PHYSICAL REVIEW B VOLUME 23, NUMBER 2 15 JANUARY 1981

Dynamics of translations and rotations in molecular crystals: Macroscopic and microscopic approaches

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(Received 2 September 1980)

Starting from a Hamiltonian for an orientationally disordered crystal with bilinear coupling between translational and orientational coordinates, a nonequilibrium macroscopic free energy is calculated. It is used to obtain coupled dynamic equations for translations and rotations by methods of irreversible thermodynamics. The corresponding dynamic response functions are in full agreement with those derived using a microscopic Mori-type projection-operator method. The coefficients of the macroscopic free energy are related to the static susceptibilities obtained from the Hamiltonian in the framework of molecular-field theory. Dynamic sum rules for translational-rotational motion are given.

I. INTRODUCTION

Hydrodynamic equations can be derived by means of Onsager's method of irreversible processes.[1] As a starting point, one writes down a nonequilibrium free energy or equivalently a minimum work function $\mathcal{R}$ in terms of the relevant dynamic variables. Then, one obtains dynamic equations for these variables by using generalized Langevin equations.[2] This type of approach has also been applied in solid-state physics for the study of pseudospin-phonon coupled systems, for instance, cooperative Jahn-Teller crystals[3] and molecular crystals such as NH_4Br.[4] In molecular crystals, the pseudospin variables are most appropriate whenever the molecules (or molecular ions) are well localized in a small number of orientational positions. On the other hand, in shallow or dynamically changing potentials, pseudospin variables are not adequate. In fact, in molecular liquids one often uses the anisotropic molecular polarizability density.[5]

Starting from a phenomenological nonequilibrium free energy with a bilinear static coupling between orientational coordinates (molecular polarizability) and translations (lattice strains), one of the present authors has derived a coupled set of dynamic equations for translations and rotations in molecular crystals.[6] As a consequence of the bilinear coupling, the acoustic-phonon modes enter, as additional resonances, the polarizability-polarizability or equivalently the orientation-orientation correlation function. This was first observed by Rayleigh-Brillouin measurements in succinonitrile,[7] and was explained by the theory of Ref. 6.

Besides the Onsager method, a more microscopic approach for the derivation of dynamic equations is provided by the projection-operator technique[8] of Mori and Zwanzig. This method has the advantage that, in principle, all static and dynamic coefficients can be calculated from a Hamiltonian. In practice, however, the explicit calculation of transport coefficients is often an extremely difficult task, and one has to make use of severe approximations. The case of molecular liquids is described in Ref. 5 in terms of polarizability orientational variables. In crystals, the preferred orientational dynamic variables will, in general, be based on symmetry-adapted functions.[9] It is then possible to describe orientationally disordered phases, as well as partially ordered phases in a unified way.[10]

Using as a starting point a Hamiltonian[11] with bilinear coupling between translations (acoustic phonons) and orientations (symmetry-adapted functions), a coupled set of dynamic equations was derived by means of the projection-operator method in Ref. 12. Since the molecular polarizability, as used in Ref. 6, admits a linear expansion in terms of symmetry-adapted functions, and since the dynamic equations derived in Refs. 6 and 12 describe the same physical phenomena, they should correspond term by term. Recently, Wang,[13] following essentially the approach of Ref. 12, and including explicitly anharmonic lattice-displacement terms in his Hamiltonian, came to the conclusion that the equations of Ref. 6 were inconsistent with his microscopic orientational correlation functions. It is the aim of the present paper to investigate this problem in detail and to clarify the correspondence between macroscopic and microscopic approaches. In fact, we demonstrate that there is *no* inconsistency. In addition, we relate the phenomenological coefficients occurring in the free energy to static susceptibilities obtained from the microscopic Hamiltonian. The subdivision of the paper is as follows.

In Sec. II, we derive a nonequilibrium free energy from a microscopic Hamiltonian with bilinear coupling of translations and orientations. Static susceptibilities are calculated by means of molecular-field theory. All coefficients entering the free energy are identified. Next (Sec. III), we follow the macroscopic approach to derive the set of hydrodynamic equations, using a molecular-polarizability density orthogonalized to the translational coordinates as orientational dynamic variable. This allows a direct comparison with the dynamic equations obtained with the projection-operator technique in Refs. 12 and 13. In Sec. IV, we discuss correlation functions and sum rules. In particular, it is shown that if one correctly takes into account mixed dynamic correlations between translations and orientations, there is full agreement between the hydrodynamic and the microscopic approaches.

