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# Propagation of Sound at Continuous Structural Phase Transitions[1]

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Structural phase transitions of second order can be divided into two groups: (i) distortive phase transitions, with a soft (ultimately overdamped) optic mode, and (ii) elastic phase transitions, with an acoustic soft mode or no soft phonon for shear or isostructural transitions, respectively. The propagation of sound shows significantly different features in these two cases. We consider the theory of the critical variation of the velocity of ultrasonic modes as well as the damping and dispersion near transitions of second order.

**KEY WORDS:** Critical dynamics; structural phase transitions; sound propagation; soft modes.

## 1. INTRODUCTION

Structural phase transitions can be divided into two groups: (i) distortive phase transitions and (ii) elastic phase transitions.

At distortive phase transitions some of the ions or molecular groups are displaced with respect to each other. The order parameter of the phase transition is a collective coordinate which characterizes this displacement. The soft mode is an optic phonon, which gets overdamped at least very close to the phase transition temperature $T_c$. Famous examples of this group of structural phase transitions are found among perovskites (simple cubic $ABO_3$), which undergo ferroelectric ($BaTiO_3$), antiferroelectric ($NaNbO_3$), and antiferrodistortive $R_{25}$($SrTiO_3$) phase transitions. At distortive transitions the elastic degrees of freedom are secondary variables.

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Their interaction with the critical order parameter fluctuations is quadratic in the order parameter and linear in the strains.

At an elastic phase transition (also called ferroelastic) the unit cell undergoes an elastic deformation. Thus the order parameter is a linear combination of components of the strain tensor. In the majority of cases this elastic deformation is a shear deformation and then the soft mode is the corresponding transverse acoustic phonon. The other possibility, isostructural elastic phase transitions, are related to those elastic stability limits where all transverse and necessarily all longitudinal sound velocities remain finite. For instance, if the bulk modulus of an isotropic or cubic elastic medium vanishes, only the macroscopic uniform dilatation and gradient modes soften but none of the phonons. In this report we will consider only the more interesting and prevalent case of elastic phase transitions accompanied by a soft transverse acoustic phonon. A substance undergoing an elastic phase transition is $KH_2PO_4$ (KDP), which is better known for its ferroelectric properties. However, the $z$ component of the electric dipole moment $P_z$ couples linearly to (belongs to the same representation as) the $\varepsilon_{12}$ shear deformation. Consequently, the transition, although driven by the ordering of the hydrogen bonding protons and the $P_z$ motion, becomes ultimately an elastic phase transition with the shear coefficient $c_{66} \to 0$. A situation analogous to KDP, where an optical soft mode is responsible for the instability and "drives" the elastic transitions is rather common, e.g., $LaP_5O_{14}$. But there are also cases of pure acoustic elastic phase transitions, where the instability is driven by local fluctuations (NaOH).

Distortive phase transitions in materials with short-range interactions and elastic phase transitions belong to different universality classes concerning their behavior near the critical point. This difference will be particularly significant when one is concerned with sound propagation. In the former case the sound waves are secondary degrees of freedom, while in the latter case the soft mode is a transverse sound wave. Hence these two cases must be studied separately.

The experimental investigation of sound propagation near distortive structural transitions intensified in the late sixties.[1–3] Early theories were based on the random phase approximation[4] and the dynamical scaling and the mode coupling theory.[5] The invention of new experimental techniques[6,7] and increasingly precise results[8,6,7] prompted the application of the dynamical renormalization group (RNG) technique to this problem.[9,10] Also, elastic phase transitions have experienced increasing experimental[11–20] and theoretical (static[21,23] and dynamic[22] RNG) attention.

Our main goal is to review the present status of the theory. We do not go into any details of the underlying RNG calculations but emphasize the basic features of the Hamiltonian and the dynamical equations of motion and the results derived therefrom. At appropriate places we will compare the theory with a limited number of experiments. Further experiments can be found in the review by Cummins[24] and in Refs. 22 and 25. The material covered in the present overview is based mainly on Refs. 9, 10, 21, and 22, which should be consulted for details of the derivations and for further discussions and applications of the theory.

Now we turn to the outline of this paper. In Section 2 we consider distortive phase transitions and discuss the velocity, the damping, and the dispersion of sound waves. In Section 3, we study the elastic phase transitions. In Section 4, we discuss and summarize the results, emphasizing the information derivable from ultrasonic experiments and the relation to phase transitions beyond the realm of the structural ones.

## 2. DISTORTIVE STRUCTURAL PHASE TRANSITIONS

### 2.1. The Hamiltonian and the Dynamics

Before starting the discussion of sound propagation we would like to remind the reader of some basic features of structural transitions.

We shall denote the local order parameter of the system by $\phi_\alpha(\mathbf{x})$ with $\alpha = 1,\ldots, n$. Here $\phi_\alpha(\mathbf{x})$ may represent the electric moment, the staggered moment, or the rotation angle for the ferroelectric, antiferroelectric, or $R_{25}$ transitions, respectively. In a cubic system the number of components $n$ of the order parameter equals 3. As usual the starting point in the modern theory of critical phenomena is the Ginzburg–Landau free energy functional

$$H(\phi) = k_B T_c^{\,0} \int d^3x \left[ \tfrac{1}{2} r_0 \boldsymbol{\phi}^2 + \tfrac{1}{2}(\nabla\boldsymbol{\phi})^2 + u_0(\boldsymbol{\phi}^2)^2 + v_0 \sum_\alpha \phi_\alpha^4 \right] \qquad (2.1)$$

with the mean field transition temperature $T_c^{\,0}$ and $r_0 \propto (T - T_c^{\,0})$.

