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Coupled hydrodynamic modes near structural phase transitions in crystals

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THE thermo-elastic description of a crystal is discussed and applied in the vicinity of a structural phase transition of the displacive type. The associated soft phonon mode causes a strong temperature dependence of certain elastic parameters which gives rise to a new coupling between the elastic and the thermal variables. This new coupling is responsible for a central peak in the elastic response and may explain recent neutron scattering data of $SrTiO_3$ and Nb_3Sn.

Przedyskutowano termo-sprężyste zachowanie się kryształu i zastosowano je do opisu zjawiska w otoczeniu przejścia fazy strukturalnej typu przemieszczeniowego. Związana z tym gasnąca postać drgań (mode) fononu powoduje silną zależność od temperatury niektórych parametrów sprężystych, które prowadzą do powstania nowego sprzężenia między zmiennymi sprężystymi i termicznymi. To nowe sprzężenie jest odpowiedzialne za centralne maksimum w rozwiązaniu sprężystym i może wyjaśnić ostatnie dane dotyczące rozpraszania neutronów $SrTiO_3$ i Nb_3Sn.

Обсуждено термо-упругое поведение кристалла и оно применено для описания явления в окрестности перехода структурной фазы типа перемещений. Связанный с этим затухающий вид колебаний (мод) фонона вызывает сильную зависимость от температуры некоторых упругих параметров, которые приводят к возникновению нового сопряжения между упругими и термическими переменными. Это новое сопряжение ответственно за центральный максимум в упругом решении и может выяснить последние данные, касающиеся рассеяния нейтронов $SrTiO_3$ и Nb_3Sn.

1. Continuum description of ordered systems

THE ordered systems we shall consider here consist of condensed matter of a long-range order in configuration space (crystals), in direction (magnetic bodies, nematic liquid crystals), or in momentum space (superfluids, superconductors) [1]. A continuum description of such systems applies to perturbations of long wavelength, $\lambda = 2\pi/q$ ($\mathbf{q}$ is the wave vector), as compared to the dimension a of the microscopic structure. Such perturbations have a thermal aspect, expressed by local and time-dependent values of temperature, $T(\mathbf{r}, t)$, and entropy per unit mass, $s(\mathbf{r}, t)$, as well as a dynamical aspect described by the hydrodynamic equations of motion [1].

The latter express local conservation of mass or magnetization, etc.,

$$\dot{\varrho} + \nabla \cdot \mathbf{j} = 0 \tag{1.1}$$

(ϱ is the density and $\mathbf{j}$ the associated flux), local energy conservation

$$(\varrho\varepsilon)^{\cdot} + \nabla \cdot \mathbf{J}_\varepsilon = 0 \tag{1.2}$$

(ε is the energy per unit mass and $\mathbf{J}_\varepsilon$ the associated flux), local momentum balance

$$\dot{\mathbf{j}} + \nabla\pi = \frac{1}{\tau}\mathbf{j} \tag{1.3}$$

(π is the momentum flux, τ is a relaxation time) and the motion of the ordered phase

$$\dot{\mathbf{v}}_0+\nabla\mu = 0 \tag{1.4}$$

($\mathbf{v}_0$ is the velocity of the ordered phase, while μ plays the role of a chemical potential). The non-ordered phase consists of the thermal excitations of the system as described by the entropy balance

$$(\varrho s)^{\cdot}+\nabla\cdot \mathbf{J}_s = \sigma \tag{1.5}$$

(J_s is the entropy flux and σ the entropy production density) which follows from the energy conservation equation and thermodynamic relations [1].