II. NONEQUILIBRIUM FREE ENERGY

The main idea of the present approach is to obtain a macroscopic nonequilibrium free energy depending only on the fluctuating variables of interest, this starting from a microscopic Hamiltonian that, in principle, might contain a greater number of operators. The fluctuating variables of interest are assumed to be thermodynamic in the sense of Landau and Lifshitz, i.e., their evolution towards equilibrium is slow compared to the other variables of the system which are thus called fast.[14] The nonequilibrium free energy is calculated by assuming that the fast variables have come into equilibrium with nonequilibrium expectation values of the slow variables of interest. This free energy, for which the new variables are those nonequilibrium expectation values, can be taken as a minimum work function[14] in terms of which the correlations of those expectation values will later be calculated.

Specifically, we will show that the nonequilibrium free energy postulated in Ref. 6 can be derived from the Hamiltonian of Ref. 11. The calculation follows closely the method used by Feder and Pytte for the statistical description of collective Jahn-Teller transitions.[3]

We start from the Hamiltonian

$$H = H^T + H^R + H^{TR} . \tag{2.1}$$

Here H^T describes the pure translational part

$$H^T = \sum_{\vec{q}} \left(\frac{p_i^\dagger(\vec{q}) p_i(\vec{q})}{2m} + \tfrac{1}{2} M_{ij} s_i^\dagger(\vec{q}) s_j(\vec{q}) \right) , \tag{2.2a}$$

where $s_i(\vec{q})$ denotes the Fourier-transformed center of mass displacements of the unit cell, $p_i(\vec{q})$ is the conjugate momentum, m stands for the total mass per unit cell, and $i,j = x,y,z$ are Cartesian indices. The summation convention for repeated indices applies. The coupling factor $M_{ij}(\vec{q})$ accounts for the harmonic part of the translational interaction. Since we restrict ourselves to long-wavelength phenomena (e.g., elastic properties), we need only to consider the translational center-of-mass motion, and $\vec{q}$ then denotes a small wave vector near the zone center in reciprocal space.

The pure, orientational part of the Hamiltonian is taken to be

$$H^R = K + V^R . \tag{2.2b}$$

Here, K stands for the kinetic energy of rotations

$$K = \sum_{\vec{q}} \frac{L_\alpha^\dagger(\vec{q}) L_\alpha(\vec{q})}{2 I_\alpha} . \tag{2.2c}$$

The angular momentum components L_α and the momenta of inertia components I_α are taken along the principal axes of the molecules. The second term on the right-hand side (rhs) of Eq. (2.2b) stands for the single-particle orientational potential

$$V^R = \sum_{\vec{n}} V[\Omega(\vec{n})] . \tag{2.2d}$$

The coupling of translations and orientations H^{TR} is taken to be

$$H^{TR} = \sum_{\vec{q}} i v_{j\nu}(\vec{q}) s_j(\vec{q}) Y_\nu^\dagger(\vec{q}) . \tag{2.2e}$$

Here, $Y_\nu(\vec{q})$ is the Fourier-transformed orientational coordinate

$$Y_\nu(\vec{q}) = \frac{1}{\sqrt{N}} \sum_{\vec{n}} Y_\nu(\vec{n}) e^{-i\vec{q}\cdot\vec{X}(\vec{n})} . \tag{2.3}$$

