C_{13}e_1e_3+C_{13}e_2e_3+\tfrac{1}{2}C_{66}e_6^2+\tfrac{1}{2}C_{44}e_4^2+\tfrac{1}{2}C_{44}e_5^2-e_i\sigma_i$$
$$+\tfrac{1}{2}C_{166}e_1e_6^2+\tfrac{1}{2}C_{166}e_2e_6^2+\tfrac{1}{2}C_{366}e_3e_6^2+C_{456}e_4e_5e_6+\frac{1}{4!}C_{6666}e_6^4\ . \tag{2.4}$$

Here, the $C$'s are elastic stiffnesses at constant $T$ and $P$, and Brugger's definition of the higher-order elastic constants has been used.[29] Note that $G_E$ above does not contain *all* third- and fourth-order terms in *all* strains. It just contains all quadratic terms in the strains, and only those third- and fourth-order terms that give quadratic contributions in strain fluctuations under the application of a static electric field $E$, or of a static stress $\sigma_6$. An easy way to see that Eq. (2.4) is complete in the above sense is to consider the elastic-constant tensor of the distorted phase (obtained by application of a static $\sigma_6$ to the parent phase) as shown in Fig. 2(a). This tensor is then rotated to the coordinate system of the parent phase [Fig. 2(b)]. Those elements that appear in addition to the usual ones of the parent point group ($\bar{4}2m$) are proportional to $e_6$ and are included in Eq. (2.4).

(4) $G_{PE}$ contains the mixed polarization and strain terms, that is, piezoelectricity and electrostriction, to fourth order in $P$ and $e_6$. One has

$$G_{PE}=-h_{36}Pe_6-\delta_6P^3e_6-\delta_6'Pe_6^3-\delta_1P^2e_1-\delta_1P^2e_2$$
$$-\delta_3P^2e_3+\tfrac{1}{2}\Delta_{16}Pe_1e_6+\tfrac{1}{2}\Delta_{16}Pe_2e_6+\tfrac{1}{2}\Delta_{36}Pe_3e_6$$
$$+\tfrac{1}{2}\Delta_{66}P^2e_6^2\ . \tag{2.5}$$



(a) (b)

FIG. 2. Diagrams of allowed tensor coefficients for second-, third-, and fourth-rank tensors. Bars connect equal elements: (a) Point group $mm2$, which is the orthorhombic point group of the low-temperature phase of KDP. (b) The same as (a) but with the $(\hat{x}-\hat{y})$ axes rotated by 45° about $\hat{z}$: here full dots represent the point group $\bar{4}2m$ of the high-temperature phase, open dots represent additional elements produced by the lower $mm2$ symmetry, and squares indicate elements whose nonlinearities are important for the considerations of Eqs. (2.4) and (2.5). The line indices are indicated between (a) and (b).

Here, $h_{36}$ is the usual piezoelectric coefficient, and the subscripts (36) will be dropped for notational simplicity. The other coefficients are denoted by $\delta$ and $\Delta$, with the polarization subscript 3 omitted for the same reason. There seems to be no standard notation for these coefficients. Their existence derives from a consideration of the third column of the piezoelectric tensor in Fig. 2(b). The omission of terms in $P_1$ and $P_2$ amounts to neglecting the tensor coefficients in the first and second columns of the piezoelectric tensor of Fig. 2(b). These only play a role for waves with appreciable $e_4$ and $e_5$ components.

(5) Finally, $G_{TE}$ accounts for thermal expansion. It is written

$$G_{TE}=-[\alpha_1(e_1+e_2)+\alpha_3e_3]\Delta T\ , \tag{2.6}$$

where the following definitions are used

$$\alpha_1\equiv\alpha_{11}(C_{11}+C_{12})+\alpha_{33}C_{13}\ , \tag{2.7a}$$

$$\alpha_3\equiv2\alpha_{11}C_{13}+\alpha_{33}C_{33}\ , \tag{2.7b}$$

$$\Delta T\equiv T-T_a\ . \tag{2.7c}$$

Here, $\alpha_{ij}$ is the thermal expansion tensor at constant $P$.[30] The effect of thermal expansion being altogether small, no nonlinear term has been included in Eq. (2.6). Note that Eq. (2.7c) is consistent with our choice of the parent phase at $T=T_a$.

This completes the Landau expansion which will allow us to calculate both macroscopic and microscopic responses. In spite of the vast knowledge accumulated on KDP, several coefficients appearing in Eqs. (2.4) and (2.5) have never been measured. As will be shown below, this does not prevent the comparison of theory and experiment, as these coefficients will occur in final results in combinations which have actually been established experimentally.

## III. MACROSCOPIC RESPONSE AND THE PHASE DIAGRAM

The equilibrium state is obtained by elimination of all strains from Eq. (2.1) using

$$\frac{\partial G}{\partial e_i}=0\quad(i=1\text{ to }6)\ . \tag{3.1}$$

After elimination of the $e_i$'s the expression $\partial G/\partial\eta=0$ becomes the equation of state connecting the order parameter to the external force. Here, it is assumed that, as in the case of KDP, the order parameter is not a strain. Otherwise the relation $\partial G/\partial\eta=0$ would already be one (or several) of the equations (3.1). The derivative in $\eta$ of $\partial G/\partial\eta$ is the inverse of the macroscopic susceptibility. In practice, the equations (3.1) are nonlinear and clumsy to solve. Furthermore, the coefficients $a_{in}$ of the expansion

$$e_i=\sum_n a_{in}\eta^n \tag{3.2}$$

are generally accessible to experiment. Hence, it is preferable to consider Eq. (3.2) as experimentally established, and to introduce these equations in Eq. (3.1) to derive relations between the experimentally known $a_{in}$'s and the coefficients that apppear in $G$. If convenient, these relations can also be introduced in $\partial G/\partial\eta=0$ in order to express the equation of state, inasmuch as possible, in terms of measured quantities.

Let us see how this works out for KDP. As we will also discuss the effect of hydrostatic pressure, we take $\sigma_1=\sigma_2=\sigma_3=-p$ where $p$ is the pressure. The symmetry of the low-temperature phase imposes $e_1=e_2$ and $e_4=e_5=0$. Then Eq. (3.1) reduces to the three independent equations

$$(C_{11}+C_{12})e_1+C_{13}e_3+\tfrac{1}{2}C_{166}e_6^2-\delta_1P^2+\tfrac{1}{2}\Delta_{16}Pe_6-\alpha_1\Delta T+p=0\ , \tag{3.3a}$$

$$2C_{13}e_1+C_{33}e_3+\tfrac{1}{2}C_{366}e_6^2-\delta_3P^2+\tfrac{1}{2}\Delta_{36}Pe_6-\alpha_3\Delta T+p=0\ , \tag{3.3b}$$

$$C_{66}e_6+2C_{166}e_1e_6+C_{366}e_3e_6+\tfrac{1}{6}C_{6666}e_6^3-hP-\delta_6P^3-3\delta_6'Pe_6^2+\Delta_{16}Pe_1+\tfrac{1}{2}\Delta_{36}Pe_3+\Delta_{66}P^2e_6=0\ . \tag{3.3c}$$

These equations were obtained from $\partial G/\partial e_1=0$, $\partial G/\partial e_3=0$, in which $e_2$ has been replaced by $e_1$. Similarly, from $\partial G/\partial P=0$, one obtains

$$E=a(T-T_c)P+BP^3-he_6-3\delta_6P^2e_6-\delta_6'e_6^3-4\delta_1Pe_1-2\delta_3Pe_3+\Delta_{16}e_1e_6+\tfrac{1}{2}\Delta_{36}e_3e_6+\Delta_{66}Pe_6^2\ . \tag{3.4}$$

The symmetry of the low-temperature phase, and also the symmetry of Eq. (3.3), give for the expansion (3.2) in the present case

$$e_1=\epsilon_1+\alpha P^2+\cdots\ , \tag{3.5a}$$

$$e_3=\epsilon_3+\beta P^2+\cdots\ , \tag{3.5b}$$

$$e_6=bP+mP^3+\cdots\ . \tag{3.5c}$$

Here, $\epsilon_1$ and $\epsilon_3$ are independent of $P$ and are proportional to the source terms $\alpha_1\Delta T-p$ and $\alpha_3\Delta T-p$ in Eqs. (3.3a) and (3.3b), respectively.

Let us first discuss the case $p=0$ and neglect thermal expansion contributions [set $\Delta T=0$ in Eq. (3.3) and $\epsilon_1=\epsilon_3=0$ in Eq. (3.5)]. Introducing Eq. (3.5) in Eqs. (3.3a) and (3.3b), and observing that the result should be an identity to order $P^2$, one obtains

$$\delta_1=(C_{11}+C_{12})\alpha+C_{13}\beta+\tfrac{1}{2}C_{166}b^2+\tfrac{1}{2}\Delta_{16}b\ , \tag{3.6a}$$

$$\delta_3=2C_{13}\alpha+C_{33}\beta+\tfrac{1}{2}C_{366}b^2+\tfrac{1}{2}\Delta_{36}b\ . \tag{3.6b}$$

Similarly, with Eq. (3.3c), to order $P$ and $P^3$, one obtains

$$h=C_{66}b\ , \tag{3.6c}$$

$$\delta_6+3b^2\delta_6'=C_{66}m+2C_{166}\alpha b+C_{366}\beta b+\Delta_{16}\alpha+\tfrac{1}{2}\Delta_{36}\beta+\Delta_{66}b+\tfrac{1}{6}C_{6666}b^3\ . \tag{3.6d}$$

Finally, Eqs. (3.5) are introduced in Eq. (3.4), and Eqs. (3.6) can be used to eliminate some of the unknown coefficients. We chose to eliminate from the result the coefficients $\delta_1$, $\delta_3$, and $m$. The resulting equation of state is of the form

$$E=AP+B_MP^3+CP^5+\cdots\ , \tag{3.7}$$

where

$$A\equiv a(T-T_c)-bh=a(T-T_a)\ , \tag{3.8a}$$

with

$$T_a-T_c=h^2/aC_{66}\ , \tag{3.8b}$$

and

$$B_M\equiv B+2\Delta_{66}b^2+\tfrac{1}{6}C_{6666}b^4-4\delta_6'h^3-4\delta_6b-4[(C_{11}+C_{12})\alpha^2+2C_{13}\alpha\beta+\tfrac{1}{2}C_{33}\beta^2]\ . \tag{3.8c}$$

Here, $A$ and $B_M$ are the macroscopic "free" Landau parameters determined by polarization measurements.[18] Equation (3.8c) demonstrates that elastic terms can have a major contribution to $B_M$. Indeed, the constants $\alpha$ and $\beta$ are known from accurate x-ray measurements.[31] Using the well-established values of the elastic constants,[32] the expression within the square bracket in Eq. (3.8c) has the value $1.53\times10^{-11}$ esu. Four times that value is thus much larger than $-B_M$ which is of the order of $1.8\times10^{-11}$ esu.[8,18] Unfortunately, the right-hand side (RHS) of

Eq. (3.8c) cannot be evaluated fully as the constants $\Delta_{66}$, $C_{6666}$, $\delta_6'$ and $\delta_6$ are not known. It should be noted, however, that it is well possible for the clamped Landau coefficient $B$ to be positive, which would mean that the transition would be continuous in the absence of elastic couplings. Our lack of knowledge of all constants in Eq. (3.8c), fortunately, does not prevent a comparison of the macroscopic $B_M$ with the microscopic $B_m$ (Sec. V) as it is the same combination of unknown constants that enters both expressions.

