

## Slow modes in crystals: A method to study elastic constants

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We propose a microscopic expression for a displacement field in a crystal and derive nondissipative equations of motion for the slow hydrodynamic and broken-symmetry modes, including the vacancy-diffusion mode. Comparing these equations with the macroscopic ideal equations of elasticity we obtain exact expressions for isothermal elastic constants.

### I. INTRODUCTION

For a one-component crystal consisting of spherically symmetric particles there are in general eight slow hydrodynamiclike modes.<sup>1</sup> These are five densities of conserved quantities, i.e., number, momentum (three components), and energy densities, and in addition three modes due to broken continuous symmetry, corresponding to the macroscopic displacement field. On the other hand, on the macroscopic level<sup>2</sup> one introduces six propagating sound modes or elastic waves (three branches for a given wave vector, two possible velocity signs for a given branch) and a diffusive energy mode, usually neglecting existence of the eighth mode, the vacancy-diffusion mode.

Martin, Parodi, and Pershan<sup>1</sup> clearly recognized the deficiency of the usual macroscopic description. Starting from general ideas of hydrodynamiclike description of broken-symmetry phases they derived the full set of evolution equations for all the eight slow modes. They argued that vacancy diffusion is possibly due to the distinction between the displacement field and the mass transport.

The analysis of Martin, Parodi, and Pershan was purely phenomenological. In particular they did not calculate any reactive or dissipative coefficients. The problem of deriving the full macroscopic description of a crystal from a microscopic theory remained unsolved.

Here we study the time evolution of the slow modes in crystals using techniques developed in nonequilibrium statistical mechanics of systems with broken continuous symmetry. We identify all eight slow hydrodynamiclike modes: We propose a *microscopic* expression for the displacement field. Next we derive nondissipative equations of motion for the slow modes. The extension to include dissipative processes is straightforward and will be reported elsewhere.

We derive here exact expressions for the reactive coefficients in the evolution equations. These expressions will not change if we include dissipative processes. Next we introduce the vacancy concentration as a combination of the conserved (hydrodynamic) and broken-symmetry modes. Finally, we derive the usual equations of ideal elasticity.<sup>2</sup> By comparison of the microscopically derived evolution equations with the macroscopic ones we identify exact expressions for the elastic constants.

Elastic constants of the hard sphere solid have been calculated before by using density-functional theory.<sup>3,4</sup> The basic idea was to calculate the free energy for a strained crystal<sup>3</sup> and then to differentiate it with respect to the elements of the strain tensor. The expressions for the elastic constants obtained in this way depend sensitively on the approximate parametrization of the density field in the strained crystal. The same remark applies to the results derived from kinetic theory.<sup>5</sup> In contrast our expressions do not depend upon any parametrization of the density profile in the strained crystal. The elastic constants are explicitly expressed in terms of equilibrium quantities: the long-wavelength limit of the structure factor and integrals of the direct correlation function with derivatives of the equilibrium density profile.

Our formulas for the elastic constants are similar in structure to the Triezenberg-Zwanzig formula for the surface tension and complementary to those derived by Squire, Holt, and Hoover.<sup>6</sup> The relation between our expressions and those of Squire, Holt, and Hoover is the same as between the Triezenberg-Zwanzig<sup>7</sup> and the Kirkwood-Buff<sup>8</sup> formulas for the surface tension.

The paper is organized as follows. In Sec. II we introduce and justify a microscopic expression for the displacement field. In Sec. III equations of motion for all the eight slow hydrodynamic and broken-symmetry modes are derived. In Sec. IV we compare these equations with the phenomenological linear equations of elasticity and obtain expressions for the elastic constants. Finally in Sec. V we summarize our results and end with some comments.

### II. MICROSCOPIC DEFINITION OF THE DISPLACEMENT FIELD

To identify additional slow modes that owe their existence to broken translational invariance we follow Anderson's presentation of the spin-wave excitations.<sup>9</sup> Let  $n_e(\mathbf{r})$  be the equilibrium density profile in a crystal. It can be decomposed into components corresponding to different reciprocal-lattice vectors:

$$n_e(\mathbf{r}) = n_0 + \sum_{\{\mathbf{G}, \mathbf{G} \neq 0\}} n_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}, \quad (2.1)$$

where  $\{\mathbf{G}\}$  denotes the set of reciprocal-lattice vectors,  $n_{\mathbf{G}}$  is the amplitude of the component of the density profile corresponding to the reciprocal-lattice vector  $\mathbf{G}$ , and  $n_0$  is the average *macroscopic* density,

$$n_0 = v^{-1} \int_v d\mathbf{r} n_e(\mathbf{r}), \quad (2.2)$$

with  $v$  the volume of the unit cell.