The orientational coordinates $Y_\nu(\vec{n})$ are the coefficients of an expansion into symmetry-adapted functions at each lattice site $\vec{X}(\vec{n})$. The particular observable that is expanded is characteristic of molecular orientation. The symmetry-adapted functions are combinations of the Wigner representations of the full rotation group $D_{\lambda\lambda'}^{(l)}[\Omega(\vec{n})]$, where the Euler angles $\Omega \equiv \{\alpha, \beta, \gamma\}$ refer to the orientation. The index ν in $Y_\nu(\vec{n})$ stands for (l, λ, λ'), where l denotes the angular-momentum quantum number, $2l+1$ being the dimensionality of the representation.[15] In Eq. (2.2e), $v_{j\nu}(\vec{q})$ is the matrix of the bilinear coupling between translations and orientations. In the long-wavelength limit, where the molecular orientations couple to the lattice strains, all the elements of v are linear in q_i. A Hamiltonian of the form (2.1)–(2.2e) has been derived explicitly in the particularly simple case of a crystal consisting of dumbbell molecules in a deformable octahedral surrounding.[12] Then, for $l=2$, the basis set for Y_ν reduces to the five linear combinations of spherical harmonics with E_g and T_{2g} symmetry. The single-particle potential V^R then corresponds to the Devonshire potential.[16] Here we shall not restrict ourselves to a particular symmetry. We shall only take

$$v_{j\nu}(\vec{q}) = -v_{j\nu}^*(-\vec{q}), \tag{2.4}$$

which is the condition for H^{TR} as given in (2.2e) to be Hermitian.

Since we are using center-of-mass coordinates per unit cell, $M_{ij}(\vec{q})$ is related to the bare elastic constants by

$$M_{ij}(\vec{q}) = q_l q_k C^0_{il,jk}. \tag{2.5}$$

The lattice strains are related to the displacements by

$$\epsilon_{ij}(\vec{q}) = i[q_i s_j(\vec{q}) + q_j s_i(\vec{q})]. \tag{2.6}$$

The Helmholtz free energy is given in terms of a trace (Tr) over the density matrix by the usual expression

$$F = \mathrm{Tr}[\rho H + (1/\beta)\rho \ln\rho]. \tag{2.7}$$

Taking units such that $k_B=1$, β is also the inverse temperature T^{-1}. The density matrix satisfies the condition

$$\mathrm{Tr}\rho = 1. \tag{2.8}$$

The equilibrium density matrix, $\rho_0 = \exp(-\beta H)$, is obtained by minimizing (2.7) with respect to ρ under condition (2.8). At present, we need the nonequilibrium free energy corresponding to the instantaneous expectation values of the slow variables, denoted by the superscript e:

$$s_i^e(\vec{q}, t) = \mathrm{Tr}\rho s_i(\vec{q}), \tag{2.9a}$$

$$p_i^e(\vec{q}, t) = \mathrm{Tr}\rho p_i(\vec{q}), \tag{2.9b}$$

$$Y_\nu^e(\vec{q}, t) = \mathrm{Tr}\rho Y_\nu(\vec{q}). \tag{2.9c}$$

In what follows, the time dependence of those expectation values will be understood without always being shown explicitly. The choice of (2.9) as slow variables is essentially motivated by the experimental situation (frequency regime) one wants to describe. If we should describe optical resonances, we should include the corresponding lattice displacements and momenta in the set of "hydrodynamic" variables. If librations were important, we should also include the angular momentum $\vec{L}^e$. The conditions for a coupling of $\vec{L}^e$ and $\vec{Y}^e$ have been discussed in Ref. 10. Without coupling, the trace over the variables L_α does not have to be considered explicitly in the following.

The nonequilibrium free energy is a functional of the above expectation values

$$F = F\{\vec{s}^e, \vec{p}^e, Y_\nu^e\}. \tag{2.10}$$

Using the method of Lagrange multipliers to minimize (2.7) under the constraints (2.8) and (2.9), one obtains

$$\rho = (1/\mathfrak{z})\exp(-\beta\mathcal{K}), \tag{2.11}$$

where

$$\mathfrak{z} \equiv \mathrm{Tr}\exp(-\beta\mathcal{K}) \tag{2.12}$$

and

$$\mathcal{K} \equiv H - \sum_{\vec{q}} [\lambda_i^*(\vec{q}) s_i(\vec{q}) + \xi_i^*(\vec{q}) p_i(\vec{q}) + \gamma_\nu^*(\vec{q}) Y_\nu(\vec{q})]. \tag{2.13}$$