Let us not consider the effect of hydrostatic pressure. With $p \neq 0$, one has $\epsilon_1$ and $\epsilon_3$ proportional to $p$, and their value is determined by Eqs. (3.3a) and (3.3b) setting $P = e_6 = 0$. One finds

$$(C_{11}+C_{12})\epsilon_1 + C_{13}\epsilon_3 = -p \ , \tag{3.9a}$$

$$2C_{13}\epsilon_1 + C_{33}\epsilon_3 = -p \ . \tag{3.9b}$$

With the reference configuration of the parent phase fixed at zero pressure, the parameters appearing in $G$ are of course pressure independent. The effect of pressure is described by taking proper account of the higher-order terms, for example, of the higher-order stiffnesses in $G_E$. However, $\alpha$, $\beta$, $b$, and $m$ are now pressure dependent and can be expanded in the form

$$b = b_0 + b_1 p + \cdots \ . \tag{3.10}$$

The parameters $\alpha_0$, $\beta_0$, $b_0$, $m_0$ are given by Eqs. (3.6) previously derived for $p=0$. To obtain $b_1$, for example, one considers the terms of order one in both $p$ and $P$ in Eq. (3.3c). One finds

$$C_{66}b_1 + (2C_{166}b_0 + \Delta_{16})\dot{\epsilon}_1 + (C_{366}b_0 + \tfrac{1}{2}\Delta_{36})\dot{\epsilon}_3 = 0 \ , \tag{3.11}$$

where $\dot{\epsilon}_1$ and $\dot{\epsilon}_3$ are the first derivatives of $\epsilon_1$ and $\epsilon_3$ in $p$, respectively. Identifying Eqs. (3.4) and (3.7) also to first order in $p$ and $P$, one finds

$$a\,dT_a/dp = hb_1 + (4\delta_1 - \Delta_{16}b_0)\dot{\epsilon}_1 + (2\delta_3 - \tfrac{1}{2}\Delta_{36}b_0)\dot{\epsilon}_3 \ . \tag{3.12}$$

Replacing $b_1$ by its value from Eq. (3.11), using Eqs. (3.6a) and (3.6b), and omitting now the subscript zero on $\alpha$, $\beta$, $b$, one finally obtains

$$a\frac{dT_a}{dp} = 4[(C_{11}+C_{12})\alpha + C_{13}\beta]\dot{\epsilon}_1 + 2(2C_{13}\alpha + C_{33}\beta)\dot{\epsilon}_2 \ , \tag{3.13a}$$

where $\dot{\epsilon}_1$ and $\dot{\epsilon}_2$ are obtained from Eq. (3.9),

$$\dot{\epsilon}_1 = \frac{C_{13}-C_{33}}{(C_{11}+C_{12})C_{33} - 2C_{13}^2} \ , \tag{3.13b}$$

$$\dot{\epsilon}_3 = \frac{2C_{13} - (C_{11}+C_{12})}{(C_{11}+C_{12})C_{33} - 2C_{13}^2} \ . \tag{3.13c}$$

Using the known constants[18,31,32] ($a$ is taken equal to $3.9 \times 10^{-3}$ esu), one obtains $dT_a/dp = -5.4$ K/kbar. This compares well with the experimental literature values,[33–35] as well as with our own recent determination.[36] Note that Eq. (3.13) simply expresses the pressure derivative of the Curie temperature in terms of the Curie constant and the volume electrostriction as already pointed out in Ref. 34. A determination of $dB_M/dp$ would require an expansion of the free energy complete to sixth order in $P$. Indeed, terms such as $P^4 e_1$ would have to be included. Unfortunately, we do not have sufficient information on the various constants involved to predict in this way the tricritical point around 2.5 kbar.[18]

Let us now turn to the effect of thermal expansion at zero pressure. With $p = P = e_6 = 0$, Eqs. (3.3a) and (3.3b), together with Eq. (2.7), give

$$\epsilon_1 = \alpha_{11}\Delta T, \quad \epsilon_3 = \alpha_{33}\Delta T \ . \tag{3.14}$$

This produces a temperature dependence of $b$, $\alpha$, $\beta$, etc. The effect can be treated similarly to that of pressure in Eqs. (3.10) and (3.11), but now with $\dot{\epsilon}_1 = \alpha_{11}$ and $\dot{\epsilon}_3 = \alpha_{33}$. Identifying terms of order one in $\Delta T$ and $P$ in Eqs. (3.4) and (3.7), one obtains a modification of the Curie constant

$$A \equiv a'(T - T_a) \ , \tag{3.15a}$$

with

$$a' - a = -4\alpha_{11}[(C_{11}+C_{12})\alpha + C_{13}\beta] - 2\alpha_{33}(2C_{13}\alpha + C_{33}\beta) \ . \tag{3.15b}$$

Using known values of the expansion coefficients of KDP,[37] one calculates $a' - a = -0.54 \times 10^{-3}$ esu, which is more than 10% of the measured value of $a'$ ($3.9 \times 10^{-3}$ esu). This effect comes from having fixed the reference configuration at $T = T_a$. In the following discussion of the spectra, *the reference configuration will be taken at the measurement temperature T.* Then the coefficients of $G$ all depend on $T$. With $\Delta T$ in Eq. (2.6) equal to the fluctuation about $T$, one then obtains $a' = a$ in Eq. (3.15), and the only effect of $G_{TE}$ is on the spectral shapes (Sec. VI).

Finally, let us discuss briefly the phase diagram and the exponents associated with the macroscopic free energy,

$$G = G_0 + \tfrac{1}{2}a(T - T_a)P^2 + \tfrac{1}{4}B_M P^4 + \tfrac{1}{6}CP^6 - EP \ , \tag{3.16}$$

where $B_M < 0$. For this discussion, it is convenient to use reduced variables

$$g \equiv \frac{C^2}{|B_M|^3} G \ , \tag{3.17a}$$

$$e \equiv \frac{C^{3/2}}{|B_M|^{5/2}} E \ , \tag{3.17b}$$

$$r \equiv \left[ \frac{C}{|B_M|} \right]^{1/2} P \ , \tag{3.17c}$$

$$t \equiv \frac{aC}{B_M^2} T \ , \tag{3.17d}$$

which give

$$g = g_0 + \tfrac{1}{2}(t - t_a) r^2 - \tfrac{1}{4} r^4 + \tfrac{1}{6} r^6 - er \ . \tag{3.18}$$

In this notation, the equation of state (3.7) becomes

$$e = (t - t_a) r - r^3 + r^5 \ . \tag{3.19}$$

For given $t$ and $e$, the real root of Eq. (3.19) that gives the smallest $g$ value corresponds to the stable phase. A point $(t,e)$ for which two roots give the smallest $g$ value belongs to the thermodynamic transition line. For $|e|$ smaller than the critical value $e_{\text{cr}}$, the curve $(t - t_a)$ vs $r^2$ is as shown in Fig. 3(a). If $r_1$ and $r_2$ are two roots for which $g(r_1) = g(r_2)$ at the same value $t_{\text{tr}}$ of $t$, it follows from Eqs. (3.18) and (3.19) that

$$\int_{r_1}^{r_2} (t - t_a) r \, dr = \tfrac{1}{2}(t_{\text{tr}} - t_a)(r_2^2 - r_1^2) \ . \tag{3.20}$$

Hence, $t_{\text{tr}}$ is given by a Maxwell construction as shown in Fig. 3(a). The stability limits of either the high-temperature phase, or of the low-temperature phase, which we call the spinodal of the down transition ($\downarrow$) and the spinodal of the up transition ($\uparrow$), respectively, occur when the minimum of Eq. (3.18) is also an inflection point: $\partial^2 g/\partial r^2 = 0$. This condition, combined with Eq. (3.19), gives $d(t - t_a)/d(r^2) = 0$, so that the extrema of $t$ in Fig. 3(a) correspond to the spinodal points as shown. The numerical determination of the temperatures $t_{\downarrow}$, $t_{\text{tr}}$, $t_{\uparrow}$ is, however, easier by considering the curve $g(t)$ at fixed $e$. For that curve, $dg/dt = r^2/2$ so that, considering Fig. 3(a), it follows that the shape includes two cusps corresponding to the spinodal points as shown in Fig. 3(b). The intercept of the two branches in Fig. 3(b) is of course the thermodynamic transition point.

The full phase diagram is as shown in Fig. 4. The positions of the end points are easily calculated.[18] For $e = 0$, $g(t_{\text{tr}}) - g_0 = 0$ with $r = r_1$ and $r = r_2$, so that $r_1 = 0$ and $r_2 = (\frac{3}{2})^{1/2}$. It results that $t_{\text{tr}} - t_a = \frac{3}{16}$. As with $e = 0$, $r_{\downarrow} = 0$, one also finds $t_{\downarrow} - t_a = 0$. Using $\partial^2 g/\partial r^2 = 0$ and $e = 0$ it also follows that $r_{\uparrow} = 1/\sqrt{2}$ with $t_{\uparrow} - t_a = \frac{1}{4}$. For small $e$, using $\partial g/\partial r = \partial^2 g/\partial^2 r = 0$, one finds $e_{\downarrow} = \pm(2/3\sqrt{3})\ (t_{\downarrow} - t_a)^{3/2}$ so that the down spinodal is cusped at $e = 0$. The exact shape of the down spinodal is best represented by plotting $e^2/(t - t_a)^3$ versus the reduced temperature, as shown in Fig. 5 . That curve is implicitly given by the relation

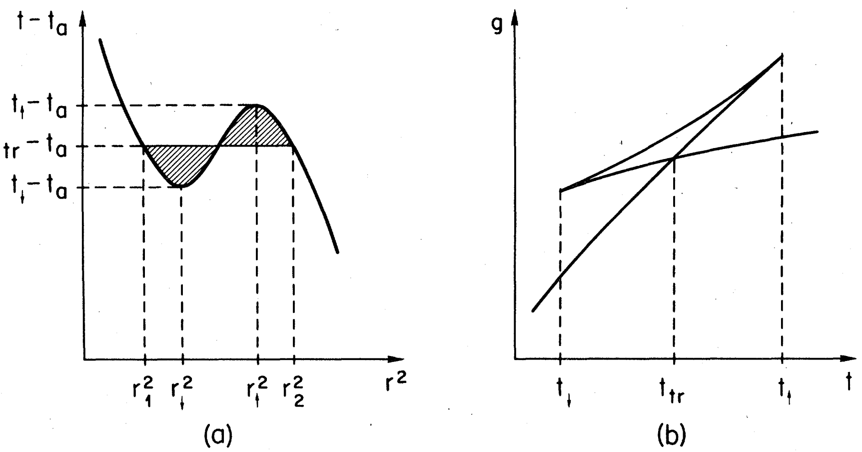
$$\frac{e_{\downarrow}^2}{(t_{\downarrow} - t_a)^3} = \frac{4}{27} \frac{(1 - 2r^2)^2}{(1 - \frac{5}{3} r^2)^3} \ , \tag{3.21a}$$

together with

$$t_{\downarrow} - t_a = 3r^2 - 5r^4 \ . \tag{3.21b}$$

The critical point occurs where all three temperatures $t_{\downarrow}$, $t_{\text{tr}}$, and $t_{\uparrow}$ coincide. The condition for this is $\partial^3 g/\partial r^3 = 0$, which gives

$$r_{\text{cr}}^2 = \tfrac{3}{10}, \ t_{\text{cr}} - t_a = \tfrac{9}{20}, \ e_{\text{cr}} = (2.3^3/5^5)^{1/2} \ . \tag{3.22}$$



(a) (b)

FIG. 3. (a) Temperature vs polarization squared. The two hatched areas are equal, illustrating the Maxwell construction. (b) The free energy vs temperature, illustrating the spinodal cusps and the intercept at the thermodynamic transition temperature.

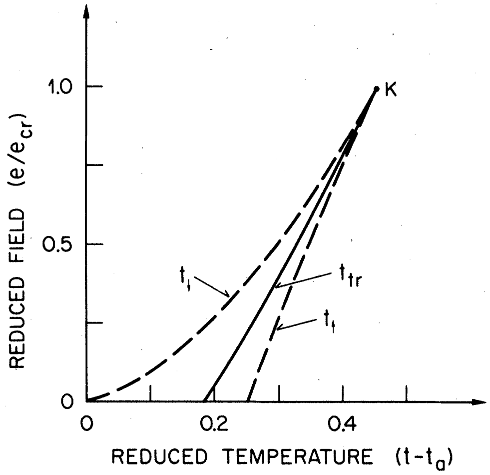


FIG. 4. Phase diagram in an $e,t$ plane. Only the $e \geq 0$ side is shown.

The free energy can be expanded about that point using

$$\tau \equiv t - t_{cr} \ , \tag{3.23a}$$

$$\epsilon \equiv e_{cr} - e \ , \tag{3.23b}$$

$$\pi \equiv r_{cr} - r \ . \tag{3.23c}$$

One finds

$$g = g_0 - \tfrac{9}{400} + \tfrac{3}{20}\tau + \epsilon r_{cr} - (\epsilon + r_{cr}\tau)\pi + \tfrac{1}{2}\tau\pi^2 + \tfrac{1}{2}\pi^4 - r_{cr}\pi^5 + \tfrac{1}{6}\pi^6 \ . \tag{3.24}$$

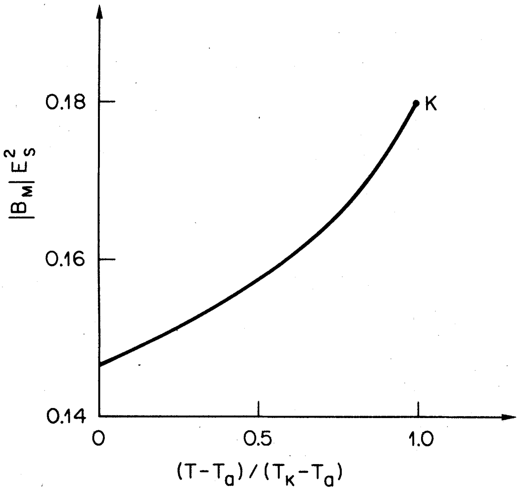


FIG. 5. Curve giving the field value vs temperature for the spinodal of the high-temperature phase. The scaled field $E_S$ is defined in Eq. (5.17). $T_K$ is the temperature of the critical point.

With $\partial g/\partial \pi = 0$, the equation of state becomes

$$\epsilon + r_{cr}\tau = \tau\pi + 2\pi^3 - 5r_{cr}\pi^4 + \pi^5 \ . \tag{3.25}$$

For $\epsilon = 0$, the leading term on the RHS is $2\pi^3$ giving

$$\pi = (\tfrac{1}{2} r_{cr}\tau)^{1/3} \ . \tag{3.26a}$$

For $\tau = 0$, one finds, similarly,

$$\pi = (\tfrac{1}{2}\epsilon)^{1/3} \ . \tag{3.26b}$$

It follows that with $e = e_{cr}$ ($\epsilon = 0$) the specific-heat divergence is in $\tau^{-2/3}$, and with $\tau = 0$, the susceptibility divergence is in $\epsilon^{-2/3}$, as already pointed out in Ref. 8.

It should also be pointed out that the definition of the stability limit used above ($\partial^2 g/\partial r^2 = 0$), combined with the strain elimination following Eq. (3.1), is identical to Cowley's definition $\det|C_{ij}| = 0$, where the $C_{ij}$'s are here the isothermal elastic constants at fixed orienting field.[1] This is shown in detail in Appendix A.