The amplitudes  $n_{\mathbf{G}}$ , with  $\mathbf{G} \neq \mathbf{0}$ , specify a particular state from a manifold of equivalent broken-symmetry states. They are the order parameters of the crystal.<sup>9</sup> By changing the phases of *all* the order parameters,

$$n_{\mathbf{G}} \rightarrow n_{\mathbf{G}} e^{-i\mathbf{G} \cdot \mathbf{a}} \quad \text{for all } \mathbf{G} \neq \mathbf{0}, \quad (2.3)$$

we obtain an equivalent but different state of the crystal. This state corresponds to the original crystal moved by a vector  $\mathbf{a}$ . The important fact is that changing the order parameters through a uniform translation  $\mathbf{a}$  does not change the free energy. Now we consider small perturbations of the equilibrium state with a slowly varying displacement field,

$$\mathbf{a}(\mathbf{r}) = \mathbf{a} e^{-i\mathbf{k} \cdot \mathbf{r}} \quad (2.4)$$

of small magnitude  $|\mathbf{a}|$ ; i.e., we move different parts of the crystal out of phase using different displacement vectors in different positions. Here and in the following lower-case letters  $\mathbf{k}, \mathbf{q}, \dots$  denote wave vectors from the first Brillouin zone of the reciprocal lattice. Using displacement field (2.4) we change the order parameters,

$$n_{\mathbf{G}} \rightarrow n_{\mathbf{G}} e^{-i\mathbf{G} \cdot \mathbf{a} \exp(-i\mathbf{k} \cdot \mathbf{r})} \approx n_{\mathbf{G}} (1 - i\mathbf{G} \cdot \mathbf{a} e^{-i\mathbf{k} \cdot \mathbf{r}}). \quad (2.5)$$

As the relevant free-energy change vanishes at  $\mathbf{k} = \mathbf{0}$  and is a scalar quantity, it must be of the order of at most  $k^2$  for small wave vectors. Hence we have a low-energy excitation.

Note that in order to get the low-energy excitation we need to change *only* the order parameters  $n_{\mathbf{G}}, \mathbf{G} \neq \mathbf{0}$ . There is no change of the average density  $n_0$ .

Although we have identified relevant low-energy excitations, finding a microscopic expression for the displacement field is not as simple, unless one restricts oneself to a model situation in which every lattice site is occupied by a specified atom. Unfortunately there are no vacancies in this case and one is left with seven slow modes only. Density is not an independent variable anymore.

A sensible *microscopic* expression for the displacement field  $\mathbf{u}(\mathbf{k})$  should satisfy the following conditions: Consider a strained state of a crystal with the average density

$$n'_e(\mathbf{r}) = n_e[\mathbf{r} - \mathbf{a}(\mathbf{r})] = n_e(\mathbf{r}) - \frac{\partial n_e(\mathbf{r})}{\partial \mathbf{r}} \cdot \mathbf{a}(\mathbf{r}), \quad (2.6)$$

where function  $\mathbf{a}(\mathbf{r})$  has no Fourier components outside the first Brillouin zone of the reciprocal lattice [note that  $n_e(\mathbf{r})$  is the density field of the unstrained crystal]. The density field (2.6) can be obtained as a linear combination of the transformations (2.5). Now the important

requirement is that the ensemble-averaged displacement field  $\langle \mathbf{u}(\mathbf{k}) \rangle$  calculated for the considered state should have form

$$\langle \mathbf{u}(\mathbf{k}) \rangle = \int d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} \mathbf{a}(\mathbf{r}). \quad (2.7)$$

Here and in the following brackets  $\langle \dots \rangle$  denote an average over a nonequilibrium (strained) ensemble compatible with the prescribed displacement field  $\mathbf{a}(\mathbf{r})$ .

It is clear from the above discussion that the displacement manifests itself in the change of the rapidly varying components of the microscopic density field,  $n(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{R}_i)$ , where  $\mathbf{R}_i$  denotes the position of the  $i$ th particle. Guided by this fact we propose a definition that essentially is a projection of the microscopic density on the equilibrium density gradient:

$$\begin{aligned} \mathbf{u}(\mathbf{k}) &= -V \frac{(h_{\alpha}, n)}{(h_{\alpha}, h_{\alpha})} = -\frac{1}{\mathcal{N}} \int d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} \frac{\partial n_e(\mathbf{r})}{\partial \mathbf{r}} n(\mathbf{r}) \\ &= -\frac{1}{\mathcal{N}} \sum_{\mathbf{G}} i\mathbf{G} n_{\mathbf{G}} \delta n(\mathbf{k} - \mathbf{G}), \end{aligned} \quad (2.8)$$

where  $h_{\alpha}(\mathbf{k}, \mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) (\partial/\partial r_{\alpha}) n_e(\mathbf{r})$ . The inner product is defined as

$$(a, b) = \frac{1}{V} \int d\mathbf{r} a^*(\mathbf{r}) b(\mathbf{r}) \quad (2.9)$$

and the constant  $\mathcal{N}$  as

$$\begin{aligned} \mathcal{N} &= (h_{\alpha}, h_{\alpha}) = \frac{1}{3} \sum_{\mathbf{G}} G^2 |n_{\mathbf{G}}|^2 \\ &= \frac{1}{3v} \int_v d\mathbf{r} \left( \frac{\partial n_e(\mathbf{r})}{\partial \mathbf{r}} \right)^2. \end{aligned} \quad (2.10)$$

Note that there is no summation over  $\alpha$  in Eq. (2.10). In general  $\mathcal{N}$  has to be replaced by a second-rank tensor. Here we have assumed cubic symmetry. It can be easily checked that definition (2.8) agrees with our intuitive discussion above: For a state in which the average density has the form  $n_e(\mathbf{r}) - (\partial n_e(\mathbf{r})/\partial \mathbf{r}) \cdot \mathbf{a}(\mathbf{r})$  one gets  $\langle \mathbf{u}(\mathbf{k}) \rangle = \int d\mathbf{r} \exp(-i\mathbf{k} \cdot \mathbf{r}) \mathbf{a}(\mathbf{r})$ .