2. Dielectric crystals as thermo-elastic medium

A dielectric (or insulating) crystal does not contain any free electrons, therefore, the only thermal excitations are long wavelength phonons. The ordered phase consists of the periodic atomic lattice (lattice constant a) the perturbations of which are described by the displacements $\mathbf{u}(\mathbf{R}, t)$ of the atoms from their equilibrium position $\mathbf{R}$. In a long-wave approximation $aq \ll 1$, these positions, $\mathbf{R}$, may be replaced by the continuum variable $\mathbf{r}$. The displacement field $\mathbf{u}(\mathbf{r}, t)$ then satisfies the equation of motion of the elasticity theory which can be cast into the form (1.4) by identifying $\mathbf{v}_0$ with the "lattice velocity" $\dot{\mathbf{u}}$ and $\nabla\mu$ with $\frac{1}{\varrho}\nabla\Sigma$. Here, Σ is the stress tensor which, expressed in terms of the deformations

$$\theta_{ij} = \frac{1}{2}(\nabla_i u_j+\nabla_j u_i) \tag{2.1}$$

and the temperature variation $\delta T = T(\mathbf{r}, t)-T$ around the equilibrium value T, has the form

$$\Sigma_{ij} = \sum_{kl} C_{ij,kl}\theta_{kl}-\beta_{ij}\delta T. \tag{2.2}$$

Here, $C_{ij,kl}$ are the isothermal elastic constants and β_{ij} the tension coefficients.

In terms of a lattice free energy functional [2]

$$F_L[\mathbf{u}, \delta T] = \int d^3r\left\{\frac{1}{2}\sum_{ijkl} C_{ij,kl}\theta_{ij}\theta_{kl}-\sum_{ij}\beta_{ij}\theta_{ij}\delta T-\varrho\mathbf{u}\cdot\mathbf{f}\right\}, \tag{2.3}$$

where we have added the contribution due to an external force per unit mass, $\mathbf{f}$, the gradient of the stress tensor may be expressed as

$$(\nabla\Sigma)_i = -\frac{\delta F_L}{\delta u_i}. \tag{2.4}$$

Adding a dissipative term resulting from the lattice viscosity $\eta_{ij,kl}$ the equation of motion (1.4) of the ordered phase then becomes

$$\varrho\ddot{u}_i = \sum_{jkl}\eta_{ij,kl}\nabla_j\nabla_k\dot{u}_l-\frac{\delta F_L}{\delta u_i} \tag{2.5}$$

which, in view of (2.1)–(2.3), has a form familiar to that of the elasticity theory.

The thermal part of the lattice free energy (2.3) which is proportional to δT gives rise to a lattice entropy per unit volume

$$s_L = -\frac{1}{\varrho}\frac{\delta F_L}{\delta(\delta T)} \tag{2.6}$$

which, however, is only part of the total entropy variation δs. The main part of δs is due to the specific heat of the thermal fluctuations, C_V, so that

$$\delta s = \frac{C_V}{T}\,\delta T + s_L. \tag{2.7}$$

Unless the crystal is near to perfect and the temperature is quite low the thermal phonons will dissipate their momentum very fast. This means that the relaxation time τ in Eq. (1.3) is very small and the excitation fluid cannot support a flow. In this case Eq. (1.3) has to be discarded and the entropy flux in Eq. (1.5) has no convective contribution but results entirely from the thermal conductivity λ,

$$\mathbf{J}_s = -\frac{\lambda}{T}\nabla T. \tag{2.8}$$

Physically, this means that heat does not propagate as second sound [1]. With (2.6), (2.7), and (2.8) and neglecting the entropy production σ the entropy balance (1.5) then takes the form

$$\left(\frac{\partial}{\partial t} - D\nabla^2\right)\delta T = \frac{T}{\varrho C_V}\frac{\partial}{\partial t}\left(\frac{\partial F_L}{\partial(\delta T)}\right), \tag{2.9}$$

where $D = \lambda/\varrho C_V$ is the heat diffusion constant.

Equations (2.5) and (2.9) together with (2.3) contain the continuum description of dielectric crystals as thermo-elastic medium [1].