Here $\vec{\lambda}$, $\vec{\xi}$, and $\vec{\gamma}$ are the Lagrange multipliers to be determined by conditions (2.9). It is convenient to define a new thermodynamic potential

$$F^e \equiv -T\ln\mathfrak{z}. \tag{2.14}$$

Note that F in (2.7) is related to F^e by

$$F = F^e + \mathrm{Tr}[\rho(H - \mathcal{K})]. \tag{2.15}$$

To obtain the explicit expression for F, the Lagrange multipliers must be calculated. To this effect, it is practical to separate the phonon and the orientational variables by a canonical transformation:

$$\hat{s}_j(\vec{q}) = s_j(\vec{q}) + M_{jk}^{-1}[iv_{k\nu}(-\vec{q})Y_\nu(\vec{q}) - \lambda_k(\vec{q})], \tag{2.16a}$$

$$\hat{p}_j(\vec{q}) = \frac{p_j(\vec{q})}{\sqrt{m}} - \xi_j(\vec{q})\sqrt{m}. \tag{2.16b}$$

In terms of these new variables, one has

$$\mathcal{K} = \hat{H}_{\mathrm{ph}} + H_R(\vec{b}) - \frac{m}{2}\sum_{\vec{q}} \xi_i^*(\vec{q})\xi_i(\vec{q}) - \frac{1}{2}\sum_{\vec{q}} \lambda_i^*(\vec{q}) M_{ij}^{-1} \lambda_j(\vec{q}). \tag{2.17}$$

Here the phonon Hamiltonian is

$$\hat{H}_{\mathrm{ph}} = \sum_{\vec{q}} [\tfrac{1}{2}\hat{p}^\dagger(\vec{q})\hat{p}(\vec{q}) + \tfrac{1}{2}M_{ij}(\vec{q})\hat{s}_i^\dagger(\vec{q})\hat{s}_j(\vec{q})], \tag{2.18}$$

whereas the effective orientational interaction Hamiltonian is

$$H_R(\vec{b}) = -\sum_{\vec{q}} [\tfrac{1}{2}Y_\nu^\dagger(\vec{q}) C^R_{\nu\mu} Y_\mu(\vec{q}) + b_\nu^* Y_\nu(\vec{q})] + V_R. \tag{2.19}$$

In the last expression, the effective orientational interaction is given by

$$C^R_{\nu\mu}(\vec{q}) = v^*_{i\nu}(\vec{q}) M^{-1}_{ij}(\vec{q}) v_{j\mu}(\vec{q}) \,, \tag{2.20}$$

and the "external" field b_ν is defined by

$$b_\nu(\vec{q}) = \gamma_\nu(\vec{q}) - i\lambda_i(\vec{q}) M^{-1}_{ij}(\vec{q}) v_{j\nu}(\vec{q}) \,. \tag{2.21}$$

Equation (2.20) expresses the fact that a bilinear interaction of type (2.2e) between translations and orientations leads to an effective interaction between reorienting molecules.[11] The last two terms on the rhs of Eq. (2.17) are c numbers. Note that by writing down Eqs. (2.18) and (2.19), we have achieved a separation in phonon and in orientational coordinates.

We now rewrite the thermodynamic potential (2.14) as

$$F^e = F^e_{\rm ph} + F^e_R(\vec{b}) + F' \,, \tag{2.22}$$

with

$$F^e_{\rm ph} = - T \ln \operatorname{Tr} \exp(- \beta \hat{H}_{\rm ph}) \,, \tag{2.23a}$$

$$F^e_R(\vec{b}) = - T \ln \operatorname{Tr} \exp[- \beta H_R(\vec{b})] \,, \tag{2.23b}$$

and

$$F' = - \frac{m}{2} \sum_{\vec{q}} \xi^*_i(\vec{q}) \xi_i(\vec{q}) - \tfrac{1}{2} \sum_{\vec{q}} \lambda^*_i(\vec{q}) M^{-1}_{ij}(\vec{q}) \lambda_j(\vec{q}) \,. \tag{2.23c}$$

In (2.23a), the trace over the orientational degrees of freedom is trivial, and only the trace over the phonon coordinates remains. Since $H_{\rm ph}$, Eq. (2.18), represents a harmonic phonon Hamiltonian, the resulting thermodynamic potential reads

$$F^e_{\rm ph} = - \sum_{q,\alpha} [\, \tfrac{1}{2} \hbar \omega_\alpha(\vec{q}) + T \ln n_\alpha(\vec{q})] \,, \tag{2.24}$$

where the phonon frequencies $\omega_\alpha(\vec{q})$ are the eigenvalues of the dynamical matrix M, and where $n_\alpha(\vec{q})$ is the Bose-Einstein distribution for phonons of energy $\hbar\omega_\alpha(\vec{q})$.[17]

