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Statistical Mechanics of Dissipative Transport in Crystals

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We present a microscopic derivation of dissipative (nonideal) hydrodynamic-like equations for crystals. The local density changes and the lattice displacement (distortion) are treated as independent. In this way we take into account all the eight slow modes predicted by the phenomenological theory, including the so-called vacancy diffusion mode. However, microscopically derived hydrodynamic-like equations are simpler than those postulated in the phenomenological theory. We also derive the exact formal expressions for the solid-state transport coefficients in terms of the Green-Kubo integrals.

KEY WORDS: Statistical mechanics; nonequilibrium statistical mechanics; crystals; slow (hydrodynamic and broken symmetry) modes; transport coefficients.

1. INTRODUCTION

The purpose of this paper is to provide a statistical mechanical basis for the phenomenological theory of dissipative transport in (classical) crystals.

The long-time large-scale dynamics of a macroscopic system can be described in terms of a few collective variables. These are so-called slow modes of the system of interest. They owe their existence to the local conservation laws and to spontaneous breaking of continuous symmetries.(1)

In the simplest case of a one-component fluid there are three conservation laws: number of particles, momentum (three components), and energy. These conservation laws are local, i.e., the densities of the conserved quantities can change only due to flow of these quantities. More precisely, time

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This paper is dedicated to Prof. Matthieu Ernst on the occasion of his 60th birthday. His advice and encouragement were invaluable in early stages of the research described here.

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derivatives of the densities can be expressed as divergences of the corresponding currents. Hence, the deviations of the number, momentum, and energy densities from their equilibrium values have lifetimes that are proportional to their characteristic wavelengths. In the long-wavelength limit these lifetimes become larger than lifetimes of all of the other variables. Therefore, after the initial (slip) period, the dynamics of the fluid can be completely described in terms of the number, momentum, and energy densities. The corresponding equations of motion are known as hydrodynamic equations.

This simple picture changes if in the equilibrium state of the system of interest a continuous symmetry is spontaneously broken:(2) First, there appear low energy excitations that correspond to fluctuations in the subspace *orthogonal* to the direction in which the system has ordered. These excitations are known as Goldstone modes. Second, the transverse correlation functions(2) are long-ranged: they decay algebraically. Third, a *rigidity* emerges: the system exerts a restoring force in response to a nonuniform displacement in the subspace orthogonal to the direction of the ordering. One of the consequences of the new equilibrium behavior is emergence of the additional slow modes. These modes are the above-mentioned low energy excitations (Goldstone modes). Hereafter we will use the name *hydrodynamic-like* equations for the (coupled) equations of motion for both the densities of the conserved quantities and the Goldstone modes.

The time evolution of the densities of the conserved quantities is slow because of the existence of the conservation laws. The Goldstone modes belong to the set of slow modes due to small (vanishing in the long wavelength limit) energy cost associated with them. More precisely, it is the long-wavelength divergence of the transverse correlation functions that makes their relaxation times arbitrary large.

Our aim in this paper is to present a complete statistical mechanical description of the dissipative transport in one of the most common broken symmetry states: crystalline solids. Let us first introduce the problem. The general theory as outlined above disagrees with the standard theory of elasticity. The theory of elasticity deals with six sound modes or elastic waves (three branches for a given wavevector, two possible velocity signs for a given branch) and an energy mode, a total of seven slow modes. On the contrary, the general theory clearly says that there should be eight modes: we have five densities of conserved quantities (number, three components of momentum, and energy) and three modes associated with broken translational symmetry (the original symmetry group is three parameter, hence the three broken symmetry modes).

The deficiency of the standard approach was first discussed in a seminal paper by Martin *et al.*(3) They argued that the mode missing in the usual description should be associated with the vacancy diffusion. To include this mode it was necessary to treat the particle density and the displacement field independently.

Both the analysis of Martin *et al.* and a later study by Fleming and Cohen(4) of the spectrum of the light scattered by crystals were purely phenomenological. In particular the reactive and dissipative coefficients were treated as parameters. The problem of deriving the full macroscopic description of the long-time large-scale crystal dynamics from the microscopic statistical mechanical theory remained unsolved.[2]

It seems now that the main stumbling block was the lack of a microscopic expression for the slow mode associated with broken symmetry, i.e., for the displacement field. It should be emphasized that such an expression cannot identify the lattice sites with the (averaged) positions of specific particles. Such a procedure would necessarily lead to a relation between the displacement field and the density, and to the neglect of the vacancy diffusion mode.(4)

Recently, in collaboration with Matthieu Ernst, we postulated a microscopic expression for the displacement field in crystals.(7) WE showed that the displacement field correlation function is long-ranged, derived the nondissipative equations of motion for the density, momentum and broken symmetry modes (the energy mode was neglected), and obtained new exact expressions for the isothermal elastic constants.

In this paper we complement the study of ref. 6 with a derivation of the dissipative equations of motion for all the eight slow modes, including the energy mode. We assume that only the correlation functions that *have* to diverge in the long-wavelength limit (due to broken translational symmetry of the crystalline state) are singular and all the other ones are regular in this limit. We note that this assumption leads to a frequency matrix that is considerably simpler than that postulated in the phenomenological approaches. As a result, the hydrodynamic-like equations derived here, while having the same general structure as those postulated in the phenomenological theory, are also simpler.

As a by-product of the derivation of the hydrodynamic-like equations we obtain exact expressions for the transport coefficients. In particular we derive for the first time the transport coefficients associated with the Goldstone modes of crystals.

The paper is organized as follows. In Section 2 we briefly review the microscopic definition of the displacement field. The review is followed by a derivation of the dissipative equations of motion in Section 3, and an

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[2] In a very interesting paper Kirkpatrick *et al.*(5) considered a kinetic theory of transport in a hard-sphere crystal. However, they included only the seven standard modes.

analysis of the vacancy diffusion in Section 4. Next, in Section 5 we analyze the Green–Kubo expressions for the transport coefficients. We conclude with a summary of the results and some comments.