Finally, let us remark that the heat of transition is related to the Landau coefficients $a$, $B_M$, and $C$. With $E = 0$, using Eq. (3.16), one obtains

$$S = -\frac{\partial G}{\partial T} = -\frac{\partial G_0}{\partial T} - \tfrac{1}{2} a P^2 \ . \tag{3.27}$$

The heat of transition is then

$$T\Delta S = \tfrac{1}{2} a T P_{tr}^2 = \tfrac{3}{8} a \frac{|B_M|}{C} T \ , \tag{3.28}$$

where $P_{tr}$ is the polarization jump at the transition, which by the above considerations is given by $P_{tr}^2 = 3|B_M|/4C$. Using the value $4.8 \times 10^8$ ergs/mole for the heat of transition of KDP,[38] one finds $T\Delta S = 8.56 \times 10^6$ ergs/cm$^3$. With $a = 3.9 \times 10^{-3}$ esu and $B_M = -1.8 \times 10^{-11}$ esu, it follows that $C = 3.7 \times 10^{-19}$ esu in good agreement with direct determinations.[18] In particular, the ratio $B_M/C = -4.38 \times 10^7$ obtained here is in very good agreement with the recent polarization determination of Western *et al.*[18]

## IV. QUANTITIES MEASURED IN LIGHT SCATTERING

The acoustic modes becoming soft at elastic transitions are commonly observed either with ultrasound or with Brillouin scattering. In the latter case, and for transparent materials, the wavelength of the observed modes is usually smaller than both the sample volume and the illuminated volume. Hence, one investigates a *microscopic* response of well-defined finite $\vec{q}$ vector, which is calculated by solving the appropriate wave-propagation equations. For $kT \gg \hbar\omega$, where $\omega$ is the frequency shift of interest, the scattered intensity is proportional to thermal occupation.

The expressions below will be restricted to that classical case. It is the fluctuations $\delta\epsilon$ of the dielectric constant that give rise to light scattering. In the plane-wave approximation, the spectrum is proportional to the space-time Fourier transform of the correlation function.[39]

$$I(\omega) \propto m_i n_j m_k n_l \int dt\, d\vec{r}\, e^{i\omega t - i\vec{q}\cdot\vec{r}} \langle \delta\epsilon_{ij}(\vec{r}+\vec{r}', t+t')\delta\epsilon_{kl}(\vec{r}', t')\rangle \equiv m_i n_j m_k n_l \langle \delta\epsilon_{ij}\delta\epsilon_{kl}\rangle_{\omega,\vec{q}} \quad . \tag{4.1}$$

Here, $\hat{m}$ and $\hat{n}$ are the polarization vectors of the incident and scattered waves, respectively, and an abbreviated notation is introduced for the Fourier transform. It is assumed that $\hat{m}$ and $\hat{n}$ are along principal directions of vibration associated with the corresponding wave normals for the incident, $\hat{k}_i$, and scattered, $\hat{k}_s$, waves, respectively. The proportionality factor in Eq. (4.1), other effects of sample birefringence, of sample surface, and of the finite illuminated volume have been extensively discussed in the literature.[40] They will not be considered explicitly here in order not to obscure the discussion of the main effect which is fluctuation quenching by the application of the ordering force.

The fluctuations $\delta\epsilon$ are related to fluctuations in $\eta$, $\vec{e}$, and $T$ by tensorial equations of the type

$$\delta\epsilon_{ij} = a_{ijk}\delta\eta_k + p_{ijkl}\delta e_{kl} + \left(\frac{\partial\epsilon_{ij}}{\partial T}\right)_{\eta,e} \delta T \quad . \tag{4.2}$$

Here, for notational convenience, we depart from the ususal conventions that relate the Pockel's coefficients to the inverse rather than to the direct dielectric constant. For completeness, the direct coupling to temperature fluctuations is indicated. The effect of rotations, which only plays an important role in strongly birefringent materials,[41] is neglected. Under the applied ordering field, the tensors $\vec{a}$ and $\vec{p}$ will, in general, depend on the induced value of $\eta$, and they will also contain new elements. For example, in the case of KDP, the structure of $p_{ijkl}$ is just that of $C_{ijkl}$ in Fig. 2(b), and $a_{ijk}$ corresponds to $h_{ijk}$ in the same figure. Using Eq. (4.2) in Eq. (4.1), the spectrum is expressed in terms of correlation functions of the type $\langle\delta\eta\delta\eta\rangle_{\vec{q},\omega}$, $\langle\delta\eta\delta\vec{e}\rangle_{\vec{q},\omega}$, and $\langle\delta\vec{e}\delta\vec{e}\rangle_{\vec{q},\omega}$. By the fluctuation-dissipation therorem, these are related to the generalized susceptibility $\chi$.[42] For example,

$$\langle\delta\eta\delta\eta\rangle_{\vec{q},\omega} = \frac{kT}{\pi\omega}\operatorname{Im}\chi_{\eta\eta}(\vec{q},\omega) \quad , \tag{4.3}$$

with the sum rule

$$\int d\omega\, \langle\delta\eta\delta\eta\rangle_{\vec{q},\omega} = kT\operatorname{Re}\chi_{\eta\eta}(\vec{q},\omega=0) \quad , \tag{4.4}$$

which allows calculation of the integrated scattered intensity. With respect to this sum rule, one should recall the two different limits[43]

$$\lim_{\vec{q}\to 0}\lim_{\omega\to 0}\chi(\vec{q},\omega) \equiv \chi_T \quad , \tag{4.5a}$$

$$\lim_{\omega\to 0}\lim_{\vec{q}\to 0}\chi(\vec{q},\omega) \equiv \chi_s \quad . \tag{4.5b}$$

Taking first the long-time limit (4.5a), the response becomes isothermal, whereas taking first the large sample limit (4.5b), it is adiabatic. Clearly, from Eq. (4.4), the integral of the scattered spectrum is at finite $q$ and it is thus proportional to the *isothermal* susceptibility.

The scattering geometry will be labeled using the standard notation

$$\hat{k}_i(\hat{m},\hat{n})\hat{k}_s \quad . \tag{4.6}$$

By this, we mean that the momentum exchange $\vec{q} \equiv \vec{k}_i - \vec{k}_s$ has the exact direction of $\hat{k}_i - \hat{k}_s$. This also means that $\vec{k}_i$ and $\vec{k}_s$ are only *approximately* in the (usually simple) directions of the two unit vectors $\hat{k}_i$ and $\hat{k}_s$, respectively. The exact directions of $\vec{k}_i$ and $\vec{k}_s$ needed to achieve this result depend on their length difference caused by birefringence. For what follows, they do not need to be further specified. Experimentally, this becomes relevant as one approaches the elastic instability sufficiently closely. For instance, in the type-I transition of KDP, the critical scattering becomes concentrated in very narrow cones with $\vec{q}$ parallel to $\hat{x}$ and $\hat{y}$ (as shown in Sec. V). For observation of the soft shear mode, one can take an ordinary incident beam and look at the extraodinary scattered light (*VH* geometry) or vice versa (*HV* geometry). With KDP near its TCP, taking spectra with a 1-GHz free-spectral-range spherical Fabry Perot, we observed considerable spectral broadening upon going from *VH* geometry with $\vec{q}$ well lined up, to *HV* geometry. The amount of collection-aperture realignment necessary to recover the narrow spectrum exactly corresponded to the change in the length of $\vec{k}_i$ and $\vec{k}_s$ that could be calculated using the known KDP birefringence.

In the case of KDP, one is particularly interested in the following three scattering geometries[21]:

(1) $(\hat{z}-\hat{x})/\sqrt{2}\,[\hat{y}, (\hat{z}-\hat{x})/\sqrt{2}\,](\hat{z}+\hat{x})/\sqrt{2}$: depolarized scattering from shear modes propagating parallel to $\hat{x}$. Here $\hat{x}$ and $\hat{y}$ correspond to the *a* axes of the body-centered tetragonal cell, and $\hat{z}$ is parallel to the *c* axis. For this geometry,

$$\delta\epsilon_{ij}m_i n_j = \frac{1}{\sqrt{2}}(\delta\epsilon_{23} - \delta\epsilon_{12}) \quad . \tag{4.7}$$

For modes propagating along $\hat{x}$, only three strain components exist: $\delta e_1 = iq\,\delta u_i$, $\delta e_6 = iq\,\delta u_2$, $\delta e_5 = iq\,\delta u_3$, where the $\delta u_i$'s are the fluctuating displacements of wave vector $(q,0,0)$. Using Fig. 2(b), one has

$$\delta\epsilon_{12}=p_{61}\delta e_1+p_{66}\delta e_6+a_{63}\delta P_3+\left(\frac{\partial\epsilon_{12}}{\partial T}\right)\delta T \ , \qquad (4.8a)$$

$$\delta\epsilon_{23}=p_{45}\delta e_5+a_{41}\delta P_1+a_{42}\delta P_2 \ . \qquad (4.8b)$$

Note that the coefficients $p_{61}$, $\partial\epsilon_{12}/\partial T$, $p_{45}$, and $a_{42}$ are all proportional to the ordering field (or better to the static value of $P_3$). Fluctuations $\delta P_1$ along $\hat{x}$ are strongly suppressed due to the div$P$ term in the free energy of ferroelectrics. Hence, in the absence of applied field, one measures in this geometry the correlation of

$$\delta\epsilon_{ij}m_in_j=-\frac{1}{\sqrt{2}}(p_{66}\delta e_6+a_{63}\delta P_3) \ . \qquad (4.9)$$

In the presence of the ordering field, it turns out that all the additional terms mentioned above remain negligible in comparison with the main effect which is a quenching of the correlation function $\langle\delta P_3\delta P_3\rangle$. This will be discussed in some detail in the following sections.

(2) $(\hat{z}-\hat{x})/\sqrt{2}(\hat{y},\hat{y})(\hat{z}+\hat{x})/\sqrt{2}$: polarized scattering from modes along $\hat{x}$. For

$$\delta\epsilon_{ij}m_in_j=\delta\epsilon_{22} \ . \qquad (4.10)$$

Using Fig. 2(b), one has

$$\delta\epsilon_{22}=p_{12}\delta e_1+p_{16}\delta e_6+a_{13}\delta P_3 \ . \qquad (4.11)$$

Again, $p_{16}$ and $a_{13}$ are proportional to the static value of $P_3$. In the absence of ordering field, one measures in this geometry the correlation of $\delta e_1$ with itself, which is noncritical. In principle, with a small ordering field, a critical contribution mixes in with a coefficient proportional to $P_3^2$. In practice, the measurement might be difficult for two reasons: (i) As this geometry corresponds to polarized scattering, it is more prone to be perturbed by defect scattering and stray light. (ii) As depolarized scattering in the same direction is critical and strong, appreciable leakage of the depolarized component into the polarized component might be hard to prevent. To avoid the first difficulty, one can select the depolarized geometry

$$\frac{\hat{z}-\hat{x}}{\sqrt{2}}\left(\frac{\hat{z}+\hat{x}}{\sqrt{2}},\frac{\hat{z}-\hat{x}}{\sqrt{2}}\right)\frac{\hat{z}+\hat{x}}{\sqrt{2}}$$

for which

$$\begin{aligned}\delta\epsilon_{ij}m_in_j&=\tfrac{1}{2}(\delta\epsilon_{33}-\delta\epsilon_{11})\\&=\tfrac{1}{2}(p_{31}-p_{11})\delta e_1+\tfrac{1}{2}(p_{36}-p_{16})\delta e_6\\&\quad+\tfrac{1}{2}(a_{33}-a_{13})\delta P_3 \ .\end{aligned}$$

(3) $(\hat{y}-\hat{x})/\sqrt{2}[(\hat{x}+\hat{y})/\sqrt{2},(\hat{y}-\hat{x})/\sqrt{2}]$ $(\hat{x}+\hat{y})/\sqrt{2}$: alternate geometry for depolarized scattering along $\hat{x}$. Here,

$$\delta\epsilon_{ij}m_in_j=\tfrac{1}{2}(\delta\epsilon_{22}-\delta\epsilon_{11}) \ , \qquad (4.12)$$

$\delta\epsilon_{22}$ is given by Eq. (4.11), and $\delta\epsilon_{11}$ is

$$\delta\epsilon_{11}=p_{11}\delta e_1+p_{16}\delta e_6+a_{13}\delta P_3 \ . \qquad (4.13)$$

Hence,

$$\delta\epsilon_{ij}m_in_j=\tfrac{1}{2}(p_{12}-p_{11})\delta e_1 \ , \qquad (4.14)$$

and in this manner one can obtain the pure $\langle\delta e_1\delta e_1\rangle$ correlation, also in presence of the ordering field. The only disadvantage is that this geometry will require a different crystal cut from the previous two.

## V. STATIC MICROSCOPIC SUSCEPTIBILITIES

As seen above, the term "microscopic" refers to modes of nonzero wave vector $\vec{q}$. The static response observed in scattering experiments is the isothermal response, as discussed below Eq. (4.5). Hence, in the present section, the fluctuations of interest will be restricted to $\delta T=0$. As shown in Eq. (4.4), the static microscopic response is proportional to the integral of the spectrum. Thus, in the present section, we calculate how the integral of the spectrum varies with the application of the ordering force.

