Hydrodynamics of solids*

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The hydrodynamic equations for solids are derived from the connection between hydrodynamic variables (and linearized hydrodynamic modes) and continuous broken symmetries. A simple fluid has five hydrodynamic variables (and modes), one for each conservation law (mass, three components of momentum and energy). As pointed out by Martin, Pershan, and Parodi a crystal must have three additional hydrodynamic variables (and modes) because it does not possess the (threefold) continuous translational invariance of the underlying Hamiltonian of the system. Previous treatments of the hydrodynamics of solids gave only seven hydrodynamic modes. As suggested by Martin, Pershan, and Parodi, the additional mode which was omitted from other earlier treatments, is associated with vacancy diffusion. Previous treatments of vacancy diffusion failed to recognize its coupling with the other hydrodynamic variables. The recognition of the necessity of inclusion of vacancy diffusion leads to the identification of two tensor transport coefficients (in addition to the usual viscosity and thermal conductivity). One is associated with the vacancy flux while the other is connected with the cross effect of thermal diffusion of vacancies (or equivalently a heat flow in a vacancy concentration gradient). The linearized equations are solved for propagation along the [100], [110], and [111] directions in cubic crystals. For these directions the longitudinal equations are isomorphic with those in a binary mixture when vacancy concentration is identified with the concentration in the mixture. In these cases the identification of the additional mode with vacancy diffusion is most clear. It is suggested that this additional mode should appear in the spectrum of light scattered from such crystals.

I. INTRODUCTION

It is well known^{1,2} that the slowly varying spatial and temporal disturbances of a mechanical system can be described in terms of local (in space and time) thermodynamic variables of that system. The best-known example of such a description is that of ordinary fluid mechanics, in which the slowly varying nonequilibrium behavior of a fluid is given in terms of five partial differential equations.³ This description is referred to as hydrodynamic because of its extensive application to fluid flow. By analogy the equations which describe the slowly varying (in space and time) disturbances of any system, be it a normal fluid¹ or superfluid, ⁴ magnet, ⁵ crystal, ^{2,6,7} or liquid crystal, ^{2,8} are usually referred to as the hydrodynamic equations of that system.

The hydrodynamic behavior of a system is conveniently described in terms of a few "hydrodynamic modes" (sound waves, thermal conduction, etc.). These collective modes are characterized by slow decay in times proportional to some power of their wavelength. The existence and number of such modes is determined by the sum of the number of conservation laws and the number of "continuous broken symmetries."² An example of the contribution of the latter is provided by the long-wavelength spin waves in an isotropic antiferromagnet, which behave hydrodynamically because the continuous rotational symmetry of the spin system (relative to the lattice) is broken in the ordered phase. The importance of the continuous nature of the broken symmetry is that it ensures the system has equal energy for all orientations of the staggered spin arrangement relative to the lattice (i. e., the Hamiltonian is invariant under rotation). Liquid crystals^{2,8} and superfluids⁴ are other examples of ordered systems in which continuous broken symmetries are responsible for hydrodynamic modes.

Since the hydrodynamic description of a system is a consequence of the assumption of local thermodynamic equilibrium and slowly varying disturbances, it follows that there must be a thermodynamic variable corresponding to each hydrodynamic variable (or vice versa). Thus the description of ordered systems must include additional thermodynamic variables, one corresponding to each continuous symmetry broken.

In this paper we wish to consider in some detail the thermodynamic and hydrodynamic equations for solids. A simple crystalline solid, unlike a simple fluid, is not translationally invariant even though the underlying Hamiltonian of the system is translationally invariant. Therefore, since translation is a three-dimensional continuous transformation, we say that a crystalline phase has three continuous broken symmetries. Since the system still possesses the five conservation laws (mass, mo-

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mentum, and energy), a crystal must have eight hydrodynamic modes. This fact was pointed out by Martin *et al.*² In particular they argued that a distortion (or displacement) vector must be treated as a hydrodynamic variable along with the five conserved variables.

Earlier treatments^{6,7} of hydrodynamics in solids have included the distortion as a hydrodynamic variable. However it has been generally assumed that the fluctuations in the divergence of the distortion are simply proportional to those of the particle (or mass) density. It is easy to see how such an identification is made. Suppose in a simple crystal that the number of lattice sites denoted by the running index α and the number of particles (atoms or molecules) denoted by the running index *i* are the same and that each particle is associated with a particular lattice site (i.e., there is an $\boldsymbol{\alpha}$ associated with each *i*). Then if \vec{R}_{α} labels a lattice vector, the particle number density $n(\mathbf{r}t)$ is given in terms of the isotropic component $\nabla \cdot \vec{\mathbf{R}}(\vec{\mathbf{r}}t)$ of the strain $\nabla \vec{\mathbf{R}}(\vec{\mathbf{r}}t)$ by

$$n(\mathbf{\vec{r}}t) = \sum_{\mathbf{i}} \delta(\mathbf{\vec{r}} - \mathbf{\vec{r}}_{\mathbf{i}}(t)) = \sum_{\alpha} \delta(\mathbf{\vec{r}} - \mathbf{\vec{R}}_{\alpha} - \delta \mathbf{\vec{r}}_{\alpha}(t))$$
$$\approx \sum_{\alpha} \delta(\mathbf{\vec{r}} - \mathbf{\vec{R}}_{\alpha}) - \nabla \cdot \mathbf{\vec{R}}(\mathbf{\vec{r}}t) , \qquad (1.1)$$

where

$$\vec{\mathbf{R}}(\vec{\mathbf{r}}t) = \sum_{\alpha} \delta \vec{\mathbf{r}}_{\alpha}(t) \delta(\vec{\mathbf{r}} - \vec{\mathbf{R}}_{\alpha}) ,$$

with

$$\delta \vec{\mathbf{r}}_{\alpha}(t) = \vec{\mathbf{r}}_{i} - \vec{\mathbf{R}}_{\alpha} .$$

Thus in a perfect crystal (one with no vacancies) the fluctuations in the particle density are the same as those in the divergence of the distortion. However, a real crystal has vacancies, so that even classically⁹ it is impossible to identify each particle with a particular lattice site. Therefore (1.1) is not valid in a real crystal and there are indeed eight independent thermodynamic and hydrodynamic variables (along with a like number of hydrodynamic modes). Indeed the general mode theorem implies, in accordance with thermodynamics, that any crystal in thermal equilibrium must have vacancies. We shall see that the hydrodynamic mode site from conventional treatments is related to diffusion of vacancies.¹⁰

Of course, vacancy diffusion is a well-known phenomenon in solids. In particular, Allnatt and Chadwick¹¹ have discussed the effect of a temperature gradient on vacancy diffusion. This was utilized to discuss the coupling of vacancy and heat diffusion. They were not, however, concerned with the full set of hydrodynamic equations which involve these diffusions. In Sec. II the thermodynamics of solids is discussed without the constraint implied by (1.1). In Sec. III the constitutive equations relating the currents of the hydrodynamic variables to the thermodynamic variables are derived from the entropyproduction formalism. In Sec. IV the general hydrodynamic equations for solids are derived and discussed. In Sec. V the equations for cubic crystals are discussed in some detail for particular directions of propagation. In Sec. VI our results are discussed and the number of thermodynamic derivatives and transport coefficients necessary to describe a crystal of a particular symmetry are exhibited.

II. THERMODYNAMICS OF SOLIDS

As argued in the Introduction and in Ref. 2 the (lattice) distortion R must be treated as a thermodynamic and hydrodynamic variable. It is totally equivalent² and more convenient to work with the symmetric strain as a variable.¹² Hence, we define a strain-tensor density $\overline{u}(\overline{r}t)$ whose variation is given by

$$\delta u_{ij}(\mathbf{\vec{r}}t) = -\frac{1}{2} \left[\partial_i R_j(\mathbf{\vec{r}}t) + \partial_j R_i(\mathbf{\vec{r}}t) \right] , \qquad (2.1)$$

where \vec{R} is the distortion density.

In addition we must introduce an additional variable which is thermodynamically conjugate to the strain. It is most simply defined in terms of the energy density ϵ by

$$\vec{\phi} = \left(\frac{\partial \epsilon}{\partial \vec{u}}\right)_{\mathbf{s},\rho} \,. \tag{2.2}$$

Clearly $\overline{\phi}$ can be taken symmetric without loss of generality. The requirement that the energy be stationary with respect to strain variations fixes the equilibrium value of $\overline{\phi}$ to be zero. A similar recognition is present in conventional elasticity theory.^{6,7}

We introduce the auxiliary quantity $n_0(\tilde{\mathbf{f}}t)$, which we shall refer to as the lattice-site density. Its fluctuations are assumed to be related to the local strain by

$$\delta n_0(\mathbf{r}t) = \mathrm{Tr}\,\delta\,\mathbf{\vec{u}}(\mathbf{r}t) = -\,\nabla\,\boldsymbol{\cdot}\,\mathbf{\vec{R}}(\mathbf{r}t)\,\,. \tag{2.3}$$

This identification is motivated by (1.1), with $\delta \vec{r}_{\alpha}(t)$ identified with a fluctuating lattice-site position rather than a fluctuating particle position. This variable allows us to identify the vacancy-(or hole-) concentration variable

$$c = 1 - n/n_0$$
, (2.4)

where n is the particle number density.

We specify the thermodynamics of a solid in terms of the energy-density differential

$$d\boldsymbol{\epsilon} = Td(\rho s) + \mu \, d\rho + \vec{\mathbf{v}} \cdot d\vec{\mathbf{g}} + \mathrm{Tr}\vec{\phi} \cdot d\vec{\mathbf{u}} , \qquad (2.5)$$

$$\rho \mu = P + \epsilon - T\rho s - \vec{g} \cdot \vec{v} - Tr \vec{\phi} \cdot \vec{u} . \qquad (2.6)$$

Galilean invariance requires that

$$\vec{\mathbf{g}} = \rho \vec{\mathbf{v}} \tag{2.7a}$$

and

$$\boldsymbol{\epsilon} = \boldsymbol{\epsilon}^0 + \frac{1}{2} \rho v^2 , \qquad (2.7b)$$

where ϵ^0 is the energy density in the rest frame. The differential of the chemical potential is seen to be

$$\rho d(\mu + \frac{1}{2}v^2) = dP - \rho s \, dT - \operatorname{Tr} \vec{\mathbf{u}} \cdot d\vec{\phi} \, . \tag{2.8}$$

This is alternatively interpreted as a Gibbs-Duhem relation since it can be rewritten as

$$\rho s dT - dP + \vec{g} \cdot d\vec{v} + Tr \vec{u} \cdot d\vec{\phi} + \rho d\mu = 0. \quad (2.9)$$

Note that the finite-strain chemical potential (2.6) and its differential (2.8) arise naturally in the development presented here. The chemical potential (2.6) allows absolute comparison of relative stability of strained states. This is to be contrasted with recent discussions¹³ of stressed solids involving finite strain which have appeared in the geophysical literature.

It is instructive to examine the energy differential when the vacancy concentration is employed as a variable. We see that

$$de = d\left(\frac{\epsilon}{\rho}\right) = T \, ds + \frac{P - \mathrm{Tr}\,\vec{\mathrm{u}} \cdot \vec{\phi}}{\rho^2} \, d\rho$$
$$+ \vec{\mathrm{v}} \cdot d\vec{\mathrm{v}} + \mathrm{Tr}\,\frac{\vec{\phi}}{\rho} \cdot d\vec{\mathrm{u}} \, . \tag{2.10}$$

We see from the definition (2.4)

$$dc = \frac{\rho \, dn_0}{mn_0^2} - \frac{d\rho}{mn_0} \, . \tag{2.11}$$

Then (2.10) becomes

$$de = T ds - \frac{mn_0}{\rho^2} \prod dc + \vec{\nabla} \cdot d\vec{\nabla} + \operatorname{Tr} \frac{\vec{\sigma}^R}{n_0 \rho} \cdot d\vec{u} , \qquad (2.12)$$

where

 $\Pi = P - \mathbf{Tr} \, \mathbf{\vec{u}} \cdot \, \mathbf{\vec{\phi}}$

and

$$\overline{\sigma}^R = \Pi \overline{1} + n_0 \overline{\phi} .$$

In Sec. III we shall see that $\overline{\sigma}^R$ is the reactive (reversible or thermodynamic) part of the stress tensor. Thus equation (2.12) reduces to the energy differential usually employed in elasticity theory if there are no fluctuations in the vacancy concentration. II, the variable conjugate to the vacancy concentration, is essentially a "vacancy pressure." The stress $\overline{\sigma}^R$ is conjugate to the strain only when the energy is considered as a function of entropy, vacancy concentration, and strain. The variables II and $\overline{\sigma}^R$ are related to the energy by the corresponding derivatives

$$\Pi = -\frac{\rho^2}{mn_0} \left(\frac{\partial e}{\partial c}\right)_{s,\vec{u}}$$
(2.13a)

and

$$\overline{\sigma}^{R} = n_{0} \rho \left(\frac{\partial e}{\partial \overline{u}} \right)_{s,c} .$$
(2.13b)

We can use equations (2.5), (2.8), or (2.12), or their Legendre transforms to derive sets of Maxwell relations amongst the variables s, ρ , \vec{v} , and \vec{u} or s, c, \vec{v} , and \vec{u} and their conjugate variables. For example, (2.5) can be written in a form convenient for deriving Maxwell relations with use of (2.6),

$$d\epsilon = T\rho \, ds + \frac{P + \epsilon - \vec{g} \cdot \vec{v} - Tr \, \vec{u} \cdot \phi}{\rho} \, d\rho$$
$$+ \vec{v} \cdot d\vec{g} + Tr \, \vec{\phi} \cdot d\vec{u} \, . \qquad (2.14)$$

By equating the appropriate cross derivatives we obtain (neglecting terms which vanish for an equilibrium system at rest)

$$\begin{pmatrix} \frac{\partial T}{\partial \rho} \end{pmatrix}_{s,\vec{u}} = \frac{1}{\rho^2} \begin{pmatrix} \frac{\partial P}{\partial s} \end{pmatrix}_{\rho,\vec{u}} - \operatorname{Tr} \frac{\vec{u}}{\rho^2} \cdot \begin{pmatrix} \frac{\partial \overline{\phi}}{\partial s} \end{pmatrix}_{\rho,\vec{u}},$$

$$\begin{pmatrix} \frac{\partial T}{\sigma \vec{u}} \end{pmatrix}_{s,\rho} = \frac{1}{\rho} \begin{pmatrix} \frac{\partial \overline{\phi}}{\partial s} \end{pmatrix}_{\rho,\vec{u}},$$

$$(2.15a)$$

$$(2.15b)$$

and

$$\left(\frac{\partial P}{\partial \overline{u}}\right)_{s,\rho} = \rho \left(\frac{\partial \overline{\phi}}{\partial \rho}\right)_{s,\overline{u}} + \operatorname{Tr} \overline{u} \cdot \left(\frac{\partial \overline{\phi}}{\partial \overline{u}}\right)_{s,\rho} \quad (2.15c)$$

We have assumed $\vec{\nabla} = 0$ and $\vec{\phi} = 0$ in equilibrium and that¹⁴

$$\vec{u} = \frac{1}{3}n_0 \vec{1} \neq 0$$
 . (2.16)

We can neglect cross derivatives involving the velocity or momentum and omit the symbol indicating that derivatives are taken at constant \vec{v} when all derivatives are evaluated at $\vec{v} = 0$. The thermodynamic variables for nonzero \vec{v} can be obtained from (2.7). The remaining Maxwell relations amongst the appropriate variables are derived in Appendix A.