In a tetragonal system $n$ equals either 1 or 2. The tetragonal structure is imposed on a cubic crystal by applying uniaxial pressure. For the particular and frequently studied case of $SrTiO_3$, positive uniaxial pressure favors the order parameter perpendicular to the axis and thus leads to $n = 2$.[26] Negative uniaxial pressure (which is more readily realized by applying biaxial pressure) favors the order parameter along this axis and thus $n = 1$. The possiblity of changing the universality class by applying pressure is an attractive feature of experimental structural phase transition research.

One of the basic quantities in critical phenomena is the correlation length $\xi=\xi_0\tau^{-\nu}$ which diverges at $T_c$, where $\tau=(T-T_c)/T_c$. $\xi$ is the only significant length scale in the problem and associated with the growth of $\xi$ is the critical slowing down of the characteristic frequency of the order parameter dynamics

$$\omega_c=\gamma\tau^{\nu z} \tag{2.2}$$

where in addition to the exponent $\nu$ we have introduced the dynamical critical exponent $z$. We will describe the dynamics in the context of sound propagation shortly [Eq. (2.11)], but already at this point we mention that the dynamical renormalization group theory of Halperin *et al.*[27] gives

$$z=2+c\eta \tag{2.3}$$

in $O((4-d)^2)$ with $c=6\ln\frac{4}{3}-1\approx 0.726$. Thus $z$ is slightly higher than 2, while the conventional mode coupling theory gave $z=2-\eta$. For most purposes $z\approx 2$ since the correlation length exponent $\eta$ is extremely small in three dimensions.

Ultrasonic experiments on $SrTiO_3$,[1-3] $KMnF_3$,[6,7] and other substances of the distortive variety show a strong anomalous increase of the sound attenuation when approaching the critical point. Taking into account the usual increase with the frequency $\omega$ of the ultrasonic wave one might in a first attempt fit the coefficient of ultrasonic attenuation by

$$\alpha(\omega)\sim\tau^{-\rho}\omega^{x} \tag{2.4}$$

The exponents $\rho$ and $x$ characterize the temperature and the frequency dependence, respectively. Very close to the transition the critical increase with $\tau$ arrests and levels off. It is important to determine whether this rounding is due to imperfections or is an intrinsic consequence of dynamical scaling which requests that the $\tau^{-\rho}$ dependence has to go over into a $\omega^{-\rho/z\nu}$ dependence as soon as one is so close to $T_c$ that the characteristic critical soft mode frequency $\omega_c$ becomes comparable to and finally smaller than $\omega$.

In the hydrodynamic region $x$ equals 2 and $\rho$ is given by Eq. (2.14a) below. The interpretation of ultrasonic experiments was plagued by the fact that even in cases where agreement was found with the theoretical value of $\rho$ there were significant deviations from the hydrodynamic $x=2$. This is immediately related to the above-mentioned rounding. Therefore it is important to have a theory which gives the complete dynamical scaling function for the attenuation in the whole frequency range.

We shall now discuss the total Hamiltonian including the interaction with acoustic waves. The latter are characterized by the wave vector $\mathbf{k}$, the polarization $\lambda$, the polarization vector $\mathbf{e}(\mathbf{k}, \lambda)$, and the normal coordinate $Q_{\mathbf{k},\lambda}$. Then the total Hamiltonian is

$$H = H(\phi) + H(Q) + H_{a,s} \tag{2.5}$$

with $H(\phi)$ given in Eq. (2.1), the acoustic part

$$H(Q) = \sum_{\mathbf{k},\lambda} \frac{\bar{\rho}}{2} [kc_0(\hat{k}, \lambda)]^2 |Q_{\mathbf{k},\lambda}|^2 \tag{2.6}$$

with the mass density $\bar{\rho}$ and the bare sound velocity $c_0(\hat{k}, \lambda)$ and the interaction $H_{a,s}$. Since the interaction is analogous to the magnetostrictive interaction in magnets it is linear in $Q$ and quadratic in $\phi$.

The interaction is most easily expressed in terms of the Lagrangian strain tensor

$$\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} + \frac{\partial u_l}{\partial x_i}\frac{\partial u_l}{\partial x_j}\right) \tag{2.7}$$

with the displacement field

$$u_i = \frac{1}{(\Omega\bar{\rho})^{1/2}} \sum_{\mathbf{k},\lambda} e^{i\mathbf{kx}} e_i(\mathbf{k}, \lambda)\, Q_{\mathbf{k},\lambda} \tag{2.8}$$

and $\Omega$ the total volume.

The following three cases are of primary interest.

(I) $n = 3$: For a three-component order parameter in a cubic crystal the interaction part is[28]

$$H_{a,s} = \int d^3x[A\varepsilon_{11}\phi_1^2 + B\varepsilon_{11}(\phi_2^2 + \phi_3^2) + 2C\varepsilon_{12}\phi_1\phi_2 + \text{cycl}] \tag{2.9a}$$

with interaction coefficients $A$, $B$, and $C$. In tetragonal crystals $n$ equals 2 or 1.

II) $n = 2$:

$$H_{a,s} = \int d^3x[A'(\varepsilon_{11}\phi_1^2 + \varepsilon_{22}\phi_2^2) + B'(\varepsilon_{11}\phi_2^2 + \varepsilon_{22}\phi_1^2) + 2C'\varepsilon_{12}\phi_1\phi_2 + B''\varepsilon_{33}(\phi_1^2 + \phi_2^2)] \tag{2.9b}$$

(III) $b = 1$:

$$H_{a,s} = \int d^3x[\bar{A}\varepsilon_{33} + \bar{B}(\varepsilon_{11} + \varepsilon_{22})]\phi^2 \tag{2.9c}$$

For $SrTiO_3$ under uniaxial pressure one finds $A' = A$, $B' = B'' = B$, $C' = C$ and under biaxial pressure $\bar{A} = A$, $\bar{B} = B$. Here we have neglected higher-order anharmonicities. We also note that in the computation of sound attenuation we may omit the quadratic term in the Lagrangian strain tensor (2.7). Thus in all three cases the interaction is linear in $Q_{\mathbf{k},\lambda}$ and quadratic in $\phi$.