In a plane-wave representation where $\mathbf{u}$ and δT are proportional to $e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}$ these equations may be written as [1]

$$[\omega^2 - c_1^2(1-i\omega\tau_1)q^2]\mathbf{u} - \frac{i}{\varrho}(\beta\mathbf{q})\,\delta T = -\mathbf{f} \tag{2.10}$$

and

$$(-i\omega + Dq^2)\,\delta T = -\frac{T\omega}{\varrho C_V}(\beta\mathbf{q})\mathbf{u}, \tag{2.11}$$

where c_1 is the isothermal (first) sound velocity tensor defined by

$$(c_1^2(\hat{q}))_{ij} = \frac{1}{\varrho}\sum_{mn} C_{im,nj}\,\hat{q}_m\hat{q}_n, \tag{2.12}$$

$\hat{q} = \mathbf{q}/q$ and the relaxation time matrix τ_1 describes sound attenuation according to

$$(c_1^2(\hat{q})\,\tau_1(\hat{q}))_{ij} = \frac{1}{\varrho}\sum_{mn} \eta_{im,nj}\,\hat{q}_m\hat{q}_n. \tag{2.13}$$

The elastic and thermal equations (2.10) and (2.11) are coupled through the tensor of tension coefficients β. In the limit $Dq^2 \ll \omega$ this coupling has the well-known effect of transforming the isothermal quantities $C_{ij,kl}$ and c_{1ij} into adiabatic quantities $C_{ij,kl}$ and $\tilde{c}_{1ij}$ according to

$$\tilde{C}_{ij,kl} - \tilde{C}_{ij,kl} = \frac{T}{\varrho C_V} \beta_{ij} \beta_{kl} \tag{2.14}$$

and

$$(c_1^2 \theta)_{ij} \equiv (c_1^2)_{ij} - (c_1^2)_{ij} = \frac{T}{\varrho^2 C_V} (\beta \hat{q})_i (\beta \hat{q})_j . \tag{2.15}$$

If we eliminate δT from Eq. (2.10) with the help of (2.11) we find the elastic response function

$$\varrho \chi_{ij}(\mathbf{q}, \omega) = \frac{\delta u_i}{\delta f_j} = \left\{ c_1^2 q^2 - \omega^2 - i\omega \left[c_1^2 \tau_1 q^2 + \frac{c_1^2 \theta q^2}{Dq^2 - i\omega} \right] \right\}_{ij}^{-1} . \tag{2.16}$$

In order to see the structure of this function we assume isotropy so that c_1, τ_1 and θ become multiples of the unit tensor and are independent of $\hat{q}$. It is then easily seen that for fixed $\mathbf{q}$ Eq. (21) has three poles:

$$\omega \cong \pm \tilde{c}_1 q - \frac{i}{2} c_1^2 \tau_1 q^2, \quad \omega \cong -i \frac{c_1}{\tilde{c}_1} \sqrt{D} q \tag{2.17}$$

which correspond, respectively, to damped adiabatic sound and to heat diffusion. These three poles give rise to two symmetric Brillouin peaks and a central Rayleigh peak, well-known from both light scattering and from neutron scattering.

3. Structural phase transitions

For most temperatures, the elastic constants $C_{ij,kl}$ and, hence, also the sound velocities c_{1ij} are almost temperature independent. However, a strong temperature dependence may occur for certain critical values T_c of the temperature which signals an instability or softening of the crystal lattice. Such a structural phase transition may be of the order-disorder type, corresponding to the transformation between a compound and an alloy, or of the displacive type in which a transformation between two crystalline structures of different symmetries takes place.

A *displacive* change of the crystal lattice may be described by a particular homogeneous and static displacement field $\mathbf{u} = \text{const}$, that is, by an infinitely slow ($\omega \to 0$) and infinitely long wavelength ($q \to 0$) lattice vibration or phonon of a given mode and polarization, called a *soft mode*. An example of a displacive change of structure due to a transverse acoustic soft mode is sketched in Fig. 1 where the softening of the dispersion curve $\omega = \omega_{TA}(\mathbf{q}, T)$ near $T = T_C$ and $\mathbf{q} = 0$ is also shown. Such a transition occurs, e.g., in Nb_3Sn at $T_c = 45$ K [3] which, above T_c, is a cubic crystal.