In Sec. III we shall use the thermodynamic equations in this section to derive the constitutive equations from the entropy-production formalism.

III. DERIVATION OF CONSTITUTIVE EQUATIONS

In this section we shall obtain the constitutive equations which couple the currents (or fluxes) of the hydrodynamic variables back to the hydrodynamic variables themselves. For solids, these currents are defined by the usual five local conservation laws plus equations of motion for the strain. These equations are

mass:
$$\frac{\partial \rho(\mathbf{\tilde{r}}t)}{\partial t} + \nabla \cdot \mathbf{\tilde{g}}(\mathbf{\tilde{r}}t) = 0$$
; (3.1a)

momentum:
$$\frac{\partial \vec{g}(\vec{r}t)}{\partial t} + \nabla \cdot \vec{\sigma}(\vec{r}t) = 0$$
; (3.1b)

energy:
$$\frac{\partial \epsilon(\mathbf{r}t)}{\partial t} + \nabla \cdot \mathbf{J}^{\epsilon}(\mathbf{r}t) = 0$$
; (3.1c)

strain:
$$\frac{\partial \vec{u}(\vec{r}t)}{\partial t} + \nabla \cdot \underline{J}^{u}(\vec{r}t) = 0$$
; (3.1d)

where $\overline{\sigma}$ is the stress tensor, $\overline{J}^{\varepsilon}$ is the energy current, and <u>J</u>^u plays the role of strain current. In particular

$$J_{ijk}^{u}(\mathbf{\tilde{r}}t) = \frac{1}{2} \left[\delta_{ki} J_{j}^{R}(\mathbf{\tilde{r}}t) + \delta_{kj} J_{i}^{R}(\mathbf{\tilde{r}}t) \right] , \qquad (3.2)$$

where we have assumed that the distortion satisfies the dynamical equation²

$$\frac{\partial \vec{\mathbf{R}}(\vec{\mathbf{r}}t)}{\partial t} = \vec{\mathbf{J}}^{R}(\vec{\mathbf{r}}t) .$$
 (3.3)

We see that one advantage of working with the strain as a variable instead of the distortion itself is that (3.1d) has the appearance of a local conservation law. Of course (3.1d) contains no more information than (3.3).

Although Eqs. (3.1) are formally exact and apply to arbitrary disturbances, they are of use only when the currents can be related back to the hydrodynamic variables themselves. This can be done when these variables are slowly varying in space and time. For sufficiently slowly varying disturbances it is possible to assume that the system is in local thermodynamic equilibrium. Then Eqs. (2.5), (2.6), and (2.8) are valid locally around each point in space and time. This allows us to write for the rate of entropy production (temporarily suppressing spatial and temporal arguments)

$$\frac{\partial(\rho s)}{\partial t} = \frac{1}{T} \frac{\partial \epsilon}{\partial t} - \frac{\mu}{T} \frac{\partial \rho}{\partial t} - \frac{\vec{v}}{T} \cdot \frac{\partial \vec{g}}{\partial t} - \operatorname{Tr} \frac{\vec{\phi}}{T} \cdot \frac{\partial \vec{u}}{\partial t}.$$
(3.4)

The requirement that the work done on the system by external forces must be positive for a stable system² implies that

$$R = T \frac{d}{dt} \int d\vec{\mathbf{r}} \, \rho s \ge 0 \, . \tag{3.5}$$

When we use (3.1) R can be written in terms of the currents as

$$\frac{R}{T} = \int d\vec{\mathbf{r}} \left(-\frac{1}{T} \nabla \cdot \vec{\mathbf{J}}^{\epsilon} + \frac{\mu}{T} \nabla \cdot \vec{\mathbf{g}} + \frac{\vec{\nabla}}{T} \cdot \nabla \cdot \vec{\sigma} + \operatorname{Tr} \frac{\vec{\phi}}{T} \cdot \nabla \vec{\mathbf{J}}^{R} \right).$$
(3.6)

If we integrate (3.6) by parts we obtain using (2.8), (2.6) and neglecting surface terms

$$\frac{R}{T} = -\int d\vec{r} \left(\frac{[\vec{J}^{\epsilon} - (\epsilon - \vec{g} \cdot \vec{v} - Tr\vec{u} \cdot \vec{\phi})\vec{v} - \vec{\sigma} \cdot \vec{v} - \vec{J}^{R} \cdot \vec{\phi}] \cdot \nabla T}{T^{2}} + \frac{Tr(\vec{\sigma} - P\vec{1} - \rho\vec{v}\vec{v}) \cdot \nabla\vec{v}}{T} + \frac{\vec{J}^{R}}{T} \cdot (\nabla \cdot \vec{\phi}) - \frac{Tr\vec{v} \cdot \nabla\vec{\phi} \cdot \vec{u}}{T} \right).$$
(3.7)

Since we shall only be concerned with the linearized hydrodynamic equations we can drop all terms in (3.7) which are of higher order than quadratic in fluctuations from equilibrium. Then (3.7) becomes

$$R = -\int d\vec{\mathbf{r}} \left(\frac{\left[\vec{\mathbf{J}}^{\epsilon} - (\epsilon + P)\vec{\mathbf{v}}\right] \cdot \nabla T}{T} + \mathrm{Tr}\left(\vec{\sigma} - P\vec{\mathbf{1}} - n_0\vec{\phi}'\right) \cdot \nabla\vec{\mathbf{v}} + \left(\vec{\mathbf{J}}^R - n_0\vec{\mathbf{v}}\right) \cdot \left(\nabla \cdot \vec{\phi}\right) \right),$$
(3.8)

where

$$\vec{\phi}' = \vec{\phi} - \phi_0 \vec{1} \tag{3.9}$$

is the symmetric-traceless part of ϕ with $\phi_0 = \frac{1}{3} \text{Tr} \phi$. In (3.8) we have used the fact that

$$\nabla \phi_0 = \nabla \cdot (\vec{\phi} - \vec{\phi}') \tag{3.10}$$

and integrated $n_0 \mathbf{\bar{v}} \cdot (\nabla \cdot \mathbf{\vec{\phi}'})$ by parts, neglecting the surface term.

The requirement that R be positive restricts the currents to be of the form (putting the spatial and temporal variables into the nonequilibrium quantities and denoting equilibrium quantities as those without such variables)

$$\vec{\mathbf{J}}^{\epsilon}(\vec{\mathbf{r}}t) = (\boldsymbol{\epsilon} + P)\vec{\boldsymbol{\nabla}}(\vec{\mathbf{r}}t) - \vec{\boldsymbol{\alpha}} \circ \nabla T(\vec{\mathbf{r}}t) - \vec{\boldsymbol{\xi}} \cdot [\nabla \circ \vec{\boldsymbol{\phi}}(\vec{\mathbf{r}}t)],$$
(3.11a)

$$\vec{\sigma}(\vec{\mathbf{r}}t) = P(\vec{\mathbf{r}}t) \mathbf{1} + n_0 \vec{\phi}'(\vec{\mathbf{r}}t) - \underline{\eta} : \nabla \vec{\nabla}(\vec{\mathbf{r}}t) , \qquad (3.11b)$$
$$\mathbf{j}^R(\vec{\mathbf{r}}t) = n_0 \vec{\nabla}(\vec{\mathbf{r}}t) - \vec{\boldsymbol{\xi}} \cdot [\nabla \cdot \vec{\phi}(\vec{\mathbf{r}}t)] - \vec{\boldsymbol{\xi}}^T / T \cdot \nabla T(\vec{\mathbf{r}}t) .$$

(3.11c)

 $\vec{\alpha}$, a second-rank tensor, is related to the pure thermal conductivity $\vec{\kappa}$ as will be shown below. $\underline{\eta}$, a fourth-rank tensor, is the viscosity. $\vec{\xi}$ and $\vec{\xi}$ $(\vec{\xi}^T \text{ is the transpose of } \vec{\xi})$ are new (tensor) transport coefficients which appear because $\nabla \cdot \vec{R}$ is a variable independent of the density (mass or particle). $\vec{\xi}$ is related to the vacancy diffusion constant while $\overline{\xi}$ is related to the cross effect of "thermal diffusion" of vacancies.

Note there are no cross terms coupling \overline{J}^{ϵ} to $\nabla \vec{v}$, etc., because \vec{J}^{ϵ} and \vec{v} have the same behavior under time reversal. A fundamental property of transport coefficients is that they always relate quantities with opposite time-reversal behavior² (e.g., $\overline{\sigma}$ is even and \overline{v} is odd under time reversal).

We see that the reactive or reversible part (that which is simply proportional to thermodynamic quantities with no gradients) of the stress tensor is

$$\vec{\sigma}^{R}(\vec{r}t) = \left[P(\vec{r}t) - n_{0}\phi_{0}(\vec{r}t) \right] \vec{1} + n_{0}\vec{\phi}(\vec{r}t)$$
$$= \Pi(\vec{r}t) \vec{1} + n_{0}\vec{\phi}(\vec{r}t)$$
(3.12)

to linear order in fluctuations from equilibrium. As was seen in Sec. II $\overline{\sigma}^{R}$ is conjugate to the strain when the vacancy concentration is used as a variable.

Equations (3.11) are the desired constitutive equations relating the currents to the hydrodynamic variables. When combined with the assumption that the fluctuations of the local thermodynamic variables are related to one another by thermodynamic derivatives, they close our system of hydrodynamic equations. In Sec. IV we will derive and discuss these equations.

IV. GENERAL HYDRODYNAMIC EQUATIONS

In this section we will derive the general hydrodynamic equations for solids. We can obtain these equations by substitution of (3.11) into (3.1). This yields the four equations

$$\frac{\partial \rho(\mathbf{\vec{r}}t)}{\partial t} + \nabla \cdot \mathbf{\vec{g}}(\mathbf{\vec{r}}t) = 0 , \qquad (4.1a)$$

$$\left(\vec{1}\frac{\partial}{\partial t} - \frac{\nabla \cdot \underline{\eta} \cdot \nabla}{\rho}\right) \cdot \vec{g}(\vec{r}t) + \nabla \cdot \vec{\sigma}^{R}(\vec{r}t) = 0, \quad (4.1b)$$

$$\frac{\partial \epsilon(\mathbf{\vec{r}}t)}{\partial t} + \frac{\epsilon + P}{\rho} \nabla \cdot \mathbf{\vec{g}}(\mathbf{\vec{r}}t) - \mathbf{\vec{\alpha}} : \nabla \nabla T(\mathbf{\vec{r}}t) - \mathbf{\vec{\zeta}} : \nabla [\nabla \cdot \mathbf{\vec{\phi}}(\mathbf{\vec{r}}t)] = 0 , \qquad (4.1c)$$

$$\frac{\partial \vec{u}(\vec{r}t)}{\partial t} + \frac{n_0}{\rho} [\nabla \vec{g}(\vec{r}t)] - [\nabla \nabla \cdot \vec{\phi}(\vec{r}t) \cdot \vec{\xi}] - \left(\nabla \frac{\vec{\xi}^T}{T} \cdot \nabla T(\vec{r}t)\right) = 0 , \qquad (4.1c)$$

where

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$$\begin{split} \left[\nabla \mathbf{g}(\mathbf{\vec{r}}t)\right]_{ij} &= \frac{1}{2} \left[\partial_i g_j(\mathbf{\vec{r}}t) + \partial_j g_i(\mathbf{\vec{r}}t)\right] , \\ \left[\nabla \nabla \cdot \vec{\phi}(\mathbf{\vec{r}}t) \cdot \mathbf{\vec{\zeta}}\right]_{ij} &= \frac{1}{2} (\zeta_{1j}\partial_i + \zeta_{1i}\partial_j) \partial_k \phi_{kl}(\mathbf{\vec{r}}t) , \end{split}$$

$$\left(\nabla \frac{\vec{\xi}^T}{T} \cdot \nabla T(\vec{\mathbf{r}}t)\right)_{ij} = \frac{1}{2} (\xi_{kj} \partial_i + \xi_{ki} \partial_j) \frac{\partial_k T(\vec{\mathbf{r}}t)}{T} .$$

A summation convention over repeated indices has been employed.

We can close these equations if we assume that the small fluctuations of the conjugate variables $\vec{\sigma}^R$, $\vec{\phi}$, and T are related to the variables ρ , \vec{u} , and ϵ by a linear combination of thermodynamic derivatives. It is convenient, however, to first replace the scalar variables ρ and ϵ by two other scalar variables which to linear order are given by

$$q(\mathbf{\tilde{r}}t) = T\rho s(\mathbf{\tilde{r}}t) = \epsilon(\mathbf{\tilde{r}}t) - \frac{\epsilon + P}{\rho}\rho(\mathbf{\tilde{r}}t) , \qquad (4.2)$$

$$c(\mathbf{\vec{r}}t) = \frac{\rho}{mn_0^2} \left(n_0(\mathbf{\vec{r}}t) - \frac{n_0}{\rho} \rho(\mathbf{\vec{r}}t) \right) \,. \tag{4.3}$$

The first, $q(\mathbf{r}t)$, has been introduced by Kadanoff and Martin¹ as the heat-energy density and is proportional to the fluctuation in entropy; the second, $c(\mathbf{r}t)$, is the fluctuation in vacancy concentration. We can then write

$$\frac{\partial c(\mathbf{\tilde{r}}t)}{\partial t} - \frac{\rho}{mn_0^2} \operatorname{Tr} \mathbf{\tilde{\xi}} \cdot \nabla [\nabla \cdot \vec{\phi}(\mathbf{\tilde{r}}t)] - \frac{\rho}{mn_0^2} \operatorname{Tr} \mathbf{\tilde{\xi}} \cdot \nabla \nabla T(\mathbf{\tilde{r}}t) = 0 , \qquad (4.1a')$$

$$\frac{\partial q(\mathbf{r}t)}{\partial t} - \operatorname{Tr}\vec{\alpha} \cdot \nabla \nabla T(\vec{\mathbf{r}}t) - \operatorname{Tr}\vec{\xi} \circ \nabla [\nabla \cdot \vec{\phi}(\vec{\mathbf{r}}t)] = 0 .$$
(4.1c')

We now note that if the vacancy diffusion flux $(\rho/mn_0^2)[\vec{J}^R(r,t) - n_0\vec{v}(r,t)]$ is zero, we have pure thermal conduction since

$$\operatorname{Tr} \vec{\xi} \cdot \nabla [\nabla \cdot \vec{\phi}(\vec{\mathbf{r}}t)] + \operatorname{Tr} \frac{\vec{\xi}^{T}}{T} \cdot \nabla \nabla T(\vec{\mathbf{r}}t) = 0 , \quad (4.4)$$

which when substituted in (4.1c') yields

$$\frac{\partial q(\vec{\mathbf{r}}t)}{\partial t} - \operatorname{Tr}\left(\vec{\alpha} - \frac{\vec{\xi} \cdot \vec{\zeta}^{-1} \cdot \vec{\xi}^{T}}{T}\right) \cdot \nabla \nabla T(\vec{\mathbf{r}}t) = 0.$$
(4.5)

This equation may be rewritten as

$$\frac{\partial q(\vec{\mathbf{r}}t)}{\partial t} - \operatorname{Tr}\vec{\kappa} \cdot \nabla \nabla T(\vec{\mathbf{r}}t) = 0 , \qquad (4.6)$$

which defines the thermal conductivity tensor $\vec{\kappa}$ of the system.