It is convenient to introduce the symmetry-adapted two mode fields[9,10]

$$\psi_1 = \frac{1}{(n\Omega)^{1/2}} \sum_{\mathbf{k}} \sum_{\alpha=1}^{n} \phi_{\alpha,\mathbf{k}} \phi_{\alpha,-\mathbf{k}}, \qquad \psi_3 = \left(\frac{2}{\Omega}\right)^{1/2} \sum_{\mathbf{k}} \phi_{1,\mathbf{k}} \phi_{2,-\mathbf{k}}$$
$$\psi_2 = \frac{1}{[n(n-1)\Omega]^{1/2}} \sum_{\mathbf{k}} \left( \sum_{\alpha=1}^{n} \phi_{\alpha,\mathbf{k}} \phi_{\alpha,-\mathbf{k}} - n\phi_{n,\mathbf{k}} \phi_{n,-\mathbf{k}} \right) \tag{2.10}$$

In intermediate steps of the calculation it is necessary to introduce $(n-1)$ additional such fields, the correlation functions of which are identical with those of $\psi_2$.

The dynamics are based on two coupled Langevin equations for the acoustic and soft phonons

$$\bar{\rho} \ddot{Q}_{\mathbf{k},\lambda} = -\frac{\delta H}{\delta Q_{-\mathbf{k},\lambda}} - \bar{\rho} D k^2 \dot{Q}_{\mathbf{k},\lambda} + \eta_{\mathbf{k},\lambda}$$
$$\dot{\phi}_{\alpha,\mathbf{k}} = -\Gamma \frac{\delta H}{\delta \phi_{\alpha,-\mathbf{k}}} + \xi_{\alpha,\mathbf{k}} \tag{2.11}$$

Here $\eta$ and $\xi$ are Gaussian white noises, whose variances are connected with the bare damping terms $Dk^2$ and $\Gamma$ by Einstein relations.

## 2.2. Renormalization Group Theory

The quantity of interest is the response function of the acoustic phonons

$$G(\mathbf{k}, \omega) = \left[ G_0^{-1}(k, \omega) - \mathbf{k}^2 \sum_{\sigma=1}^{3} A_\sigma^{(n)}(\hat{k}, \lambda)\, \Sigma_\sigma(\omega) \right]^{-1} \tag{2.12}$$

where the free response function is $G_0^{-1}(k, \omega) = \bar{\rho}[-\omega^2 - i\omega D k^2 + c_0^2(\hat{k}, \lambda) k^2]$. The interactions (2.9a, b, c) lead to the self-energy $\Sigma_\sigma(\omega)$, which equals the Fourier-transformed response function

$$\Sigma_\sigma(\omega) = -\int_0^\infty dt\, e^{i\omega t} \frac{d}{dt} \frac{\langle \psi_\sigma(t)\, \psi_\sigma(0) \rangle}{k_B T} \tag{2.13}$$

**Table I. Critical Exponents of Sound Propagation**

| $n$ | $\sigma$ | $\alpha_\sigma$ | $\rho_\sigma$ | $\rho_\sigma/z\nu$ | $1-\alpha_\sigma/z\nu$ | $\nu$ | $\eta$ | $\phi$ | $z$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 0.086 | 1.381 | 1.066 | 0.934 | 0.638 | 0.0413 | — | 2.029 |
| 2 | 1 | −0.027 | 1.341 | 0.980 | 1.02 | 0.674 | 0.0426 | 1.175 | 2.031 |
| | 2 | 0.223 | 1.591 | 1.163 | 0.837 | | | | |
| 3 | 1 | −0.125 | 1.306 | 0.913 | 1.087 | 0.705 | 0.0419 | 1.25 | 2.03 |
| | 2 | 0.375 | 1.806 | 1.262 | 0.738 | | | | |

and $k^2 A_\sigma^{(n)}(\hat{k}, \lambda)$ is the square of the coupling coefficient of $\psi_\sigma$ and $Q_{\mathbf{k},\lambda}$. Equation (2.13) may be also regarded as a Kubo formula. A quick estimate[5,9,29] for the anomalous damping in the hydrodynamic region is obtained by noting that the right-hand side of Eq. (2.13) is proportional to $i\omega\omega_c^{-1}\langle\psi_\sigma^2\rangle \sim i\omega\tau^{-z\nu-\alpha_\sigma}$ in the low-frequency limit.[5,9] Thus the exponent

$$\rho_\sigma = z\nu + \alpha_\sigma \tag{2.14a}$$

$$\alpha_\sigma = \alpha + 2(\phi - 1)(1 - \delta_{\sigma,1}) \tag{2.14b}$$

where $\alpha$ is the exponent of the specific heat and $\phi$ the crossover exponent.[30,9],4 This relation is confirmed by the dynamical RNG theory using the $\varepsilon$ expansion.[9,10] The combinations of critical exponents which govern sound propagation are tabulated in Table I for $n = 1, 2, 3$. The static exponents are taken from Refs. 32 and 33 and Eq. (2.3) has been used.

To determine the scaling function a matching method similar to the one introduced by Nelson in the statics[34] has been used[10]:

$$\mathrm{Im}\, \Sigma_\sigma(\omega, r_0, u^*)/\omega = e^{l\rho_\sigma/\nu}\, \mathrm{Im}\, \Sigma_\sigma(\omega e^{zl}, r_l, u^*)/\omega e^{zl} \tag{2.15a}$$

In Eq. (2.15a) $l$ is chosen such, that the arguments on the right-hand side are away from criticality and perturbation theory can be used. To this end one requires

$$(\omega e^{zl}/\tilde{\gamma})^2 + t^2 e^{2l/\nu} = 1 \tag{2.15b}$$

where $\tilde{\gamma} = \Gamma k_B T_c^0 A^2$ and $t$ is related to $r$.[34,10]

4 We assume the stability of the Heisenberg fixed point (Ref. 31) in which case there is only one crossover exponent, and $\Sigma_3(\omega) = \Sigma_2(\omega)$ plus corrections to scaling.