To discuss the projection in definition (2.8) in a slightly more formal manner we define the following set of functions:

$$\begin{aligned} h_0(\mathbf{k}, \mathbf{r}) &= e^{i\mathbf{k} \cdot \mathbf{r}} n_e(\mathbf{r}), \\ h_{\alpha}(\mathbf{k}, \mathbf{r}) &= e^{i\mathbf{k} \cdot \mathbf{r}} \frac{\partial}{\partial r_{\alpha}} n_e(\mathbf{r}), \\ h_{\alpha\beta}(\mathbf{k}, \mathbf{r}) &= e^{i\mathbf{k} \cdot \mathbf{r}} \left( \frac{\partial^2}{\partial r_{\alpha} \partial r_{\beta}} \right) n_e(\mathbf{r}), \\ &\dots, \end{aligned} \quad (2.11)$$

where  $[\partial^n n_e(\mathbf{r})/(\partial r_{\alpha} \partial r_{\beta} \partial r_{\gamma} \dots)]$  denote orthogonalized higher-order gradients and  $\alpha, \beta, \dots$  denote Cartesian components  $\{x, y, z\}$ . We decompose the difference between the microscopic density field and its equilibrium average along the basis (2.11), using the inner product (2.9). The result is

$$n(\mathbf{r}) - n_e(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k}} v(\mathbf{k}) h_0(\mathbf{k}, \mathbf{r}) - \frac{1}{V} \sum_{\mathbf{k}, \alpha} u_\alpha(\mathbf{k}) h_\alpha(\mathbf{k}, \mathbf{r}) + \dots \quad (2.12)$$

The  $\mathbf{k}$  summations in Eq. (2.12) are restricted to the first Brillouin zone. The expansion coefficients are the projections of  $\delta n(\mathbf{r}) \equiv n(\mathbf{r}) - n_e(\mathbf{r})$  on the basis functions (2.11), where  $v(\mathbf{k})$  is given by an expression similar to (2.8) with  $h_\alpha$  replaced by  $h_0$ . An alternative way to write (2.12) is

$$\delta n(\mathbf{k} + \mathbf{G}) = [v(\mathbf{k}) - i\mathbf{G} \cdot \mathbf{u}(\mathbf{k}) + \dots] n_{\mathbf{G}}, \quad (2.13)$$

where  $\mathbf{k}$  belongs to the first Brillouin zone and  $\delta n(\mathbf{k} + \mathbf{G})$  is the Fourier transform of  $\delta n(\mathbf{r})$  with the wave vector  $\mathbf{k} + \mathbf{G}$ . Multiplication of (2.13) with  $n_{\mathbf{G}}^*$  or  $iG_\alpha n_{\mathbf{G}}^*$  yields again  $v(\mathbf{k})$  and  $u_\alpha(\mathbf{k})$  as in (2.8).

The second term is the component  $n_{\parallel}(\mathbf{r})$  of the density field, parallel to the equilibrium density gradient, i.e.,

$$n_{\parallel}(\mathbf{r}) \equiv -\frac{1}{V} \sum_{\mathbf{k}, \alpha} u_\alpha(\mathbf{k}) h_\alpha(\mathbf{k}, \mathbf{r}) = -\sum_{\alpha} u_\alpha(\mathbf{r}) \frac{\partial}{\partial r_\alpha} n_e(\mathbf{r}) \simeq n_e[\mathbf{r} - \mathbf{u}(\mathbf{r})] - n_e(\mathbf{r}). \quad (2.14)$$

To further justify definition (2.8) we show that the Fourier transform of the correlation function of the displacement field diverges in the long-wavelength limit. To do so we use Bogolyubov's inequality<sup>10</sup>

$$\langle |A|^2 \rangle_{\text{eq}} \langle |B|^2 \rangle_{\text{eq}} \geq |\langle AB \rangle_{\text{eq}}|^2, \quad (2.15)$$

with  $A = V^{-1/2} \hat{\mathbf{n}} \cdot \mathbf{u}(-\mathbf{k})$  and  $B = V^{-1/2} \hat{\mathbf{n}} \cdot \dot{\mathbf{g}}(\mathbf{k})$ . Here brackets  $\langle \dots \rangle_{\text{eq}}$  denote the equilibrium ensemble average,  $\hat{\mathbf{n}}$  is a unit vector, and  $N = n_0 V$  denotes the number of particles (the thermodynamic limit is implied). Finally  $\mathbf{g}(\mathbf{k})$  is the Fourier transform of the microscopic momentum density,

$$\mathbf{g}(\mathbf{r}) = \sum_i m \mathbf{V}_i \delta(\mathbf{r} - \mathbf{R}_i), \quad (2.16)$$

with  $\mathbf{V}_i$  the velocity of the  $i$ th particle and  $m$  its mass, and a dot denotes the time derivative. We consider the cross correlation

$$\begin{aligned} \langle AB \rangle_{\text{eq}} &= \frac{1}{V} \langle \hat{\mathbf{n}} \cdot \mathbf{u}(-\mathbf{k}) \hat{\mathbf{n}} \cdot \dot{\mathbf{g}}(\mathbf{k}) \rangle_{\text{eq}} \\ &= -\frac{1}{V} \langle \hat{\mathbf{n}} \cdot \dot{\mathbf{u}}(-\mathbf{k}) \hat{\mathbf{n}} \cdot \mathbf{g}(\mathbf{k}) \rangle_{\text{eq}} \end{aligned} \quad (2.17)$$