2. MICROSCOPIC DEFINITION OF THE DISPLACEMENT FIELD

In the crystalline phase the translational symmetry of the Hamiltonian is spontaneously broken. The general theory predicts that the symmetry breaking leads to emergence of the new set of slow modes that correspond to displacements[3] of the broken symmetry state in the direction orthogonal to the direction of the ordering.

The displacement in the direction orthogonal to the ordering is a change of the broken symmetry state that leads to a different state of the same energy as the original state. For a crystalline solid this is a uniform translation. A translation by a vector **a** of small magnitude $|\mathbf{a}|$ changes the density profile $n_e(\mathbf{r})$ of the original state to the density profile $n'_e(\mathbf{r})$ of the new (but equivalent) state:

$$n_e(\mathbf{r}) \to n'_e(\mathbf{r}) = n_e(\mathbf{r}) - \frac{\partial n_e(\mathbf{r})}{\partial \mathbf{r}} \cdot \mathbf{a} \tag{2.1}$$

Let us now assume that translation vector changes slowly in space, or more accurately, that $\mathbf{a}(\mathbf{r})$ is a periodic function, $\mathbf{a}(\mathbf{r}) = \mathbf{a}e^{i\mathbf{k}\cdot\mathbf{r}}$. In this case we generalize (2.1) to

$$n_e(\mathbf{r}) \to n'_e(\mathbf{r}) = n_e(\mathbf{r}) - \frac{\partial n_e(\mathbf{r})}{\partial \mathbf{r}} \cdot \mathbf{a}(\mathbf{r}) = n_e(\mathbf{r}) - e^{i\mathbf{k}\cdot\mathbf{r}} \frac{\partial n_e(\mathbf{r})}{\partial \mathbf{r}} \cdot \mathbf{a} \tag{2.2}$$

We conclude that slowly varying displacement of the crystalline state in the direction perpendicular to the direction of the ordering is signaled by the change of the density that is proportional to $-e^{i\mathbf{k}\cdot\mathbf{r}} \nabla n_e(\mathbf{r})$. Note that the average *macroscopic* density is *not* changed.

It follows that in order to get the **k** Fourier component of the lattice displacement from the microscopic density field one should project the microscopic density change onto (appropriately normalized) $-e^{i\mathbf{k}\cdot\mathbf{r}} \nabla n_e(\mathbf{r})$. The question arises as to what kind of a scalar product should be used for the projection. It should be noted that this projection should express *geometrical* similarity between the two quantities, not the thermodynamic

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[3] Note that in this section we use the word displacement in two different meanings: to denote a deviation from the original equilibrium state and to denote a distortion of the lattice. It should be clear from the context which of these two meanings is intended.

one. Thus it does not seem appropriate to use here the standard scalar product induced by the equilibrium average [see Eq. (3.2)].

We proposed in ref. 6 to use the following scalar product:

$$(a, b)=\frac{1}{V}\int d\mathbf{r}\, a^*(\mathbf{r})\, b(\mathbf{r}) \tag{2.3}$$

Using the scalar product (2.3), we arrived at the following expression for the microscopic (lattice) displacement field:$^{(6)}$

$$\mathbf{u}(\mathbf{k})=\frac{V}{\mathcal{N}}\left(-e^{i\mathbf{k}\cdot\mathbf{r}}\frac{\partial n_e(\mathbf{r})}{\partial\mathbf{r}}, \delta n\right)=-\frac{1}{\mathcal{N}}\sum_{\mathbf{G}} i\mathbf{G}n_{\mathbf{G}}\,\delta n(\mathbf{k}-\mathbf{G}) \tag{2.4}$$

here δn is the difference between the microscopic density field n,

$$n(\mathbf{r})=\sum_i \delta(\mathbf{r}-\mathbf{R}_i) \tag{2.5}$$

and its average equilibrium value n_e,

$$\delta n(\mathbf{r})=n(\mathbf{r})-n_e(\mathbf{r}) \tag{2.6}$$

and $\mathcal{N}$ is the normalization constant,

$$\mathcal{N}=\frac{1}{3}\left(-e^{i\mathbf{k}\cdot\mathbf{r}}\frac{\partial n_e(\mathbf{r})}{\partial r_\alpha}, -e^{i\mathbf{k}\cdot\mathbf{r}}\frac{\partial n_e(\mathbf{r})}{\partial r_\alpha}\right) \tag{2.7}$$

Greek indices denote the Cartesian components of vectors and tensors, and the summation over repeated indices is always assumed. Finally, in Eq. (2.4) $\sum_{\mathbf{G}}$ denotes summation over the reciprocal lattice vectors $\mathbf{G}$ and $n_{\mathbf{G}}$ is the amplitude of the component of the density profile corresponding to $\mathbf{G}$.

Note that in general $\mathcal{N}$ should be replaced by a second-rank tensor. Here we have assumed cubic symmetry. Moreover, to the leading order in the wavevector $\mathcal{N}$ can be replaced by its $\mathbf{k}=\mathbf{0}$ value,

$$\mathcal{N}=\frac{1}{3}\sum_{\mathbf{G}} G^2\,|n_{\mathbf{G}}|^2+\mathcal{O}(k^2)=\frac{1}{3v}\int_v d\mathbf{r}\left(\frac{\partial n_e(\mathbf{r})}{\partial\mathbf{r}}\right)^2+\mathcal{O}(k^2) \tag{2.8}$$

Here v is the volume of the unit cell.