### 2.3. Results

Now we summarize the results of this renormalization group theory.

**2.3.1. Attenuation.** The most spectacular feature in experiments is the attenuation. The critical contribution to the coefficient of attenuation following from (2.12) can be represented by

$$\alpha^{(n)}(\hat{k}, \omega, \lambda) = \frac{\omega^2}{2c^3(\hat{k}, \lambda)\bar{\rho}} \sum_{\sigma=1}^{3} A_\sigma^{(n)}(\hat{k}, \lambda) \frac{\operatorname{Im} \Sigma_\sigma(\omega)}{\omega} \tag{2.16}$$

where

$$\operatorname{Im} \Sigma_\sigma(\omega)/\omega = R_\sigma \tau^{-\rho_\sigma} g_\sigma^{(n)}(\omega/\gamma\tau^{z\nu}) \tag{2.17}$$

with a nonuniversal amplitude $R_\sigma$. The dynamical scaling functions $\hat{g}_\sigma^{(n)}(y)$ versus $y = \omega/\omega_c$ are shown in Fig. 1a. With the singular prefactors separated, the flat part corresponds to the hydrodynamic region. For $y \gg 1$ the critical result $\hat{g}_\sigma^n(y) \sim y^{-\rho_\sigma/z\nu}$ anticipated above is found. Figure 1b shows a comparison of what is believed to be the leading contribution in Eq. (2.16) with experiments by Fossheim and Holt[6,7] on $KMnF_3$. From this the nonuniversal prefactor in Eq. (2.2)

$$\gamma = 0.66 \times 10^{12} \text{ rad/sec}$$

was found.[10]

We are now able to comment on the varying values of $x$ found in early experiments. Clearly, if data in the crossover region ($\omega \approx \omega_c$) are used, anything between 2 and 1 can be obtained. The above-mentioned puzzle is resolved by noting that probably $\rho$ has been determined in the hydrodynamic and $x$ in the crossover region in some of the earlier experiments.

**2.3.2. Velocity of Sound.** From the classical field theory defined by Eqs. (2.5) and (2.11) one finds for the isothermal sound velocity

$$c_T(\hat{k}, \lambda)^2 = c_0(\hat{k}, \lambda)^{-2} - \left[ c_0(\hat{k}, \lambda)^{-2} + \bar{\rho} k_B T \Big/ \sum_\sigma A_\sigma^{(n)}(\hat{k}, \lambda) \langle |\psi_\sigma|^2 \rangle \right]^{-1} \tag{2.18}$$

The expectation values on the right-hand side of Eq. (2.18) have the scaling behavior

$$\langle \psi_\sigma^2 \rangle \propto A_0 + B_0 \tau + C_0 \tau^{-\alpha_\sigma} \tag{2.19}$$

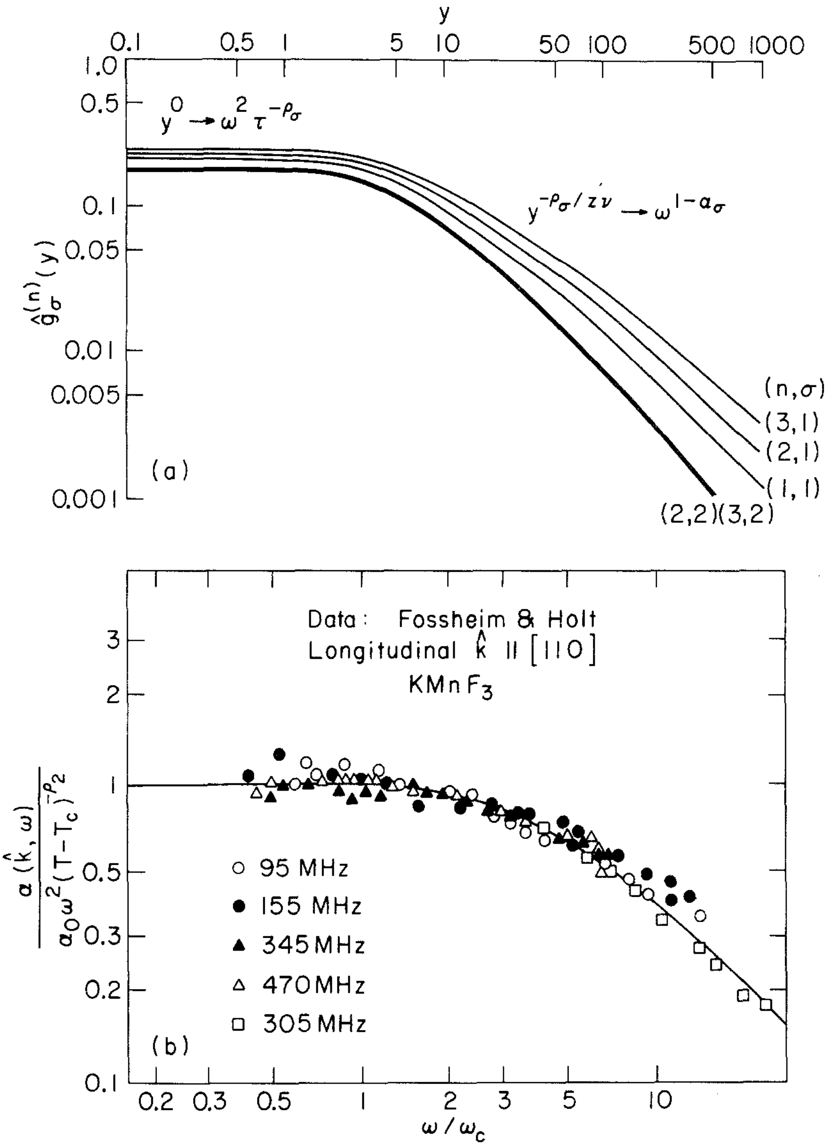


Fig. 1. (a) The scaling functions $\hat{g}_\sigma^{(n)}(y)$ for the damping in three dimensions. The values $(n, \sigma)$ are indicated on the graph. We recall $\hat{g}_3^{(n)}(y) = \hat{g}_2^{(n)}(y)$. The curves $\hat{g}_2^{(2)}$ and $\hat{g}_2^{(3)}$ almost coincide and cannot be distinguished in this plot. (b) Comparison of the theoretical curves for $\sigma = 2$, 3 and $n = 3$ with the data of Ref. 6.