Many displacive phase transitions are described by a static displacement field which alternates between neighbouring unit cells of the lattice. This corresponds to a phonon

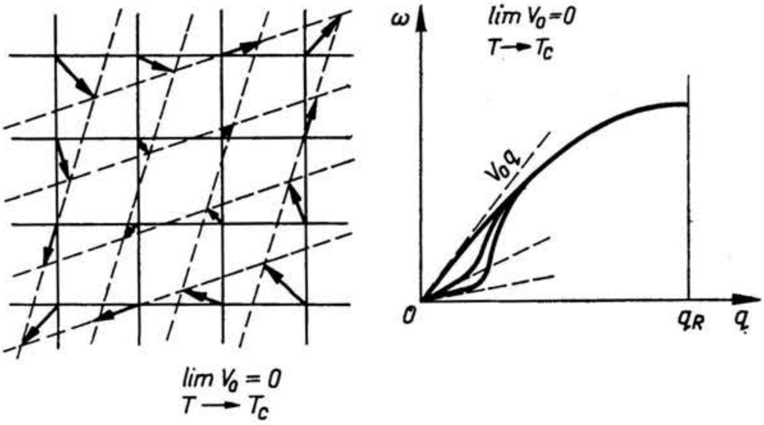

FIG. 1.

with $\omega \to 0$ but $\mathbf{q} \to \mathbf{q}_R = \frac{\pi}{a}(1, 1, 1)$; this is called a soft *staggered* mode. An example of a displacive change of structure due to a transverse optic soft staggered mode is shown in Fig. 2 together with the softening of the dispersion curve $\omega = \omega_{TO}(\mathbf{q}, T)$ near $T = T_c$ and $\mathbf{q} = \mathbf{q}_R$. Such a transition occurs, e.g., in $SrTiO_3$ at $T_c \cong 105$ K [4] which, above T_c, is also cubic.

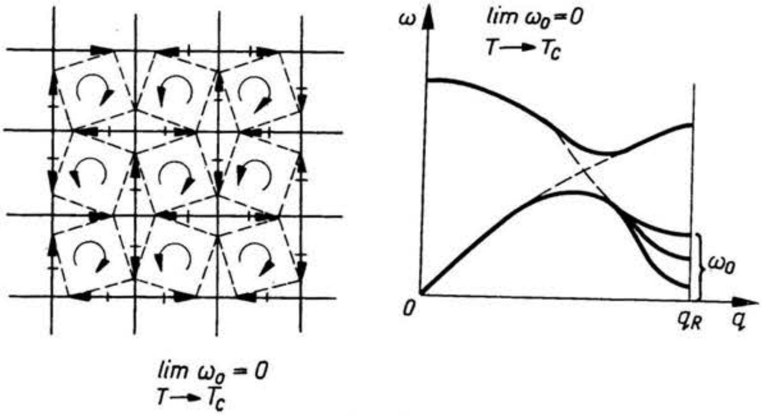

FIG. 2.

Of course, such a change of structure cannot occur abruptly. What happens in reality is that in approaching the critical point T_c the atoms fluctuate more and more around their equilibrium positions, that is, the number of soft phonons has increasing fluctuations. At T_c the atomic positions become completely diffuse, the soft phonons dominate, extending over the whole crystal and freezing into the new structure.

In neutron scattering soft phonon modes give rise to Brillouin-type peaks which, at T_c, merge into the center $\omega = 0$. The new fact discovered in recent years is that near T_c a very narrow central peak also appears for *transverse* soft phonons in the *cubic* crystals $SrTiO_3$ [5] and Nb_3Sn [6] and others. This is surprizing because the coupling constant $c_1^2\theta$ which is responsible for the heat diffusion pole in the elastic response function (2.16) is zero in this case. Indeed, for cubic crystals β is proportional to the unit tensor so that $\beta\hat{q}$ is parallel to $\hat{q}$ and, according to (2.15), $c_1^2\theta$ has no transverse component. It is clear, therefore, that the conventional thermo-elastic theory described in the last section is incapable of explaining these new central peaks.