To justify definition (2.4) we showed$^{(6)}$ that the Fourier transform of the correlation function of the displacement field diverges in the long-wavelength limit. To this end we used Bogoliubov's inequality$^{(1)}$

$$\langle |A|^2\rangle_{\mathrm{eq}}\,\langle |B|^2\rangle_{\mathrm{eq}}\geqslant |\langle AB\rangle_{\mathrm{eq}}|^2 \tag{2.9}$$

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 $\langle \cdots \rangle_{\text{eq}}$ denote the equilibrium ensemble average, $\hat{\mathbf{n}}$ is a unit vector, V denotes the volume of the system (the thermodynamic limit is implied), and $\mathbf{g}(\mathbf{k})$ is the Fourier transform of the microscopic momentum density

$$\mathbf{g}(\mathbf{r}) = \sum_i m\mathbf{V}_i\, \delta(\mathbf{r} - \mathbf{R}_i) \tag{2.10}$$

with $\mathbf{V}_i$ the velocity of the ith particle and m its mass, and a dot denotes the time derivative. We argued that the cross-correlation tends to a finite number at $\mathbf{k} \to 0$.

$$\lim_{\mathbf{k} \to 0} |\langle AB \rangle_{\text{eq}}| = \frac{k_{\text{B}} T}{3\mathcal{N}} \left(\frac{\partial n_e(\mathbf{r})}{\partial r_\alpha}, \frac{\partial n_e(\mathbf{r})}{\partial r_\alpha} \right) = k_{\text{B}} T \tag{2.11}$$

Furthermore, we expressed $\langle |B|^2 \rangle_{\text{eq}}$ in terms of the correlation function of the stress tensor $\vec{\sigma}(\mathbf{k})$ that is defined through the continuity equation for the momentum:

$$\dot{\mathbf{g}}(\mathbf{k}; t) = -i\mathbf{k} \cdot \vec{\sigma}(\mathbf{k}; t) \tag{2.12}$$

Explicitly, we got

$$\langle |B|^2 \rangle_{\text{eq}} = \frac{1}{V} \langle |\dot{\mathbf{g}}(\mathbf{k}) \cdot \hat{\mathbf{n}}|^2 \rangle_{\text{eq}} = k^2 \frac{1}{V} \langle |\hat{\mathbf{k}} \cdot \vec{\sigma}(\mathbf{k}) \cdot \hat{\mathbf{n}}|^2 \rangle_{\text{eq}} \tag{2.13}$$

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

Finally, we considered Bogoliubov's inequality (2.9) at small wave vectors. We estimated the cross-correlation $\langle AB \rangle_{\text{eq}}$ using relation (2.11) and arrived at the inequality

$$\frac{1}{V} \langle |\hat{\mathbf{n}} \cdot \mathbf{u}(\mathbf{k})|^2 \rangle_{\text{eq}} \geqslant \frac{1}{k^2} \frac{(k_{\text{B}} T)^2}{\lim_{\mathbf{k} \to 0} (1/V) \langle |\hat{\mathbf{k}} \cdot \vec{\sigma}(\mathbf{k}) \cdot \hat{\mathbf{n}}|^2 \rangle_{\text{eq}}} \tag{2.14}$$

Equation (2.14) shows 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 $\mathbf{k} \to 0$.

The correlations of the displacement field (2.4) are the only correlations that, on the basis of the Bogoliubov's inequality, *have* to diverge as $\mathbf{k} \to 0$. Indeed, if one replaces $(-e^{i\mathbf{k} \cdot \mathbf{r}}\, \nabla n_e(\mathbf{r}), \delta n)$ in (2.4) by a more general expression $(f, \delta n)$, then one easily verifies that the expression corresponding to (2.11) is proportional to $(f, \hat{\mathbf{n}} \cdot \nabla n_e)$. 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 therefore follow Occam razor and *assume* that only the correlations $\langle u_\alpha(-\mathbf{k})\, u_\beta(\mathbf{k})\rangle_{\text{eq}}$ are singular, and more explicitly we assume that they diverge exactly like k^{-2}. Furthermore, we assume that other correlation functions are regular for $\mathbf{k}\to 0$.

3. DISSIPATIVE EVOLUTION EQUATIONS FOR THE SLOW VARIABLES

Apart from the displacement field we also have the usual five slow hydrodynamic variables.(1, 8) These are number, momentum, and energy densities. These variables satisfy local conservation laws: their time derivatives equal the divergences of the corresponding currents, and therefore their time evolution is slow in the long-wavelength limit.

We study the time evolution of the deviations of the slow variables from their equilibrium values, $\delta n(\mathbf{k})$, $\mathbf{g}(\mathbf{k})$, $\delta e(\mathbf{k})$, and $\mathbf{u}(\mathbf{k})$, for small wavevectors $\mathbf{k}\to\mathbf{0}$. Here $\delta n(\mathbf{k})$ and $\mathbf{g}(\mathbf{k})$ are Fourier transforms of the density change (2.5) and the momentum (2.10), respectively, and $\mathbf{u}(\mathbf{k})$ is given by (2.4). Finally, $\delta e(\mathbf{k})$ is the Fourier transform of the deviation of the energy e,

$$e(\mathbf{r})=\sum_i\left(\tfrac{1}{2}mV_i^2+\tfrac{1}{2}\sum_{j\neq i}\phi(R_{ij})\right)\delta(\mathbf{r}-\mathbf{R}_i) \tag{3.1}$$

from its equilibrium value. In Eq. (3.1) $\phi(R)$ is the pair potential and $R_{ij}=|\mathbf{R}_i-\mathbf{R}_j|$. Note that $\langle\mathbf{g}(\mathbf{k})\rangle_{\text{eq}}$ and $\langle\mathbf{u}(\mathbf{k})\rangle_{\text{eq}}$ are vanishing.

To derive the equations of motion we use the projection operator method(1) we define a scalar product[4]

$$\langle a_i\,|\,a_j\rangle=\frac{1}{V}\,\langle\delta a_i(-\mathbf{k})\,\delta a_j(\mathbf{k})\rangle_{\text{eq}} \tag{3.2}$$

Here $\delta a_i(\mathbf{k})$, $i=1,\ldots,8$, denote the deviations of the slow variables from their equilibrium values.