The essential difference between microscopic and macroscopic responses arises from the fact that, for finite $\vec{q}$, the six strains $e_i$ ($i=1$ to 6) are not independent variables but are related to the three displacements $u_i$ ($i=1$ to 3) by equations which, for the spatial Fourier transforms of the fluctuations, take the form

$$\delta e_i=iq_i\delta u_i \quad (i=1 \text{ to } 3) \ , \qquad (5.1a)$$

$$\delta e_{i+3}=iq_j\delta u_k+iq_k\delta u_j \qquad (5.1b)$$

$$(i\neq j\neq k=1 \text{ to } 3) \ .$$

The approach will be to express the free energy in presence of the ordering force in terms of both the macroscopically induced variables and the Fourier components of their fluctuations. For the strain fluctuations, one uses Eq. (5.1), and instead of the stress-times-strain term in Eq. (2.4), one introduces the force $\delta\vec{F}(\vec{q})$ conjugated to the displacement $\delta\vec{u}(\vec{q})$, giving a term

$$-\sum_{\vec{q}}\delta\vec{F}(\vec{q})\cdot\delta\vec{u}(-\vec{q}) \qquad (5.2)$$

in the free energy. The static responses are obtained by writing the equilibrium conditions on the free energy. Limiting oneself to energy contributions quadratic in the fluctuations, a set of linear equations relating the forces to the fluctuating variables of interest results. The corresponding matrix is the inverse of the generalized susceptibility. It remains to invert it to complete the solution of the proposed problem.

Let us see how this program works in the particular case of KDP with the free energy of Sec. II. As we will be interested not only in what happens to the soft mode propagating in the [100] direction, but more generally in the soft scattering cone, we allow $\vec{q}$ to be in a general direction and define the three cosine directors $l$, $m$, and $n$:

$$\vec{q} \equiv q(l,m,n) \quad . \tag{5.3}$$

For the isothermal response, one only needs to consider the contributions (2.3), (2.4), and (2.5) to the free energy. Taking spatial Fourier transforms, one obtains

$$G_P = \sum_{\vec{q}} \tfrac{1}{2} \chi_P^{-1}(\vec{q})\, \delta P(\vec{q})\, \delta P(-\vec{q}) - \delta E(\vec{q})\, \delta P(-\vec{q}) \quad , \tag{5.4a}$$

where

$$\chi_P^{-1}(\vec{q}) = a(T-T_c) + 3BP^2 + \cdots + K\frac{q_\lambda q_\mu \delta P_\lambda(\vec{q})\, \delta P_\mu(-\vec{q})}{q^2 \delta P(\vec{q})\, \delta P(-\vec{q})} + \tfrac{1}{2}M_1(q_x^2+q_y^2) + \tfrac{1}{2}M_2 q_z^2 \quad . \tag{5.4b}$$

The $\vec{q}$ dependent terms above follow from consideration of the electrostatic energy of a dipole distribution and from spatial dispersion. The nonanalytic electrostatic part is a straightforward generalization of the well-known term $Kq_z^2/q^2$ which occurs when $\delta\vec{P}$ points in the $\hat{z}$ direction.[44] A simple electrostatic calculation gives $K = 4\pi$.[44] It is necessary to generalize this term to other $\delta\vec{P}$ directions, as discussed below, as soon as $\vec{q}$ departs from the $(xy)$ plane, although this is not often done.[44,45] It is then also necessary to generalize Eq. (5.4a) to other $\delta\vec{P}$ components in a straightforward way.

Using Eq. (2.4), one obtains

$$\begin{aligned} G_E = \sum_{\vec{q}} [ & \tfrac{1}{2}C_{11}\delta e_1^2 + \tfrac{1}{2}C_{11}\delta e_2^2 + C_{12}\delta e_1 \delta e_2 + \tfrac{1}{2}C_{33}\delta e_3^2 + C_{13}\delta e_1\delta e_3 + C_{13}\delta e_2 \delta e_3 + \tfrac{1}{2}C_{66}\delta e_6^2 + \tfrac{1}{2}C_{44}\delta e_4^2 \\ & + \tfrac{1}{2}C_{44}\delta e_5^2 - \delta F_i \delta u_i + \alpha P^2 C_{166}\delta e_6^2 + bPC_{166}(\delta e_1 \delta e_6 + \delta e_2 \delta e_6) + \tfrac{1}{2}C_{366}\beta P^2 \delta e_6^2 \\ & + bPC_{366}\delta e_3 \delta e_6 + bPC_{456}\delta e_4 \delta e_5 + \tfrac{1}{4}b^2P^2C_{6666}\delta e_6^2 ] \quad . \end{aligned} \tag{5.5}$$

Here, we use the abbreviated notation $\delta e_1(\vec{q})\delta e_1(-\vec{q}) = \delta e_1^2$, etc., and the static values of $e_1$, $e_2$, $e_3$, $e_6$ have been replaced by their expressions (3.5). Finally, using Eq. (2.5), one obtains

$$\begin{aligned} G_{PE} = \sum_{\vec{q}} [ & -h\,\delta P \delta e_6 + (\Delta_{16}\alpha + \tfrac{1}{2}\Delta_{36}\beta + 2\Delta_{66}b - 3\delta_6 - 3b^2\delta_6')P^2\delta P \delta e_6 + (\tfrac{1}{2}\Delta_{66}b^2 - 2\alpha\delta_1 - \beta\delta_3 - 3b\,\delta_6)P^2\delta P^2 \\ & + (\tfrac{1}{2}\Delta_{66} - 3b\,\delta_6')P^2\delta e_6^2 + (\tfrac{1}{2}\Delta_{16}b - 2\delta_1)P\delta P(\delta e_1 + \delta e_2) + (\tfrac{1}{2}\Delta_{36}b - 2\delta_3)P\delta P \delta e_3 \\ & + \tfrac{1}{2}\Delta_{16}P\delta e_6(\delta e_1 + \delta e_2) + \tfrac{1}{2}\Delta_{36}P\delta e_6 \delta e_3 ] \quad . \end{aligned} \tag{5.6}$$

The stabililty equations are obtained by equating to zero the derivative of $G = G_P + G_E + G_{PE}$ in $\delta P(-\vec{q})$, $\delta u_1(-\vec{q})$, $\delta u_2(-\vec{q})$, and $\delta u_3(-\vec{q})$. To this effect, one uses the relations (5.1) in the above expressions. The resulting equations are conveniently presented in matrix form

$$\begin{bmatrix} \delta E \\ \delta F_1 \\ \delta F_2 \\ \delta F_3 \end{bmatrix} = \chi^{-1} \begin{bmatrix} \delta P \\ \delta u_1 \\ \delta u_2 \\ \delta u_3 \end{bmatrix} \quad , \tag{5.7a}$$

where $\chi^{-1}$ is the inverse susceptibility matrix. It has the following structure:

$$\chi^{-1} \equiv \begin{bmatrix} \chi_0^{-1} & iqV_1 & iqV_2 & iqV_3 \\ -iqV_1 & q^2 m_{11} & q^2 m_{12} & q^2 m_{13} \\ -iqV_2 & q^2 m_{12} & q^2 m_{22} & q^2 m_{23} \\ -iqV_3 & q^2 m_{13} & q^2 m_{23} & q^2 m_{33} \end{bmatrix} \quad , \tag{5.7b}$$

with

$$\chi_0^{-1} \equiv \chi_P^{-1} + (\Delta_{66} b^2 - 6\delta_6 b - 4\alpha\delta_1 - 2\beta\delta_3) P^2 \ , \tag{5.8a}$$

$$V_1 \equiv l(\tfrac{1}{2}\Delta_{16} b - 2\delta_1) P - mh + m(\alpha\Delta_{16} + \tfrac{1}{2}\beta\Delta_{36} + 2b\Delta_{66} - 3\delta_6 - 3b^2\delta_6') P^2 \ , \tag{5.8b}$$

$$V_2 \equiv -lh + l(\alpha\Delta_{16} + \tfrac{1}{2}\beta\Delta_{36} + 2b\Delta_{66} - 3\delta_6 - 3b^2\delta_6') P^2 + m(\tfrac{1}{2}\Delta_{16} b - 2\delta_1) P \ , \tag{5.8c}$$

$$V_3 \equiv n(\tfrac{1}{2}\Delta_{36} b - 2\delta_3) P \ , \tag{5.8d}$$

$$m_{11} \equiv l^2 C_{11} + lm(2C_{166} b + \Delta_{16}) P + m^2 C_{66} + m^2(2C_{166}\alpha + C_{366}\beta + \tfrac{1}{2}C_{6666} b^2 + \Delta_{66} - 6b\delta_6') P^2 + n^2 C_{44} \ , \tag{5.8e}$$

$$\begin{aligned} m_{12} \equiv {} & l^2(C_{166} b + \tfrac{1}{2}\Delta_{16}) P + lm(C_{12} + C_{66}) + lm(2C_{166}\alpha + C_{366}\beta + \tfrac{1}{2}C_{6666} b^2 + \Delta_{66} - 6b\delta_6') P^2 \\ & + m^2(C_{166} b + \tfrac{1}{2}\Delta_{16}) P + n^2 C_{456} bP \ , \end{aligned} \tag{5.8f}$$

$$m_{13} \equiv ln(C_{13} + C_{44}) + mn(\tfrac{1}{2}\Delta_{36} + C_{366} b + C_{456} b) P \ , \tag{5.8g}$$

$$m_{22} \equiv l^2 C_{66} + l^2(2C_{166}\alpha + C_{366}\beta + \tfrac{1}{2}C_{6666} b^2 + \Delta_{66} - 6b\delta_6') P^2 + lm(2C_{166} b + \Delta_{16}) P + m^2 C_{11} + n^2 C_{44} \ , \tag{5.8h}$$

$$m_{23} \equiv ln(\tfrac{1}{2}\Delta_{36} + C_{366} b + C_{456} b) P + mn(C_{13} + C_{44}) \ , \tag{5.8i}$$

$$m_{33} \equiv (l^2 + m^2) C_{44} + 2lmC_{456} bP + n^2 C_{33} \ . \tag{5.8j}$$

The full analytic inversion of Eq. (5.7b) would be a sizable task, and would not be too helpful in the sense that many of the above parameters are not known. It is wise to proceed by steps to obtain successively:

A. An expression for the scattering intensity for $l = 1$, $m = n = 0$, with $P = 0$.

B. The similar expression with $P \neq 0$.

C. An estimate of the shape of the scattering cone with $P = 0$.

D. An estimate of the motion of the scattering cone about $l = 1$, $m = n = 0$, under small applied field.

### A. Critical scattering

The first point is very simple, as Eq. (5.8) reduces to

$$\chi_0^{-1} = \chi_P^{-1}, \quad V_2 = -h, \quad m_{11} = C_{11},$$

$$m_{22} = C_{66}, \quad m_{33} = C_{44} \ ,$$

with all other elements equal to zero. Hence, only $\delta P$ and $\delta e_6$ are coupled. From Eqs. (4.1), (4.4), and (4.9), the integrated intensity in the scattering geometry

$$\frac{\hat{z} - \hat{x}}{\sqrt{2}} \left( y, \frac{\hat{z} - \hat{x}}{\sqrt{2}} \right) \frac{\hat{z} + \hat{x}}{\sqrt{2}}$$

is given by

$$I(q) \propto kT(a_{63} \ iqp_{66}) \begin{pmatrix} \chi_P^{-1} & -iqh \\ iqh & q^2 C_{66} \end{pmatrix}^{-1} \begin{pmatrix} a_{63} \\ -iqp_{66} \end{pmatrix} \ . \tag{5.9}$$

Note that the imaginary terms in Eq. (5.9) result from spatial Fourier transformation and should not be removed by the operation "Re" in Eq. (4.4) that applies to the *time* Fourier transforms, They are related to the linear $q$ dependence of

$$\begin{aligned} \langle \delta P(q) \delta u_2(-q) \rangle &= \frac{iqh}{q^2(\chi_P^{-1} C_{66} - h^2)} \\ &= \frac{i}{q} \langle \delta P(q) \delta e_6(-q) \rangle \ , \end{aligned} \tag{5.10}$$

whereas the latter correlation function is not linearly dependent on $q$ and, hence, is real.

Using Eq. (5.4b) with $P = 0$ and $q \to 0$, Eq. (5.9) is written

$$I(q) \propto kT \frac{p_{66}^2}{C_{66}} \left[ 1 + (1 + \Upsilon)^2 \frac{T_a - T_c}{T - T_a} \right] \ , \tag{5.11}$$

where one has defined

$$\Upsilon \equiv a_{63} C_{66} / h p_{66} \ , \tag{5.12}$$

and where the definition of $T_a - T_c$ in Eq. (3.8b) has been used. Equation (5.11) emphasizes that the scattering consists of a normal piezo-optic contribution, which is the only one seen in the high-temperature limit, and a critical part proportional to $(T - T_a)^{-1}$. Both the strain wave and the polarization wave contribute to the critical part. However, if $\Upsilon$ is large, which is the case for KDP ($\Upsilon \simeq 6.5$),[24] the critical scattering is mainly related to polarization fluctuations. In fact, for KDP, one finds that ~75% of the scattering is due to polarization fluctuations, ~23% is due to polarization-strain cross correlation, and only ~2% is due to pure strain fluctuations. One should also note that the "normal" contribution becomes negligible compared to the "critical" one as soon as $T$ is close enough to $T_a$, e.g., $0 < T - T_a < T_a - T_c$.