Our set of hydrodynamic equations for the fluctuations of the thermodynamic variables may be taken to consist of (4.1a'), (4.1b), (4.1c'), and (4.1d). We can close these equations by relating the variables $\vec{\sigma}^R$, T, and $\vec{\phi}$ to the variables \vec{u} , c, and q via thermodynamic derivatives. Thus we assume in accordance with local equilibrium

$$\vec{\sigma}^{R}(\vec{\mathbf{r}}t) = \left(\frac{\partial \vec{\sigma}^{R}}{\partial \vec{\mathbf{u}}}\right)_{s,c} : \vec{\mathbf{u}}(\vec{\mathbf{r}}t) + \frac{1}{T\rho} \left(\frac{\partial \vec{\sigma}^{R}}{\partial s}\right)_{\vec{\mathbf{u}},c} q(\vec{\mathbf{r}}t) + \left(\frac{\partial \vec{\sigma}^{R}}{\partial c}\right)_{\vec{\mathbf{u}},c} c(\vec{\mathbf{r}}t) , \qquad (4.7a)$$

$$\vec{\phi}(\vec{\mathbf{r}}t) = \left(\frac{\partial\vec{\phi}}{\partial\vec{\mathbf{u}}}\right)_{s,c} : \vec{\mathbf{u}}(\vec{\mathbf{r}}t) + \frac{1}{T\rho} \left(\frac{\partial\vec{\phi}}{\partial s}\right)_{\vec{\mathbf{u}},c} q(\vec{\mathbf{r}}t) + \left(\frac{\partial\vec{\phi}}{\partial c}\right)_{\vec{\mathbf{u}},s} c(\vec{\mathbf{r}}t) , \qquad (4.7b)$$

$$T(\mathbf{\vec{r}}t) = \mathrm{Tr}\left(\frac{\partial T}{\partial \mathbf{\vec{u}}}\right)_{s,c} \cdot \mathbf{\vec{u}}(\mathbf{\vec{r}}t) + \frac{1}{T\rho}\left(\frac{\partial T}{\partial s}\right)_{\mathbf{\vec{u}},c} q(\mathbf{\vec{r}}t) + \left(\frac{\partial T}{\partial c}\right)_{\mathbf{\vec{u}},s} c(\mathbf{\vec{r}}t) .$$
(4.7c)

When these relations are substituted into our chosen set of Eqs. (4.1) we obtain

$$\left(\vec{1} \frac{\partial}{\partial t} - \nabla \cdot \underline{D}^{\boldsymbol{s}} \circ \nabla\right) \cdot g(\vec{\mathbf{r}}t) + \frac{1}{n_0} \nabla \cdot [\underline{C} : \vec{\mathbf{u}}(\vec{\mathbf{r}}t)] + \frac{1}{n_0} \overrightarrow{C}^{\boldsymbol{q}} \cdot \nabla q(\vec{\mathbf{r}}t) + \frac{1}{n_0} \overrightarrow{C}^{\boldsymbol{c}} \cdot \nabla c(\vec{\mathbf{r}}t) = 0, \qquad (4.8a)$$

$$\left(\underline{1}^{4} \frac{\partial}{\partial t} - \underline{D}^{u} : \nabla \nabla\right) : \vec{u}(\vec{r}t) + \frac{n_{0}}{\rho} [\nabla \vec{g}(\vec{r}t)] - \underline{D}^{uq} : \nabla \nabla q(\vec{r}t) - \underline{D}^{uc} : \nabla \nabla c(\vec{r}t) = 0 , \qquad (4.8b)$$

$$\left(\frac{\partial}{\partial t} - \operatorname{Tr}\vec{\mathbf{D}}^{q} \circ \nabla\nabla\right) q(\vec{\mathbf{r}}t) - \operatorname{Tr}\vec{\mathbf{D}}^{qc} \cdot \nabla\nabla c(\vec{\mathbf{r}}t) - \nabla\nabla : \underline{\mathbf{D}}^{qu} : u(\vec{\mathbf{r}}t) = 0 , \qquad (4.8c)$$

$$\left(\frac{\partial}{\partial t} - \operatorname{Tr}\vec{\mathbf{D}}^{c} \circ \nabla\nabla\right) c(\vec{\mathbf{r}}t) - \operatorname{Tr}\vec{\mathbf{D}}^{c_{q}} \cdot \nabla\nabla q(\vec{\mathbf{r}}t) - \nabla\nabla : \underline{\mathbf{D}}^{c_{u}} : u(\vec{\mathbf{r}}t) = 0 , \qquad (4.8d)$$

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where

$$\begin{split} C_{ijkl} &= n_0 \left(\frac{\partial \sigma_{ij}^{i}}{\partial u_{kl}} \right)_{s,c}, \qquad C_{ij}^{q} = \frac{n_0}{T\rho} \left(\frac{\partial \sigma_{ij}^{R}}{\partial s} \right)_{u,c}, \\ C_{ij}^{c} &= n_0 \left(\frac{\partial \sigma_{ij}^{R}}{\partial c} \right)_{\vec{u}_{*}s}, \qquad D_{ijkl}^{q} = \frac{\eta_{ijkl}}{\rho}, \\ D_{ijklmn}^{u} &= \frac{1}{2} (\delta_{im} \xi_{jj'} + \delta_{jm} \xi_{ij'}) \left(\frac{\partial \phi_{j'n}}{\partial u_{kl}} \right)_{s,c} + \frac{1}{2T} (\delta_{im} \xi_{jn} + \delta_{jm} \xi_{in}) \left(\frac{\partial T}{\partial u_{kl}} \right)_{s,c}, \\ D_{ijkl}^{u} &= \frac{1}{2T\rho} (\delta_{ik} \xi_{jj'} + \delta_{jk} \xi_{ij'}) \left(\frac{\partial \phi_{j'1}}{\partial s} \right)_{\vec{u}_{*}c} + \frac{1}{2T^2\rho} (\delta_{ik} \xi_{jl} + \delta_{jk} \xi_{il}) \left(\frac{\partial T}{\partial s} \right)_{\vec{u}_{*}c}, \\ D_{ijkl}^{u} &= \frac{1}{2} (\delta_{ik} \xi_{jj'} + \delta_{jk} \xi_{ij'}) \left(\frac{\partial \phi_{j'1}}{\partial c} \right)_{s,\vec{u}} + \frac{1}{2T} (\delta_{ik} \xi_{jl} + \delta_{jk} \xi_{il}) \left(\frac{\partial T}{\partial s} \right)_{\vec{u}_{*}c}, \\ D_{ijkl}^{u} &= \frac{1}{2} (\delta_{ik} \xi_{jj'} + \delta_{jk} \xi_{ij'}) \left(\frac{\partial \phi_{j'1}}{\partial c} \right)_{s,\vec{u}} + \frac{1}{2T} (\delta_{ik} \xi_{jl} + \delta_{jk} \xi_{il}) \left(\frac{\partial T}{\partial c} \right)_{s,\vec{u}}, \\ D_{ijkl}^{q} &= \frac{\alpha_{ij}}{\rho c_{u,c}} + \frac{\xi_{ik}}{T\rho} \left(\frac{\partial \phi_{kj}}{\partial s} \right)_{c,\vec{u}}, \qquad C_{\vec{u},c} = T \left(\frac{\partial s}{\partial T} \right)_{\vec{u},c}, \\ D_{ij}^{q} &= \alpha_{ij} \left(\frac{\partial T}{\partial c} \right)_{s,\vec{u}} + \xi_{ik} \left(\frac{\partial \phi_{kj}}{\partial c} \right)_{s,\vec{u}}, \qquad D_{ijkl}^{q} &= \alpha_{ij} \left(\frac{\partial T}{\partial u_{kl}} \right)_{s,c} + \xi_{ij} \left(\frac{\partial \phi_{kj}}{\partial u_{kl}} \right)_{s,c}, \\ D_{ij}^{cq} &= \frac{\rho}{mn_0^2} \zeta_{ik} \left(\frac{\partial \phi_{kj}}{\partial c} \right)_{s,\vec{u}} + \frac{\rho}{mn_0^2 T} \xi_{ij} \left(\frac{\partial T}{\partial c} \right)_{s,\vec{u}}, \\ D_{ijkl}^{cq} &= \frac{1}{Tmn_0^2} \xi_{ik} \left(\frac{\partial \phi_{kj}}{\partial s} \right)_{\vec{u},c} + \frac{\xi_{ij}}{mn_0^2 Tc_{\vec{u},c}}, \\ D_{ijkl}^{cq} &= \frac{\rho}{mn_0^2 T} \xi_{ij} \left(\frac{\partial T}{\partial u_{kl}} \right)_{s,c} + \frac{\rho}{mn_0^2} \zeta_{ii'} \left(\frac{\partial \phi_{i'j}}{\partial u_{kl}} \right)_{s,c}, \end{split}$$

and

$$1^4_{ijkl} = \frac{1}{2} \left(\delta_{ik} \delta_{jl} + \delta_{jk} \delta_{il} \right) .$$

These equations are a set of complicated coupled equations which describe the hydrodynamic modes of a general crystal. It is not obvious that they describe six propagating sound modes and two diffusive modes. However, we can identify the propagating modes of a general crystal by examining the reversible Euler equations (i.e., the equations obtained by neglecting all terms involving transport coefficients). These equations are

$$\frac{\partial \vec{g}(\vec{r}t)}{\partial t} + \frac{1}{n_0} \nabla \cdot \underline{C} : \vec{u}(\vec{r}t) + \frac{1}{n_0} \vec{C}^q \cdot \nabla q(\vec{r}t) + \frac{1}{n_0} \vec{C}^c \cdot \nabla c(\vec{r}t) = 0 , \qquad (4.9a)$$

$$\frac{\partial \vec{\mathbf{u}}(\vec{\mathbf{r}}t)}{\partial t} + \frac{n_0}{\rho} [\nabla \vec{\mathbf{g}}(\vec{\mathbf{r}}t)] = 0 , \qquad (4.9b)$$

$$\frac{\partial q(\vec{x}t)}{\partial t} = 0 , \qquad (4.9c)$$

$$\frac{\partial c(\mathbf{\bar{r}}t)}{\partial t} = 0 \quad . \tag{4.9d}$$

These can be reduced to one nontrivial secondorder equation by taking $\partial/\partial t$ of (4.9a),

$$\left(\overline{1} \frac{\partial^2}{\partial t^2} - \frac{1}{\rho} \nabla \cdot \underline{C} \cdot \nabla\right) \cdot \overline{g}(\overline{r}t) = 0 . \qquad (4.10)$$

Equation (4.10) is the usual^{6,7,15} equation describing sound propagation in solids. We can most easily solve (4.10) by Fourier-Laplace transformation. The transformed equation is

$$\left(-z^{2}\vec{1}+\frac{\vec{k}\cdot\underline{C}\cdot\vec{k}}{\rho}\right)\cdot\vec{g}(\vec{k}z)=\dot{\vec{g}}(\vec{k})-iz\vec{g}(\vec{k}),$$
(4.11)

where

$$\vec{g}(\vec{k}z) = \int_0^\infty dt \int d\vec{r} \, e^{izt} \, e^{-i\vec{k}\cdot\vec{r}} \vec{g}(\vec{r}t) ,$$
$$\vec{g}(\vec{k}) = \int d\vec{r} \, e^{i\vec{k}\cdot\vec{r}} \vec{g}(\vec{r}, t=0) ,$$
$$\vec{g}(\vec{k}) = \int d\vec{r} \, e^{i\vec{k}\cdot\vec{r}} \left[\frac{\partial}{\partial t} \, \vec{g}(\vec{r}t)\right]_{t=0} .$$

The sound velocities are obtained from the solution to the eigenvalue problem

$$\left(\frac{\hat{k}\cdot\underline{C}\cdot\hat{k}}{\rho}-c_{\lambda}^{2}\right)\cdot\hat{e}_{\lambda}=0, \qquad (4.12)$$

where \hat{k} is the unit vector along \vec{k} , $\lambda = 1, 2, 3$ labels

the eigenvalues, and the eigenvectors are denoted by $\hat{e}_{\lambda}.$

We can solve (4.8) in terms of these eigenvalues and eigenvectors,

$$g_{\lambda}(\mathbf{k}z) = \mathbf{g}(\mathbf{k}z) \cdot \mathbf{\hat{e}}_{\lambda} = \frac{\mathbf{\hat{g}}_{\lambda}(\mathbf{k}) - izg_{\lambda}(\mathbf{k})}{-z^2 + c_{\lambda}^2 k^2} \quad . \tag{4.13}$$

Thus (4.13) describes six propagating sound modes, $z = \pm c_{\lambda}k$, of the system. These modes are not attenuated in this approximation since we have neglected the dissipative coefficients.

When dissipation is included, (4.9c) and (4.9d)are replaced by (coupled) diffusion equations. In the Sec. V the full equations, including dissipation for certain selected directions of propagation in cubic crystals, will be discussed. In a subsequent paper¹⁰ the solutions of these equations will be discussed for isotropic amorphous solids.

V. HYDRODYNAMIC EQUATIONS FOR CUBIC CRYSTALS

In this section we will discuss the hydrodynamic equations for the particular case of cubic crystals. We shall see that the equations simplify somewhat and can be analytically solved for certain directions of propagation.