The variables $\delta n(\mathbf{k})$, $\mathbf{g}(\mathbf{k})$, $\delta e(\mathbf{k})$, and $\mathbf{u}(\mathbf{k})$ are not mutually orthogonal with respect to the scalar product (3.2). First, the energy variable contains a part parallel to the density variable. Second, the submatrix $\langle u_\alpha\,|\,u_\beta\rangle$ has nonvanishing off-diagonal elements.

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[4] Note that for a broken symmetry state we have two scalar products. One has been defined by Eq. (2.3); it determines the value of the slow mode in terms of the geometrical structure of the broken symmetry phase. The other, defined through Eq. (3.2), is the standard scalar product induced by the equilibrium ensemble average that is used in the projection operator method.

It is convenient to subtract from the energy $\delta e(\mathbf{k})$ the part parallel to the density $\delta n(\mathbf{k})$ [in the sense of the scalar product (3.2)]:

$$\delta e(\mathbf{k}) \rightarrow \delta e(\mathbf{k}) - \delta n(\mathbf{k}) \langle n | n \rangle^{-1} \langle n | e \rangle \tag{3.3}$$

The new variable $\delta e(\mathbf{k}) - \delta n(\mathbf{k}) \langle n | n \rangle^{-1} \langle n | e \rangle$ has a natural interpretation: in the long-wavelength limit it is proportional to the deviation of the temperature from its equilibrium value,

$$n_0 c_V \delta T(\mathbf{k}) = \delta e(\mathbf{k}) - \delta n(\mathbf{k}) \langle n | n \rangle^{-1} \langle n | e \rangle \tag{3.4}$$

In Eq. (3.4) no is the average macroscopic density and c_V is the specific heat per particle at constant volume.

The derivation of the dissipative equations of motion is fairly standard. Here we will only sketch the actual calculations. The Laplace transform of the equations of motion have the following form:

$$z\langle a_i(\mathbf{k}; z)\rangle - \langle a_i(\mathbf{k}; t=0)\rangle = \sum_j (\Omega_{ij}(\mathbf{k}) + U_{ij}(\mathbf{k}; z)) \langle a_j(\mathbf{k}; z)\rangle \tag{3.5}$$

In (3.5) $\Omega_{ij}(\mathbf{k})$ is the frequency matrix and $U_{ij}(\mathbf{k}; z)$ is the transport matrix,

$$\Omega_{ij}(\mathbf{k}) = \sum_l \langle a_j | a_l \rangle^{-1} \langle a_l | \mathcal{L} a_i \rangle \tag{3.6}$$

$$U_{ij}(\mathbf{k}, z) = \sum_l \langle a_j | a_l \rangle^{-1} \left\langle a_l \,\middle|\, \mathcal{L}\mathcal{Q} \frac{1}{z - \mathcal{Q}\mathcal{L}\mathcal{Q}} \mathcal{Q}\mathcal{L} a_i \right\rangle \tag{3.7}$$

Here $\langle a_i | a_j \rangle^{-1}$ denotes the inverse of the matrix $\langle a_j | a_j \rangle$, $\mathcal{L}$ is the Liouville operator,$^{(8)}$ and $\mathcal{Q}$ is the projection operator on the subspace orthogonal to the slow variables,

$$\mathcal{Q} = \mathcal{I} - \mathcal{P} \tag{3.8}$$

where $\mathcal{I}$ is the identity and $\mathcal{P}$ is the projection operator on the slow subspace,

$$\mathcal{P} f(\mathbf{k}) = \sum_{i,j} \delta a_i(\mathbf{k}) \langle a_i | a_j \rangle^{-1} \langle a_j | f \rangle \tag{3.9}$$

To get the explicit form of the nondissipative part of the evolution equations we have to calculate the inverse of the correlation matrix and the matrix elements of the Liouville operator $\mathcal{L}$.

The calculation of the inverse matrix $\langle a_i \mid a_j \rangle^{-1}$ is relatively simple. First, the densities of the conserved quantities $\delta n(\mathbf{k})$, $\mathbf{g}(\mathbf{k})$, and $n_0 c_V \delta T(\mathbf{k})$ are mutually orthogonal. Second, the correlations between the number and energy densities and the displacement field vanish in the $\mathbf{k} \to \mathbf{0}$ limit,

$$\langle n \mid u_\alpha \rangle \sim \mathcal{O}(k), \qquad \langle e \mid u_\alpha \rangle \sim \mathcal{O}(k) \tag{3.10}$$

This fact follows from the assumption that these correlations are regular in the $\mathbf{k} \to \mathbf{0}$ limit and therefore can be expanded around the $\mathbf{k} = \mathbf{0}$ wavevector. Third, the correlations of the displacement field $\langle u_\alpha \mid u_\beta \rangle$ are the *only* divergent correlations. It can then be shown that the off-diagonal elements of the inverse matrix $\langle a_i \mid a_j \rangle^{-1}$ are (i) zero, when both a_i and a_j are the densities of the conserved quantities, (ii) of the order of k^3, when one of a_i, a_j is the displacement mode, or (iii) of the order of k^2, when both a_i and a_j are the displacement modes. Therefore the only elements of the inverse matrix that contribute to the hydrodynamic-like equations are

$$\begin{aligned}
\langle n \mid n \rangle^{-1} &= (n_0 S(0))^{-1} \\
\langle g_\alpha \mid g_\beta \rangle^{-1} &= (n_0 m k_B T)^{-1} \delta_{\alpha\beta} \\
\langle n_0 c_V T \mid n_0 c_V T \rangle^{-1} &= (n_0 c_V k_B T^2)^{-1} \\
\langle u_\alpha \mid u_\beta \rangle^{-1} &= (k_B T)^{-1} \lambda_{\alpha\beta\gamma\delta} k_\gamma k_\delta
\end{aligned} \tag{3.11}$$

where the last equality was proven in ref. 6. In Eqs. (3.11) $S(0)$ is the $k = 0$ value of the structure factor, and the tensor $\lambda_{\alpha\beta\gamma\delta}$ is defined as

$$\lambda_{\alpha\beta\gamma\delta} = \frac{k_B T}{2V} \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, \frac{\partial n_e(\mathbf{r}_1)}{\partial r_{1\alpha}} \frac{\partial n_e(\mathbf{r}_2)}{\partial r_{2\beta}} c_2(\mathbf{r}_1, \mathbf{r}_2) \, r_{12\gamma} r_{12\delta} \tag{3.12}$$