### B. Fluctuation quenching

With $P \neq 0$ and $l = 1$, one still has $V_3 = m_{13} = m_{23} = 0$ so that $\delta u_3$ remains decoupled. For the same scattering geometry as above, Eq. (5.9) now reads

$$I(q) \underset{\sim}{\propto} kT(a_{63}\; iqp_{61}\; iqp_{66}) \begin{pmatrix} \chi_0^{-1} & iqV_1 & iqV_2 \\ -iqV_1 & q^2C_{11} & q^2m_{12} \\ -iqV_2 & q^2m_{12} & q^2m_{22} \end{pmatrix}^{-1} \begin{pmatrix} a_{63} \\ -iqp_{61} \\ -iqp_{66} \end{pmatrix} = kT(a_{63}\; p_{61}\; p_{66}) \begin{pmatrix} \chi_0^{-1} & V_1 & V_2 \\ V_1 & C_{11} & m_{12} \\ V_2 & m_{12} & m_{22} \end{pmatrix}^{-1} \begin{pmatrix} a_{63} \\ p_{61} \\ p_{66} \end{pmatrix} . \tag{5.13}$$

The approximation in Eq. (5.13) consists in keeping only the $\delta\epsilon_{12}$ contribution of Eq. (4.8a), although $p_{45}$ and $a_{42}$ in Eq. (4.8b) are now both proportional to $P$. Close to the transition, this is fully justified by the fact that Eq. (5.13) is the only contribution exhibiting critical increases. The second equality in Eq. (5.13) shows how $q$ drops out with the convenient definitions (5.7b).

The evaluation of Eq. (5.13) using Eqs. (5.8) and (3.6) is lengthy but straightforward. The result can be written, to order $P^2$,

$$I(q) - I(q,P=0) \propto \frac{LP^2}{a(T-T_a)} - kT\frac{p_{66}^2}{C_{66}}(1+\Upsilon)^2\frac{T_a - T_c}{(T-T_a)^2}\frac{3B_m}{a}P^2 . \tag{5.14}$$

Here $L$ is a constant that can be expressed in terms of the various coefficients entering Eqs. (2.4) and (2.5) together with the linear dependence of $p_{61}$ on $P$. $B_m$ is also such a constant, however, its relation to $B_M$ in Eq. (3.8c) is remarkably simple:

$$B_m - B_M = \tfrac{8}{3}[(C_{11}+C_{12})\alpha^2 + 2C_{13}\alpha\beta + \tfrac{1}{2}C_{33}\beta^2] - \frac{4}{3}\frac{1}{C_{11}}[(C_{11}+C_{12})\alpha + C_{13}\beta]^2 . \tag{5.15}$$

Note that it involves only well-known constants. For $T$ close to $T_a$, the second term in Eq. (5.14) becomes more important than the first one in view of the different $T - T_a$ power dependence. For $T - T_a$ sufficiently small, keeping only the most critical parts in $I(q,P=0)$ and in Eq. (5.14), one obtains

$$I(q)^{-1} = I^{-1}(q,P=0)\left[1 + 3B_m\frac{P^2}{a(T-T_a)} + \cdots\right] = I^{-1}(q,P=0)(1 + 3B_mE_s^2 + \cdots) , \tag{5.16}$$

where

$$E_s^2 \equiv E^2/a^3(T-T_a)^3 . \tag{5.17}$$

$E_s$ is the scaled variable in terms of which intensity results at many $E$ and $T$'s can be expressed. The experimental verification of this scaling[8] supports the contention that the term proportional to $L$ in Eq. (5.4) is sufficiently small compared to the term proportional to $B_m$ in the measured region. The experimental value of $B_m$ ($0.72 \times 10^{-11}$ esu)[8] is also in good agreement with the most reliable $B_M$ measurements ($-1.3 \ldots -1.9 \times 10^{-11}$ esu)[18] and the theoretical difference calculated using Eq. (5.15) $B_m - B_M = 2.48 \times 10^{-11}$ esu.

The effect of the ordering field is to *quench* microscopic fluctuations. To be specific, quenching means that the microscopic fluctuations are smaller than expected on the basis of the macroscopic susceptibility $\chi_M$ which, using Eq. (3.7), can be expressed in a form similar to (5.16):

$$\chi_M^{-1} = \chi_M^{-1}(P=0)(1 + 3B_ME_s^2 + \cdots) . \tag{5.18}$$

Indeed, the right-hand side of Eq. (5.15) is a quadratic form in $(\alpha, \beta)$ which is positive definite in view of the requirements on the elastic constants imposed by crystal stability. It can be written

$$B_m - B_M = \frac{4}{3C_{11}}[(C_{11}+C_{12})(C_{11}-C_{12})\alpha^2 + 2C_{13}(C_{11}-C_{12})\alpha\beta + (C_{11}C_{33} - C_{13}^2)\beta^2] . \tag{5.19a}$$

The determinant $\Delta$ of the quadratic form within brackets is

$$\Delta = (C_{11}-C_{12})C_{11}[(C_{11}+C_{12})C_{33} - 2C_{13}^2] . \tag{5.19b}$$

$\Delta$ is positive definite since each one of its factors is. For the last factor, this is easily seen by considering the stability of the elastic-constant tensor when the coordinates are rotated by 45° around $\hat{z}$. This demonstrates that the only circumstance in which quenching would not occur is $\alpha=\beta=0$, i.e., if there were no electrostriction at all.

### C. Scattering cone

It should be noticed that Eq. (5.16) could also have been obtained with the approximation $I(q) \propto \langle \delta P_q \delta P_{-q} \rangle$, as actually done in Ref. 8. The reason this works is that the above correlation contains all important critical contributions. As the calculation of that correlation is more straightforward [just one element of the inverse of Eq. (5.7b) is needed], use of that simplification will be made for the following considerations. Note that, from Eqs. (4.4) and (5.7b), one can conveniently write

$$\langle \delta P_q \delta P_{-q} \rangle^{-1} = \frac{1}{kT}\left[\chi_0^{-1} - (V_1\ V_2\ V_3)\begin{pmatrix} m_{11} & m_{12} & m_{13} \\ m_{12} & m_{22} & m_{23} \\ m_{13} & m_{23} & m_{33} \end{pmatrix}^{-1}\begin{pmatrix} V_1 \\ V_2 \\ V_3 \end{pmatrix}\right] . \tag{5.20}$$

Now, consider again the case $P=0$ and the scattering geometry $(\hat{z}-\hat{x})/\sqrt{2}\,(\hat{y}, (\hat{z}-\hat{x})/\sqrt{2})\ (\hat{z}+\hat{x})/\sqrt{2}$, but allow for slight deviations from exact alignment. Birefringence effects will be neglected, and we shall only consider what effect a deviation of $\vec{q}$ from the exact $\hat{x}$ direction has on the correlation (5.20). To be specific, we maintain the incident wave-vector direction, and scan the scattering cone as shown in Fig. 6. The incident wave vector $\vec{k}_i$ points in the $\hat{z}-\hat{x}$ direction, and the reference position of the scattered wave vector $\vec{k}_s^0$ points in the $\hat{z}+\hat{x}$ direction. The wave vector $\vec{k}_s$ is displaced from $\vec{k}_s^0$ by an internal angle $\theta$ in the $(\hat{x},\hat{z})$ plane and by an internal angle $\varphi$ perpendicular to that plane. We consider the two cases $(\theta \neq 0,\ \varphi=0)$ and $(\theta=0,\ \varphi\neq 0)$ separately, whereas the general case is better handled numerically.

With $\varphi=0$, one has $l=\cos(\theta/2)$, $m=0$, $n=\sin(\theta/2)$, and Eq. (5.20) reduces to

$$\langle \delta P_q \delta P_{-q} \rangle^{-1} = (kT)^{-1}\left[\chi_P^{-1} - \frac{h^2}{C_{66}}\left(1+\frac{C_{44}}{C_{66}}\tan^2\frac{\theta}{2}\right)^{-1}\right] . \tag{5.21}$$

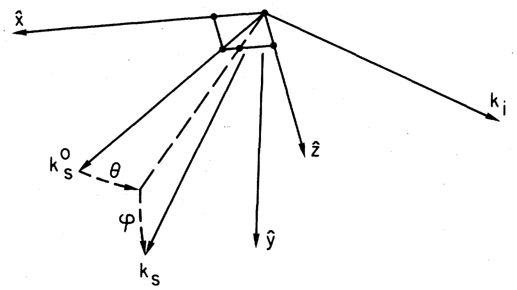


FIG. 6. Definition of the angles $\theta$ and $\varphi$ of the scattering cone. $\hat{x}$, $\hat{y}$, $\hat{z}$ are the tetragonal axes, $\vec{k}_i$, $\vec{k}_s^0$ and $\vec{k}_s$ are described in the text.

The nonanalytic term in $\chi_P^{-1}$ must be handled carefully. It couples fluctuations along $\hat{z}$ (noted here $\delta P_3$) with fluctuations along $\hat{x}$ ($\delta P_1$). This term is so strong that, considering the quite large polarizability in the $\hat{x}$ direction ($\epsilon_{11} \simeq 80$ for KDP), the fluctuations $\delta P$ leading to the lowest free energy will be approximately those for which the term is zero. Using Eq. (5.4b), this means $\delta P_3 = [\cos(\theta/2)]\delta P$ and $\delta P_1 = [\sin(\theta/2)]\delta P$. To lowest order, the polarization contribution to the free energy for such a fluctuation is simply

$$G_P = \tfrac{1}{2}\chi_{33}^{-1}\cos^2\frac{\theta}{2}\,\delta P^2 + \tfrac{1}{2}\chi_{11}^{-1}\sin^2\frac{\theta}{2}\,\delta P^2 - \left(\delta E_3 \cos\frac{\theta}{2} - \delta E_1 \sin\frac{\theta}{2}\right)\delta P , \tag{5.22}$$

where $\chi_{33}^{-1} = a(T-T_c)$ as in Eq. (5.4b), whereas $\chi_{11}^{-1} \simeq 4\pi/\epsilon_{11}$ when $\epsilon_{11} >> 1$. The parentheses in Eq. (5.22) contains just the field conjugated to $\delta P$, i.e., the projection of $\delta\vec{E}$ on $\delta\vec{P}$. Neglecting spatial dispersion in Eq. (5.4b), and for $\theta$ small, one finally writes in Eq. (5.21)

$$\begin{aligned} \chi_p^{-1} &\simeq a(T-T_c) + (\chi_{11}^{-1} - \chi_{33}^{-2})\sin^2\frac{\theta}{2} \\ &\simeq a(T-T_c) + \frac{4\pi}{\epsilon_{11}}\sin^2\frac{\theta}{2} . \end{aligned} \tag{5.23}$$

The second form of writing Eq. (5.23) takes into account the fact that $\chi_{11}^{-1} >> \chi_{33}^{-1}$. In other words, the effect of the $\delta P_1$ fluctuation component is approximately to reduce the nonanalytic term from $4\pi q_z^2/q^2$ to $4\pi q_z^2/\epsilon_{11} q^2$, which is a sizable effect. Combining Eqs. (5.23) and (5.21), one can write for small $\theta$,

$$\frac{I(\theta=0)}{I(\theta)} \simeq 1 + \frac{\theta^2}{T-T_a}\left(\frac{\pi}{\epsilon_{11} a} + \tfrac{1}{4}(T_a - T_c)\frac{C_{44}}{C_{66}}\right) . \tag{5.24}$$

For KDP, the first term within the brackets equals 10.1 K, whereas the second term equals 2.3 K. At 50 mK, from $T_a$ the half-width at half-height of $I(\theta)$ is then 3.6° internal angle, or 5.5° external angle. This corresponds fairly well to our experimental observations, and confirms the need for the $\epsilon_{11}^{-1}$ factor in the nonanalytic term: without it the theoretical width would be much too narrow compared to experiment.

With $\theta=0$, one has $l=\cos^2(\varphi/2)$, $m=\sqrt{2}[\sin(\varphi/2)]\cos(\varphi/2)$, and $n=-\sin^2(\varphi/2)$. Now, the nonanalytic term is proportional to $\varphi^4$ and turns out to be negligible compared to the elastic terms. To order $\varphi^2$, one obtains

$$\langle \delta P_q \delta P_{-q} \rangle^{-1} \simeq \frac{1}{kT}\left[a(T-T_a)+a(T_a-T_c)\frac{C_{11}^2-C_{12}^2}{2C_{11}C_{66}}\varphi^2\right] . \tag{5.25}$$

This gives the intensity ratio

$$\frac{I(\varphi=0)}{I(\varphi)} \simeq 1+\frac{\varphi^2}{T-T_a}\frac{T_a-T_c}{2C_{11}C_{66}}(C_{11}^2-C_{12}^2) . \tag{5.26}$$

For KDP, the coefficients of $\varphi^2/(T-T_a)$ equals 26 K. Hence, the half-width at 50 mK above $T_a$ is 2.5° internal angle, or 3.8° external angle. Again, this is in good agreement with our observations.