The Lagrange parameters λ and ξ are immediately obtained by noting that the instantaneous expectation values $\hat{s}^e_i$ and $\hat{p}^e_i$ must vanish in view of the separation of variables and of the form of (2.18). Using (2.16), it follows that

$$\lambda_i(\vec{q}) = M_{ij} s^e_j(\vec{q}) - i v^*_{i\nu}(\vec{q}) Y^e_\nu(\vec{q}) \tag{2.25}$$

and

$$\xi_i(\vec{q}) = \frac{1}{m} p^e_i(\vec{q}) \,. \tag{2.26}$$

Using these relations, F' is rewritten as

$$F' = - \sum_{\vec{q}} \Big(\frac{1}{2m} p^{e*}_i(\vec{q}) p^e_i(\vec{q}) + \tfrac{1}{2} s^{e*}_i(\vec{q}) M_{ij} s^e_j(\vec{q}) + i s^e_i(\vec{q}) v_{i\nu}(\vec{q}) Y^{e*}_\nu(\vec{q}) + \tfrac{1}{2} Y^{e*}_\nu(\vec{q}) C^R_{\nu\mu}(\vec{q}) Y^e_\mu(\vec{q}) \Big) \,. \tag{2.27}$$

Calculation of the Lagrange parameter γ is more delicate in view of the linear term in Y_ν in (2.19). To obtain an explicit expression for Y^e_ν, we use a molecular-field approximation in (2.23b). Note that the trace over the phonon variables in that equation is trivial, and that only the trace over the orientational variables remains. Assume that Y_ν undergoes only small fluctuations about its mean Y^e_ν and write (2.19) in terms of the difference

$$\Delta_\nu \equiv Y_\nu - Y^e_\nu \,. \tag{2.28}$$

One obtains the molecular-field approximation of (2.19),

$$H^{\rm MF}_R = - \tfrac{1}{2} \sum Y^{e*}_\nu C^R_{\nu\mu} Y^e_\mu - \sum b^*_\nu Y^e_\nu + V_R - \sum a^*_\mu \Delta_\mu \,, \tag{2.29}$$

where only terms linear in the operator Δ_μ have been retained, and where

$$a_\nu(\vec{q}) \equiv C^R_{\nu\mu}(\vec{q}) Y^e_\mu(\vec{q}) + b_\nu(\vec{q}) \,, \tag{2.30}$$

with b_ν defined in (2.21). Now, the exponential in (2.23b) is expanded and the trace is taken. To this effect, it is useful to define the following operation on any function A of the orientational variables:

$$\langle A \rangle_0 \equiv \operatorname{Tr}[A \exp(-\beta V_R)] / \operatorname{Tr}[\exp(-\beta V_R)] \,. \tag{2.31}$$

The symmetry of V_R leads to

$$\langle Y_\nu \rangle_0 = 0 \,, \tag{2.32a}$$

$$\langle Y^\dagger_\mu Y_\nu \rangle_0 = \delta_{\mu\nu} \langle Y^\dagger_\mu Y_\mu \rangle_0 \,. \tag{2.32b}$$

Note that the last trace is independent of $\vec{q}$ by (2.2d). It represents the single-particle orientational susceptibility multiplied by the temperature T.[11] Using (2.32) one also finds

$$\langle \Delta_\nu \rangle_0 = - Y^e_\nu \,, \tag{2.33a}$$

$$\langle \Delta^\dagger_\mu \Delta_\nu \rangle_0 = Y^{e*}_\mu Y^e_\nu + \delta_{\mu\nu} \langle Y^\dagger_\mu Y_\mu \rangle_0 \,. \tag{2.33b}$$