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.(9)

Furthermore it can be shown that the only nonzero matrix elements of the Liouville operator $\mathcal{L}$ are

$$\begin{aligned}
\langle g_\alpha \mid \mathcal{L} n \rangle &= -\langle n \mid \mathcal{L} g_\alpha \rangle = -i k_\alpha n_0 k_B T \\
\langle g_\alpha \mid \mathcal{L} n_0 c_V \delta T \rangle &= -\langle n_0 c_V \delta T \mid \mathcal{L} g_\alpha \rangle = -i k_\alpha (k_B T^2) \left(\frac{\partial p}{\partial T} \right)_n \\
\langle g_\alpha \mid \mathcal{L} u_\beta \rangle &= -\langle u_\alpha \mid \mathcal{L} g_\beta \rangle = \delta_{\alpha\beta} (k_B T)
\end{aligned} \tag{3.13}$$

Note that to write down (3.13) we again used cubic symmetry, which leads to $\langle \sigma_{\alpha\beta} \rangle_{\text{eq}} = p \, \delta_{\alpha\beta}$.

It is worth emphasizing here that the elements of the inverse matrix $\langle a_i | a_j \rangle^{-1}$ involving the densities of the conserved quantities are finite in the $\mathbf{k} \to \mathbf{0}$ limit, and the matrix elements of the Liouville operator involving the densities of the conserved quantities are proportional to the wavenumber, i.e., they vanish in the former limit. On the other hand; the matrix elements $\langle u_\alpha | u_\beta \rangle^{-1}$ vanish as k^2 in the $\mathbf{k} \to \mathbf{0}$ limit and the matrix elements of the Liouville operator involving the displacement field are finite. Correspondingly, the elements of the frequency matrix involving the densities of the conserved quantities vanish as k because of the vanishing matrix elements of the Liouvillian and the elements of the frequency matrix involving the displacement field vanish as k^2 because of the vanishing inverse static correlations or are finite: As was announced in the Introduction, the two subsets of the slow modes are slow because of the two different reasons.

To make the dissipative part of the equations of motion slightly more explicit we define transport coefficients. We note that the time derivatives of the densities of the conserved quantities are proportional to the wavevector,

$$\begin{aligned} \mathscr{L}\,\delta n(\mathbf{k};t) &= -i\mathbf{k}\cdot\mathbf{g}(\mathbf{k};t) \\ \mathscr{L}\mathbf{g}(\mathbf{k};t) &= -i\mathbf{k}\cdot\overleftrightarrow{\sigma}(\mathbf{k};t) \\ \mathscr{L}n_0 c_V\,\delta T(\mathbf{k};t) &= -n_0 c_V \mathbf{k}\cdot\mathbf{j}^T(\mathbf{k};t) \end{aligned} \tag{3.14}$$

where the last equality serves to define the temperature current $\mathbf{j}^T$. As usual this wavevector dependence of the time derivatives (3.14) will be separated out while defining the transport coefficients. On the other hand the time derivatives $\mathscr{L}u_\alpha$ of the components of the displacement field remain finite in the $\mathbf{k} \to \mathbf{0}$ limit. Therefore we will use the full time derivative $\mathscr{L}\mathbf{u}$ in the definition of the transport coefficients.

We define the transport coefficients as follows:

$$\eta_{\alpha\beta\gamma\delta} = \frac{1}{k_B T} \lim_{z\to 0} \lim_{\mathbf{k}\to\mathbf{0}} \left\langle \sigma_{\alpha\beta} \middle| \mathscr{Q} \frac{1}{z - \mathscr{Q}\mathscr{L}\mathscr{Q}} \mathscr{Q}\sigma_{\gamma\delta} \right\rangle \tag{3.15}$$

$$\kappa_{\alpha\beta} = \frac{(n_0 c_V)^2}{k_B T^2} \lim_{z\to 0} \lim_{\mathbf{k}\to\mathbf{0}} \left\langle j^T_\alpha \middle| \mathscr{Q} \frac{1}{z - \mathscr{Q}\mathscr{L}\mathscr{Q}} \mathscr{Q} j^T_\beta \right\rangle \tag{3.16}$$

$$\xi_{\alpha\beta} = \frac{n_0 c_V}{k_B T} \lim_{z\to 0} \lim_{\mathbf{k}\to\mathbf{0}} \left\langle j^T_\alpha \middle| \mathscr{Q} \frac{1}{z - \mathscr{Q}\mathscr{L}\mathscr{Q}} \mathscr{Q}\mathscr{L}u_\beta \right\rangle \tag{3.17}$$

$$\zeta_{\alpha\beta} = \frac{1}{k_B T} \lim_{z\to 0} \lim_{\mathbf{k}\to\mathbf{0}} \left\langle \mathscr{L}u_\alpha \middle| \mathscr{Q} \frac{1}{z - \mathscr{Q}\mathscr{L}\mathscr{Q}} \mathscr{Q}\mathscr{L}u_\beta \right\rangle \tag{3.18}$$