The thermodynamic derivatives and transport coefficients for cubic crystals are simpler than for any other type of crystal. The simplifications are summarized in Appendix B. With these simplifications of coefficients, the Fourier-Laplace transforms of the hydrodynamic equations are of the form

$$(-iz\vec{1}+\vec{k}\cdot\underline{D}^{e}\cdot\vec{k})\cdot\vec{g}(\vec{k}z)+\frac{i}{n_{0}}\vec{k}\cdot[\underline{C}:\vec{u}(\vec{k}z)]+\frac{i}{n_{0}}C^{e}\vec{k}q(\vec{k}z)+\frac{i}{n_{0}}C^{e}\vec{k}c(\vec{k}z)=\vec{g}(\vec{k}), \qquad (5.1a)$$

$$(-iz\underline{1}^{4} + \underline{D}^{u}:\vec{k}\vec{k}):\vec{u}(\vec{k}z) + \frac{in_{0}}{2\rho}[\vec{k}\vec{g}(\vec{k}z) + \vec{g}(\vec{k}z)\vec{k}] + D^{uq}\vec{k}\vec{k}q(\vec{k}z) + D^{uc}\vec{k}\vec{k}c(\vec{k}z) = \vec{u}(\vec{k}), \qquad (5.1b)$$

$$(-iz+D^{a}k^{2})q(\vec{k}z)+D^{ac}k^{2}c(\vec{k}z)+\vec{k}\vec{k}:\underline{D}^{au}:\vec{u}(\vec{k}z)=q(\vec{k}), \qquad (5.1c)$$

$$(-iz+D^{c}k^{2})c(\vec{k}z)+D^{cq}k^{2}q(\vec{k}z)+\vec{k}\vec{k}:D^{cu}:\vec{u}(\vec{k}z)=c(\vec{k}).$$
(5.1d)

Although these equations are simpler than in a general crystal, they still involve couplings amongst all of the eight hydrodynamic variables for most directions of propagation. However, for certain special directions of \vec{k} , the equations separate into subsets. When the directions of propagation (\vec{k}) are the [100], [110], [111], or equivalent directions, the equations can be separated into longitudinal and transverse components. Then the equations separate into one set of four equations and two sets of two equations each. For these directions we have the set of four longitudinal equations:

$$(-iz + D_L^{\mathscr{E}}k^2)g_L(\mathbf{k}z) + \frac{ik}{n_0}C_L n_0(\mathbf{k}z) + i\frac{C^{\mathscr{E}}k}{n_0}q(\mathbf{k}z) + i\frac{C^c k}{n_0}c(\mathbf{k}z) = g_L(\mathbf{k}), \qquad (5.2a)$$

$$(-iz + D_L^{u}k^2)n_0(\vec{k}z) + i\frac{n_0}{\rho}kg_L(\vec{k}z) + D^{uq}k^2q(\vec{k}z) + D^{uc}k^2c(\vec{k}z) = n_0(\vec{k}) , \qquad (5.2b)$$

$$(-iz + D^{q}k^{2})q(\vec{k}z) + D^{qc}k^{2}c(\vec{k}z) + D_{L}^{qu}k^{2}n_{0}(\vec{k}z) = q(\vec{k}) , \qquad (5.2c)$$

$$(-iz + D^{c}k^{2})c(\vec{k}z) + D^{ca}k^{2}q(\vec{k}z) + D_{L}^{ca}k^{2}n_{0}(\vec{k}z) = c(\vec{k}) , \qquad (5.2d)$$

where

 $g_L(\vec{\mathbf{k}}z) = \vec{\mathbf{g}}(\vec{\mathbf{k}}z) \cdot \hat{k} , \qquad n_0(\vec{\mathbf{k}}z) = u_L(\vec{\mathbf{k}}z) = \hat{k} \cdot \vec{\mathbf{u}}(\vec{\mathbf{k}}z) \cdot \hat{k} ,$

$$D_{L}^{g} = \begin{cases} \eta_{11}/\rho & \text{if } \hat{k} = \hat{e}_{x}, \ \hat{e}_{y}, \text{ or } \hat{e}_{z}, \\ [\eta_{44} + \frac{1}{2}(\eta_{11} + \eta_{12})]/\rho & \text{if } \hat{k} = \frac{1}{2}\sqrt{2}(\hat{e}_{x} + \hat{e}_{y}), \text{ etc. }, \\ (\frac{1}{3}\eta_{12} + \frac{2}{3}\eta_{12} + \frac{4}{3}\eta_{44})/\rho & \text{if } \hat{k} = \frac{1}{3}\sqrt{3}(\hat{e}_{x} + \hat{e}_{y} + \hat{e}_{z}), \\ \\ C_{L} = \begin{cases} C_{11} & \text{if } \hat{k} = \hat{e}_{x}, \text{ etc. }, \\ C_{44} + \frac{1}{2}(C_{11} + C_{12}) & \text{if } \hat{k} = \frac{1}{2}\sqrt{2}(\hat{e}_{x} + \hat{e}_{y}), \text{ etc. }, \\ \frac{1}{3}C_{11} + \frac{2}{3}C_{12} + \frac{4}{3}C_{44} & \text{if } \hat{k} = \frac{1}{3}\sqrt{3}(\hat{e}_{x} + \hat{e}_{y} + \hat{e}_{z}), \\ \\ \frac{1}{3}C_{11} + \frac{2}{3}C_{12} + \frac{4}{3}C_{44} & \text{if } \hat{k} = \frac{1}{3}\sqrt{3}(\hat{e}_{x} + \hat{e}_{y} + \hat{e}_{z}), \\ \\ D_{L}^{g} = \begin{cases} D_{11} & \text{if } \hat{k} = \hat{e}_{x}, \text{ etc. }, \\ D_{44} + \frac{1}{2}(D_{11} + D_{12}) & \text{if } \hat{k} = \frac{1}{2}\sqrt{2}(e_{x} + e_{y}), \text{ etc. }, \\ \\ \frac{1}{3}D_{11} + \frac{2}{3}D_{12} + \frac{4}{3}D_{44} & \text{if } \hat{k} = \frac{1}{3}\sqrt{3}(\hat{e}_{x} + \hat{e}_{y} + \hat{e}_{z}), \\ \\ \\ D_{L}^{gu} - \alpha\left(\frac{\partial T}{\partial n_{0}}\right)_{s,c} - \xi \frac{\rho}{n_{0}}\left(\frac{\partial \phi}{\partial \rho}\right)_{s,u} = \frac{\xi}{n_{0}^{2}}G_{L} = \begin{cases} (\xi/n_{0}^{2})G_{11} & \text{if } \hat{k} = \frac{1}{2}\sqrt{2}(\hat{e}_{x} + \hat{e}_{y}), \text{ etc. }, \\ (\xi/n_{0}^{2})[G_{44} + \frac{1}{2}(G_{11} + G_{12})] & \text{if } \hat{k} = \frac{1}{3}\sqrt{3}(\hat{e}_{x} + \hat{e}_{y} + \hat{e}_{z}), \\ \\ (\xi/n_{0}^{2})(\frac{1}{3}G_{11} + \frac{2}{3}G_{12} + \frac{4}{3}G_{44}) & \text{if } \hat{k} = \frac{1}{3}\sqrt{3}(\hat{e}_{x} + \hat{e}_{y} + \hat{e}_{z}), \end{cases}$$

and

$$D_L^{cu} - \frac{\rho \xi}{mn_0^2 T} \left(\frac{\partial T}{\partial n_0}\right)_{s,c} - \frac{\zeta \rho^2}{mn_P^3} \left(\frac{\partial \phi}{\partial \rho}\right)_{s,u} = \frac{\rho \zeta}{mn_0^4} G_L .$$

The quantities η_{11} , C_{11} , G_{11} , etc., are defined in Appendix B. The two pairs of transverse equations are of the form

$$(-iz + D_i^{g}k^2)g_i(\vec{k}z) + \frac{2i}{n_0}kC_iu_i(\vec{k}z) = g_i(\vec{k}), \qquad (5.3a)$$
$$(-iz + D_i^{u}k^2)u_i(\vec{k}z) + \frac{in_0}{2\rho}kg_i(\vec{k}z) = u_i(\vec{k}), \qquad (5.3b)$$

where

$$g_i(\vec{k}z) = \hat{e}_i \cdot \vec{g}(\vec{k}z), \qquad u_i(\vec{k}z) = \hat{k} \cdot \vec{u}(\vec{k}z) \cdot \hat{e}_i, \qquad i = 1, 2,$$

$$\hat{e}_{1} = \begin{cases} \hat{e}_{y}, & \hat{e}_{2} = \begin{cases} \hat{e}_{z} & \text{if } \hat{k} = \hat{e}_{x}, \\ \hat{e}_{z} & \text{if } \hat{k} = \frac{1}{2}\sqrt{2} (\hat{e}_{x} + \hat{e}_{y}), \\ \text{any unit vector orthogonal to } \hat{k}, & \hat{e}_{2} = \begin{cases} \hat{e}_{z} & \text{if } \hat{k} = \frac{1}{2}\sqrt{2} (\hat{e}_{x} + \hat{e}_{y}), \\ \hat{k} \times \hat{e}_{1}/|\hat{k} \times \hat{e}_{1}| & \text{if } \hat{k} = \frac{1}{2}\sqrt{2} (\hat{e}_{x} + \hat{e}_{y}), \\ \hat{k} \times \hat{e}_{1}/|\hat{k} \times \hat{e}_{1}| & \text{if } \hat{k} = \frac{1}{3}\sqrt{3} (\hat{e}_{x} + \hat{e}_{y} + \hat{e}_{z}), \end{cases}$$

$$D_{1}^{g} = \begin{cases} \eta_{44}/\rho, & D_{1}^{g} = \begin{cases} D_{1}^{g} & \text{if } \hat{k} = \hat{e}_{x}, \\ (\eta_{11} - \eta_{12})/2\rho, & D_{2}^{g} = \begin{cases} D_{1}^{g} & \text{if } \hat{k} = \frac{1}{2}\sqrt{2} (\hat{e}_{x} + \hat{e}_{y}), \\ (\frac{1}{3}\eta_{44} + \frac{1}{3}\eta_{11} - \frac{1}{3}\eta_{12})/\rho, & D_{1}^{g} \end{cases} \\ (\frac{1}{3}\eta_{44} + \frac{1}{3}\eta_{11} - \frac{1}{3}\eta_{12})/\rho, & C_{2} = \begin{cases} C_{1} & \text{if } \hat{k} = \hat{e}_{x}, \\ D_{1}^{g} & \text{if } \hat{k} = \frac{1}{2}\sqrt{2} (\hat{e}_{x} + \hat{e}_{y}), \\ (\frac{1}{3}C_{44} + \frac{1}{3}C_{11} - \frac{1}{3}C_{12}, & C_{2} = \begin{cases} C_{1} & \text{if } \hat{k} = \frac{1}{2}\sqrt{2} (\hat{e}_{x} + \hat{e}_{y}), \\ C_{1} & \text{if } \hat{k} = \frac{1}{3}\sqrt{3} (\hat{e}_{x} + \hat{e}_{y} + \hat{e}_{z}), \end{cases} \\ D_{1}^{g} & \text{if } \hat{k} = \frac{1}{2}\sqrt{2} (\hat{e}_{x} + \hat{e}_{y}), \\ \frac{1}{3}D_{44} + \frac{1}{3}D_{11} - \frac{1}{3}D_{12}, & D_{2}^{g} = \begin{cases} D_{1}^{g} & \text{if } \hat{k} = \frac{1}{2}\sqrt{2} (\hat{e}_{x} + \hat{e}_{y}), \\ D_{1}^{g} & \text{if } \hat{k} = \frac{1}{2}\sqrt{2} (\hat{e}_{x} + \hat{e}_{y}), \\ D_{1}^{g} & \text{if } \hat{k} = \frac{1}{3}\sqrt{3} (\hat{e}_{x} + \hat{e}_{y} + \hat{e}_{z}) \end{cases} \\ \end{pmatrix}$$

The two transverse equations can be solved immediately. It is easy to show that

$$g_{i}(\vec{k}z) = \frac{(-iz + D_{i}^{u}k^{2})g_{i}(\vec{k}) + (2iC_{i}k/n_{0})u_{i}(\vec{k})}{-z^{2} - izD_{i}^{T}k^{2} + c_{i}^{2}k^{2}},$$
(5.4a)

$$u_{i}(\vec{\mathbf{k}}z) = \frac{(-iz + D_{i}^{g}k^{2})u_{i}(\vec{\mathbf{k}}) + \frac{1}{2}(i)(n_{0}/\rho)kg_{i}(\vec{\mathbf{k}})}{-z^{2} - izD_{i}^{T}k^{2} + c_{i}^{2}k^{2}} , \qquad (5.4b)$$

where

$$c_i^2 = \frac{C_i}{\rho}$$
 and $D_i^T = D_i^u + D_i^g$.

These solutions are identical to those obtained in the usual treatment^{6,7,16} of the transverse sound equations in solids except for the appearance of the new transport coefficient (in D_i^u).

The longitudinal equations can also be solved in a reasonably transparent form. The equations can be put in a more suggestive form in terms of the variables ρ , g_L , q, and c instead of the variables n_0 , g_L , q, and c. The transformed equations are

$$-iz\rho(\mathbf{k}z) + ikg_L(\mathbf{k}z) = \rho(k) , \qquad (5.5a)$$

$$(-iz+D_L^g k^2)g_L(\mathbf{\bar{k}}z) + \frac{ik}{\rho}C_L\rho(\mathbf{\bar{k}}z) + \frac{ik}{n_0}C^q(\mathbf{\bar{k}}z) + \frac{ik}{n_0}\overline{C}^c c(\mathbf{\bar{k}}z) = g_L(\mathbf{\bar{k}}), \qquad (5.5b)$$

$$(-iz+D^{q}k^{2})q(\vec{k}z)+\overline{D}^{qc}k^{2}c(\vec{k}z)+D^{qc}k^{2}\rho(\vec{k}z)=q(\vec{k}), \qquad (5.5c)$$

$$(-iz+\overline{D}^{c}k^{2})c(\overline{k}z)+D^{cq}k^{2}q(\overline{k}z)+D^{cr}k^{2}\rho(\overline{k}z)=c(\overline{k}), \qquad (5.5d)$$

where

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$$\begin{split} \overline{C}^{c} &= C^{c} + \frac{mn_{0}^{2}}{\rho} C_{L} = n_{0} \overline{k} \cdot \left(\frac{\partial \overline{\sigma}^{R}}{\partial c} \right)_{s,\rho} \cdot \overline{k} ,\\ \overline{D}^{ac} &= D^{ac} + \frac{mn_{0}^{2}}{\rho} D_{L}^{au} = \alpha \left(\frac{\partial T}{\partial c} \right)_{s,\rho} + \frac{mn_{0}\xi}{\rho} G_{L} ,\\ D^{a\rho} &= \frac{n_{0}}{\rho} D_{L}^{au} , \qquad D^{c\rho} = \frac{n_{0}}{\rho} D_{L}^{cu} ,\\ \overline{D}^{c} &= D^{c} + \frac{mn_{0}^{2}}{\rho} D_{L}^{cu} = \mathbf{k} \, \mathbf{k} : \left[\frac{\xi\rho}{mn_{0}^{2}} \left(\frac{\partial \overline{\phi}}{\partial c} \right)_{s,\rho} + \frac{\rho\xi}{mn_{0}^{2}} \left(\frac{\partial T}{\partial c} \right)_{s,\rho} \overline{1} \right]. \end{split}$$