Combining this with (2.29), one obtains

$$\operatorname{Tr} e^{-\beta H^{\rm MF}_R} \simeq \Big\{ \exp\Big[\beta \Big(\tfrac{1}{2} \sum Y^{e*}_\nu C^R_{\nu\mu} Y^e_\mu + b^*_\mu Y^e_\mu \Big) \Big] \Big\} \times \{ \operatorname{Tr}[\exp(-\beta V_R)] \} \times \Big(1 - \beta \sum a^*_\mu Y^e_\mu + \tfrac{1}{2} \beta^2 \sum a^*_\mu a_\nu \langle \Delta_\mu \Delta^\dagger_\nu \rangle_0 \Big) \,. \tag{2.34}$$

Finally, one calculates the logarithm of this expression, expanding the last factor. The self-consistency equation can simply be written

$$\Delta^e_\mu = - T \frac{\partial \ln \operatorname{Tr} e^{-\beta H^{\rm MF}_R}}{\partial a^*_\mu} = 0 \,, \tag{2.35}$$

from which

$$Y^e_\mu = \beta a_\mu \langle Y^\dagger_\mu Y_\mu \rangle_0 + \beta \sum_\nu a_\nu Y^e_\mu Y^{e^*}_\nu . \qquad (2.36a)$$

As Y^e_μ itself is a small nonequilibrium fluctuation, this equation is linearized to

$$Y^e_\mu = \beta a_\mu \langle Y^\dagger_\mu Y_\mu \rangle_0 \quad (\mu \text{ fixed}), \qquad (2.36b)$$

from which

$$Y^e_\nu = \beta \sum_\mu G^{-1}_{\nu\mu} b_\mu \langle Y^\dagger_\mu Y_\mu \rangle_0 , \qquad (2.37a)$$

where

$$G_{\mu\nu} \equiv \delta_{\mu\nu} - \beta C^R_{\mu\nu} \langle Y^\dagger_\mu Y_\mu \rangle_0 \quad (\mu \text{ fixed}). \qquad (2.37b)$$

Equation (2.36b) represents the change in Y^e induced by the complete Weiss molecular field. To find the response to the orienting field, we have to subtract the Onsager reaction field.[18] Therefore we write, instead of Eq. (2.36b),

$$Y^{ec}_\mu = \beta a^c_\mu \langle Y^\dagger_\mu Y_\mu \rangle_0 , \qquad (2.38a)$$

where a^c_μ is the cavity field, defined by

$$a^c_\mu = a_\nu - l_{\mu\nu} Y^{ec}_\nu \qquad (2.38b)$$

with

$$l_{\nu\mu} = \frac{1}{N} \sum_{\vec{q}} C^R_{\nu\mu}(\vec{q}) . \qquad (2.38c)$$

The last term on the rhs in Eq. (2.38b) represents the Onsager reaction field. Then, the static susceptibility is given by

$$\chi_{\mu\nu}(q) = \frac{\partial Y^{ec}_\nu}{\partial b_\mu} = \beta E^{-1}_{\nu\mu} \langle Y^\dagger_\mu Y_\mu \rangle_0 \quad (\mu \text{ fixed}), \qquad (2.38d)$$

where $E_{\mu\nu}$ is defined by

$$E_{\mu\nu} = \delta_{\mu\nu} - \beta (C^R_{\mu\nu} - l_{\mu\nu}) \langle Y^\dagger_\mu Y_\mu \rangle_0 \quad (\mu \text{ fixed}). \qquad (2.38e)$$

Combining (2.25) and (2.37) with (2.21), one finds

$$\gamma_\mu = \beta^{-1} \langle Y^\dagger_\mu Y_\mu \rangle_0^{-1} Y^e_\mu + i v_{j\mu} s^e_j . \qquad (2.39)$$

It remains to calculate the molecular-field value F^{MF}_R of (2.23b). From (2.34), using (2.36), one immediately finds

$$F^{\mathrm{MF}}_R = F^0_R - \tfrac{1}{2} T \langle Y^\dagger_\mu Y_\mu \rangle_0^{-1} Y^{e^*}_\mu Y^e_\mu + \tfrac{1}{2} C^R_{\mu\nu} Y^{e^*}_\mu Y^e_\nu , \qquad (2.40a)$$

where

$$F^0_R \equiv - T \ln \operatorname{Tr} \exp(-\beta V_R) . \qquad (2.40b)$$

Combining (2.15), (2.22), (2.27), and (2.40), using the values of the Lagrange parameters (2.25), (2.26), and (2.39) in (2.15), and after cancellation of terms, the nonequilibrium free energy in the molecular-field approximation follows:

$$F^{\mathrm{MF}}\{s^e, p^e, Y^e\} = F^e_{\mathrm{ph}} + F^0_R + \mathcal{T} + \mathcal{V}, \qquad (2.41)$$

where we have used the definitions

$$\mathcal{T} \equiv \frac{1}{2m} \sum_{\vec{q}} p^{e^*}_i(\vec{q}) p^e_i(\vec{q}) , \qquad (2.42a)$$

$$\mathcal{V} \equiv \sum_{\vec{q}} \big[\tfrac{1}{2} s^{e^*}_i(\vec{q}) M_{ij}(\vec{q}) s^e_j(\vec{q}) + i v_{i\nu}(\vec{q}) s^e_i Y^{e^*}_\nu + \tfrac{1}{2} T \langle Y^\dagger_\mu Y_\mu \rangle_0^{-1} Y^{e^*}_\mu Y^e_\mu \big] . \qquad (2.42b)$$

Only $\mathcal{T}$ and $\mathcal{V}$ in (2.41) depend on the nonequilibrium expectation values. The nonequilibrium thermodynamic Lagrangian can thus be written

$$\mathcal{L} = \mathcal{T} - \mathcal{V} . \qquad (2.43)$$

This expression corresponds to the phenomenological Lagrangian density, Eq. (2) of Ref. 6. By comparing both expressions term by term, we arrive at the following identification:

$$i q_i s^e_j \longleftrightarrow \epsilon_{ij} , \qquad (2.44a)$$

$$M_{ij} \longleftrightarrow q_k q_l C_{ik,jl} , \qquad (2.44b)$$

$$\vec{\mathrm{Y}}^e \longleftrightarrow \overleftrightarrow{\alpha} , \qquad (2.44c)$$

$$\langle Y^\dagger Y \rangle_0 / T \longleftrightarrow \overleftrightarrow{B}^{-1} , \qquad (2.44d)$$

$$v(\vec{q}) \longleftrightarrow q \overleftrightarrow{D} . \qquad (2.44e)$$

On the rhs of these identifications, we have shown the symbols used in Eq. (2) of Ref. 6. Recalling Eq. (2.5), we recover the result that C of Ref. 6 corresponds to the bare elastic constants (high-frequency elastic tensor). From Eq. (2.44d), we see that $\overleftrightarrow{B}$ is the inverse of the single-particle orientational susceptibility.

Once given a Hamiltonian of the form (2.1), we are able to write down the nonequilibrium free energy. The explicit form of the functions Y_ν and of the matrices v and M depends on the symmetry of the system and on the details of the potential. For complicated systems, we do not have a complete knowledge of the force laws. Nevertheless, we can use the relevant symmetries of the problem to write down a free energy F, where the nonzero elements of the matrices M, v, and $\langle Y^\dagger Y \rangle_0$ are taken as parameters.

For the sake of completeness, we mention an extension of the previous theory if a direct orientational interaction is taken into account. This amounts to addition of a term

$$H^{RR} = \tfrac{1}{2} \sum_{\vec{q}} J_{\mu\nu}(\vec{q}) Y^\dagger_\mu(\vec{q}) Y_\nu(\vec{q}) \qquad (2.45)$$

to the Hamiltonian (2.1). Then Eq. (2.19) becomes

$$H_R(\vec{b}) = - \sum_{\vec{q}} \big[\tfrac{1}{2} Y^\dagger_\nu(\vec{q}) K^R_{\nu\mu} Y_\mu(\vec{q}) + b^*_\nu Y_\nu(\vec{q}) \big] + V^R , \qquad (2.46a)$$

where we have defined

$$K^R_{\nu\mu}(\vec{q}) = C^R_{\nu\mu}(\vec{q}) + J_{\nu\mu}(\vec{q}) . \tag{2.46b}$$