and demonstrate that at  $\mathbf{k} = \mathbf{0}$  the cross correlation  $\langle AB \rangle_{\text{eq}}$  equals  $k_B T$  where  $k_B$  is the Boltzmann constant and  $T$  is the temperature. The quantity  $\dot{\mathbf{u}}(-\mathbf{k})$  can be calculated from (2.8) and the microscopic continuity equation

$$m \dot{\mathbf{n}}(\mathbf{r}; t) = -\nabla \cdot \mathbf{g}(\mathbf{r}; t), \quad (2.18)$$

and one finds

$$\dot{\mathbf{u}}(-\mathbf{k}) = \frac{1}{mN} \int d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} \frac{\partial n_e(\mathbf{r})}{\partial \mathbf{r}} \cdot \nabla \cdot \mathbf{g}(\mathbf{r}; t). \quad (2.19)$$

Then we set  $\mathbf{k} = \mathbf{0}$ , carry out the velocity integrations in Eq. (2.17), and use the definitions of the displacement field (2.8) and the normalization constant (2.10). In this way the relation  $\langle AB \rangle_{\text{eq}} = k_B T$  follows at  $\mathbf{k} = \mathbf{0}$ .

In using the Bogolyubov inequality, we *assume* in fact the stronger result

$$\lim_{\mathbf{k} \rightarrow \mathbf{0}} \langle AB \rangle_{\text{eq}} = (k_B T / n_0). \quad (2.20)$$

In general one can prove (2.20) if the equality at  $\mathbf{k} = \mathbf{0}$  holds unless there are long-range interparticle interactions.<sup>9,10</sup> Note that result (2.20) follows from the fact that the translational symmetry is broken; i.e., the Hamiltonian is invariant under all translations and the equilibrium state is not.

To evaluate  $\langle |B|^2 \rangle_{\text{eq}}$  we express the correlation function of the time derivatives of the momentum in terms of the correlation function of the stress tensor  $\vec{\sigma}(\mathbf{k})$ . The stress tensor is defined through the continuity equation for the momentum:

$$\dot{\mathbf{g}}(\mathbf{k}; t) = -i\mathbf{k} \cdot \vec{\sigma}(\mathbf{k}; t). \quad (2.21)$$

In this way we obtain

$$\langle |B|^2 \rangle_{\text{eq}} = \frac{1}{V} \langle |\dot{\mathbf{g}}(\mathbf{k}) \cdot \hat{\mathbf{n}}|^2 \rangle_{\text{eq}} = k^2 \frac{1}{V} \langle |\hat{\mathbf{k}} \cdot \vec{\sigma}(\mathbf{k}) \cdot \hat{\mathbf{n}}|^2 \rangle_{\text{eq}}, \quad (2.22)$$

where  $\hat{\mathbf{k}} = \mathbf{k}/k$ .

Finally we consider Bogolyubov's inequality (2.15) at small wave vectors. We estimate the cross correlation  $\langle AB \rangle_{\text{eq}}$  using relation (2.20) and arrive at the inequality

$$\frac{1}{V} \langle |\hat{\mathbf{n}} \cdot \mathbf{u}(\mathbf{k})|^2 \rangle_{\text{eq}} \geq \frac{1}{k^2} \frac{(k_B T)^2}{\lim_{\mathbf{k} \rightarrow \mathbf{0}} \frac{1}{V} \langle |\hat{\mathbf{k}} \cdot \vec{\sigma}(\mathbf{k}) \cdot \hat{\mathbf{n}}|^2 \rangle_{\text{eq}}}. \quad (2.23)$$

For general potentials the denominator is bounded. The tensor character of  $\langle \mathbf{u}(-\mathbf{k}) \mathbf{u}(\mathbf{k}) \rangle_{\text{eq}}$  implies that in general all the functions  $\langle u_\alpha(-\mathbf{k}) u_\beta(\mathbf{k}) \rangle_{\text{eq}}$  diverge at least as  $k^{-2}$  as  $\mathbf{k} \rightarrow \mathbf{0}$  (Greek indices denote the Cartesian components of vectors and tensors). The divergence of the susceptibility  $\langle u_\alpha(-\mathbf{k}) u_\beta(\mathbf{k}) \rangle_{\text{eq}}$  implies that there exists long-range order in the displacements fields and that the time evolution of the long-wavelength components of the displacement field are slow: The characteristic relaxation time is directly proportional to the static correlations.