4. Thermo-elastic description of displacive transitions

Near a phase transition driven by a soft mode at $\mathbf{q} = 0$, the thermoelastic description of Sect. 2 remains valid except for the fact that a certain combination of the elastic constants $C_{ij,kl}$ and the corresponding sound velocity c_1 goes to zero at T_c. The resulting strong temperature dependence of these $C_{ij,kl}$ near T_c brings about a new coupling between the elastic variable $\mathbf{u}$ and the thermal variable δT in Eq. (2.3), since, at the local temperature $T+\delta T$,

$$C_{ij,kl}(T+\delta T) = C_{ij,kl}(T) + \frac{\partial C_{ij,kl}}{\partial T}\,\delta T + \dots. \tag{4.1}$$

As compared to this coupling the thermal expansion coupling $\beta\theta\delta T$ is negligible in (2.3).

Retaining δT only in the first order, Eqs. (2.5) and (2.9) become respectively [2]

$$\left\{-\frac{1}{\varrho}C\nabla\otimes\nabla-\frac{1}{\varrho}\frac{\partial C}{\partial T}[(\nabla\delta T)+\delta T\nabla]\otimes\nabla+\frac{\partial^2}{\partial t^2}-\frac{1}{\varrho}\eta\nabla\otimes\nabla\frac{\partial}{\partial t}\right\}\mathbf{u} = \mathbf{f}, \tag{4.2}$$

where we have used the notation $(Aa\otimes b)_{ij} = \sum\limits_{mn} A_{im,nj}a_m b_n$, and

$$\left(\frac{\partial}{\partial t} - D\nabla^2\right)\delta T = \frac{1}{2\varrho C_V}\sum_{ijkl}\frac{\partial C_{ij,kl}}{\partial T}\frac{\partial}{\partial t}(\theta_{ij}\theta_{kl}). \tag{4.3}$$

The non-linearity of these equations in the variables $\mathbf{u}$ and δT excludes a plane-wave solution as in Eqs. (2.10) and (2.11), and this is why more sophisticated methods have to be used. Since, physically, only equilibrium averages without the external field $\mathbf{f}$ are observed and since the fluctuations $\mathbf{u}$ and δT have zero average,

$$\langle\mathbf{u}(\mathbf{r},t)\rangle_0 = 0, \quad \langle\delta T(\mathbf{r},t)\rangle_0 = 0, \tag{4.4}$$

it is natural to study the response functions [2]

$$\tilde{\chi}_{ij}(\mathbf{r},t;\mathbf{r};t') = \frac{1}{\varrho}\frac{\delta u_i(\mathbf{r},t)}{\delta f_j(\mathbf{r}',t')}, \quad \phi_j(\mathbf{r},t;\mathbf{r}',t') = \frac{1}{\varrho}\frac{\delta\big(\delta T(\mathbf{r},t)\big)}{\delta f_j(\mathbf{r}',t')}. \tag{4.5}$$

By functional derivation of Eqs. (4.2) and (4.3) with respect to f_j we obtain two equations relating $\tilde{\chi}_{ij}$ and ϕ_j, from which ϕ_j may, in principle, be eliminated. Then, we can put $\mathbf{f} = 0$ and take averages. However, in order to obtain closed expressions it is necessary to introduce an approximation by factorizing the higher correlation functions. In this way it is possible to calculate the Fourier transformed averaged elastic response function

$$\chi_{ij}(\mathbf{q},\omega) = \int d^3r\int dt\langle\tilde{\chi}_{ij}(\mathbf{r},t;0,0)\rangle_0\cdot e^{-i(\mathbf{q}\cdot\mathbf{r}-\omega t)}. \tag{4.6}$$

It turns out [2] that the factorization approximation reduces the problem to finding the auto-correlation function

$$\langle \nabla_r u_i(\mathbf{r}, t) \nabla_s u_j(\mathbf{r}, t) \rangle_0 = \psi_{ri} \delta_{rs} \delta_{ij} \tag{4.7}$$

which, in turn, may be derived from $\chi_{ij}(\mathbf{q}, \omega)$ using the fluctuation-dissipation theorem [2]. The result is again of the form [2.16] but the coupling constant $c_1^2 \theta$ is now determined by Eq. (4.7) instead of Eq. (2.15).