This analysis shows that the critical scattering, close to $T_a$, concentrates in a rather narrow cone. The effect becomes even more striking under hydrostatic pressure as it is then possible to approach $T_a$ very closely. For a general $\vec{q}$, it is more expedient to obtain $I(\theta,\varphi)$ numerically using Eq. (5.20) with

$$l=\frac{1+\cos\varphi(\cos\theta-\sin\theta)}{(2-4\cos\varphi\sin\theta)^{1/2}} , \tag{5.27a}$$

$$m=\frac{\sin\varphi}{(1-2\cos\varphi\sin\theta)^{1/2}} , \tag{5.27b}$$

$$n=\frac{-1+\cos\varphi(\cos\theta+\sin\theta)}{(2-4\cos\varphi\sin\theta)^{1/2}} . \tag{5.27c}$$

### D. Motion of the softest direction

The fact that the [100] direction in the crystal does not remain truly soft under the application of the ordering force also means that the softest crystal direction does not generally remain parallel to [100]. For KDP, motion of the softest direction in $\varphi$ is dominant as it is proportional to $P$, whereas, by symmetry, motion along $\theta$ is proportional to $P^2$ only.

Restricting the calculation to small $P$ and $\varphi$, one takes $l=1$, $m=\varphi/\sqrt{2}$, and $n=0$ in Eq. (5.13), where now $C_{11}$ is replaced by $m_{11}$. Keeping only the most divergent term in the spirit of the discussion following Eq. (5.14), one obtains

$$I(\varphi) \simeq I(0)(1+S\varphi E+\cdots) , \tag{5.28a}$$

where

$$S=\frac{2\sqrt{2}(C_{11}-C_{12})[(C_{11}+C_{12})\alpha+C_{13}\beta]b}{C_{11}a^2(T-T_a)^2} . \tag{5.28b}$$

For the measurement of this effect, it is convenient to consider the following ratio

$$R_\varphi=\frac{I^{-1}(\varphi,-E)-I^{-1}(\varphi,E)}{2I^{-1}(\varphi,E=0)}=S\varphi E . \tag{5.29}$$

The terms in the numerator are easily obtained experimentally by switching adiabatically the sign of the applied electric field. It should be noted that the angle $\varphi$ in the above Eq. (5.28) is referenced to the original tetragonal direction of the crystal. Depending on the clamping condition, this reference direction might itself move due to the static $xy$ shear. The angle measured in the laboratory frame, for a crystal resting on a (010) plane, will be

$$\varphi_L=\varphi+\tfrac{1}{2}e_6=\varphi+bE/2a(T-T_a) .$$

However, this effect cancels out by taking the difference in the numerator of Eq. (5.29). Hence, the ratio can also be written $R_\varphi=SE\,\varphi_L$. Furthermore, the difference between $\varphi$ and $\varphi_L$ becomes negligible compared to the angular shift of the softest direction as $T_a$ is approached, since the former is proportional to $(T-T_a)^{-1}$, while the latter to $(T-T_a)^{-2}$. For KDP, one calculates $S=0.30/(T-T_a)^2$, where the units are esu, radians, and degrees kelvin. This gives $S=26.5$ esu/rad for $T-T_a=106$ mK in excellent agreement with observation.[8]

## VI. DYNAMIC MICROSCOPIC SUSCEPTIBILITIES

Under the ordering force, the transition is nonsymmetry breaking, as discussed in previous sections. Hence, a bilinear coupling between order-parameter fluctuations and temperature fluctuations is symmetry allowed. Consequently, the heat-diffusion dynamics is reflected on the order-parameter correlation function in the form of a thermal central peak. This means that it is essential to consider temperature fluctuations $\delta T$ in order to obtain the dynamic response, even though their effect drops out from the integrated spectrum. In distinction with the previous section, the dynamics cannot be derived from the free energy alone, and additional phenomenological or microscopic considerations are needed to obtain the equations of motion.

Let us see how this works out for KDP. For simplicity, we now restrict the analysis to $l=1$, $m=n=0$

in Eq. (5.3). The coupling between $\delta P$ and $\delta T$ is immediately evident in the first term on the RHS of Eq. (2.3). In Fourier-transform notation this leads to an additional term on the RHS of Eq. (5.4a) which is

$$\sum_{\vec{q}} aP\,\delta P(\vec{q})\,\delta T(-\vec{q}) \ . \tag{6.1}$$

Equations (5.5) and (5.6) are unchanged, but the contributions of $F_0$ in Eq. (2.2), and $G_{TE}$ in Eq. (2.6), should also be added to $G$. They are

$$F_0 = -\sum_{\vec{q}} \frac{1}{2}\frac{\rho C_{P,e}}{T}\,\delta T(\vec{q})\,\delta T(-\vec{q}) \ , \tag{6.2}$$

$$G_{TE} = -\sum_{\vec{q}} [\alpha_1(\delta e_1 + \delta e_2) + \alpha_3 \delta e_3]\delta T \ . \tag{6.3}$$

The equations of motion are now written using phenomenological considerations similar to those of Ref. 28. Polarization dynamics in the form of a Debye relaxation is introduced in Eq. (5.4a) by writing

$$\chi_P^{-1} = \frac{a(T-T_c)}{\omega_c^2}(\omega_c^2 - i\gamma\omega) + 3BP^2 + \cdots \ . \tag{6.4a}$$

Here $a(T-T_c)/\omega_c^2$ is just a proportionality constant, as $\omega_c^2$ follows a Curie law

$$\omega_c^2 = \bar{\omega}^2 (T-T_c)/(T_a - T_c) \ , \tag{6.4b}$$

where $\bar{\omega}$ is the value of $\omega_c$ at $T = T_a$. Although a more elaborate frequency dependence is necessary to account for Raman results, the Debye approximation is sufficient in the frequency range of interest, where $\omega << \bar{\omega} < \gamma$.[22] This has been confirmed by quantitative measurements at $E = 0$.[24] Dynamics is introduced in the elastic equations by taking into account inertia. No further friction is needed as the main source of damping is already in Eq. (6.4a). Inertia reduces the effect of the external force from $\delta\vec{F}$ to $\delta\vec{F} - \rho d^2 \delta\vec{u}/dt^2$. In the time-Fourier transform notation, this amounts to the substitution

$$\delta\vec{F} \rightarrow \delta\vec{F} + \rho\omega^2 \delta\vec{u} \tag{6.5}$$

in Eq. (5.7a). Finally the heat dynamics is described in terms of the entropy fluctuation $\delta S$, thermal conductivity $\vec{\Lambda}$, and an external force $\delta F_T$ given by

$$\delta F_T \equiv \delta W / i\omega T \ , \tag{6.6}$$

where $\delta W(\vec{q}, \omega)$ is an applied power source. $\delta F_T$ is the appropriate force conjugated to $\delta T$ that leads to correct fluctuation-dissipation relations as shown in Appendix B. The entropy fluctuations are obtained from $\delta S = -\partial G / \partial \delta T$ using Eqs. (6.1) to (6.3)

$$\delta S = -aP\delta P + \frac{\rho C_{P,e}}{T}\delta T + iq\alpha_1 \delta u_1 \ . \tag{6.7}$$

The heat-conductivity equation including the external power source is

$$T\frac{d}{dt}\delta S = \vec{\nabla}\cdot(\vec{\Lambda}\cdot\vec{\nabla} T) + \delta W \ , \tag{6.8a}$$

which in Fourier-transformed notation, and combined with Eq. (6.7) gives

$$\delta F_T = aP\delta P - iq\alpha_1 \delta u_1 + \frac{q^2\Lambda}{i\omega T} - \frac{\rho C_{P,e}}{T}\delta T \ . \tag{6.8b}$$

Here, $\Lambda$ stands for the component $\Lambda_{11}$ of the thermal-conductivity tensor.

Introducing the above modifications in Eq. (5.7), and taking systematic account of $\delta T$, one obtains the set of equations

$$\begin{pmatrix} \delta E \\ \delta F_1 \\ \delta F_2 \\ \delta F_T \end{pmatrix} = \begin{pmatrix} \chi_0^{-1} & iqV_1 & iqV_2 & aP \\ -iqV_1 & q^2 M_{11} & q^2 M_{12} & iq\alpha_1 \\ -iqV_2 & q^2 M_{12} & q^2 M_{22} & 0 \\ aP & -iq\alpha_1 & 0 & M_{33} \end{pmatrix}^{-1} \begin{pmatrix} \delta P \\ \delta u_1 \\ \delta u_2 \\ \delta T \end{pmatrix} , \tag{6.9}$$

where $\chi_0^{-1}$ is given by Eq. (5.8a), with $\chi_P^{-1}$ given by Eq. (6.4), and

$$V_1 \equiv (\tfrac{1}{2}\Delta_{16} b - 2\delta_1)P \ , \tag{6.10a}$$

$$V_2 \equiv -h + (\alpha\Delta_{16} + \tfrac{1}{2}\beta\Delta_{36} + 2b\Delta_{66} - 3\delta_6 - 3b^2\delta_6')P^2 \ , \tag{6.10b}$$

$$M_{11} \equiv C_{11} - \rho\omega^2/q^2 \ , \tag{6.10c}$$

$$M_{12} \equiv (C_{166} b + \tfrac{1}{2}\Delta_{16})P \ , \tag{6.10d}$$

$$M_{22} \equiv C_{66} - \rho\omega^2/q^2 + (2C_{166}\alpha + C_{366}\beta + \tfrac{1}{2}C_{6666} b^2 + \Delta_{66} - 6b\delta_6')P^2 \ , \tag{6.10e}$$

$$M_{33} \equiv \frac{q^2\Lambda}{i\omega T} - \frac{\rho C_{P,e}}{T} \ . \tag{6.10f}$$

The equation for $\delta u_3$ is not written explicitly as for $\vec{q}$ parallel to $\hat{x}$ it decouples from Eq. (6.9) as it did for the statics in Eq. (5.13). It should be noted that the phenomenological dynamics was introduced only in the diagonal terms in Eq. (6.9), assuming that local piezoelectric and thermal responses are fast compared to the ferroelectric response in the frequency range of interest to the Brillouin experiment.

One recognizes in $M_{33}$ the thermal response whose width will depend on

$$Dq^2 \equiv \tau_{\text{th}}^{-1} \ , \tag{6.11a}$$

where the thermal diffusion constant is

$$D \equiv \Lambda/\rho C_{P,e} \ . \tag{6.11b}$$

With that notation

$$M_{33}^{-1} = \frac{T}{\rho C_{P,e}} \frac{i\omega\tau_{\text{th}}}{1 - i\omega\tau_{\text{th}}} \ . \tag{6.11c}$$

### A. Critical scattering

With $P=0$, one has $V_1 = M_{12} = 0$, and both $\delta T$ and $\delta u_1$ decouple from $\delta P$ in Eq. (6.9). The scattering in the usual depolarized geometry is found in the same spirit as in Eq. (5.9), but now using Eq. (4.3) instead of the sum rule (4.4):

$$I(q,\omega) \propto \frac{kT}{\pi\omega} \operatorname{Im}(a_{63}\ p_{66}) \begin{pmatrix} \chi_P^{-1} & -h \\ -h & C_{66} - \rho\dfrac{\omega^2}{q^2} \end{pmatrix}^{-1} \begin{pmatrix} a_{63} \\ p_{66} \end{pmatrix} \ . \tag{6.12}$$

Defining the relaxation time

$$\tau \equiv \gamma/\overline{\omega}^2 \ , \tag{6.13a}$$

the bare-phonon frequency $\omega_a$ by

$$\omega_a^2 \equiv q^2 C_{66}/\rho \ , \tag{6.13b}$$

and the reduced distance to the clamped Curie temperature

$$Q = (T - T_c)/(T_a - T_c) \ , \tag{6.13c}$$

the intensity is finally written in the convenient form

$$I(q,\omega) \propto \frac{kT}{\pi} \frac{p_{66}^2}{C_{66}} \times \tau \frac{(1 + \Upsilon - \Upsilon\omega^2/\omega_a^2)^2}{(Q - 1 - Q\omega^2/\omega_a^2)^2 + \omega^2\tau^2(1 - \omega^2/\omega_a^2)^2} \ . \tag{6.14}$$

The validity of Eq. (6.14) does not depend on the Curie-law assumptions of Eqs. (6.4b) and (6.13c), but just on the Debye assumption (6.4a) which at $P=0$ can be written

$$\chi_p^{-1} = a(T_a - T_c)(Q - i\omega\tau) \ . \tag{6.15}$$

The expression (6.14) was found to give statistically perfect fits to observed spectra, with $Q$ following the Curie law (6.13c), and with $\tau$ constant.[24] The integration of Eq. (6.14) gives

$$I(q) \propto kT\frac{p_{66}^2}{C_{66}} \left[ 1 + \frac{(1+\Upsilon)^2}{Q-1} \right] \ , \tag{6.16}$$

which is exactly Eq. (5.11).