Equations (5.5) are isomorphic with the hydrodynamic equations in a binary mixture.¹⁷ The vacancy concentration c is identified with the concentration of one of the species in the mixture. The longitudinal part of ϕ is to be identified with the chemical potential. In particular we identify

$$\mu(kz) \equiv \frac{\mu_1(\bar{k}z)}{m_1} - \frac{\mu_2(\bar{k}z)}{m_2} \longrightarrow \frac{mn_0^2}{\rho} \,\hat{k} \cdot \vec{\phi}(\bar{k}z) \cdot \hat{k} \equiv \frac{mn_0^2}{\rho} \,\phi_L(\bar{k}z) \tag{5.6}$$

for the mixture and the solid, respectively. $(mn_0^2/\rho^2)\phi_L$ is essentially a "chemical potential" of vacancies.¹¹ The pressures in the binary mixtures must here be identified with the longitudinal stress (a kind of "longi-tudinal pressure")

$$P(kz) \leftrightarrow P_L(\vec{k}z) = \hat{k} \cdot \vec{\sigma}^R(\vec{k}z) \cdot \hat{k} = P(kz) + n_0 \hat{k} \cdot \vec{\phi}'(\vec{k}z) \cdot \hat{k} .$$
(5.7)

On the other hand, one can show that (Appendix C)

$$\hat{k} \cdot \hat{\phi}'(\bar{k}z) \cdot \hat{k} = \frac{2}{3} \phi_L(\bar{k}z) .$$
(5.8)

We then have for the longitudinal pressure

$$P_L(kz) = P(kz) + \frac{2}{3}n_0\phi_L(kz) .$$
 (5.9)

With these identifications we can easily solve Eqs. (5.5) by following the corresponding solution in the binary-mixture case. The full solutions are complicated and will not be explicitly provided here. However, it is instructive to display the mode structure of the solution. This structure is seen most easily in the determinant of the 4×4 matrix defined by the left-hand side of (5.5). This determinant, which when set equal to zero gives the dispersion relation for the hydrodynamic modes, is seen to be of the form¹⁷

$$\det M = (-iz + D_1k^2)(-iz + D_2k^2)(-iz + ic_0k + \Gamma k^2)(-iz - ic_0k + \Gamma k^2),$$
(5.10)

where

$$c_{0} = (C_{L}/\rho)^{1/2} \text{ (sound velocity) ,}$$

$$2\Gamma = D_{L}^{\ell} + D_{T}(\gamma_{L} - 1) + Dmn_{0}^{2}c_{P}^{2} \left(\frac{\partial\phi_{L}}{\partial c}\right)_{P_{L},T} \Phi^{2}, \qquad D_{T} = \frac{\kappa}{\rho c_{P_{L},c}} ,$$

$$\kappa = \alpha - \frac{\xi^{2}}{T\zeta}, \qquad \gamma_{L} = \frac{c_{P_{L},c}}{c_{\rho,c}}, \qquad c_{P_{L},c} = T\left(\frac{\partial s}{\partial T}\right)_{P_{L},c}, \qquad c_{\rho,c} = T\left(\frac{\partial s}{\partial T}\right)_{\rho,c},$$

$$D = \frac{\zeta\rho}{mn_{0}^{2}} \left(\frac{\partial\phi_{L}}{\partial c}\right)_{T,P_{L}}, \qquad \Phi = \frac{k_{p}}{P} + \frac{k_{T}\alpha_{T}}{\rho c_{P_{L},c}}, \qquad k_{p} = P\left(\frac{\partial\phi_{L}}{\partial P_{L}}\right)_{T,c} / \left(\frac{\partial\phi}{\partial c}\right)_{T,P_{L}},$$

$$k_{T} = \left[\xi + T\zeta\left(\frac{\partial\phi_{L}}{\partial T}\right)_{c,P_{L}}\right] \frac{\rho}{mn_{0}^{2}D}, \qquad \alpha_{T} = -\frac{1}{\rho} \left(\frac{\partial\rho}{\partial T}\right)_{P_{L},c}, \qquad D_{1} = \frac{1}{2}(D_{T} + \mathfrak{D}) + \frac{1}{2}[(D_{T} + \mathfrak{D})^{2} - 4D_{T}\mathfrak{D}]^{1/2},$$
ith

with

$$\mathfrak{D} = D \left[1 + \frac{k_T^2 m n_0^2}{T c_{P_L,c} \rho^2} \left(\frac{\partial \phi_L}{\partial c} \right)_{P_L,T} \right]$$

The thermodynamic derivatives evaluated at constant P_L are not easily identified with a simple experiment. However, we can easily relate these to the corresponding constant-pressure derivatives with use of (5.9). For example,

$$\left(\frac{\partial \phi_L}{\partial c}\right)_{P_L,T} = \hat{k} \cdot \left(\frac{\partial \phi}{\partial c}\right)_{P_L,T} \cdot \hat{k}$$

$$= \left(\frac{\partial \phi_L}{\partial c}\right)_{P,T} + \left(\frac{\partial \phi_L}{\partial P}\right)_{T,c} \left(\frac{\partial P}{\partial c}\right)_{P_L,T} \cdot$$

$$(5.11)$$

But from (5.9)

$$\left(\frac{\partial P}{\partial c}\right)_{P_{L},T} = -\frac{2}{3}n_{0}\left(\frac{\partial \phi_{L}}{\partial c}\right)_{P_{L},T} .$$
 (5.12)

Substituting into (5.11) and solving for $(\partial \phi_L / \partial c)_{P_L,T}$ we obtain

$$\left(\frac{\partial\phi_L}{\partial c}\right)_{P_L,T} = \frac{(\partial\phi_L/\partial c)_{P,T}}{1 + \frac{2}{3}n_0(\partial\phi_L/\partial P)_{T,c}} \quad . \tag{5.13}$$

In a similar manner we can show that

$$c_{P_L,c} = c_{P,c} - \frac{\frac{2}{3}(\partial S/\partial P)_{c,T}(\partial \phi_L/\partial T)_{P,c}n_0T}{1 + \frac{2}{3}n_0(\partial \phi_L/\partial P)_{T,c}},$$
(5.14a)

$$\left(\frac{\partial \phi_L}{\partial P_L}\right)_{T,c} = \frac{(\partial \phi_L/\partial P)_{T,c}}{1 + \frac{2}{3}n_0(\partial \phi_L/\partial P)_{T,c}} , \qquad (5.14b)$$

$$\left(\frac{\partial \phi_L}{\partial T}\right)_{c,P_L} = \frac{(\partial \phi_L/\partial T)_{P,c}}{1 + \frac{2}{3}n_0(\partial \phi_L/\partial P)_{T,c}}, \qquad (5.14c)$$

$$\alpha_{T} = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_{P,c} + \frac{\frac{2}{3} (n_{0}/\rho) (\partial \rho/\partial P)_{c,T} (\partial \phi_{L}/\partial T)_{P,c}}{1 + \frac{2}{3} n_{0} (\partial \phi_{L}/\partial P)_{T,c}}$$
(5.14d)

Equations (5.4) and (5.10) constitute a complete description of the hydrodynamic mode structure of

a cubic crystal when the wave vector is along certain special directions. For these directions of propagation, we do see the predicted eight hydrodynamic modes; two longitudinal diffusive modes, two longitudinal propagating sound modes, and four transverse propagating sound modes. We would expect that the spectrum of light scattered with momentum transfer in the [100], [110], [111], or equivalent directions would be indicative of this mode structure. The sound modes are well known as the Brillouin components of both polarized and depolarized spectra. 7,18 In the case of the polarized Brillouin components, the width of these components $(2\Gamma k^2)$, which represents the sound-absorption coefficient, contains an extra term due to vacancy diffusion. The two coupled diffusive modes described by D_1 and D_2 should appear as the central (unshifted) Rayleigh component of the spectra. This component could be resolved into two components (exponential in time or Lorentzian in frequency) described by D and D_T if the thermal diffusion coefficient k_T is negligible or if¹⁷ $D_T \gg D$; both are reasonable assumptions.

To our knowledge, these components have not been resolved for the spectrum of any crystalline system. Such a resolution may be possible in the spectra of light scattered from crystals near their melting point. At these relatively high temperatures the vacancy concentration should be high enough that their diffusion will give an appreciable contribution to the scattering.

VI. DISCUSSION

In this paper we have derived the general hydrodynamic equations for solids. This derivation has been based on the recognition that a crystal has three continuous broken symmetries in addition to the usual conservation laws of mass, momentum, and energy. Since a crystal breaks the translational invariance of the Hamiltonian of the system, it is necessary to treat the distortion \vec{R} (here actually its gradient) as a hydrodynamic variable. The recognition that lattice motion and particle motion need not be identical² required that n_0 = $-\nabla \cdot \vec{R}$ and the density ρ be independent variables. This led us naturally to introduce the vacancy concentration as an auxiliary variable. The additional hydrodynamic mode omitted from previous^{6, 7} treatments of hydrodynamics of solids was identified with vacancy diffusion.

For particular propagation directions in cubic crystals the longitudinal hydrodynamic equations obtained are identical to those of a binary mixture. In that case vacancy diffusion indeed plays the role of particle diffusion in a binary mixture. It is reasonable to expect that this interpretation is still approximately valid for arbitrary directions of propagation even in anisotropic crystals.

As in ordinary simple fluids, the hydrodynamics of solids are characterized by two kinds of coefficients, thermodynamic (reactive) and dissipative. The dissipative coefficients can be represented as a symmetric matrix of transport coefficients which connect the currents $\overline{\sigma}$, \overline{J}^e , and \overline{J}^R [cf. Eq. (3.11)] to the gradients of \overline{v} , T, and $\overline{\phi}$:

$$\begin{pmatrix} \underline{\eta} & 0 & 0\\ 0 & \overline{\alpha} & \overline{\xi}\\ 0 & \overline{\xi}^{T} & \overline{\xi} \end{pmatrix}.$$
(6.1)

The reactive coefficients can be represented by a matrix of thermodynamic derivatives which relate the fluctuations of the conjugate variables to those of the direct hydrodynamic variables²:

$$\begin{pmatrix} \left(\frac{\partial P}{\partial \rho}\right)_{\mathbf{s},\vec{u}} & \left(\frac{\partial T}{\partial \rho}\right)_{\mathbf{s},\vec{u}} & \left(\frac{\partial \overline{\phi}}{\partial \rho}\right)_{\mathbf{s},\vec{u}} \\ \left(\frac{\partial P}{\partial s}\right)_{\rho,\vec{u}} & \left(\frac{\partial T}{\partial s}\right)_{\rho,\vec{u}} & \left(\frac{\partial \overline{\phi}}{\partial s}\right)_{\rho,\vec{u}} \\ \left(\frac{\partial P}{\partial \overline{u}}\right)_{\mathbf{s},\rho} & \left(\frac{\partial T}{\partial \overline{u}}\right)_{\mathbf{s},\rho} & \left(\frac{\partial \overline{\phi}}{\partial \overline{u}}\right)_{\mathbf{s},\rho} \end{pmatrix}.$$
(6.2)

As seen in Sec. IV it is often convenient to work in terms of the equivalent matrix

$$\begin{pmatrix} \left(\frac{\partial \,\overline{\sigma}^{\,R}}{\partial \,\overline{u}}\right)_{s,c} & \left(\frac{\partial \,\overline{u}}{\partial \,\overline{u}}\right)_{s,c} & \left(\frac{\partial \,\overline{u}}{\partial \,\overline{u}}\right)_{s,c} \\ \left(\frac{\partial \,\overline{\sigma}^{\,R}}{\partial s}\right)_{\overline{u},c} & \left(\frac{\partial \,T}{\partial s}\right)_{\overline{u},c} & \left(\frac{\partial \,\Pi}{\partial s}\right)_{\overline{u},c} \\ \left(\frac{\partial \,\overline{\sigma}^{\,R}}{\partial c}\right)_{\overline{u},s} & \left(\frac{\partial \,T}{\partial c}\right)_{\overline{u},s} & \left(\frac{\partial \,\Pi}{\partial c}\right)_{\overline{u},s} \end{pmatrix}.$$
(6.3)

The Maxwell relations require that these matrices

be equivalent to symmetric matrices. One thermodynamic derivative,

$$\frac{\vec{1}}{\rho} = \frac{\vec{1}}{mn} = \frac{\partial \vec{\nabla}}{\partial \vec{g}} , \qquad (6.4)$$

is omitted from the matrices (6.2) and (6.3) since it is trivially separated from the others by Galilean invariance.

For a general (anisotropic) crystal there are 21 + 6 + 6 + 9 = 42 independent elements in the dispative matrix (6.1) and 21+6+6+3=36 independent elements in the reactive matrix (6.2) or (6.3). This is too large a number to reasonably sort out in any set of experiments. However, for a uniaxial crystal these numbers reduce to 5+2+2+2=11transport coefficients and 5+2+2+3=12 thermodynamic derivatives. In a cubic crystal there are 3+1+1+1=6 transport and 3+1+1+3=8 reactive coefficients. For an isotropic (amorphous) solid there is one less viscosity and one less elastic constant than in a cubic crystal. This count of coefficients is summarized in Table I. In cubic and amorphous solids it seems reasonable to hope to determine the reactive and dissipative coefficients in a small set of mechanical or scattering experiments.

As pointed out in Ref. 2 the hydrodynamic equations for smectic *B* liquid crystals are identical to those in a uniaxial crystal except that two of the five elastic constants, $(\partial \overline{\sigma}^R / \partial \overline{u})_{s,c}$, must be of order k^2 . Thus our equations are formally valid, with the appropriate modification for smectic *B* liquid crystals. Recently¹⁹ it has been shown that the low-temperature "crystal" phase in phospholipid bilayers and biological membranes may be described essentially as a smectic *B* liquid crystal. Our equations would hence also describe the mechanical and hydrodynamic properties of certain biological membranes.

In a subsequent paper we will apply our equations specifically to amorphous solids. In particular we will discuss in detail the expected spectrum of scattered light in amorphous solids.

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APPENDIX A: MAXWELL RELATIONS

In this appendix we derive the other Maxwell relations which must be employed in the thermodynamics of solids. We have already derived the relations involving the variables ρ , s, \vec{g} , and \vec{u}

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TABLE I. Number of independent components associated with the various dissipative (transport) and reactive (thermodynamic) coefficients.