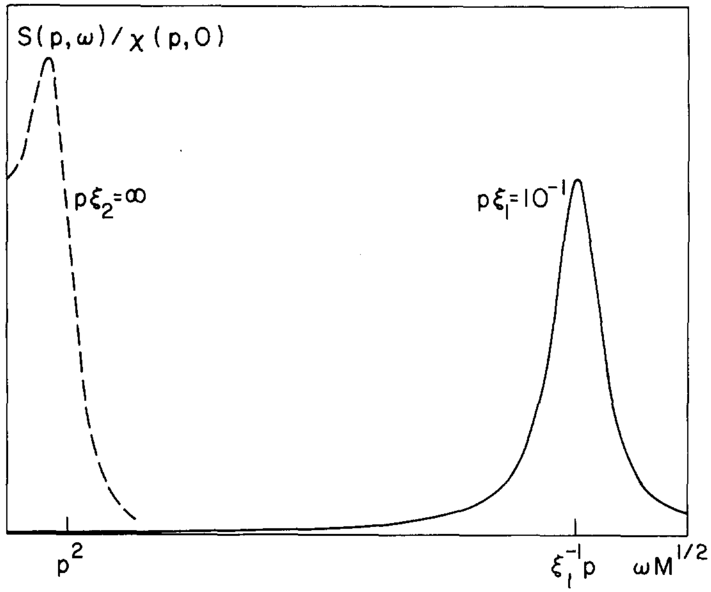


Fig. 2. Dynamic structure factor for the soft acoustic phonon versus $\omega M^{1/2}$ for two values of the correlation length and $M^{1/2}D = 1.0$ [Eq. (3.12) with $q = 0$]. Solid, $p\xi_1 = 10^{-1}$ (hydrodynamic); dashed, $p\xi_2 = \infty$ (critical).

with $\alpha_\sigma$ defined in Eq. (2.14b) and cofficients $A_0$, $B_0$, and $C_0$. In a region where the critical modification of the sound velocity is still small compared to the bare velocity $c_0$ one may approximate (2.18) by

$$c_T^2 = c_0^2 - \sum_\sigma A_\sigma^{(n)}(\hat{k}, \lambda)\langle|\psi_\sigma|^2\rangle/\bar{\rho}k_B T \tag{2.20}$$

So far we have considered the isothermal velocity of sound. However, it is well known that owing to the slowness of the heat diffusion sound propagates adiabatically. In special symmetry directions the adiabatic and isothermal sound velocities of transverse phonons coincide; however, they are distinct for longitudinal phonons. The general thermodynamic relation between adiabatic and isothermal elastic constants is

$$c_{iklm}^{ad} = c_{iklm}^{is} + \beta_{ik}\beta_{lm}/C_\varepsilon \tag{2.21}$$

where $\beta_{ik} = (\partial\sigma_{ik}/\partial T)_\varepsilon$ and $C_\varepsilon = (\partial s/\partial T)_\varepsilon$ are the derivative of the stress tensor and the specific heat at constant strain, respectively. For instance it is evident from Eq. (2.21) that (switching back to the Voigt notation) $c_{11}^{ad} - c_{12}^{ad} = c_{11}^{is} - c_{12}^{is}$, but $c_{11}^{ad} = c_{11}^{is} + \beta^2/C_\varepsilon$ in a cubic crystal. If one is fitting experimental data over a wide temperature range the use of the full formula, Eq. (2.19), may be important and also the additional "adiabatic contribution" in Eq. (2.21) should be noticeable.

Table II. The Coefficients $A_\sigma^{(n)}(\hat{k}, \lambda)$ in High-Symmetry Directions, Wave Vector $k$, Polarization $\lambda$

| k | $\lambda$ | $A_1^{(3)}$ | $A_2^{(3)}$ | $A_3^{(3)}$ | $A_1^{(2)}$ | $A_2^{(2)}$ | $A_3^{(2)}$ | $A_1^{(1)}$ |
|---|---|---|---|---|---|---|---|---|
| (100) | $l$ | $(1/3)(A+2B)^2$ | $(2/3)(A-B)^2$ | 0 | $(1/2)(A'+B')^2$ | $(1/2)(A'-B')^2$ | 0 | $\bar{B}^2$ |
| | $t(0,1,0)$ | 0 | 0 | $(1/2)C^2$ | 0 | 0 | $(1/2)C'^2$ | 0 |
| | $t(0,0,1)$ | 0 | 0 | $(1/2)C^2$ | 0 | 0 | 0 | 0 |
| (110) | $l$ | $(1/3(A+2B)^2$ | $(1/6)(A-B)^2$ | $(1/2)C^2$ | $(1/2)(A'+B')^2$ | 0 | $(1/2)C'^2$ | $\bar{B}^2$ |
| | $t(1,\bar{1},0)$ | 0 | $(1/2)(A-B)^2$ | 0 | 0 | $(1/2)(A'-B')^2$ | 0 | 0 |
| | $t(0,0,1)$ | 0 | 0 | $(1/2)C^2$ | 0 | 0 | 0 | 0 |
| (111) | $l$ | $(1/3)(A+2B)^2$ | 0 | $(2/3)C^2$ | — | — | — | — |
| | $t$ | 0 | $(1/3)(A-B)^2$ | $(1/6)C^2$ | — | — | — | — |
| (001) | $l$ | $(1/3)(A+2B)^2$ | $(2/3)(A-B)^2$ | 0 | $2B''^2$ | 0 | 0 | $\bar{A}^2$ |
| | $t$ | 0 | 0 | $(1/2)C^2$ | 0 | 0 | 0 | 0 |