### B. Coupling to temperature fluctuations

For $P \neq 0$, let us consider only the main contribution to spectral changes, in the spirit of the discussion preceding Eq. (5.20). If we call $\chi_{PP}$ the upper left-hand corner of the inverse of the matrix in Eq. (6.9), we can write

$$\chi_{PP}^{-1} = \chi_0^{-1} - (V_1\ V_2\ aP) \begin{pmatrix} M_{11} & M_{12} & -\alpha_1 \\ M_{12} & M_{22} & 0 \\ -\alpha_1 & 0 & M_{33} \end{pmatrix}^{-1} \begin{pmatrix} V_1 \\ V_2 \\ aP \end{pmatrix} \ . \tag{6.17}$$

First make the approximation $\alpha_1 = 0$. Then Eq. (6.17) can be written

$$\chi_{PP}^{-1} = \chi_0^{-1} - (V_1\ V_2) \begin{pmatrix} M_{11} & M_{12} \\ M_{12} & M_{22} \end{pmatrix}^{-1} \begin{pmatrix} V_1 \\ V_2 \end{pmatrix} - \frac{a^2P^2}{M_{33}} \ . \tag{6.18}$$

The elements $M_{11}$ and $M_{22}$ both contain $\omega^2$ in accordance with Eqs. (6.10c) and (6.10e). However, $C_{11} >> C_{66}$, and $\omega_a^2 >> \omega^2$, where $\omega$ is the frequency of interest when observing the soft mode near $T_a$. It follows that a reasonable approximation of Eq. (6.18) is obtained by maintaining the $\omega^2$ terms for the constant ($P=0$) contribution and neglecting it for the $P^2$ corrections, which are small anyway. Then one finds

$$(1 - \omega^2/\omega_a^2)\chi_{PP}^{-1} \simeq a(T_a - T_c)[(Q - 1 - Q\omega^2/\omega_a^2) - i\omega\tau(1 - \omega^2/\omega_a^2)] + (3B_mP^2 - M_{33}^{-1}a^2P^2)(1 - \omega^2/\omega_a^2) \ . \tag{6.19}$$

The $P$-independent terms in Eq. (6.19) are immediately recognized as those that lead to the denominator in Eq. (6.14). Using Eq. (6.11c), the parentheses containing $P^2$ in Eq. (6.19) is written

$$(3B_mP^2 - M_{33}^{-1}a^2P^2) = 3B_mP^2 + \delta^2 - \frac{\delta^2}{1 - i\omega\tau_{\text{th}}} \ , \tag{6.20a}$$

where we defined

$$\delta^2 \equiv a^2P^2T/\rho C_{P,e} \ . \tag{6.20b}$$

It follows that Eq. (6.14) remains a good approximation to the spectrum provided one uses for $Q$ and $\tau$ the following expressions

$$Q = Q_{\text{iso}} + \frac{\delta^2}{a(T_a - T_c)} - \frac{\delta^2}{a(T_a - T_c)} \frac{1}{1+\omega^2\tau_{\text{th}}^2} \ , \tag{6.21a}$$

$$\tau = \frac{\gamma}{\bar{\omega}^2} + \frac{\delta^2}{a(T_a - T_c)} \frac{\tau_{\text{th}}}{1+\omega^2\tau_{\text{th}}^2} \ , \tag{6.21b}$$

where $Q_{\text{iso}}$ is the $\omega = 0$ limit (isothermal) of Eqs. (6.21a)

$$Q_{\text{iso}} = Q_0 + 3B_m P^2/a(T_a - T_c) \ , \tag{6.21c}$$

and $Q_0$ is the $P = 0$ value as given in Eq. (6.13c) or Eq. (6.15). One should note that the integration of Eq. (6.14) gives the isothermal response

$$I_{\text{iso}}(q) \propto kT\frac{p_{66}^2}{C_{66}}\left[1 + \frac{(1+\Upsilon)^2}{Q_{\text{iso}} - 1}\right] \ , \tag{6.22}$$

which is just Eq. (5.11) combined with Eq. (5.16).

For $\alpha_1 \neq 0$, the inverse matrix in Eq. (6.17) is approximated by

$$\begin{vmatrix} H_{11} & H_{12} & H_{11}M_{33}^{-1}\alpha_1 \\ H_{12} & H_{22} & H_{12}M_{33}^{-1}\alpha_1 \\ H_{11}M_{33}^{-1}\alpha_1 & H_{12}M_{33}^{-1}\alpha_1 & M_{33}^{-1} \end{vmatrix} \ , \tag{6.23}$$

where $H$ is the inverse of the $(2\times 2)$ $M$ matrix in Eq. (6.18). Using Eqs. (6.10) and (3.6a), one finds that the coefficient of $P^2/M_{33}$ in Eq. (6.18) is modified. This leads to a modified definition of $\delta^2$, with Eq. (6.20b) replaced by

$$\delta^2 \equiv \left\{\frac{a^2P^2T}{\rho C_{P,e}}\right\}\left\{1 - \frac{4\alpha_1}{aC_{11}}[(C_{11}+C_{12})\alpha + 2C_{13}\beta]\right\} \ . \tag{6.24}$$

For KDP, all parameters entering Eq. (6.24) are, in principle, known. In particular, the thermal-expansion correction within curly brackets can be calculated using Eq. (2.7a) and the values of Refs. 32 and 37. One finds that the curly bracket is equal to 0.904, meaning that thermal expansion reduces the adiabatic correction to the susceptibility by about 10%.

### C. Adiabatic response and the thermal central peak

Consider the spectrum (6.14), where $Q$ and $\tau$ are given by Eq. (6.21), and $\delta^2$ by Eq. (6.24). For $\omega\tau_{\text{th}} \gg 1$, the terms with $1+\omega^2\tau_{\text{th}}^2$ in the denominator in Eq. (6.21) can be neglected, leading to the adiabatic values

$$Q_\infty \equiv Q_{\text{iso}} + N \ , \tag{6.25a}$$

$$\tau_\infty \equiv \gamma/\bar{\omega}^2 \ , \tag{6.25b}$$

where

$$N \equiv \delta^2/a(T_a - T_c) \ . \tag{6.25c}$$

The corresponding spectrum, $I_\infty(q,\omega)$, is given by Eq. (6.14) where $Q$ and $\tau$ are replaced by $Q_\infty$ and $\tau_\infty$, respectively. This is the adiabatic spectrum which can also be obtained by equating Eq. (6.7) to zero and introducing the corresponding value of $\delta T$ in the first three equations (6.9). This spectrum is just like the critical spectrum obtained at $P = 0$, but with a downward shift of the critical temperature. For KDP, this shift is mainly due to the adiabatic correction, as $N$ in Eq. (6.25a) is much larger than $Q_{\text{iso}} - Q_0$ which is the fluctuation-quenching contribution. The adiabatic spectrum integrates to

$$I_\infty(q) \propto kT\frac{p_{66}^2}{C_{66}}\left[1 + \frac{(1+\Upsilon)^2}{Q_\infty - 1}\right] \ . \tag{6.26}$$

The difference between $I_{\text{iso}}(q)$ in Eq. (6.22) and $I_\infty(q)$ in Eq. (6.26) is the strength of the thermal central peak

$$I_{\text{CP}}(q) \propto kT\frac{p_{66}^2}{C_{66}}\frac{(1+\Upsilon)^2N}{(Q_{\text{iso}}-1)(Q_\infty - 1)} \ . \tag{6.27}$$

Neglecting the "noncritical" contribution in Eq. (6.26), i.e., the term 1 within the large parenthese, one finds the ratio of central-peak to adiabatic Brillouin-peak intensities

$$R_I = \frac{I_{\text{CP}}}{I_\infty} \simeq \frac{N}{Q_{\text{iso}} - 1} = 0.904\frac{a^2T}{\rho C_{P,e}}E_s^2 \ . \tag{6.28}$$

The last expression takes account of the value derived for KDP in Eq. (6.24) and of the definition of $E_s$ in Eq. (5.17).

The above spectral decomposition assumes that the thermal response is slower than the critical response. To obtain the width of the thermal central peak, one first notes that for light scattering, $Dq^2 \ll \omega_a = q\sqrt{C_{66}/\rho}$. For KDP, equality of these two frequencies is only obtained for $\lambda = 2\pi/q \simeq 40$ Å, which is the domain of neutron scattering. Hence, in the low-frequency limit, $\omega^2/\omega_a^2$ in expressions such as Eqs. (6.14) or (6.19) can be neglected with respect to 1. The width $\Gamma$ of the central peak is then given by the lowest root $-i\Gamma$ of the expression

$$Q_{\text{iso}} - 1 - i\omega\tau - i\omega N\tau_{\text{th}}/(1 - i\omega\tau_{\text{th}}) \ , \tag{6.29}$$

which is derived from Eq. (6.19). This gives, to order $P^2$,

$$\Gamma = \tau_{\text{th}}^{-1}\left[1 - \frac{N}{Q_\infty - 1 - \tau/\tau_{\text{th}}} + \cdots\right] \tag{6.30}$$

under the condition

$$Q_\infty - 1 > \tau/\tau_{\text{th}} \ . \tag{6.31}$$

This condition is precisely that the thermal response is slower than the overdamped critical one. For KDP at 1 bar, $\tau = 0.84$ cm, whereas $\tau_{\text{th}} \simeq 220$ cm.[24,25] It follows that Eq. (6.31) is always satisfied as $Q_\infty - 1 = \tau/\tau_{\text{th}}$ means $T - T_a \simeq 20$ mK which is beyond the stability limit found experimentally.[24] If one neglects the term $\tau/\tau_{\text{th}}$ in Eq. (6.30), the expression can be rewritten

$$\Gamma = \tau_{\text{th}}^{-1}(1 + R_l + \cdots) \ , \tag{6.32}$$

with $R_l$ given by Eq. (6.28). This emphasizes the narrowing of the thermal central peak by the coupling to the phonon branch.

## VII. CONCLUDING REMARKS

In elastic solids, the critical microscopic fluctuations associated with a symmetry-breaking transition are generally quenched under the application of the ordering force. This is due to the fact that the force already breaks the symmetry, so that the order parameter couples linearly to density, and pure microscopic density fluctuations cannot occur in elastic solids due to the elastic compatibility equations. In the present paper, the above considerations have been applied to the particular case of the type-I transition in KDP, obtaining the following key results:

(i) In an expansion to lowest order in the ordering force, the macroscopic Landau parameter $B_M$ is always smaller than the microscopic Landau parameter $B_m$, i.e., $B_m - B_M > 0$ as shown in Eq. (5.19). This demonstrates that the microscopic response (5.16) is quenched compared to the macroscopic response (5.18).

(ii) Under $E$, the soft*est* direction moves in the (001) plane away from the original soft direction [100]. The sign of this motion depends on the sign of $E$. This is related to the fact that at type-0 instability the soft*est* elastic direction is not necessarily a direction of high symmetry.

(iii) Under $E$, temperature fluctuations are also linearly coupled to polarization fluctuations. A thermal central peak results whose relative strength is given by Eq. (6.28).

(iv) The width of the induced thermal central peak is the thermal diffusion width renormalized by the coupling to the polarization fluctuations, as shown in Eq. (6.30) or (6.32).

Given the large number of parameters entering Eqs. (2.4) and (2.5), it is truly remarkable that the above results, in particular Eqs. (5.15), (5.28), and (6.24), could be expressed in terms of the lowest-order elastic constants and the lowest-order coefficients $a_{in}$ of Eq. (3.2) only. This suggests underlying symmetry reasons which might generalize beyond the particular case of KDP, but which have not been established so far. On the other hand, useful analytic expressions beyond the expansions to the lowest nontrivial order in $E$ could not be obtained. In particular, the Landau coefficient $C$ in Eq. (3.16) was simply introduced phenomenologically, and expressions for the quenching in the region of the critical point have not been derived. The reason for this is simple: at the critical point, it is only macroscopic responses that diverge, whereas all microscopic responses remain finite. However, as the critical polarization is of sizable value, expansions in $P$ of the microscopic responses in that region might have to be carried to arbitrary order, and are thus not useful. In particular, it does not seem possible to determine by microscopic measurements either the exact position of the critical point, or the values of the macroscopic Landau coefficient $C$.

Finally, one should note that in real crystals, the symmetry can be locally broken by defects. Such a mechanism was invoked to explain the occurrence of quasistatic central peaks.[46] Symmetry-breaking defects will also produce a linear coupling between order parameter and density. Consideration of elastic terms might thus become important in these systems sufficiently close to their transition.