Dissipative						Reactive					
Solid	η	₩ κ	ξ	ţ.	$\left(\frac{\partial P}{\partial \rho}\right)_{\!$	$\left(\frac{\partial T}{\partial \rho}\right)_{\!$	$\left(\frac{\partial T}{\partial s}\right)_{\rho, \stackrel{\leftarrow}{u}}$	$\left(\frac{\partial \overleftarrow{\phi}}{\partial \rho}\right)_{\!\!\boldsymbol{s},\overrightarrow{\boldsymbol{u}}}$	$\left(\frac{\partial \dot{\phi}}{\partial s}\right)_{\rho, \dot{\mathbf{u}}}$	$\left(\frac{\partial \overrightarrow{\phi}}{\partial \overrightarrow{u}}\right)_{s,\rho}$	
General crystal	21	6	9	6	1	1	1	6	6	21	
Uniaxial crystal	5	2	2	2	1	1	1	2	2	5	
Cubic crystal	3	1	1	1	1	1	1	1	1	3	
Isotropic	2	1	1	1	1	1	1	1	1	2	

from the differential of the energy density. We obtain the relations appropriate for the variables P, s, \vec{v} , and \vec{u} from the enthalpy (per unit mass)

$$h = (\epsilon + P)/\rho \quad . \tag{A1}$$

Then we have

$$dh = T ds + \frac{dP}{\rho} + \vec{\nabla} \cdot d\vec{\nabla} + \mathrm{Tr}\vec{\phi} \cdot d\left(\frac{\vec{u}}{\rho}\right). \tag{A2}$$

The natural variables for h are s, P, and \overline{u}/ρ (strain per unit mass). The corresponding Maxwell relations are

$$\left(\frac{\partial T}{\partial P}\right)_{\mathbf{s},\vec{\mathbf{u}}/\rho} = -\frac{1}{\rho^2} \left(\frac{\partial \rho}{\partial s}\right)_{\mathbf{P},\vec{\mathbf{u}}/\rho}, \qquad (A3a)$$

$$\left(\frac{\partial T}{\partial(\vec{u}/\rho)}\right)_{s,P} = \left(\frac{\partial \vec{\phi}}{\partial s}\right)_{P,\vec{u}/\rho}, \quad (A3b)$$

$$\left(\frac{\partial \vec{\phi}}{\partial P}\right)_{\mathbf{s},\vec{\mathbf{u}}/\rho} = -\frac{1}{\rho^2} \left(\frac{\partial \rho}{\partial (\vec{\mathbf{u}}/\rho)}\right)_{\mathbf{s},P} . \tag{A3c}$$

We can convert these to relations involving the variables s, P, and \overline{u} via an exercise in partial derivatives. For example we have

$$\left(\frac{\partial T}{\partial P}\right)_{s,\,\overline{u}/\rho} = \left(\frac{\partial T}{\partial P}\right)_{s,\,\overline{u}} + \operatorname{Tr}\left(\frac{\partial T}{\partial \overline{u}}\right)_{s,\,\rho} \cdot \left(\frac{\partial \overline{u}}{\partial P}\right)_{s,\,\overline{u}/\rho} .$$
(A4)

But

$$\left(\frac{\partial \vec{\mathbf{u}}}{\partial P}\right)_{\mathbf{s},\vec{\mathbf{u}}/\rho} = \frac{\vec{\mathbf{u}}}{\rho} \left(\frac{\partial \rho}{\partial P}\right)_{\mathbf{s},\vec{\mathbf{u}}/\rho} \tag{A5}$$

and

$$\begin{pmatrix} \frac{\partial \rho}{\partial \rho} \end{pmatrix}_{\mathbf{s}, \mathbf{\tilde{u}}/\rho} = \begin{pmatrix} \frac{\partial \rho}{\partial \rho} \end{pmatrix}_{\mathbf{s}, \mathbf{\tilde{u}}} + \operatorname{Tr} \left(\frac{\partial \rho}{\partial \mathbf{\tilde{u}}} \right)_{\mathbf{s}, p} \cdot \frac{\mathbf{\tilde{u}}}{\rho} \begin{pmatrix} \frac{\partial \rho}{\partial P} \end{pmatrix}_{\mathbf{s}, \mathbf{\tilde{u}}/\rho}$$
$$= \frac{(\partial \rho / \partial P)_{\mathbf{s}, \mathbf{\tilde{u}}}}{1 - \operatorname{Tr}(\mathbf{\tilde{u}}/\rho) \circ (\partial \rho / \partial \mathbf{\tilde{u}})_{\mathbf{s}, p}} .$$
(A6)

So

$$\left(\frac{\partial T}{\partial P}\right)_{\mathbf{s}_{\mathbf{v}}\vec{\mathbf{u}}/\rho} = \left(\frac{\partial T}{\partial P}\right)_{\mathbf{s}_{\mathbf{v}}\vec{\mathbf{u}}} + \frac{\mathrm{Tr}(\vec{\mathbf{u}}/\rho) \cdot (\partial T/\partial \vec{\mathbf{u}})_{\mathbf{s}_{\mathbf{v}}} \rho(\partial \rho/\partial P)_{\mathbf{s}_{\mathbf{v}}\vec{\mathbf{u}}}}{1 - \mathrm{Tr}(\vec{\mathbf{u}}/\rho) \cdot (\partial \rho/\partial \vec{\mathbf{u}})_{\mathbf{s}_{\mathbf{v}}\rho}} .$$
(A7)

By a similar argument we can show that

$$\left(\frac{\partial\rho}{\partial s}\right)_{P,\vec{u}/\rho} = \frac{(\partial\rho/\partial s)_{P,\vec{u}}}{1 - (\vec{u}/\rho) \cdot (\partial\rho/\partial\vec{u})_{s,\rho}} .$$
(A8)

Thus equating (A7) and (A8) and simplifying the expressions, we obtain

$$\frac{-1}{\rho^2} \left(\frac{\partial \rho}{\partial s} \right)_{P, \overline{u}} = \left(\frac{\partial T}{\partial P} \right)_{s, \overline{u}} + \operatorname{Tr} \frac{\overline{u}}{\rho} \cdot \left(\frac{\partial T}{\partial \overline{u}} \right)_{s, \rho} \left(\frac{\partial \rho}{\partial P} \right)_{s, T} .$$
(A9)

Similarily, we have

$$\rho\left(\frac{\partial T}{\partial \overline{\mathfrak{u}}}\right)_{s,\rho} = \left(\frac{\partial \overline{\phi}}{\partial s}\right)_{\rho,\overline{\mathfrak{u}}} + \left(\frac{\partial \rho}{\partial s}\right)_{\rho,\overline{\mathfrak{u}}} \left(\frac{\partial \overline{\phi}}{\partial \overline{\mathfrak{u}}}\right)_{\rho,\rho} : \frac{\overline{\mathfrak{u}}}{\rho} \qquad (A10)$$

and

$$\left(\frac{\partial\vec{\phi}}{\partial P}\right)_{s,\vec{u}} = \left(\frac{\partial\rho}{\partial s}\right)_{p,\vec{u}} \operatorname{Tr}\left(\frac{\partial\vec{\phi}}{\partial\vec{u}}\right)_{s,p} \cdot \frac{\vec{u}}{\rho} = -\frac{1}{\rho} \left(\frac{\partial\rho}{\partial\vec{u}}\right)_{s,p}.$$
 (A11)

Next we derive the Maxwell relations appropriate for the variables T, ρ , \vec{g} , and \vec{u} . Thus we consider the Helmholtz free-energy density

$$f = \epsilon - T\rho s , \qquad (A12)$$

which has the differential

$$df = -s\rho \, dT + \left(\frac{P+f - \mathrm{Tr}\,\vec{\mathbf{u}}\cdot\vec{\phi} - \vec{g}\cdot\vec{\mathbf{v}}}{\rho}\right) d\rho$$
$$+\vec{\mathbf{v}}\cdot d\vec{g} + \mathrm{Tr}\,\vec{\phi}\cdot d\vec{\mathbf{u}} . \tag{A13}$$

This leads to the set of Maxwell relations

$$\left(\frac{\partial s}{\partial \rho}\right)_{T,\vec{u}} = -\frac{1}{\rho^2} \left(\frac{\partial P}{\partial T}\right)_{\rho,\vec{u}} + \operatorname{Tr} \frac{\vec{u}}{\rho^2} \cdot \left(\frac{\partial \vec{\phi}}{\partial T}\right)_{\rho,\vec{u}}, \quad (A14a)$$

$$\left(\frac{\partial s}{\partial \tilde{\mathbf{u}}}\right)_{T,\rho} = -\frac{1}{\rho} \left(\frac{\partial \tilde{\phi}}{\partial T}\right)_{\tilde{\mathbf{u}},\rho} , \qquad (A14b)$$

$$\left(\frac{\partial P}{\partial \overline{\mathbf{u}}}\right)_{\rho,T} = \rho \left(\frac{\partial \overline{\phi}}{\partial \rho}\right)_{T,\overline{\mathbf{u}}} + \overline{\mathbf{u}} : \left(\frac{\partial \overline{\phi}}{\partial \overline{\mathbf{u}}}\right)_{\rho,T} .$$
(A14c)

In order to obtain the Maxwell relations appropriate for the variables s, ρ , \vec{g} , and $\vec{\phi}$ we consider a quantity which is equal to the energy in equilibrium, but differs from it outside,

$$\overline{\epsilon} = \epsilon - \mathrm{Tr}\overline{\phi} \cdot \overline{u} , \qquad (A15)$$

for which

$$d\overline{\epsilon} = T\rho \, ds + \left(\frac{P + \overline{\epsilon} - \overline{g} \cdot \overline{v}}{\rho}\right) d\rho + \overline{v} \cdot d\overline{g} - \mathrm{Tr} \, \overline{u} \cdot d\overline{\phi} \, . \tag{A16}$$

Hence we obtain

$$\left(\frac{\partial T}{\partial \rho}\right)_{s,\,\vec{o}} = \frac{1}{\rho^2} \left(\frac{\partial P}{\partial s}\right)_{\rho,\,\vec{o}} , \qquad (A17a)$$

$$\left(\frac{\partial T}{\partial \vec{\phi}}\right)_{s,\rho} = -\frac{1}{\rho} \left(\frac{\partial \vec{u}}{\partial s}\right)_{\rho,\vec{\phi}} , \qquad (A17b)$$

$$\frac{1}{\rho} \left(\frac{\partial P}{\partial \vec{\phi}} \right)_{s,\rho} = \frac{\vec{u}}{\rho} - \left(\frac{\partial \vec{u}}{\partial \rho} \right)_{s,\vec{\phi}} . \tag{A17c}$$

Next, the free energy which has as its natural variables T, P, \vec{v} , and \vec{u}/ρ is the Gibbs free energy (per unit mass),

$$\overline{\mu} = \frac{\epsilon + P - T\rho s - \vec{g} \cdot \vec{v}}{\rho} \quad . \tag{A18}$$

 $\overline{\mu}$ is equal to the chemical potential in equilibrium. Its differential is

$$d(\overline{\mu} + \frac{1}{2}v^2) = dP/\rho - s \, dT + \vec{\phi} \cdot d(\vec{u}/\rho) \, . \tag{A19}$$

Thus we obtain

$$\left(\frac{\partial s}{\partial P}\right)_{T,\vec{u}/\rho} = \frac{1}{\rho^2} \left(\frac{\partial \rho}{\partial T}\right)_{P,\vec{u}/\rho} , \qquad (A20a)$$

$$\left(\frac{\partial s}{\partial(\vec{\mathbf{u}}/\rho)}\right)_{\rho,T} = -\left(\frac{\partial \vec{\phi}}{\partial T}\right)_{\rho,\vec{\mathbf{u}}/\rho}, \qquad (A20b)$$

$$\frac{1}{\rho^2} \left(\frac{\partial \rho}{\partial (\mathbf{\tilde{u}}/\rho)} \right)_{P,T} = - \left(\frac{\partial \tilde{\phi}}{\partial P} \right)_{T,\mathbf{\tilde{u}}/\rho} .$$
(A20c)

To obtain the relations involving the variables T, P, and \vec{u} we employ a procedure similar to that used to obtain (A9). This procedure yields

$$\left(\frac{\partial s}{\partial P}\right)_{T,\vec{u}} + \frac{\vec{u}}{\rho} : \left(\frac{\partial s}{\partial \vec{u}}\right)_{T,P} \left(\frac{\partial \rho}{\partial P}\right)_{T,\vec{u}} = \frac{1}{\rho^2} \left(\frac{\partial \rho}{\partial T}\right)_{\rho,\vec{u}}, \quad (A21a)$$

$$\rho\left(\frac{\partial s}{\partial \overline{u}}\right)_{P,T} = \left(\frac{\partial \phi}{\partial T}\right)_{P,\overline{u}} + \left(\frac{\partial \rho}{\partial T}\right)_{P,\overline{u}} \left(\frac{\partial \phi}{\partial \overline{u}}\right)_{P,\rho} : \frac{\overline{u}}{\rho} , \quad (A12b)$$

$$\frac{1}{\rho} \left(\frac{\partial \rho}{\partial \vec{u}} \right)_{P,T} = - \left(\frac{\partial \vec{\phi}}{\partial P} \right)_{T,\vec{u}} - \left(\frac{\partial \rho}{\partial P} \right)_{T,\vec{u}} \left(\frac{\partial \vec{\phi}}{\partial \vec{u}} \right)_{T,\rho} : \frac{\vec{u}}{\rho} .$$
(A21c)

In order to obtain the Maxwell relations appropriate for the variables T, ρ , \vec{g} , and $\vec{\phi}$ we need to consider a free energy which is equal to the Helmholtz free energy in equilibrium,

$$\overline{f} = f - \operatorname{Tr} \overline{\mathbf{u}} \cdot \overline{\phi} . \tag{A22}$$

Its differential is

$$d\overline{f} = -s dT + \frac{P + \overline{f} - \overline{g} \cdot \overline{v}}{\rho} d\rho + \overline{v} \cdot d\overline{g} - \mathrm{Tr} \overline{u} \cdot d\overline{\phi} .$$
(A23)

From this we obtain the Maxwell relations

$$\left(\frac{\partial s}{\partial \rho}\right)_{T,\,\vec{\phi}} = -\frac{1}{\rho^2} \left(\frac{\partial P}{\partial T}\right)_{\rho,\,\vec{\phi}} , \qquad (A24a)$$

$$\left(\frac{\partial s}{\partial \vec{\phi}}\right)_{T,\rho} = \left(\frac{\partial \vec{u}}{\partial T}\right)_{\rho,\vec{\phi}} , \qquad (A24b)$$

$$\frac{1}{\rho} \left(\frac{\partial P}{\partial \phi} \right)_{\rho, T} = \frac{\vec{u}}{\rho} - \left(\frac{\partial \vec{u}}{\partial \rho} \right)_{T, \phi} .$$
 (A24c)

Finally for the variables P, T, and $\overline{\phi}$ we need consider the chemical potential (2.6). From (2.8) we can obtain

$$\frac{1}{\rho^2} \left(\frac{\partial \rho}{\partial T} \right)_{\rho, \vec{\phi}} = \left(\frac{\partial s}{\partial \rho} \right)_{T, \vec{\phi}} , \qquad (A25a)$$

$$\left(\frac{\partial \widetilde{\mathbf{u}}}{\partial P}\right)_{T,\widetilde{\phi}} = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial \widetilde{\phi}}\right)_{P,T} + \frac{\widetilde{\mathbf{u}}}{\rho} \left(\frac{\partial \rho}{\partial P}\right)_{T,\widetilde{\phi}} , \qquad (A25b)$$

$$\frac{1}{\rho} \left(\frac{\partial \widetilde{\mathbf{u}}}{\partial T} \right)_{P, \widetilde{\boldsymbol{\sigma}}} = \left(\frac{\partial s}{\partial \widetilde{\boldsymbol{\phi}}} \right)_{P, T} + \widetilde{\mathbf{u}} \left(\frac{\partial s}{\partial P} \right)_{T, \widetilde{\boldsymbol{\sigma}}} .$$
(A25c)

It might seem that we could obtain additional Maxwell relations from (2.12) in terms of the variables s, c, and \overline{u} or their conjugates. For example, we could obtain

$$\left(\frac{\partial T}{\partial c}\right)_{s,\vec{u}} = -\frac{mn_0}{\rho^2} \left(\frac{\partial \Pi}{\partial s}\right)_{c,\vec{u}} .$$
(A26)

But (2.15a)

$$\left(\frac{\partial T}{\partial \rho}\right)_{s,\vec{u}} = \frac{1}{\rho^2} \left(\frac{\partial \Pi}{\partial s}\right)_{\rho,\vec{u}} = \frac{1}{\rho^2} \left(\frac{\partial \Pi}{\partial s}\right)_{c,\vec{u}}$$
(A27)

and

$$\left(\frac{\partial T}{\partial \rho}\right)_{\mathbf{s},\mathbf{\bar{u}}} = \frac{-1}{mn_0} \left(\frac{\partial T}{\partial c}\right)_{\mathbf{s},\mathbf{\bar{u}}} . \tag{A28}$$

Substitution into (A27) yields (A26).