From the above description of the procedure it follows that the explicit form of the probability density which defines the equilibrium average is not required. This is of some importance in view of the non-trivial determination of this probability density which is the stationary solution of the Fokker-Planck equation [7] associated to the hydrodynamic equations. For this association, fluctuating random forces should actually be added to the hydrodynamic equations (4.2), (4.3) which then take the form of Langevin equations [7]. Physically, this addition of random forces just compensates for the drastic reduction of the number of degrees of freedom in going from the discrete microscopic description to the continuous thermo-elastic description.

The above factorization is reminiscent of the random-phase approximation which is known to be insufficient in the critical region near T_c. It is, therefore, quite possible that this factorization is not good enough for the problem of critical dynamics and that renormalization group techniques [8] have to be used.

The method described above is also applicable to a soft *staggered* mode. In this case, the lattice free energy (2.3) must be replaced by

$$F_L[\mathbf{u}, \delta T] = \int d^3 r \left\{ \frac{\varrho}{2} \omega_0^2 \mathbf{u}^2 + \frac{1}{2} \sum_{ijkl} C_{ij,kl} \theta_{ij} \theta_{kl} - \varrho \mathbf{u} \cdot \mathbf{f} \right\} \tag{4.8}$$

and the elastic equation of motion (2.5) by

$$\varrho \ddot{u}_i = -\varrho \Gamma \dot{u}_i - \frac{\delta F_L}{\delta u_i}. \tag{4.9}$$

Here, ω_0 is the soft staggered mode frequency at $\mathbf{q} = \mathbf{q}_R$, Γ the associated damping and $C_{ij,kl}$ are the staggered elastic constants. The coupling between $\mathbf{u}$ and δT now comes from the strong temperature dependence of ω_0 near T_c,

$$\omega_0^2(T + \delta T) = \omega_0^2(T) + \frac{\partial \omega_0^2}{\partial T} \delta T + \ldots . \tag{4.10}$$

From (4.8)–(4.10) and (2.9) we obtain, instead of (4.2), (4.3), [9]

$$\left\{ \omega_0^2 + \frac{\delta \omega_0^2}{\partial T} \delta T - \frac{1}{\varrho} C \nabla \otimes \nabla + \frac{\partial^2}{\partial t^2} + \Gamma \frac{\partial}{\partial t} \right\} \mathbf{u} = \mathbf{f} \tag{4.11}$$

and

$$\left(\frac{\partial}{\partial t} - D \nabla^2 \right) \delta T = \frac{T}{2 C_V} \frac{\partial \omega_0^2}{\partial T} \frac{\partial \mathbf{u}^2}{\partial t}. \tag{4.12}$$

Using the same technique as before we arrive again at a response function of the form (2.16) [2, 9]

$$\varrho\chi_{ij}(\mathbf{q},\omega)=\left\{\omega_0^2+c_{1i}^2(\hat{q})q^2-\omega^2-i\omega\left[\Gamma+\frac{\delta^2}{Dq^2-i\omega}\right]\right\}^{-1}\delta_{ij}, \tag{4.13}$$

where δ^2 is determined by the auto-correlation function

$$\langle u_i(\mathbf{r}t)u_j(\mathbf{r}t)\rangle_0=\phi\delta_{ij}. \tag{4.14}$$

The comparison of Eqs. (2.16) and (4.13) with the experimental results for Nb_3Sn and $SrTiO_3$, respectively, has been quite satisfactory [2, 9]. More recently, other explanations for these new central peaks in terms of clusters [10] and domain walls or solitons [11, 12] have been advanced for one and two dimensional models. While these explanations have been successful in computer simulations of molecular dynamics [10, 11], a quantitative application to real crystals has still to be made. It is, of course, possible that such mechanisms dominate over the hydrodynamic effect described in this paper. However, the latter is so general that it is expected to be present in all cases including those where it does not actually explain the experimental facts.

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