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## APPENDIX A: EQUIVALENCE OF TWO STABILITY-LIMIT CONDITIONS

Consider a free energy

$$G = G_0(\eta, e_i) - \eta f - e_i \sigma_i \ , \tag{A1}$$

where $f$ is the force conjugated to $\eta$. In Sec. III, the strains were eliminated from $G$ using, at $\sigma_i = 0$,

$$\frac{\partial G_0}{\partial e_i} = 0 \ . \tag{A2}$$

The solutions $e_i(\eta)$ of these equations are reintroduced in $G$ to obtain a free energy depending on $\eta$ alone. Its first derivative in $\eta$ is the equation of state

$$f = \frac{dG_0(\eta, e_i(\eta))}{d\eta} = \frac{\partial G_0}{\partial \eta} \ . \tag{A3}$$

The system becomes unstable when the derivative of Eq. (A3) vanishes. This condition is

$$\frac{\partial^2 G_0}{\partial\eta^2}+\frac{\partial^2 G_0}{\partial\eta\partial e_i}\frac{de_i}{d\eta}=0 \ . \tag{A4}$$

Let us demonstrate that Eq. (A4) is identical to the stability-limit condition $\det(C_{ij})=0$, where here the $C_{ij}$'s are the isothermal elastic constants at fixed $f$.[1] To obtain the $C_{ij}$'s, consider how the equilibrium values $e_i(\eta)$ are modified to $e_i+\delta e_i$ by application of small stresses $\delta\sigma_j$. Under constant $f$, the stresses also modify $\eta$ to $\eta+\delta\eta$. Rewriting the equilibrium conditions (A2) and (A3) for the perturbed system, one obtains

$$\frac{\partial^2 G_0}{\partial e_i\partial e_j}\delta e_j+\frac{\partial^2 G_0}{\partial e_i\partial\eta}\delta\eta=\delta\sigma_i \ , \tag{A5a}$$

$$\frac{\partial^2 G_0}{\partial\eta 2}\delta\eta+\frac{\partial^2 G_0}{\partial e_j\partial\eta}\delta e_j=0 \ , \tag{A5b}$$

where repeated indices are summed on. Introducing $\delta\eta$ from the second equation into the first one, and observing that $C_{ij}\delta e_j=\delta\sigma_i$, one obtains

$$C_{ij}=\frac{\partial^2 G_0}{\partial e_i\partial e_j}-\left[\frac{\partial^2 G_0}{\partial e_i\partial\eta}\right]\left[\frac{\partial^2 G_0}{\partial e_j\partial\eta}\right]\Big/\frac{\partial^2 G_0}{\partial\eta^2} \ . \tag{A6}$$

We assume that the uncoupled system is stable so that both $(\partial^2 G_0/\partial e_i\partial e_j)$ and $(\partial^2 G_0/\partial\eta^2)$ do not vanish. Note that $C_{ij}$ is of the form

$$\begin{aligned}C_{ij}&=a_{ij}-v_iv_j=a_{im}(\delta_{mj}-a_{mk}^{-1}v_kv_j)\\&=a_{im}(\delta_{mj}-V_mv_j) \ .\end{aligned} \tag{A7}$$

Here, $a_{ij}$ is nonsingular, $a_{ij}^{-1}$ is the inverse matrix of $a_{ij}$, and $v_i$, $V_j$ are vectors as shown. From Eq. (A7), the condition $\det(C_{ij})=0$ is simply

$$\det(\delta_{ij}-V_iv_j)=0 \ . \tag{A8a}$$

It is not difficult to see that in all generality the value of this determinant is simply $(1-V_iv_i)$, so that Eq. (A8a) can be rewritten

$$V_iv_i=a_{ik}^{-1}v_kv_i=1 \ , \tag{A8b}$$

or,

$$a_{ij}^{-1}\frac{\partial^2 G_0}{\partial e_i\partial\eta}\frac{\partial^2 G_0}{\partial e_j\partial\eta}=\frac{\partial^2 G_0}{\partial\eta^2} \ . \tag{A9}$$

To see that Eqs. (A4) and (A9) are identical conditions, it suffices to take the total derivative in $\eta$ of Eq. (A2) to obtain

$$\frac{\partial^2 G_0}{\partial e_i\partial\eta}+a_{ij}\frac{de_j}{d\eta}=0 \ . \tag{A10}$$

Introducing the value of $de_i/d\eta$ from Eq. (A10) into Eq. (A4), one recovers Eq. (A9) which completes the proof.

## APPENDIX B: DYNAMIC CORRELATIONS INVOLVING $\delta T$

Correlation functions involving temperature fluctuations are comparatively rarely observed experimentally. This might explain that their calculation following a fluctuation-dissipation approach does not seem to be much documented in the literature. The alternate approach, which is the one usually used in this case, in particular for the description of light-scattering results, goes as follows:

(i) Obtain the equal-time correlation functions from thermodynamics, for example following Sec. 111 of Ref. 42.

(ii) Set up dynamical equations and Laplace transform them taking due account of the initial values.

(iii) Multiply the resulting equations by the initial values and ensemble average.

In this manner, a set of equations for the Laplace transforms of the dynamic correlation functions is obtained. They are expressed in terms of the known static correlation. In the present Appendix, it is shown how identical results can be obtained by the shorter route offered by the fluctuation-dissipation theorem.

Following the approach of Callen and Greene,[47] one finds rather readily which is the external force conjugated to energy fluctuations $\delta E$. The quantity $Y(\omega)/i\omega T$ in their notation [Eq. (3.6) in Ref. 48] corresponds to $-\chi(\omega)$ in the present notation, where account is taken of the different sign of the imaginary exponent in the Fourier-transform definition. The fluctuations in their $X_0$, that is $\delta E$, which in their definitions are conjugated to the external force $-\delta T/T^2$, are in the present definitions conjugated to the force $\delta T/T$. Here, instead of taking $\delta E$ as response to the force $\delta T/T$, we take the temperature as response to an external energy source. This introduces an additional minus sign just as when one interchanges independent and dependent variables in a thermodynamic potential. It results that the force conjugated to $\delta T$ is $\delta F_T=-\delta E/T$. Introducing an external power source $\delta W$, one has $\delta\dot{E}=-i\omega\delta E=\delta W$ or

$$\delta F_T=-\frac{\delta E}{T}=\frac{\delta W}{i\omega T} \tag{B1}$$

as indicated in Eq. (6.6).

It is instructive to discuss somewhat further the implications of Eq. (B1). For simplicity, consider the case where temperature fluctuations are decoupled from the other variables of the problem. One immediately has

$$T\delta S=\rho C\delta T \ , \tag{B2a}$$

where $C$ is the appropriate heat capacity per unit weight and

$$T\delta\dot{S} = -q^2\Lambda\delta T + \delta W \;, \tag{B2b}$$

where $\Lambda$ is the thermal conductivity. This gives straightforwardly

$$\delta T = \frac{T}{\rho C}\frac{i\omega\tau}{1-i\omega\tau}\delta F_T = \chi(\omega)\delta F_T \;, \tag{B3}$$

where $\tau \equiv \rho C/\Lambda q^2$. The fluctuation-dissipation theorem then gives

$$\langle \delta T \delta T \rangle_{q,\omega} = \frac{kT}{\pi\omega}\,\mathrm{Im}\chi = \frac{kT^2}{\rho C}\frac{\tau/\pi}{1+\omega^2\tau^2} \;. \tag{B4}$$

The sum rule on Eq. (B4) is

$$\begin{aligned}\langle \delta T(0)\delta T(0) \rangle_q &= kT\,\mathrm{Re}[\chi(\omega\to 0) - \chi(\omega\to\infty)] \\ &= \frac{kT^2}{\rho C} \;. \end{aligned} \tag{B5}$$

The modification of the Kramers-Kronig relation in Eq. (B5) should be noted. It arises from the fact that $\chi(\omega\to\infty)$ is different from zero, and is explained in Ref. 42, in the footnote following Eqs. (122.15) and (122.16).

The simplicity with which the results (B4) and (B5) have been derived should be stressed. If one had followed the route indicated at the beginning of this Appendix, one would have first had to derive Eq. (B5), then one would have had to take the Laplace transforms of Eq. (B2). The work saving becomes very evident if one considers a complicated situation with many couplings such as in Eq. (6.9) above.

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[1] R. A. Cowley, Phys. Rev. B 13, 4877 (1976).

[2] S. Aubry and R. Pick, J. Phys. (Paris) 32, 657 (1971).

[3] R. A. Toupin and H. Thomas (unpublished).

[4] H. Wagner and H. Horner, Adv. Phys. 23, 587 (1974).

[5] R. L. Melcher, G. Guntherodt, T. Penney, and F. Holtzberg, IEEE Trans. Sonics Ultrason. 23, 205 (1976).

[6] H. Zabel and H. Peisl, Phys. Rev. Lett. 42, 511 (1979).

[7] D. J. Bergmann and B. I. Halperin, Phys. Rev. B 13, 2145 (1976).

[8] E. Courtens, R. Gammon, and S. Alexander, Phys. Rev. Lett. 43, 1026 (1979).

[9] R. Folk, H. Iro, and F. Schwabl. Z. Phys. B 25, 69 (1976); Phys. Rev. B 20, 1229 (1979).

[10] Y. Le Corre and L. Benguigui, Phys. Lett. 24A, 419 (1967).

[11] V. L. Ginzburg and A. P. Levanyuk, Phys. Lett. 47A, 345 (1974).

[12] M. F. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon, Oxford, 1977).

[13] F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon, Oxford, 1962).

[14] R. Blinc, J. Phys. Chem. Solids 13, 204 (1960); P. G. de Gennes, Solid State Commun. 1, 132 (1963); R. Brout, K. A. Müller, and H. Thomas, *ibid.* 4, 507 (1966).

[15] M. S. Shur, Kristollagrafiya 11, 448 (1966) [Sov. Phys. Crystallogr. 11, 394 (1966)].

[16] Abbreviated Voigt subscripts are used as defined by J. F. Nye, in *Physical Properties of Crystals, their Representation by Tensors and Matrices* (Clarendon, Oxford, 1957), Chaps. VII and VIII.

[17] B. A. Strukov, M. A. Korzhuev, A. Baddur, and V. A. Koptsik, Fiz. Tverd. Tela (Leningrad) 13, 1872 (1971) [Sov. Phys. Solid State 13, 1569 (1972)].

[18] A. B. Western, A. G. Baker, C. R. Bacon, and V. H. Schmidt, Phys. Rev. B 17, 4461 (1978).

[19] P. Bastie, M. Vallade, C. Vettier, and C. M. E. Zeyen, Phys. Rev. Lett. 40, 337 (1978).

[20] E. M. Brody and H. Z. Cummins, Phys. Rev. B 9, 179 (1974).

[21] R. L. Reese, I. J. Fritz, and H. Z. Cummins, Phys. Rev. B 7, 4165 (1973).

[22] N. Lagakos and H. Z. Cummins, Phys. Rev. B 10, 1063 (1974).

[23] L. N. Durvasula and R. Gammon, Phys. Rev. Lett. 38, 1081 (1977).

[24] E. Courtens, Phys. Rev. Lett. 41, 1171 (1978).

[25] E. Courtens (unpublished).

[26] E. Pytte and H. Thomas, Solid State Commun. 11, 161 (1972).

[27] M. D. Mermelstein and H. Z. Cummins, Phys. Rev. B 16, 2177 (1977); M. D. Mermelstein, *ibid.* 23, 3139 (1981).

[28] E. Courtens and R. Gammon, Ferroelectrics 24, 19 (1980).

[29] K. Brugger, Phys. Rev. 133, A1611 (1964).

[30] R. N. Thurston, in *Physical Acoustics,* edited by W. P. Mason (Academic, New York, 1964), Vol. IA.

[31] One has $\alpha = 3.83 \times 10^{-12}$ esu, $\beta = 2.9 \times 10^{-12}$ esu, $b = 5.0 \times 10^{-7}$ esu, from M. de Quervain, Helv. Phys. Acta 17, 509 (1944), and also A. von Arx and W. Bantle, *ibid.* 17, 298 (1944). Also cited by Jona and Shirane, Ref. 13, pp. 68–72.

[32] S. Haussühl, Z. Krist. 120, 401 (1964). As the elastic stiffnesses at constant polarization are fairly temperature independent, we use these well-established room-temperature values $C_{11} = 7.165$, $C_{12} = -0.627$, $C_{13} = 1.494$, $C_{33} = 5.640$, $C_{44} = 1.248$ times $10^{11}$ dynes/cm$^2$. For $C_{66}$ at constant polarization, we use $C_{66} = 0.73 \times 10^{11}$ dynes/cm$^2$ in agreement with Brillouin measurements (Ref. 24).

[33] H. Umebayashi, B. C. Frazer, G. Shirane, and W. B. Daniels, Solid State Commun. 5, 591 (1967), give $dT_a/dp = -4.52 \pm 0.06$ K/kbar.

[34] E. Hegenbarth and S. Ullwer, Cryogenics 7, 306 (1967), give $dT_a/dp = -5.7$ K/kbar.

[35] G. A. Samara, Phys. Rev. Lett. 27, 103 (1971), gives $dT_a/dp = -4.6 \pm 0.1$ K/kbar.

[36] R. Gammon, W. B. Daniels, and E. Courtens obtained $dT_a/dp = -4.83$ K/kbar in the course of Brillouin scattering measurements (unpublished).

[37] W. R. Cook, Jr., J. Appl. Phys. 38, 1637 (1967). The values are $\alpha_{11} = 2.49 \times 10^{-5}$ and $\alpha_{33} = 4.40 \times 10^{-5}$ $K^{-1}$.

[38] This is the mean of two values given by S. R. Garber and L. A. Smolenko, Zh. Eksp. Teor. Fiz. 64, 181 (1973) [Sov. Phys. JETP 37, 94 (1973)]. It is also in agreement with the value $4.6 \times 10^8$ ergs/mole given by W. Reese, Phys. Rev. 181, 905 (1969).

[39] See, e.g., B. J. Berne and R. Pecora, in *Dynamic Light Scattering* (Wiley, New York, 1976), Chap. 3.

[40] D. F. Nelson, P. D. Lazay, and M. Lax, Phys. Rev. B 6, 3109 (1972). See also M. Lax and D. F. Nelson, J. Opt. Soc. Am. 65, 668 (1975); and Phys. Rev. B 14, 837 (1976). For a different approach, see O. Keller, Phys. Rev. B 11, 5059 (1975); and 14, 841 (1976).

[41] D. F. Nelson and M. Lax, Phys. Rev. B 3, 2778 (1971).

[42] L. L. Landau and E. M. Lifshitz, in *Statistical Physics* (Pergamon, London, 1958), Chap. XII.

[43] See, e.g., H. Thomas, in *Anharmonic Lattices, Structural Transitions, and Melting,* edited by T. Riste (Noordhoff, Leiden, 1974), pp. 231–244.

[44] E. Pytte and H. Thomas, Phys. Rev. 175, 610 (1968).

[45] R. A. Cowley, Phys. Rev. Lett. 36, 744 (1976).

[46] B. I. Halperin and C. M. Varma, Phys. Rev. B 9, 4030 (1976).

[47] H. B. Callen and R. F. Greene, Phys. Rev. 86, 702 (1952).