**2.3.3. Dispersion.** Associated with the frequency dependent damping is sound dispersion. For $c_T k \ll \omega_c$ on finds[10]

$$\omega = \pm c_T k \left[ 1 + k^2 \sum_{\sigma=1}^{3} A_\sigma^{(n)}(\hat{k}, \lambda) \tau^{-\alpha_\sigma - 2\nu z} B_\sigma / 48 \bar{\gamma}^2 \bar{\rho} \right] \qquad (2.22)$$

The frequency dependence of the real part of $\Sigma$ is studied in the whole frequency region in Ref. 10. Measurements of the low-frequency dispersion would be complementary to those of the attenuation, which are in the asymptotic high-frequency regime.

Let us add several remarks on the directional dependence given in Table II.[10] Firstly the directional dependence should allow one to determine $n$. If the symmetry and $n$ are known from other sources, the directional dependence still could give important information. For instance, if an $n = 3$ component system would show deviations from Table II, this would be an indication of internal strains lowering the symmetry of the order parameter. Also, it would be worthwhile to determine $\Sigma_1$ and $\Sigma_2$ individually by taking appropriate combinations of data in several directions according to the table. Finally, the high-frequency behavior would give information about the damping mechanism.

We close this section by remarking that in these calculations the backreaction of the elastic modes onto the order parameter has been neglected. This is common to most theories of critical phenomena in solids and is based on the hope that the ensuing first-order character is small and that in the pseudocritical region the pure rigid critical theory applies. For the effect of cubic anisotropy see Refs. 10, 35, and 36.[5]

## 3. ELASTIC PHASE TRANSITIONS

Now we turn to the theory of[21,22] elastic phase transitions. The order parameter characterizing an elastic phase transition is a component of the strain tensor and hence the soft mode is an acoustic phonon. Prominent examples of elastic phase transitions are the martensitic transition of $Nb_3Sn$,[12] the orthorhombic to monoclinic transition of NaOH[11] and the transition from the cubic to the orthorhomic phase of KCN.[13] As already mentioned in the Introduction also KDP[14] belongs to the elastic variety. In cases like this a soft optic phonon "drives" the transition. The theory can be applied immediately to such cases.[6]

[5] Nattermann (Ref. 37) suggested that an anisotropic coupling would not only lead to a first-order transition but also to renormalized exponents giving a smaller $\rho_2$.

[6] Systems where an optic mode couples linearly to acoustic phonons, as is the case in KDP, have been treated in Ref. 39.

The anisotropy of crystals implies that the sound velocities depend on the direction of propagation and thus the velocity of the soft phonon does not vanish throughout the whole Brillouin zone but only in one or several soft sectors. These sectors are one dimensional ($Nb_3Sn$, NaOH) or two dimensional (KCN). Even in cubic crystals sound propagation is anisotropic since the tensor of elastic constants is of fourth rank.

As is appropriate for the description of long-wavelength phenomena we adopt a continuum description starting from the elastic free energy. We derive a model Hamiltonian which contains all essential features relevant near the transition, and which we use to discuss the static critical behavior. The extreme anisotropy implies that the critical fluctuations are suppressed in directions outside the soft sectors. Hence the upper critical dimensionality for these phase transitions is reduced, and the classical Ginzburg–Landau exponents apply for one-dimensional sectors and logarithmic corrections appear for two-dimensional sectors.[21]

To determine the possible elastic phase transitions for different crystal symmetries one needs the elastic free energy

$$F=\int d^3x\left(\frac{1}{2}c_{iklm}\varepsilon_{ik}\varepsilon_{lm}+\frac{1}{2}d_{iklmrs}\frac{\partial}{\partial x_r}\varepsilon_{ik}\frac{\partial}{\partial x_s}\varepsilon_{lm}+C^{(3)}\varepsilon^3+C^{(4)}\varepsilon^4\right) \qquad (3.1)$$

Here $c_{iklm}$ are the elastic constants, the second term characterizes the energy of inhomogeneous deformations and the third and fourth term represent the nonlinear interactions. The strain tensor is defined in Eq. (2.7). The point group symmetry determines the number of independent elastic constants $c_{iklm}$ and via the stability limits the possible elastic phase transitions (Table III).

We add several remarks concerning the soft mode spectrum and the characteristic Hamiltonian or free energy density following from Eq. (3.1) as written down below.

(i) The sound velocity vanishes only in one- or two-dimensional subspaces. In the vicinity of these directions the sound velocity is finite but small and it is important that the theory includes all phonons with $\mathbf{k}$, in a sector around the $m$-dimensional soft subspace.

(ii) The "gradient" (second) term in Eq. (3.1) prevents the sound frequency from vanishing throughout the whole Brillouin zone and replaces the linear by a quadratic dispersion precisely at $T_c$.

(iii) In the investigation of the critical phenomena we disregard noncritical phonons and thus retain only the normal coordinate of the soft mode.