Thus we can obtain all the relations involving s, c, and \overline{u} and their conjugates from the ones already obtained.

APPENDIX B: THERMODYNAMIC DERIVATIVES AND TRANSPORT COEFFICIENTS IN CUBIC CRYSTALS

For cubic crystals the thermodynamic derivatives and transport coefficients are more isotropic than any other crystal. In particular, we have for the fourth-rank tensor elastic constants and viscosities

$$\underline{\mathbf{C}} = n_0 \left(\frac{\partial \vec{\sigma}^R}{\partial \vec{u}}\right)_{\mathbf{s}, \mathbf{c}} = (C_{11} + 2C_{12})\vec{\Upsilon}_0 \vec{\Upsilon}_0 + (C_{11} - C_{12})(\vec{\Upsilon}_1 \vec{\Upsilon}_1 + \vec{\Upsilon}_2 \vec{\Upsilon}_2) + 2C_{44}(\vec{\Upsilon}_3 \vec{\Upsilon}_3 + \vec{\Upsilon}_4 \vec{\Upsilon}_4 + \vec{\Upsilon}_5 \vec{\Upsilon}_5) , \qquad (B1a)$$

$$\underline{\mathbf{G}} = n_0^2 \left(\frac{\partial \vec{\phi}}{\partial \vec{u}}\right)_{\mathbf{s}, \mathbf{c}} = (G_{11} + 2G_{12})\vec{\Upsilon}_0 \vec{\Upsilon}_0 + (G_{11} - G_{12})(\vec{\Upsilon}_1 \vec{\Upsilon}_1 + \vec{\Upsilon}_2 \vec{\Upsilon}_2) + 2G_{44}(\vec{\Upsilon}_3 \vec{\Upsilon}_3 + \vec{\Upsilon}_4 \vec{\Upsilon}_4 + \vec{\Upsilon}_5 \vec{\Upsilon}_5) , \qquad (B1b)$$

$$\underline{\eta} = (\eta_{11} + 2\eta_{12}) \overrightarrow{\Upsilon_0} \overrightarrow{\Upsilon_0} + (\eta_{11} - \eta_{12}) (\overrightarrow{\Upsilon_1} \overrightarrow{\Upsilon_1} + \overrightarrow{\Upsilon_2} \overrightarrow{\Upsilon_2}) + 2\eta_{44} (\overrightarrow{\Upsilon_3} \overrightarrow{\Upsilon_3} + \overrightarrow{\Upsilon_4} \overrightarrow{\Upsilon_4} + \overrightarrow{\Upsilon_5} \overrightarrow{\Upsilon_5}) ,$$

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$$\begin{split} \vec{\Upsilon}_{0} &= \frac{1}{3}\sqrt{3} \vec{1}, \quad \vec{\Upsilon}_{1} &= \frac{1}{2}\sqrt{6} \left(\hat{e}_{x}\hat{e}_{x} - \frac{1}{3}\vec{1} \right), \quad \vec{\Upsilon}_{2} &= \frac{1}{2}\sqrt{2} \left(\hat{e}_{y}\hat{e}_{y} - \hat{e}_{x}\hat{e}_{x} \right), \\ \vec{\Upsilon}_{3} &= \frac{1}{2}\sqrt{2} \left(\hat{e}_{x}\hat{e}_{y} + \hat{e}_{y}\hat{e}_{x} \right), \quad \vec{\Upsilon}_{4} &= \frac{1}{2}\sqrt{2} \left(\hat{e}_{x}\hat{e}_{x} + \hat{e}_{x}\hat{e}_{x} \right), \quad \vec{\Upsilon}_{5} &= \frac{1}{2}\sqrt{2} \left(\hat{e}_{y}\hat{e}_{x} + \hat{e}_{x}\hat{e}_{y} \right); \end{split}$$

 \hat{e}_x , \hat{e}_y , and \hat{e}_z are the unit vectors along the coordinate axes which are taken to be the principal axes of the crystal.

Equations (B1a) and (B1b) are the form that the elastic constants would take in cubic crystals if the strain \vec{u} really had six independent components. However, as we've stated before, the strain can only have three independent components. This is most easily seen in a Fourier representation in which

$$\vec{u}(\vec{k}) = \int dr \, e^{-i \vec{k} \cdot \vec{r}} \, \vec{u}(\vec{r}) = -\frac{i}{2} \left[\vec{k} \vec{R}(\vec{k}) + \vec{R}(\vec{k}) \vec{k} \right] \,, \qquad (B2)$$

It then follows that

$$\vec{u}(\vec{k}) = n_0(\vec{k})\vec{k}\vec{k} + u_1(\vec{k})(\hat{k}\hat{e}_1 + \hat{e}_1\hat{k}) + u_2(\vec{k})(\hat{k}\hat{e}_2 + \hat{e}_2\hat{k}) ,$$
(B3)

where \hat{e}_1 and \hat{e}_2 are unit vectors transverse to \vec{k} . That is \vec{u} cannot have any components which are totally transverse to \hat{k} .

Therefore when applied to the Fourier representation of the hydrodynamic equations, only the components of (B1a) and (B1b) which are compatible with (B2) and (B3) can contribute. The corrected expressions for <u>C</u> and <u>G</u> can be most easily obtained by multiplication on both left and right by the projection operation

$$P_{ijkl} = \frac{1}{2} \left(\hat{k}_i \hat{k}_k \delta_j + \hat{k}_j \hat{k}_l \delta_{ik} \right) . \tag{B4}$$

Then, for example, (B1a) becomes^{20,21}

$$\begin{split} \underline{\mathbf{C}} &= (C_{11} + 2C_{12}) \overline{\mathbf{T}}_0(\hat{k}) \overline{\mathbf{T}}_0(\hat{k}) \\ &+ (C_{11} - C_{12}) [\overline{\mathbf{T}}_1(\hat{k}) \overline{\mathbf{T}}_1(\hat{k}) + \overline{\mathbf{T}}_2(\hat{k}) \overline{\mathbf{T}}_2(\hat{k})] \\ &+ 2C_{44} [\overline{\mathbf{T}}_3(k) \overline{\mathbf{T}}_3(k) + \overline{\mathbf{T}}_4(k) \overline{\mathbf{T}}_4(k) + \overline{\mathbf{T}}_5(k) \overline{\mathbf{T}}_5(k)] , \end{split}$$
(B1a')

where

$$\vec{\Upsilon}_{\lambda}(\hat{k}) = \frac{1}{2} (\vec{\Upsilon}_{\lambda} \cdot \hat{k}\hat{k} + \hat{k}\hat{k} \cdot \vec{\Upsilon}_{\lambda}), \quad \lambda = 0-5$$

The scalar coefficients of \underline{C} and \underline{G} are not all independent of one another. We see this since

$$\underline{\mathbf{C}} = n_0 \left(\frac{\partial \overline{\sigma}^R}{\partial \overline{\mathbf{u}}} \right)_{\mathbf{s}, \mathbf{c}} = n_0 k k \left(\frac{\partial \Pi}{\partial \overline{\mathbf{u}}} \right)_{\mathbf{s}, \mathbf{c}} + n_0^2 \left(\frac{\partial \overline{\phi}}{\partial \overline{\mathbf{u}}} \right)_{\mathbf{s}, \mathbf{c}}.$$
(B5)

But

$$\left(\frac{\partial \vec{\phi}}{\partial \vec{u}}\right)_{s,c} = \left(\frac{\partial \vec{\phi}}{\partial \vec{u}}\right)_{s,\rho} + \left(\frac{\partial \vec{\phi}}{\partial \rho}\right)_{s,\vec{u}} \left(\frac{\partial \rho}{\partial \vec{u}}\right)_{s,c}$$
(B6)

and

$$\left(\frac{\partial\rho}{\partial\tilde{\mathbf{u}}}\right)_{s,c} = \frac{\rho}{n_0} \left(\frac{\partial \operatorname{Tr}\tilde{\mathbf{u}}}{\partial\tilde{\mathbf{u}}}\right)_{s,c} = \frac{\rho}{n_0} \hat{k}\hat{k} \quad . \tag{B7}$$

So

$$\underline{\mathbf{C}} = n_0 \hat{k} \hat{k} \left(\frac{\partial \Pi}{\partial \tilde{\mathbf{u}}} \right)_{\mathbf{s}, \mathbf{c}} + \rho n_0 \left(\frac{\partial \phi}{\partial \rho} \right)_{\mathbf{s}, \tilde{\mathbf{u}}} \hat{k} \hat{k} + \underline{\mathbf{G}} . \tag{B8}$$

From the Maxwell relation (2.15c)

$$\rho\left(\frac{\partial\overline{\phi}}{\partial\rho}\right)_{s,\overline{u}} = \left(\frac{\partial\Pi}{\partial\overline{u}}\right)_{s,\rho}$$
$$= \left(\frac{\partial\Pi}{\partial\overline{u}}\right)_{s,c} - \frac{\rho}{n_0} \left(\frac{\partial\Pi}{\partial\rho}\right)_{s,\overline{u}} \hat{k}\hat{k} . \tag{B9}$$

Thus we have

$$\underline{\mathbf{C}} = n_0 \hat{k} \hat{k} \left(\frac{\partial \Pi}{\partial \overline{\mathbf{u}}}\right)_{\mathbf{s}_{\mathbf{r}}\rho} + n_0 \left(\frac{\partial \Pi}{\partial \overline{\mathbf{u}}}\right)_{\mathbf{s}_{\mathbf{r}}\rho} \hat{k} \hat{k} + \rho \left(\frac{\partial \Pi}{\partial \rho}\right)_{\mathbf{s}_{\mathbf{r}}\overline{\mathbf{u}}} \hat{k} \hat{k} \hat{k} \hat{k} + \underline{\mathbf{G}}.$$
(B10)

We obtain the corresponding components by identification of components,

$$\frac{1}{3}(C_{11}+2C_{12}) = 2n_0 \left(\frac{\partial \Pi}{\partial n_0}\right)_{s_*\rho} + \rho \left(\frac{\partial \Pi}{\partial \rho}\right)_{s_*\overline{u}} + \frac{1}{3}(G_{11}+2G_{12})$$
(B11a)

$$C_{11} - C_{12} = G_{11} - G_{12} , \qquad (B11b)$$

$$C_{44} = G_{44}$$
 . (B11c)

The tensor coefficients $\vec{C}^{\, e} \, \text{and} \, \vec{C}^{\, c} \, \text{must}$ be of the form

$$\vec{C}^{q} = \frac{n_{0}}{T} \left(\frac{\partial \vec{\sigma}^{R}}{\partial s} \right)_{u,c} = C^{q} \hat{k} \hat{k} = C^{q} \underline{P} : \vec{1}$$
(B12a)

and

$$\vec{C}^{c} = n_{0} \left(\frac{\partial \vec{\sigma}^{R}}{\partial c} \right)_{u,s} = C^{c} \hat{k} \hat{k} \quad . \tag{B12b}$$

The tensor transport coefficients must be proportional to the unit tensor

$$\overline{\alpha} = \alpha \overline{1}$$
, (B13a)

$$\vec{\zeta} = \zeta \vec{1}$$
, (B13b)

$$\vec{\kappa} = \kappa \vec{1} = (\alpha - \xi^2 / T\zeta) \vec{1} \quad . \tag{B13c}$$

Similarly we have for the other tensor coefficients

$$\left(\frac{\partial\vec{\phi}}{\partial\rho}\right)_{s,\vec{u}} = \left(\frac{\partial\vec{\phi}}{\partial\rho}\right)_{s,u} \hat{k}\hat{k} , \qquad (B14a)$$

$$\left(\frac{\partial T}{\partial u}\right)_{\mathbf{s},\mathbf{c}} = \left(\frac{\partial T}{\partial n_0}\right)_{\mathbf{s},\mathbf{c}} \hat{k}\hat{k} , \qquad (B14b)$$

$$\left(\frac{\partial \vec{\phi}}{\partial s}\right)_{\vec{u},c} = \left(\frac{\partial \phi}{\partial s}\right)_{\vec{u},c} \hat{k}\hat{k} , \qquad (B14c)$$

$$\left(\frac{\partial \vec{\phi}}{\partial c}\right)_{s_{t}\vec{u}} = \left(\frac{\partial \phi}{\partial c}\right)_{s_{t}\vec{u}} \hat{k}\hat{k} \quad . \tag{B14d}$$

The sixth-rank tensor \underline{D}^{μ} then takes the simple form

(B1c)

$$\underline{D}^{u} = (D_{11} + 2D_{12})\underline{T}_{0} + (D_{11} - D_{12})(\underline{T}_{1} + \underline{T}_{2}) + D_{44}(\underline{T}_{3} + \underline{T}_{4} + \underline{T}_{5}) , \qquad (B15)$$

where

$$\begin{split} D_{11} + 2D_{12} &= \frac{\zeta}{n_0^2} (G_{11} + 2G_{12}) \\ &\quad + 3\zeta n_0 \left(\frac{\partial \phi}{\partial \rho}\right)_{s, \vec{u}} + 3\frac{\xi}{T} \left(\frac{\partial T}{\partial n_0}\right)_{s, c} , \\ D_{11} - D_{12} &= \frac{\zeta}{n_0^2} (G_{11} - G_{12}) , \\ D_{44} &= \frac{\zeta}{n_0^2} G_{44} , \end{split}$$

and

$$(T_{\lambda})_{ijklmn} = \frac{1}{2} \left[\delta_{im} \Upsilon_{\lambda}(\hat{k})_{jn} + \delta_{jm} \Upsilon_{\lambda}(\hat{k})_{in} \right] \Upsilon_{\lambda}(\hat{k})_{kl}, \quad \lambda = 0 - 5.$$

The fourth-rank tensor coefficients \underline{D}^{uq} and \underline{D}^{uc} are of the form

$$\underline{\mathbf{D}}^{uq} = \left[\frac{\xi}{T\rho} \left(\frac{\partial\phi}{\partial s}\right)_{u,c} + \frac{\xi}{T^2\rho} \left(\frac{\partial T}{\partial s}\right)_{u,c}\right] \underline{\mathbf{P}}$$
$$\equiv D^{uq} \underline{\mathbf{P}}$$
(B16a)

and

$$\underline{\mathbf{D}}^{uc} = \left[\zeta \left(\frac{\partial \phi}{\partial c} \right)_{s, \overline{u}} + \frac{\xi}{T} \left(\frac{\partial T}{\partial c} \right)_{s, \overline{u}} \right] \underline{\mathbf{P}}$$
$$\equiv D^{uc} \underline{\mathbf{P}} \quad . \tag{B16b}$$