Taking now the large-scale long-time limit of Eqs. (3.5) and using Eqs. (3.11), (3.13), and (3.15)–(3.18) we can write down the dissipative (nonideal) hydrodynamic-like equations for crystals:

$$m\frac{\partial}{\partial t}\langle n(\mathbf{k};t)\rangle = -ik_\alpha\langle g_\alpha(\mathbf{k};t)\rangle \tag{3.19}$$

$$\begin{aligned}\frac{\partial}{\partial t}\langle g_\alpha(\mathbf{k};t)\rangle = {}& -ik_\alpha\frac{k_{\mathrm{B}}T}{S(0)}\langle n(\mathbf{k};t)\rangle - ik_\alpha\left(\frac{\partial p}{\partial T}\right)_n\langle\delta T(\mathbf{k};t)\rangle \\ & -\lambda_{\alpha\beta\gamma\delta}k_\gamma k_\delta\langle u_\beta(\mathbf{k};t)\rangle - \frac{\eta_{\alpha\beta\gamma\delta}}{mn_0}k_\beta k_\delta\langle g_\gamma(\mathbf{k};t)\rangle\end{aligned} \tag{3.20}$$

$$\begin{aligned}n_0c_v\frac{\partial}{\partial t}\langle\delta T(\mathbf{k};t)\rangle = {}& -\frac{iT}{mn_0}\left(\frac{\partial p}{\partial T}\right)_n k_\alpha\langle g_\alpha(\mathbf{k};t)\rangle - \kappa_{\alpha\beta}k_\alpha k_\beta\langle\delta T(\mathbf{k};t)\rangle \\ & + i\xi_{\alpha\beta}k_\alpha\lambda_{\beta\gamma\delta\mu}k_\delta k_\mu\langle u_\gamma(\mathbf{k};t)\rangle\end{aligned} \tag{3.21}$$

$$\begin{aligned}\frac{\partial}{\partial t}\langle u_\alpha(\mathbf{k};t)\rangle = {}& \frac{\langle g_\alpha(\mathbf{k};t)\rangle}{mn_0} - \zeta_{\alpha\beta}\lambda_{\beta\gamma\delta\mu}k_\delta k_\mu\langle u_\gamma(\mathbf{k};t)\rangle \\ & -\frac{i}{T}\xi_{\alpha\beta}k_\beta\langle\delta T(\mathbf{k};t)\rangle\end{aligned} \tag{3.22}$$

The equations of motion (3.19)–(3.22) are the most important result, of this paper. It is worthwhile to compare them to the phenomenological equations.[3,4] First, it should be noted that in the phenomenological approaches an additional variable was introduced. This variable was thermodynamically conjugate to the strain (displacement gradient), see, e.g., Eqs. (2.5)–(2.6) of ref. 3. The precise identity of the new variable was not clear. Here we have not introduced any additional variable. Instead, it is the contribution to the *stress* given by $-i\lambda_{\alpha\beta\gamma\delta}k_\delta u_\beta$ that is a reversible response to a displacement gradient $\nabla_\delta u_\beta$. Second, several phenomenologically postulated reactive coefficients are absent in the microscopically derived hydrodynamic-like equations. This fact (which is closely related to the first observation) can be traced back to the assumption that the correlations between the energy and density fluctuations land the displacement field are regular in the $\mathbf{k}\to\mathbf{0}$ limit. At present we do not have any argument to the contrary. Third, all the reactive coefficients in Eqs. (3.19)–(3.22) can be easily expressed in terms of the long-wavelength limits of the microscopic correlation functions, and therefore can be measured in computer simulations or calculated from approximate theories. This is in contrast with the phenomenologically postulated reactive coefficients.

4. VACANCY DIFFUSION MODE

Finding explicit expressions for the decay rates of all the hydrodynamic-like modes for a general crystal is a tedious and thankless task. Here we will use a quick and dirty method to find the time dependence of the new mode, i.e., the vacancy diffusion mode. For even greater simplicity we will consider an isothermal situation, i.e., we will put $\delta T(\mathbf{k}; t) = 0$.

To define the nonequilibrium density of vacancies we looked in ref. 6 for a mode that does not decay on the level of ideal elasticity: on physical grounds we can expect the vacancy concentration to decay via a diffusive process that is absent on the nondissipative level of description. With this in mind we defined the nonequilibrium density of vacancies as the following linear combination of the density and displacement fields:

$$\langle \delta c(\mathbf{k}; t) \rangle = -\langle \delta n(\mathbf{k}; t) \rangle - i\mathbf{k} \cdot n_0 \langle \mathbf{u}(\mathbf{k}; t) \rangle \tag{4.1}$$

Note the difference in sign between δn and δc; the density n counts the number of particles and c counts vacancies.

As noted in ref. 6, the vacancy mode is not convected, it changes only due to the dissipative processes. Explicitly, at constant temperature,

$$\frac{\partial}{\partial t} \langle \delta c(\mathbf{k}; t) \rangle = ik_\alpha \zeta_{\alpha\beta} \lambda_{\beta\gamma\delta\mu} k_\delta k_\mu \langle u_\gamma(\mathbf{k}; t) \rangle \tag{4.2}$$

Let us now calculate the decay rate of the vacancy mode. We will look for a diffusive mode at constant temperature,

$$\begin{aligned} \langle \delta n(\mathbf{k}; t) \rangle &\sim \delta n_0(\mathbf{k})\, e^{-D_{\alpha\beta} k_\alpha k_\beta t} \\ \langle \mathbf{g}(\mathbf{k}; t) \rangle &\sim \mathbf{g}_0(\mathbf{k})\, e^{-D_{\alpha\beta} k_\alpha k_\beta t} \\ \langle \mathbf{u}(\mathbf{k}; t) \rangle &\sim \mathbf{u}_0(\mathbf{k})\, e^{-D_{\alpha\beta} k_\alpha k_\beta t} \end{aligned} \tag{4.3}$$

Substituting (4.3) into the equations of motion, we find that the lowest order k dependence of the amplitudes has to be

$$\delta n_0(\mathbf{k}) \sim 1, \qquad \mathbf{g}_0(\mathbf{k}) \sim k, \qquad \mathbf{u}_0(\mathbf{k}) \sim 1/k \tag{4.4}$$