(iv) We disregard odd anharmonic terms. This restricts the applicability of the theory to situations where these are prohibited by sym-

**Table III. Elastic Phase Transitions: The High-Temperature Phase, the Vanishing Combination of the Elastic Constants, the Strain, the Dimensionality of Soft Sectors, Third-Order Invariants, $e_2 = (\epsilon_{11} - \epsilon_{22})/\sqrt{2}$, $e_3 = (\epsilon_{11} + \epsilon_{22} - 2\epsilon_{33})/\sqrt{6}$**

| H.T.P. | El. const. | Strain | $m$ | Third-order invariants |
|---|---|---|---|---|
| Orthorhombic | $c_{44}$ | $\varepsilon_{23}$ | 1 | — |
| | $c_{55}$ | $\varepsilon_{13}$ | 1 | — |
| | $c_{66}$ | $\varepsilon_{12}$ | 1 | — |
| Tetragonal II | $c_{44}$ | $\varepsilon_{23}, \varepsilon_{13}$ | $1+2$ | — |
| Tetragonal I | $c_{44}$ | $\varepsilon_{23}, \varepsilon_{13}$ | $1+2$ | — |
| | $c_{66}$ | $\varepsilon_{12}$ | 1 | — |
| | $c_{11}-c_{12}$ | $\varepsilon_{11}-\varepsilon_{22}$ | 1 | — |
| Cubic II | $c_{44}$ | $\varepsilon_{12}, \varepsilon_{13}, \varepsilon_{23}$ | 2 | $\varepsilon_{23}\varepsilon_{13}\varepsilon_{12}$ |
| | $c_{11}-c_{12}$ | $e_3, e_2$ | 1 | $e_3(e_3^2-3e_2^2)$, $e_2(e_3^2-3e_2^2)$ |
| Cubic I | $c_{44}$ | $\varepsilon_{12}, \varepsilon_{13}, \varepsilon_{23}$ | 2 | $\varepsilon_{23}\varepsilon_{13}\varepsilon_{12}$ |
| | $c_{11}-c_{12}$ | $e_3, e_2$ | 1 | $e_3(e_3^2-3e_2^2)$ |
| Hexagonal II | $c_{44}$ | $\varepsilon_{23}, \varepsilon_{13}$ | $1+2$ | — |
| | $c_{66}=(1/2)(c_{11}-c_{12})$ | $\varepsilon_{12}, \varepsilon_{11}-\varepsilon_{22}$ | 2 | $(\varepsilon_{11}-\varepsilon_{22})^3$, $\varepsilon_{12}(\varepsilon_{11}-\varepsilon_{22})^2$, $\varepsilon_{12}^3$ |
| Hexagonal I | $c_{44}$ | $\varepsilon_{23}, \varepsilon_{13}$ | $1+2$ | — |
| | $c_{66}=(1/2)(c_{11}-c_{12})$ | $\varepsilon_{12}, \varepsilon_{11}-\varepsilon_{22}$ | 2 | $(\varepsilon_{11}-\varepsilon_{22})^3$, $\varepsilon_{12}(\varepsilon_{11}-\varepsilon_{22})^2$ |

metry as is the case for orthorhombic and tetragonal crystals or where these are sufficiently small such that the phase transition is nearly of second order.

In Ref. 21 a $d$-dimensional system was considered and the dimensionality of the soft subspace was assumed to be $m$. Hence the wave vector $\mathbf{k}$ was decomposed into an $m$-dimensional "soft" component $\mathbf{p}$ and a $(d-m)$-dimensional "stiff" component $\mathbf{q}$, i.e., $\mathbf{k}=(\mathbf{p},\mathbf{q})$. Although $m$ is either 1 or 2 in three-dimensional crystals, it is useful to develop the theory for arbitrary $m$ and $d$. Let us denote the normal coordinate of the soft acoustic mode by $Q_{\mathbf{k}}$. It has been shown in Ref. 21 that the elastic free energy functional can be mapped onto the Hamiltonian

$$H = \tfrac{1}{2}\int dk(rp^2+q^2+p^4)\,|Q_{\mathbf{k}}|^2 + u\int dk_1\cdots dk_4\, v(\mathbf{k}_1,\dots,\mathbf{k}_4)\, Q_{\mathbf{k}_1}Q_{\mathbf{k}_2}Q_{\mathbf{k}_3}Q_{\mathbf{k}_4} \tag{3.2}$$

with

$$\begin{aligned} \text{I:}\quad & v(\mathbf{k}_1,\dots,\mathbf{k}_4) = p_1p_2p_3p_4\,\delta(\mathbf{k}_1+\cdots+\mathbf{k}_4),\\ \text{II:}\quad & v(\mathbf{k}_1,\dots,\mathbf{k}_4) = (\mathbf{p}_1\mathbf{p}_2)(\mathbf{p}_3\mathbf{p}_4)\,\delta(\mathbf{k}_1+\cdots+\mathbf{k}_4) \end{aligned} \tag{3.3}$$

The characteristic features of the elastic Hamiltonian (3.1) are (a) the anisotropy of the harmonic part because of which fluctuations in the "stiff" directions $\mathbf{q}$ are suppressed and (b) the wave vector dependence of the interaction.

In Eqs. (3.2) and (3.3) we have omitted terms which are irrelevant for the critical behavior. The Hamiltonian (3.1) refers to a single soft sector. As noted above there are in general more soft sectors than one, but the interaction between different soft sectors goes to zero after repeated application of the RNG transformation and hence we may consider independent soft sectors.

The dynamical model is completed by the stochastic equations of motion[22]

$$M\ddot{Q}_{\mathbf{k}} = -\frac{\delta H}{\delta Q_{-\mathbf{k}}} - M\Gamma_{\mathbf{k}}\dot{Q}_{\mathbf{k}} + r_{\mathbf{k}} \tag{3.4}$$

appropriate for acoustic phonons, where $\Gamma_{\mathbf{k}} = Dp^2 + \tilde{D}q^2$. The random force $r_{\mathbf{k}}$ results from noncritical degrees of freedom. Its fluctuations are related to the damping coefficient by the Einstein relation

$$\langle r_{\mathbf{k}}(t)\, r_{\mathbf{k}'}(t')\rangle = 2\Gamma_{\mathbf{k}} k_B T\, \delta(\mathbf{k}+\mathbf{k}')\, \delta(\mathbf{t}-\mathbf{t}') \tag{3.5}$$

which guarantees that the equilibrium distribution is given by $\exp(-H/k_B T)$.