On physical grounds one expects that the correlations of the displacement fields are the only correlations with long-range order. Indeed, if one replaces  $(h_\alpha, n)$  in (2.8) by a more general expression  $(f, n)$ , then one easily verifies that the correlation function corresponding to (2.17) yields  $(k_B T / n_0) (f, \hat{\mathbf{n}} \cdot \nabla n_e)$ . For functions  $f(\mathbf{r})$  orthogonal to  $\nabla n_e(\mathbf{r})$ , only a trivial inequality survives, and the argument for the existence of the long-range order in  $\langle f(-\mathbf{k}) f(\mathbf{k}) \rangle_{\text{eq}}$  breaks down. We *assume* therefore that only the susceptibilities  $\langle u_\alpha(-\mathbf{k}) u_\beta(\mathbf{k}) \rangle_{\text{eq}}$  have the leading singularity, and more explicitly we assume that

they diverge exactly like  $k^{-2}$ . Furthermore, we assume that if there is no clear physical reason to expect a long-wavelength divergence then the correlation function should be regular for  $\mathbf{k} \rightarrow \mathbf{0}$ . Note that a  $k^{-2}$  divergence of  $\langle u_\alpha(-\mathbf{k}) u_\beta(\mathbf{k}) \rangle_{\text{eq}}$  agrees with the result obtained from the phenomenological Landau-type approach to the displacement fluctuations.<sup>11</sup>

### III. EVOLUTION EQUATIONS FOR SLOW VARIABLES

Apart from the displacement field we also have the five usual slow hydrodynamic variables.<sup>10,12</sup> These are number, momentum, and energy densities,  $n(\mathbf{k})$ ,  $\mathbf{g}(\mathbf{k})$ , and  $e(\mathbf{k})$ , respectively. These five variables satisfy local conservation laws: Their time derivative equals the divergence of the corresponding current, and therefore their time evolution is slow in the long-wavelength limit  $\mathbf{k} \rightarrow \mathbf{0}$ .

For simplicity we neglect energy conservation and study the time evolution of the deviations of the slow variables  $\delta n(\mathbf{k})$ ,  $\mathbf{g}(\mathbf{k})$ , and  $\mathbf{u}(\mathbf{k})$  from their equilibrium values.<sup>13</sup> Note that  $\langle \mathbf{g}(\mathbf{k}) \rangle_{\text{eq}}$  and  $\langle \mathbf{u}(\mathbf{k}) \rangle_{\text{eq}}$  are vanishing. By neglecting the energy mode we will obtain the isothermal elastic constants, instead of adiabatic ones. To derive the equations of motion we use the projection operator method.<sup>10</sup> As this technique is fairly standard we will only sketch the actual calculations. We define a scalar product

$$\langle a|b \rangle = \frac{1}{V} \langle \delta a(-\mathbf{k}) \delta b(\mathbf{k}) \rangle_{\text{eq}}. \quad (3.1)$$

Here  $\delta a(\mathbf{k})$  denotes any of the slow variables  $\delta n(\mathbf{k})$ ,  $\mathbf{g}(\mathbf{k})$ , and  $\mathbf{u}(\mathbf{k})$ . Note that for a broken-symmetry state we have two scalar products. One has been defined by Eq. (2.9); it determines the value of the slow mode in terms of the geometrical structure of the broken-symmetry phase. The other, defined through Eq. (3.1), is the usual scalar product used in the projection-operator method and is related to equilibrium fluctuations.

We define a projection operator on the slow subspace:

$$\mathcal{P}f(\mathbf{k}) = \sum_{a,b} \delta a(\mathbf{k}) \langle a|b \rangle^{-1} \langle b|f \rangle. \quad (3.2)$$

Here  $\langle a|b \rangle^{-1}$  denotes the inverse of the matrix  $\langle a|b \rangle$ , where  $a$  and  $b$  denote slow variables. In the  $\mathbf{k} \rightarrow \mathbf{0}$  limit  $\langle u_\alpha|u_\beta \rangle$  are the only nonvanishing off-diagonal elements.

To get the nondissipative equations of motion for the slow variables we project their time derivatives on the slow subspace and average over a nonequilibrium ensemble. To get the explicit form of the evolution equations we have to calculate matrix elements of the Liouville operator<sup>12</sup>  $\mathcal{L}$ . It is easy to show that the only nonzero elements are

$$\begin{aligned} \langle g_\alpha|\mathcal{L}n \rangle &= -\langle n|\mathcal{L}g_\alpha \rangle = -ik_\alpha n_0 k_B T, \\ \langle g_\alpha|\mathcal{L}u_\beta \rangle &= -\langle u_\alpha|\mathcal{L}g_\beta \rangle = \delta_{\alpha\beta} (k_B T). \end{aligned} \quad (3.3)$$

By using the basic assumption that  $\langle \mathbf{u}(-\mathbf{k}) \mathbf{u}(\mathbf{k}) \rangle_{\text{eq}}$  are the *only* divergent correlations in the limit  $\mathbf{k} \rightarrow \mathbf{0}$ , it follows that the inverse matrix  $\langle u_\alpha|u_\beta \rangle^{-1}$  reduces to

$$\begin{aligned} \langle u_\alpha|u_\beta \rangle^{-1} &\approx \frac{1}{2V} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\partial n_e(\mathbf{r}_1)}{\partial r_{1\alpha}} \mathbf{k} \cdot \mathbf{r}_{12} c_2(\mathbf{r}_1, \mathbf{r}_2) \\ &\quad \times \frac{\partial n_e(\mathbf{r}_2)}{\partial r_{2\beta}} \mathbf{k} \cdot \mathbf{r}_{12}, \end{aligned} \quad (3.4)$$

as is shown in the Appendix. Here  $c_2(\mathbf{r}_1, \mathbf{r}_2)$  is the Ornstein-Zernike direct correlation function of the solid, defined as the inverse of the density-correlation function, i.e.,

$$\int d\mathbf{r}_2 \left( \frac{\delta(\mathbf{r}_{12})}{n_e(\mathbf{r}_1)} - c_2(\mathbf{r}_1, \mathbf{r}_2) \right) \langle \delta n(\mathbf{r}_2) \delta n(\mathbf{r}_3) \rangle_{\text{eq}} = \delta(\mathbf{r}_{13}). \quad (3.5)$$