The other fourth-rank tensor coefficients \underline{D}^{au} and \underline{D}^{cu} are more complicated,

 $\underline{\mathbf{D}}^{\boldsymbol{q}\boldsymbol{u}} = \left[3\alpha \left(\frac{\partial T}{\partial n_0}\right)_{\boldsymbol{s},\boldsymbol{c}} + 3\xi \frac{\rho}{n_0} \left(\frac{\partial \phi}{\partial \rho}\right)_{\boldsymbol{s},\vec{u}}\right] \overline{\Upsilon}_0 \overline{\Upsilon}_0 (\hat{k}) + \frac{\xi}{n_0^2} \underline{\mathbf{G}}$ (B17a)

and

$$\underline{\mathbf{D}}^{\boldsymbol{c}\boldsymbol{u}} = \left[\frac{3\rho\xi}{mn_0^2 T} \left(\frac{\partial T}{\partial n_0}\right)_{\boldsymbol{s},\boldsymbol{c}} + \frac{3\zeta\rho^2}{mn_0^3} \left(\frac{\partial\phi}{\partial\rho}\right)_{\boldsymbol{s},\vec{u}}\right] \overline{\tilde{\mathbf{Y}}_0} \overline{\tilde{\mathbf{Y}}_0}(\hat{\boldsymbol{k}}) + \frac{\rho\zeta}{mn_0^4} \underline{\mathbf{G}} . \tag{B17b}$$

The remaining second-rank tensor D's are

$$\vec{\mathbf{D}}^{q} = \left[\frac{\alpha \,\vec{\mathbf{1}}}{\rho c_{\boldsymbol{u},\boldsymbol{c}}} + \frac{\xi}{T} \left(\frac{\delta \phi}{\delta S}\right)_{\boldsymbol{c},\vec{\mathbf{u}}} \hat{k} \hat{k}\right] \equiv D^{q} \hat{k} \hat{k} + \frac{\alpha}{\rho c_{\boldsymbol{u},\boldsymbol{c}}} \left(\vec{\mathbf{1}} - \hat{k} \hat{k}\right) , \tag{B18a}$$

$$\vec{\mathbf{D}}^{qc} = \left[\alpha \left(\frac{\partial T}{\partial c} \right)_{s, \vec{u}} \vec{\mathbf{1}} + \xi \left(\frac{\partial \phi}{\partial c} \right)_{s, \vec{u}} \hat{k} \hat{k} \right] \equiv D^{qc} \hat{k} \hat{k} + \alpha \left(\frac{\partial T}{\partial c} \right)_{s, \vec{u}} (\vec{\mathbf{1}} - \hat{k} \hat{k}) , \qquad (B18b)$$

$$\vec{\mathbf{D}}^{c} = \left[\frac{\xi\rho}{mn_{0}^{2}} \left(\frac{\partial\phi}{\partial c}\right)_{s,\vec{u}} \hat{k}\hat{k} + \frac{\rho\xi}{mn_{0}^{2}T} \left(\frac{\partial T}{\partial c}\right)_{s,\vec{u}} \vec{1}\right] \equiv D^{c}\hat{k}\hat{k} + \frac{\rho\xi}{mn_{0}^{2}T} \left(\frac{\partial T}{\partial c}\right)_{s,u} (\vec{1} - \hat{k}\hat{k}) , \qquad (B18c)$$

$$\vec{\mathbf{D}}^{cq} = \left[\frac{\xi}{Tmn_0^2} \left(\frac{\partial\phi}{\partial S}\right)_{c,\vec{\mathbf{u}}} \hat{k}\hat{k} + \frac{\xi}{mn_0^2 T} \left(\frac{\partial T}{\partial S}\right)_{c,\vec{\mathbf{u}}} \vec{\mathbf{1}}\right] \equiv D^{cq}\hat{k}\hat{k} + \frac{\xi}{mn_0^2 T} \left(\frac{\partial T}{\partial S}\right)_{qu} (\vec{\mathbf{1}} - \hat{k}\hat{k}) .$$
(B18d)

APPENDIX C: PROOF THAT $\hat{k} \cdot \dot{\phi}'(\vec{k}z) \cdot \hat{k} = \frac{2}{3} \hat{k} \cdot \dot{\phi}(\vec{k}z) \cdot \hat{k}$

The easiest way to see this is to recall that $\vec{\phi}$ actually appears only as $\nabla \cdot \vec{\phi}$.² That is to say, rather than having the freedom to independently specify the tensor $\vec{\phi}$, we only have the freedom to specify the vector $\nabla \cdot \vec{\phi}$. Clearly this must be the case since all that can be relevant is a vector variable conjugate to the vector distortion \vec{R} .

Therefore we can write for the Fourier transform of $\nabla \cdot \vec{\phi}$

$$F(\vec{\mathbf{k}}z) = -i\vec{\mathbf{k}}\cdot\phi(\vec{\mathbf{k}}z) = F_L(\vec{\mathbf{k}}z)\hat{k} + F_1(\vec{\mathbf{k}}z)\hat{e}_1 + F_2(\vec{\mathbf{k}}z)\hat{e}_2 ,$$
(C1)

where \hat{e}_1 and \hat{e}_2 are any two unit orthonormal vectors orthogonal to \vec{k} . (C1) allows us to identify

$$\begin{split} \vec{\phi}(kz) &= \phi_L(\vec{k}z)\hat{k}\hat{k} + \phi_1(\vec{k}z)(\hat{k}\hat{e}_1 + \hat{e}_1\hat{k}) \\ &+ \phi_2(\vec{k}z)(\hat{k}\hat{e}_2 + \hat{e}_2\hat{k}) , \end{split}$$
(C2)

where

$$\begin{split} \phi_L(\vec{k}z) &= \hat{k} \cdot \vec{\phi}(\vec{k}z) \cdot \hat{k} = \frac{F_L(\vec{k}z)}{ik} , \\ \phi_1(\vec{k}z) &= \hat{k} \cdot \vec{\phi}(\vec{k}z) \cdot \hat{e}_1 = \frac{F_1(\vec{k}z)}{ik} , \end{split}$$

and

$$\phi_2(\mathbf{k}z) = \hat{k} \cdot \vec{\phi}(\mathbf{k}z) \cdot \hat{e}_2 = \frac{F_2(\mathbf{k}z)}{ik}$$

We have symmetrized ϕ , although this is unnecessary, because we have chosen to work with the symmetric strain. Of course (C1) only determines ϕ up to terms which are totally orthogonal to \vec{k} (i.e., orthogonal in both indices). But such terms must be irrelevant and cannot contribute to either the thermodynamics or hydrodynamics.

It then follows that

$$\vec{\phi'}(kz) = \vec{\phi}(\vec{k}z) - \frac{1}{3} \operatorname{Tr} \vec{\phi}(\vec{k}z) \vec{1}$$

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$$=\phi_L(\vec{k}z)(\hat{k}\hat{k}-\frac{1}{3}\vec{1})+\phi_1(\vec{k}z)(\hat{k}e_1+\hat{e}_1\hat{k})$$

$$+\phi_2(\vec{k}z)(\hat{k}\hat{e}_2+\hat{e}_2\hat{k}) , \qquad (C3)$$

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- ⁷See also the review by A. Griffin [Rev. Mod. Phys. <u>40</u>, 167 (1968)].
- ⁸D. Forster, T. C. Lubensky, P. C. Martin, J. Swift, and P. S. Pershan, Phys. Rev. Lett. <u>26</u>, 1016 (1971).
- ⁹In fact in quantum crystals such as solid He and solid H_2 vacancies are not only important, but particle exchange cannot be neglected either. In particular, spin exchange is responsible for interesting magnetic properties of solid ³He. See, for example, the review by R. A. Guyer [Solid State Phys. 23, 413 (1969)].
- ¹⁰Actually, a more general description of the mode of motion omitted from previous treatments is one of a configurational rearrangement. In amorphous solids, where the identification of a lattice or vacancies in it is far from clear, this terminology must be employed. In a subsequent paper [C. Cohen, P. D. Fleming, and J. H. Gibbs, Phys. Rev. B 13, 866 (1976)] we will see that for any solid the density can be changed either by a uniform strain (e.g., uniform elongation of all bonds keeping bond angles fixed) or by a configurational rearrangement (e.g., bond bending or flexing at constant bond length). Since these two kinds of motion are independent, the uniform strain can be treated as an independent variable in addition to the density for any solid just as it has been here for crystalline solids. For crystalline solids configurational rearrangements are most conveniently discussed in terms of vacancy will be employed here.
- ¹¹A. R. Allnatt and A. V. Chadwick, Chem. Rev. <u>67</u>, 681 (1967).
- ¹²It is sufficient to keep the symmetric strain since its six components (not all independent) allow for all possible variations of the distortion \vec{R} (three independent components).
- ¹³Y. Ida, J. Geophys. Res. <u>74</u>, 3208 (1969); A. G.
 McLellan, *ibid*. <u>71</u>, 4341 (1966); W. B. Kamb, *ibid*.
 <u>64</u>, 1891 (1961).
- 14 In (2.6) and (2.8) we have actually assumed

 $u_{ij}(\vec{r}t) = \frac{1}{3} n_0 \,\delta_{ij} - \frac{1}{2} \left[\partial_i R_j(\vec{r}t) + \partial_j R_i(\vec{r}t) \right] \,,$

which is consistent with (2.1). This assumption is not necessary. We can take our strain variable to be any

and therefore

$$\hat{k} \cdot \vec{\phi}'(\vec{k}z) \cdot \hat{k} = \frac{2}{3}\phi_L(\vec{k}z)$$
. Q.E.D.

linear combination of $n_0(\mathbf{\hat{r}}_i) \delta_{ij}$ and $\partial_i R_j(\mathbf{\hat{r}}_i)$ whose fluctuations are consistent with (2.3). We could take, for example, the strain to be

$$\begin{split} u_{ij}^{a}(\mathbf{\tilde{r}}t) &= a \left[n_0(\mathbf{\tilde{r}}t) + \nabla \cdot \mathbf{\tilde{R}}(\mathbf{\tilde{r}}t) \right] \delta_{ij} - \frac{1}{2} \left[\partial_i R_j(\mathbf{\tilde{r}}t) + \partial_j R_i(\mathbf{\tilde{r}}t) \right] \\ &= a n_0 \delta_{ij} - \frac{1}{2} \left[\partial_i R_j(\mathbf{\tilde{r}}t) + \partial_j R_i(\mathbf{\tilde{r}}t) \right] \end{split}$$

for arbitrary *a*. Since the fluctuations in $\mathbf{\tilde{u}}^a$ are independent of *a*, the physical consequences must be insensitive to the choice of *a*. We have chosen the case $a = \frac{1}{3}$ because it has the especially convenient property that

$$\operatorname{Tr} \vec{u}(\vec{r}t) = n_0 - \nabla \cdot \vec{R}(\vec{r}t)$$
$$= n_0 + \delta n_0(\vec{r}t) = n_0(\vec{r}t).$$

To see how the development would proceed with \overline{U}^a taken as the strain variable we first note that (2, 5) and (2.10) are obtained by respectively dividing

 $dE = T \, dS - P \, dV + \mu \, dN + \vec{v} \cdot d\vec{P} + Tr \, \vec{\phi} \cdot d\vec{\Sigma}$

by V at constant V and N at constant N, where $\vec{P} = \vec{g}V$ and $\sum = \vec{u}V$. If we chose \vec{u}^a as the strain variable then for $\sum a = \vec{u}^a V$ we have

$$d\sum^{a} = d\vec{u}^{a} V + \vec{u}^{a} dV$$
$$= d\sum^{a} + (\vec{u}^{a} - \vec{u}) dV$$
$$= d\sum^{a} + (a - \frac{1}{3}) (n_{0} + \nabla \cdot \vec{R}) \vec{1} dV$$

When this is substituted into the expression for dE it becomes

$$dE = T \, dS - P^a \, dV + \mu \, dN + \vec{v} \cdot d\vec{P} + Tr \, \vec{\phi} \cdot d\sum^a$$

where

$$P^{a} = P + 3(a - \frac{1}{3})(n_{0} + \nabla \cdot \vec{R})\phi_{0}$$
,

with $\phi_0 = \frac{1}{3} \operatorname{Tr} \vec{\phi}$. Thus the only effect of transforming from \vec{u} to \vec{u}^a is to redefine the pressure. Note, however, that $P^a = P$ in equilibrium ($\phi_0 = 0$). The "integrated" form of this equation [cf. (2.6)],

$$\begin{split} E &= TS - P^{a}V + \mu N + \vec{v} \cdot \vec{P} + \mathrm{Tr} \vec{\phi} \cdot \vec{\Sigma}^{a} \\ &= TS - \left[P + 3\left(a - \frac{1}{3}\right)\left(n_{0} + \nabla \cdot \vec{R}\right)\phi_{0}\right]V + \mu N \\ &+ \vec{v} \cdot \vec{P} + \mathrm{Tr} \vec{\phi} \cdot \left[\vec{\Sigma} + V\left(a - \frac{1}{3}\right)\left(n_{0} + \nabla \cdot \vec{R}\right)\vec{1}\right] \\ &= TS - PV + \mu N + \vec{v} \cdot \vec{P} + \mathrm{Tr} \vec{\phi} \cdot \vec{\Sigma}^{*} , \end{split}$$

is independent of a.

- ¹⁵Since the main difference between our treatment and the usual one is the appearance of an additional diffusive mode, our solution of the Euler equations for the propagating modes must be identical to the usual one.
- ¹⁶P. C. Martin, in Statistical Mechanics of Equilibrium and Non-Equilibrium, edited by J. Meixner (North-Holland, Amsterdam, 1965).
- ¹⁷(a) C. Cohen, J. W. H. Sutherland, and J. M. Deutch,

Phys. Chem. Liq. 2, 213 (1971); (b) R. Mountain and J. M. Deutch, J. Chem. Phys. 50, 1103 (1969).

¹⁸R. S. Krishman, in *The Raman Effect*, edited by A.

Anderson (Marcel Dekker, New York, 1971), p. 343. ¹⁹L. Powers, Bull. Am. Phys. Soc. <u>19</u>, 374 (1974). ²⁰Note that (B1a') only contains contributions from the part of the stress $\vec{\sigma}^R$ which contributes to the hydrodynamic equations, i.e.,

 $\overset{'}{\sigma}{}^{R} = \underline{\mathbf{P}} : \overset{\leftrightarrow}{\sigma}{}^{R} = \hat{k}\hat{k} \Pi + n_{0} \overleftrightarrow{\phi} .$

[That $\underline{P}: \vec{\phi}(\vec{k}) = \phi(\vec{k})$ follows from the development of Appendix C.]

²¹It is interesting to note that when applied to spatially dependent variables (B1a') is nonlocal in space. However, when it is multiplied either left or right by the strain it becomes effectively local.