### 3.2. Renormalization Group Theory

The renormalization group theory of these systems has to take into account the anisotropy. It consists of the following steps[21,22]:

(I) Eliminate $b^{-1} < p < 1$, $b^{-2+\eta/2} < q < 1$

(II) Rescale $p' = bp$, $q' = b^{2-\eta/2}q$, $\omega' = b^z\omega$, $Q_k \to \zeta Q'_k$

Thereby one finds a new Hamiltonian with parameters $r'$, $u'$, etc. The decisive transformation is $u' = b^{4+m-2d}u$ (1 + nonlinear terms), which gives immediately the critical dimensionality of Eq. (3.6).[21]

### 3.3. Results

The anisotropy of the Hamiltonian implies that the upper critical dimensionality[21] is[7]

$$d_c(m) = 2 + \frac{m}{2} \tag{3.6}$$

[7] A different value for the critical dimensionality is obtained (Ref. 23) if in the generalization of the elastic models to arbitrary dimensions instead of $m$ the dimensionality of the stiff $k$ space $d-m$ is kept fixed (Ref. 38).

For $d > d_c(m)$ $u$ is irrelevant and the system approaches a "Gaussian fixed point" ($u^* = 0$) with classical critical behavior, whereas for $d \leqslant d_c(m)$ we have nonclassical critical exponents.

For $m = 1$, $d_c(1) = 5/2$, and consequently three-dimensional systems with one-dimensional soft sectors are characterized by classical critical exponents ($\nu = 1/2$, $\eta = 0$, $\gamma = 1$, $\beta = 1/2$, $\alpha = 0$, $\delta = 3$).

For $m = 2$, $d_c(2) = 3$, and thus one finds classical behavior with logarithmic corrections in three dimensions. For instance the static susceptibility (inverse elastic constant) and the specific heat are given by

$$\chi = \tau^{-1} |\ln \tau|^{r_\chi}, \qquad c = |\ln \tau|^{r_c} \tag{3.7}$$

The exponents $r_\chi$ and $r_c$ for models I and II are shown in Table IV.

For isotropic elastic phase transitions one finds $d_c(3) = 7/2$; i.e., nonclassical behavior for $d = 3$.

The essential results for the dynamics are the following.[22]

The sound velocity is

$$c_s = \left(\frac{C}{\bar{\rho}}\right)^{1/2} \sim \xi^{-(2-\eta)/2} \tag{3.8}$$

where $C$ is a combination of elastic constants.

For $m = 1$ the dynamical critical exponent is

$$z = 2 \tag{3.9}$$

and

$$c_s \sim (T - T_c)^{1/2} \tag{3.8}$$

The damping coefficient is

$$D_s \sim (T - T_c)^0 \tag{3.10}$$

which implies for the coefficient of attenuation

$$\alpha = \frac{D_s \omega^2}{2c_s^3} \sim (T - T_c)^{-3/2} \omega^2 \tag{3.11}$$

**Table IV. Logarithmic Corrections**

| | $r_\chi$ | $r_c$ |
|---|---|---|
| I | 1/3 | 1/3 |
| II | 4/9 | 1/9 |

The 1/2 power law in Eq. (3.8) has been confirmed by many experiments. The prediction for the damping has been verified by Brillouin scattering experiments by Errandonea[20] and by recent ultrasonic experiments by Garland *et al.*[19]

The dynamic phonon susceptibility is

$$\chi(\mathbf{k}, \omega) = [-M\omega^2 - i\omega M(Dp^2 + \tilde{D}q^2) + \xi^{-2}p^2 + p^4 + q^2]^{-1} \quad (3.12)$$

($\xi = \xi_0 \tau^{-1/2}$). Equation (3.12) applies to elastic phase transitions with one-dimensional softening ($m = 1$) for $d = 3$. For $m = 2$, $\xi^{-2}$ is replaced by $\chi^{-1}$ of Eq. (3.7). The neutron-scattering cross section, which is determined by the dynamic structure factor $S(\mathbf{k}, \omega) = \mathrm{Im}\, \chi(\mathbf{k}, \omega) k_B T/\hbar\omega$, is plotted in Fig. 2 for the hydrodynamic and for the nonhydrodynamic critical region. Although this is of no concern in crystals, it is of interest to note that the isotropic elastic models show a breakdown of dynamical scaling similar to the superfluid model and the $O(n)$-symmetric phonon model.[40–42]

## 4. DISCUSSION AND SUMMARY

### 4.1. Information Gained from Ultrasonics

To conclude, I would like to summarize the information gained from sound measurements. In distortive phase transitions the static critical exponents $\alpha$ and $\beta$ and the dynamic exponent $z$ can be determined from data in the hydrodynamic region. By comparing the measurements with the theoretical scaling function the magnitude of the critical frequency can be found. The high-frequency behavior could give information about the damping mechanism. The directional dependence gives information about the symmetry of the order parameter and allows one to detect internal strains.

In elastic phase transitions, of course, ultrasonic and Brillouin scattering experiments probe the dynamics of the order parameter.

### 4.2. Relation to Other Phase Transitions

Finally I would like to note that the theory for distortive transitions can be applied to any other system whose dynamics are purely relaxational. The examples which come to mind are anisotropic antiferromagnets and order–disorder transitions.

The theory of elastic phase transitions applies also to spin reorientation transitions as found in rare earth orthoferrites[43] and to the phason instability at 49 K in TTF–TCNQ.[44] The transition from smectic $A$ to smectic $C$ in a magnetic field belongs to the same universality class concerning the statics.[45]

Finally, it should be emphasized that we have considered the theory of pure systems. Defects or any sort of randomness can given rise to precursor effects and modified critical behavior, hence, their study is of practical as well as principal interest.

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