The approximate equalities in Eq. (3.4) are asymptotically exact in the long-wavelength limit  $\mathbf{k} \rightarrow \mathbf{0}$ . The terms neglected are higher order in the wave vector  $k$  and do not contribute to the hydrodynamiclike equations. To write the evolution equations in a compact way we define the tensor

$$\begin{aligned} \lambda_{\alpha\beta\gamma\delta} &= \frac{k_B T}{2V} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\partial n_e(\mathbf{r}_1)}{\partial r_{1\alpha}} \frac{\partial n_e(\mathbf{r}_2)}{\partial r_{2\beta}} \\ &\quad \times c_2(\mathbf{r}_1, \mathbf{r}_2) r_{12\gamma} r_{12\delta}. \end{aligned} \quad (3.6)$$

It is a fourth-rank tensor with cubic symmetry, and therefore contains only *three independent* scalars. Consequently it obeys, apart from the obvious symmetries, ( $\alpha \leftrightarrow \beta$ ) and ( $\gamma \leftrightarrow \delta$ ), also the Voigt symmetries ( $\alpha\beta \leftrightarrow \gamma\delta$ ).

Using Eqs. (3.3)–(3.4) and (3.6) we obtain the following equations of motion:

$$\begin{aligned} m \frac{\partial}{\partial t} \langle \delta n(\mathbf{k}; t) \rangle &= -i\mathbf{k} \cdot \langle \mathbf{g}(\mathbf{k}; t) \rangle, \\ \frac{\partial}{\partial t} \langle g_\alpha(\mathbf{k}; t) \rangle &= -ik_\alpha (k_B T / S(0)) \langle \delta n(\mathbf{k}; t) \rangle \\ &\quad - \lambda_{\alpha\beta\gamma\delta} k_\gamma k_\delta \langle u_\beta(\mathbf{k}; t) \rangle, \end{aligned} \quad (3.7)$$

$$mn_0 \frac{\partial}{\partial t} \langle u_\alpha(\mathbf{k}; t) \rangle = \langle g_\alpha(\mathbf{k}; t) \rangle,$$

where  $S(0) = \lim_{\mathbf{k} \rightarrow \mathbf{0}} S(\mathbf{k}) = \langle n|n \rangle / n_0$  is the static structure factor,<sup>14</sup> and the summation over repeated Greek indices is hereafter assumed. Note that Eqs. (3.7) do not contain any dissipative terms. However, the nondissipative reactive coefficients are exact. They will not change when dissipative processes are included.

In the macroscopic theory of elasticity, in which the density of vacancies is assumed to be a time-independent constant, there is the following relation between the density change and the displacement:

$$\langle \delta n(\mathbf{k}; t) \rangle = -i\mathbf{k} \cdot n_0 \langle \mathbf{u}(\mathbf{k}; t) \rangle. \quad (3.8)$$

Equations (3.7) are more general; the density and displacement are independent variables. This additional freedom allows for a vacancy diffusion.<sup>1</sup> To define the

nonequilibrium density of vacancies we are looking for a mode in (3.7) that does not decay: On physical grounds we expect the vacancy concentration to decay via a diffusive process that is absent on the present, nondissipative level of description. With this in mind we define the nonequilibrium density of vacancies as the following linear combination of the density and displacement fields:

$$\langle \delta c(\mathbf{k}; t) \rangle = - \langle \delta n(\mathbf{k}; t) \rangle - i\mathbf{k} \cdot n_0 \langle \mathbf{u}(\mathbf{k}; t) \rangle. \quad (3.9)$$

Note the difference in sign between  $\delta n$  and  $\delta c$ ; the density  $n$  counts the number of particles and  $c$  counts vacancies. Using definition (3.9) we rewrite evolution equations (3.7):

$$\begin{aligned} \frac{\partial}{\partial t} \langle \delta c(\mathbf{k}; t) \rangle &= 0, \\ \frac{\partial}{\partial t} \langle g_\alpha(\mathbf{k}; t) \rangle &= ik_\alpha (n_0 k_B T / S(0)) \langle \delta c(\mathbf{k}; t) \rangle \\ &\quad - \Lambda_{\alpha\beta\gamma\delta} k_\gamma k_\delta \langle u_\beta(\mathbf{k}; t) \rangle, \quad (3.10) \\ mn_0 \frac{\partial}{\partial t} \langle u_\alpha(\mathbf{k}; t) \rangle &= \langle g_\alpha(\mathbf{k}; t) \rangle. \end{aligned}$$

Here  $\Lambda_{\alpha\beta\gamma\delta} = \lambda_{\alpha\beta\gamma\delta} + n_0 k_B T / [2S(0)] (\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma})$ . As has been anticipated the vacancy diffusion mode does not decay in the nondissipative limit.