Equation (3.20) combined with relation (4.4) leads to

$$0 = -ik_\alpha \frac{k_B T}{S(0)} \langle n(\mathbf{k}; t) \rangle - \lambda_{\alpha\beta\gamma\delta} k_\gamma k_\delta \langle u_\beta(\mathbf{k}; t) \rangle + \mathcal{O}(k^2) \tag{4.5}$$

Next we use Eq. (4.5) and the definition of the vacancy mode (4.1) to express the right-hand side of the equation of motion (4.2) in terms of the vacancy density. In this way we get an equation of motion for the vacancy diffusion mode:

$$\frac{\partial}{\partial t}\langle \delta c(\mathbf{k};\, t)\rangle = -D_{\alpha\beta}(\hat{\mathbf{k}})\, k_\alpha k_\beta \langle \delta c(\mathbf{k};\, t)\rangle \tag{4.6}$$

Here $\vec{D}(\hat{\mathbf{k}})$ is the vacancy diffusion tensor:

$$D_{\alpha\delta}(\hat{\mathbf{k}}) = \frac{k_{\mathrm{B}} T}{S(0)}\, \zeta_{\alpha\beta} l_{\beta\gamma}(\hat{\mathbf{k}})\, L^{-1}_{\gamma\delta}(\hat{\mathbf{k}}) \tag{4.7}$$

In Eq. (4.7), $l_{\alpha\beta}(\hat{\mathbf{k}})$ is defined as

$$l_{\alpha\beta}(\hat{\mathbf{k}}) = \lambda_{\alpha\beta\gamma\delta} \hat{k}_\gamma \hat{k}_\delta \tag{4.8}$$

and $L^{-1}_{\alpha\beta}(\hat{\mathbf{k}})$ is the inverse of the wave propagation matrix,(6)

$$L_{\alpha\beta}(\hat{\mathbf{k}}) = l_{\alpha\beta}(\hat{\mathbf{k}}) + \frac{n_0 k_{\mathrm{B}} T}{S(0)} \hat{k}_\alpha \hat{k}_\beta \tag{4.9}$$

5. GREEN–KUBO EXPRESSIONS

Our definitions of the transport coefficients (3.15)–(3.18) are *not* the Green–Kubo expressions. The former involve a projected evolution operator $\mathscr{Q}\mathscr{L}\mathscr{Q}$, whereas the latter are the $z \to 0$ Laplace transforms of the correlation functions of the currents, i.e., their time evolution is governed by the original evolution operator $\mathscr{L}$. However, it can be shown(5) that in the long-wavelength $\mathbf{k} \to \mathbf{0}$ limit the projected evolution operator $\mathscr{Q}\mathscr{L}\mathscr{Q}$ in the expressions (3.15)–(3.18) can be replaced by $\mathscr{L}$. In this way the expressions (3.15)–(3.18) can be reduced to the standard Green–Kubo form,

$$\eta_{\alpha\beta\gamma\delta} = \frac{1}{k_{\mathrm{B}} T V} \int_0^\infty dt \lim_{\mathbf{k}\to\mathbf{0}} \langle \mathscr{Q}\sigma_{\alpha\beta}(-\mathbf{k};\, 0)\, \mathscr{Q}\sigma_{\gamma\delta}(\mathbf{k};\, t)\rangle_{\mathrm{eq}} \tag{5.1}$$

$$\kappa_{\alpha\beta} = \frac{(n_0 c_V)^2}{k_{\mathrm{B}} T^2 V} \int_0^\infty dt \lim_{\mathbf{k}\to\mathbf{0}} \langle \mathscr{Q}j^T_\alpha(-\mathbf{k};\, 0)\, \mathscr{Q}j^T_\beta(\mathbf{k};\, t)\rangle_{\mathrm{eq}} \tag{5.2}$$

$$\xi_{\alpha\beta} = \frac{n_0 c_V}{k_{\mathrm{B}} T V} \int_0^\infty dt \lim_{\mathbf{k}\to\mathbf{0}} \langle \mathscr{Q}j^T_\alpha(-\mathbf{k};\, 0)\, \mathscr{Q}\dot{u}_\beta(\mathbf{k};\, t)\rangle_{\mathrm{eq}} \tag{5.3}$$

$$\zeta_{\alpha\beta} = \frac{1}{k_{\mathrm{B}} T V} \int_0^\infty dt \lim_{\mathbf{k}\to\mathbf{0}} \langle \mathscr{Q}\dot{u}_\alpha(-\mathbf{k};\, 0)\, \mathscr{Q}\dot{u}_\beta(\mathbf{k};\, t)\rangle_{\mathrm{eq}} \tag{5.4}$$

The Green–Kubo expressions (5.1)–(5.4) are different from the usual ones. First, there is additional subtraction in the expression for the projected stress tensor,

$$\mathscr{Q}\sigma_{\alpha\beta}(\mathbf{k}) = (\mathscr{Q}\sigma_{\alpha\beta}(\mathbf{k}))_{\text{fluid}} - i\lambda_{\alpha\gamma\beta\delta} u_\gamma(\mathbf{k})\, k_\delta \tag{5.5}$$

The additional subtraction term is formally of the order of k but it is absolutely essential to keep it. To realize that one should, note that the integral $\int_0^\infty dt \langle u_\alpha(-\mathbf{k};0)\, u_\gamma(\mathbf{k};t)\rangle_{\text{eq}}\, k_\beta k_\delta$ diverges in the $\mathbf{k}\to\mathbf{0}$ limit: (i) the static correlations $\langle u_\alpha(-\mathbf{k})\, u_\gamma(\mathbf{k})\rangle_{\text{eq}}$ diverge as k^{-2} and hence $\lim_{\mathbf{k}\to 0}\langle u_\alpha(-\mathbf{k})\, u_\gamma(\mathbf{k})\rangle_{\text{eq}}\, k_\beta k_\delta$ is finite, and (ii) the displacement field u_α belongs to the set of slow variables and its characteristic relaxation time diverges in the long-wavelength limit. Note that this means that if one tries to calculate in the solid phase the Green–Kubo integral that gives the viscosity in the liquid phase, i.e.,

$$\int_0^\infty dt \lim_{\mathbf{k}\to 0} \langle (\mathscr{Q}\sigma_{\alpha\beta}(\mathbf{k};0))_{\text{fluid}}\, (\mathscr{Q}\sigma_{\gamma\delta}(\mathbf{k};t))_{\text{fluid}}\rangle_{\text{eq}}$$

the result *diverges*. Moreover, a subtraction term similar to (5.5) should also appear in kinetic theory expressions for the solid state viscosities.