#### IV. ELASTIC CONSTANTS

In the previous section we obtained the nondissipative equations of motion for the slow modes in the same form as the ideal equations of elasticity with the vacancy mode included.<sup>15</sup> By taking the time derivative of the last equation in (3.10) one arrives at the usual linear equations of ideal elasticity:

$$mn_0 \frac{\partial^2}{\partial t^2} \langle u_\alpha(\mathbf{k}; t) \rangle = -\Lambda_{\alpha\beta\gamma\delta} k_\gamma k_\delta \langle u_\beta(\mathbf{k}; t) \rangle. \quad (4.1)$$

Then we can identify the matrix  $\Lambda_{\alpha\beta\gamma\delta} k_\beta k_\delta$  with the so-called wave propagation matrix.<sup>16</sup> The tensor  $\Lambda_{\alpha\beta\gamma\delta}$  equals  $\hat{A}_{\alpha\beta\gamma\delta}$  in Wallace's<sup>16</sup> book, as implied by his Eqs. (3.11) and (7.20). It obeys all Voigt symmetries, as shown below Eq. (3.6), and is related to the stress-strain elastic constants<sup>17</sup>  $B_{\alpha\beta\gamma\delta}$ :

$$\begin{aligned} B_{\alpha\beta\gamma\delta} &= \Lambda_{\alpha\gamma\beta\delta} + \Lambda_{\beta\gamma\alpha\delta} - \Lambda_{\alpha\beta\gamma\delta} \\ &= (\lambda_{\alpha\gamma\beta\delta} + \lambda_{\beta\gamma\alpha\delta} - \lambda_{\alpha\beta\gamma\delta}) \\ &\quad + (n_0 k_B T / S(0)) \delta_{\alpha\beta} \delta_{\gamma\delta}. \end{aligned} \quad (4.2)$$

$B_{\alpha\beta\gamma\delta}$  are macroscopically defined as the derivatives of the elements of the stress tensor with respect to the elements of the strain tensor.

The expressions (4.2) for the isothermal elastic constants involve the long-wavelength limit of the structure factor and integrals over the direct correlation function with derivatives of the equilibrium density profile. The expression for  $B_{xyxy}$  does not involve the structure factor, so that

$$B_{xyxy} = \lambda_{xyxy}; \quad (4.3)$$

it should be easy to calculate it using results of a density-functional theory. The functional form of  $B_{xyxy}$  is essentially the same as the Triezenberg-Zwanzig formula for the surface tension. Both  $B_{xyxy}$  and the surface tension are the rigidity constants<sup>9</sup> of broken-symmetry phases. Note that  $B_{xyxy}$  is zero in the liquid state.

We expect that formula (4.2) for the elastic constants also applies to the hard sphere solid, as it is well defined for that case. However, the present derivation does not include the hard sphere case, because the right-hand side of the essential inequality (2.23) vanishes for hard spheres. The reason is that the denominator of Eq. (2.23) is divergent in the hard sphere limit, as are the expressions for the elastic coefficients of Squire, Holt, and Hoover.<sup>6</sup>

#### V. CONCLUDING REMARKS

To summarize, two main results have been presented. First we have proposed a microscopic expression for the displacement field. We showed that it agrees with an intuitive understanding of the displacement. The Fourier transform of the displacement correlation function has been proved to diverge at least as  $k^{-2}$  in the long-wavelength limit  $\mathbf{k} \rightarrow \mathbf{0}$ . Second, we obtained new exact expressions for the isothermal elastic constants. These expressions can be used to study elastic properties of crystals near the melting point where the presence of vacancies cannot be neglected.

The present theory can be straightforwardly generalized to include dissipative processes. In this way Green-Kubo expressions for the dissipative coefficients can be derived. Of particular interest would be the expression for the vacancy-diffusion tensor. One could then try to use it to understand why the characteristic time scale for the vacancy diffusion is much larger than the time scales associated with, for example, sound attenuation. With some modifications the present method could perhaps be used to study dynamics of other broken-symmetry systems, such as, for example, liquid crystals.

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#### APPENDIX

To derive approximate relation (3.4) we start with the integral equation that is equivalent to the Ornstein-Zernike equation:

$$\int d\mathbf{r}_2 \left( \frac{\delta(\mathbf{r}_{12})}{n_e(\mathbf{r}_1)} - c_2(\mathbf{r}_1, \mathbf{r}_2) \right) \langle \delta n(\mathbf{r}_2) \delta n(\mathbf{r}_3) \rangle_{\text{eq}} = \delta(\mathbf{r}_{13}). \quad (A1)$$

We multiply both sides of Eq. (A1) with

$$\frac{1}{\mathcal{N}V} e^{i\mathbf{k}\cdot\mathbf{r}_1} \frac{\partial n_e(\mathbf{r}_1)}{\partial r_{1\alpha}} \frac{\partial n_e(\mathbf{r}_3)}{\partial r_{3\beta}} e^{-i\mathbf{k}\cdot\mathbf{r}_3} \quad (\text{A2})$$

and integrate. This leads to

$$\frac{1}{\mathcal{N}V} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 e^{i\mathbf{k}\cdot\mathbf{r}_1} \frac{\partial n_e(\mathbf{r}_1)}{\partial r_{1\alpha}} \left( \frac{\delta(\mathbf{r}_{12})}{n_e(\mathbf{r}_1)} - c_2(\mathbf{r}_1, \mathbf{r}_2) \right) \langle \delta n(\mathbf{r}_2) \delta n(\mathbf{r}_3) \rangle_{\text{eq}} e^{-i\mathbf{k}\cdot\mathbf{r}_3} \frac{\partial n_e(\mathbf{r}_3)}{\partial r_{3\beta}} = \delta_{\alpha\beta}. \quad (\text{A3})$$

Now we use the assumption that the *only long-range* correlations (diverging susceptibilities) in the microscopic density field  $n(\mathbf{r}) = n_{\parallel}(\mathbf{r}) + n_{\perp}(\mathbf{r})$  are caused by the displacement field with  $n_{\parallel}(\mathbf{r})$  defined in (2.14). We neglect all remaining short-range correlations, i.e.,

$$\begin{aligned} \langle \delta n(\mathbf{r}_2) \delta n(\mathbf{r}_3) \rangle_{\text{eq}} &\simeq \langle \delta n_{\parallel}(\mathbf{r}_2) \delta n_{\parallel}(\mathbf{r}_3) \rangle_{\text{eq}} \\ &= \frac{\partial n_e(\mathbf{r}_2)}{\partial r_{2\gamma}} \langle u_{\gamma}(\mathbf{r}_2) u_{\delta}(\mathbf{r}_3) \rangle_{\text{eq}} \frac{\partial n_e(\mathbf{r}_3)}{\partial r_{3\delta}}. \end{aligned} \quad (\text{A4})$$

After substituting this in Eq. (A3), the  $\mathbf{r}_3$  integral reduces to

$$\int d\mathbf{r}_3 e^{-i\mathbf{k}\cdot\mathbf{r}_3} u_{\delta}(\mathbf{r}_3) \frac{\partial n_e(\mathbf{r}_3)}{\partial r_{3\delta}} \frac{\partial n_e(\mathbf{r}_3)}{\partial r_{3\beta}} = \mathcal{N} u_{\beta}(\mathbf{k}). \quad (\text{A5})$$

We use the identity

$$\sum_{\mathbf{Q}} \sum_{\mathbf{q}} e^{-i(\mathbf{Q}+\mathbf{q})\cdot(\mathbf{r}_2-\mathbf{r}'_2)} = V \delta(\mathbf{r}_2 - \mathbf{r}'_2) \quad (\text{A6})$$

and the spatial symmetries of the correlation matrix  $\langle u_{\gamma}(\mathbf{r}_2) u_{\delta}(\mathbf{r}_3) \rangle_{\text{eq}}$ , and we put (A3) in the form

$$\Delta_{\alpha\gamma}(\mathbf{k}) \langle u_{\gamma} | u_{\delta} \rangle = \delta_{\alpha\beta}, \quad (\text{A7})$$

where the  $(\alpha\beta)$  element of the inverse matrix  $\Delta(\mathbf{k}) = \langle \mathbf{u} | \mathbf{u} \rangle^{-1}$  is

$$\begin{aligned} \Delta_{\alpha\beta}(\mathbf{k}) &= \frac{1}{V} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\partial n_e(\mathbf{r}_1)}{\partial r_{1\alpha}} \\ &\quad \times e^{i\mathbf{k}\cdot\mathbf{r}_1} \left( \frac{\delta(\mathbf{r}_{12})}{n_e(\mathbf{r}_1)} - c_2(\mathbf{r}_1, \mathbf{r}_2) \right) \\ &\quad \times \frac{\partial n_e(\mathbf{r}_2)}{\partial r_{2\beta}} e^{-i\mathbf{k}\cdot\mathbf{r}_2}. \end{aligned} \quad (\text{A8})$$

Using the equation for the equilibrium density profile<sup>18</sup>

$$\frac{1}{n_e(\mathbf{r}_1)} \frac{\partial n_e(\mathbf{r}_1)}{\partial r_{1\alpha}} = \int d\mathbf{r}_2 c_2(\mathbf{r}_1, \mathbf{r}_2) \frac{\partial n_e(\mathbf{r}_2)}{\partial r_{2\alpha}}, \quad (\text{A9})$$

we can transform (A8) into

$$\begin{aligned} \Delta_{\alpha\beta}(\mathbf{k}) &= \frac{1}{V} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\partial n_e(\mathbf{r}_1)}{\partial r_{1\alpha}} \\ &\quad \times c_2(\mathbf{r}_1, \mathbf{r}_2) \frac{\partial n_e(\mathbf{r}_2)}{\partial r_{2\beta}} (1 - e^{i\mathbf{k}\cdot\mathbf{r}_{12}}). \end{aligned} \quad (\text{A10})$$

In the derivation of this result we have only kept the dominant terms in  $\langle \delta n \delta n \rangle_{\text{eq}}$  which are of  $\mathcal{O}(k^{-2})$ . For consistency we should only keep the dominant small  $k$  terms in (A10). As the direct correlation function is supposedly of short range, we can simply expand the integrand in (A10) in powers of  $\mathbf{k}$ . The resulting integral exists and yields for  $\mathbf{k} \rightarrow \mathbf{0}$ ,

$$\begin{aligned} \Delta_{\alpha\beta}(\mathbf{k}) &\simeq \frac{1}{2V} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\partial n_e(\mathbf{r}_1)}{\partial r_{1\alpha}} \\ &\quad \times c_2(\mathbf{r}_1, \mathbf{r}_2) \frac{\partial n_e(\mathbf{r}_2)}{\partial r_{2\alpha}} (\mathbf{k} \cdot \mathbf{r}_{12})^2 \\ &\equiv (1/k_B T) \lambda_{\alpha\beta\gamma\delta} k_{\gamma} k_{\delta}. \end{aligned} \quad (\text{A11})$$

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