Second, there are the new transport coefficients $\overleftrightarrow{\xi}$ and $\overleftrightarrow{\zeta}$. They involve the long-wavelength limits of the time derivatives of the displacement field, or more explicitly, the combinations of the large wavevector components of the momentum density,

$$\begin{aligned} \dot{u}_\alpha(\mathbf{k};t) &= \frac{1}{m_c\mathcal{N}} \int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} \frac{\delta n_c(\mathbf{r})}{\delta r_\alpha} \frac{\delta}{\delta \mathbf{r}} \cdot \mathbf{g}(\mathbf{r};t) \\ &= \frac{1}{m_c\mathcal{N}} \sum_{\mathbf{G}} G_\alpha G_\beta n_{-\mathbf{G}}\, g_\beta(\mathbf{G};t) + \mathcal{O}(k) \end{aligned} \tag{5.6}$$

Again, one should remember that it is the projected derivative that enters the expressions (5.3)–(5.4),

$$\mathscr{Q}\dot{u}_\alpha(\mathbf{k};t) = \dot{u}_\alpha(\mathbf{k};t) - \frac{g_\alpha(\mathbf{k};t)}{n_0 m} \tag{5.7}$$

Physically the subtraction (5.7) means that, for example, the contributions to the tensor $\overleftrightarrow{\zeta}$ (and to the vacancy diffusion tensor $\overleftrightarrow{D}$) come from the difference of the rate of change of the displacement field and the number density current.

6. CONCLUDING REMARKS

We presented here the first statistical mechanical analysis of dissipative transport in crystalline solids. The main results are the equations of motion for all the eight modes predicted by the general theory of systems with broken continuous symmetry. These equations have the same general form as those derived in the phenomenological (thermodynamic) approach. There are, however, notable differences that can be traced to assumptions about the long-wavelength behavior of cross correlations. We have assumed here that the cross correlations between the displacement field and the densities of the conserved quantities are regular in the long-wavelength limit. On the other hand, in order to get equations of motion postulated in the phenomenological approach one would have to assume that some of these correlations diverge in the former limit. In a sense the hydrodynamic-like equations derived here are the *simplest* equations that describe dissipative transport in crystals.

One could also phrase the difference between the two approaches in the language of the Landau theory:(2) we have assumed that the longitudinal part of the effective long-wavelength Hamiltonian is the same in both fluid and solid phases, whereas in the phenomenological approach it is effectively assumed that the qualitative form of the longitudinal part of the Hamiltonian changes.

It would be interesting to analyze the long-wavelength behavior of the cross correlations. For example, one could try to derive an upper (lower) bound that would prove (disprove) that the cross correlations are regular.

We derived the exact expressions for the transport coefficients of crystals in terms of the Green–Kubo integrals, i.e., integrals of the correlation functions of currents of the densities of the conserved quantities or of the time derivatives of the displacement field. The general form of such expressions was anticipated before.(1) Here we derived the explicit formulas for the Green–Kubo integrands. We noted that an additional subtraction term appears in the expression for the projected stress tensor. A similar subtraction term should also appear in the kinetic theory expressions for the viscosities.

The expressions (5.1)–(5.4) can be used to evaluate the transport coefficients in molecular dynamics simulations. This was impossible before when only general form of the Green-Kubo integrals was known.

The expressions (5.1)–(5.4) can also be used as a starting point for approximate theoretical estimations of the transport coefficients. The most direct way to proceed is probably to use the hard-sphere model. In this case one could use an Enskog-like approximation for the Green–Kubo integrands. Explicit calculations will, however, be hampered by the lack of reliable information about the pair distribution function in the solid state.

Finally, we hope that the analysis presented here will help to extend the kinetic theory of transport in a hard-sphere crystal of Kirkpatrick *et al.*(5) to include the vacancy diffusion.

REFERENCES

1. D. Forster, *Hydrodynamic fluctuations Broken Symmetry, and Correlation Functions* (Benjamin, Reading, Massachusetts, 1975).
2. N. Goldenfeld, *Lectures on Phase Transitions and the Renormalization Group* (Addison-Wesley, Reading, Massachusetts, 1992).
3. P. C. Martin, O. Parodi, and P. S. Pershan, *Phys. Rev. A* **6**:2401 (1972).
4. P. D. Fleming and C. Cohen, *Phys. Rev. B* **13**:500 (1976).
5. T. R. Kirkpatrick, S. P. Das, M. H. Ernst, and J. Piasecki, *J. Chem. Phys.* **92**:3768 (1990).
6. G. Szamel and M. H. Ernst, *Phys. Rev. B* **48**:112 (1993).
7. P. W. Anderson, *Basic Notions of Condensed Matter Physics* (Benjamin, Menlo Park, California, 1984).
8. J. A. McLennan, *Introduction to Nonequilibrium Statistical Mechanics* (Prentice-Hall, Englewood Cliffs, New Jersey, 1989).
9. J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, London, 1986).
10. M. H. Ernst and J. R. Dorfman, *J. Stat. Phys.* **12**:311 (1975).