Expression (2.46a) for $H_R(\vec{b})$ has to be taken into account for the calculation of the free energy, Eq. (2.23b). In molecular-field approximation, instead of Eq. (2.29), we now have

$$H_R^{\mathrm{MF}} = -\tfrac{1}{2}\sum Y^{e*}_\nu K^R_{\nu\mu} Y^e_\mu - \sum b^*_\nu Y^e_\nu + V_R - \sum a^*_\mu \Delta_\mu , \tag{2.47}$$

and the definition of a_ν, Eq. (2.30), has to be replaced by

$$a_\nu(\vec{q}) \equiv K^R_{\nu\mu}(\vec{q}) Y^e_\mu(\vec{q}) + b_\nu(\vec{q}) , \tag{2.48}$$

where b_ν is again defined by Eq. (2.21). Equations (2.36b)–(2.38e) remain valid with $C^R_{\nu\mu}$ replaced by $K^R_{\nu\mu}$. The quantity γ_μ, Eq. (2.39), now reads

$$\gamma_\mu = (\beta^{-1}\langle Y^\dagger_\mu Y_\mu\rangle_0^{-1}\delta_{\mu\nu} - J_{\mu\nu})Y^e_\nu + iv_{j\mu}s^e_j . \tag{2.49}$$

The molecular-field expression for the free energy, Eq. (2.40a), is then given by

$$F_R^{\mathrm{MF}} = F_R^0 - \tfrac{1}{2}(T\langle Y^\dagger_\mu Y_\mu\rangle_0^{-1}\delta_{\mu\nu} - K^R_{\mu\nu})Y^{e*}_\mu Y^e_\nu . \tag{2.50}$$

The final result is given by Eq. (2.41), where now the definition (2.42b) for $\mathcal{V}$ is found to be

$$\mathcal{V} \equiv \sum_{\vec{q}} \left[\tfrac{1}{2}s^{e*}_i(\vec{q})M_{ij}(\vec{q})s^e_j(\vec{q}) + iv_{i\nu}(\vec{q})s^e_i Y^{e*}_\nu \right] + \tfrac{1}{2}(T\langle Y^\dagger_\mu Y_\mu\rangle_0^{-1}\delta_{\mu\nu} - J_{\mu\nu})Y^{e*}_\mu Y^e_\nu . \tag{2.51}$$

We should mention that Eq. (2.41), with $\mathcal{V}$ given by Eq. (2.51), is a generalization of the expression of the minimum work function $R_{\min}$ which has been written down by Yamada *et al.*[4] for the case of a pseudospin-phonon coupled system. Our deviation of Eqs. (2.41) and (2.51) remains valid for the case of a coupling of orientational motion to optical phonons. The coupling matrix $iv(\vec{q})$ has to be replaced by an appropriate coupling matrix $g(\vec{q})$ with the property

$$g(\vec{q}) = g^*(-\vec{q}) . \tag{2.52}$$

III. DYNAMIC EQUATIONS

Starting from a nonequilibrium free energy as given by Eq. (2.40b), and adding dissipative terms to account for frictional forces, one of the present authors[6] has derived kinetic equations along the lines of irreversible hydrodynamics. On the other hand, the approach used in Ref. 12 starts from a microscopic Hamiltonian, Eqs. (2.1)–(2.2e), and uses a projection-operator formalism to derive transport equations. Although the approach of Ref. 12 is formally quite general, approximations had to be made to obtain useful and tractable results. The two main approximations made are, firstly, the approximation of the memory kernels by frequency-independent constants, and secondly, the use of molecular-field theory for the calculation of static susceptibilities. We shall now show that within this framework, the transport equations of Refs. 6 are in full agreement with those of Refs. 12 and 13.

To this effect, the equations of Ref. 6 are rewritten in a form that allows direct comparison with Refs. 12 and 13. One starts from the free-energy $\mathcal{R} \equiv \mathcal{T} + \mathcal{V}$, where $\mathcal{T}$ and $\mathcal{V}$ are given by (2.42). We use the identifications (2.44) and from now on drop the superscripts e that specifically designated nonequilibrium expectations in Sec. II. One obtains

$$\mathcal{R} = \mathcal{T} + \sum_{\vec{q}} \left[\tfrac{1}{2}qqC^0 s^*(q)s(q) + \tfrac{1}{2}B\alpha^*(q)\alpha(q) + \tfrac{1}{2}iqDs(q)\alpha^*(q)\right] . \tag{3.1}$$

Here $\alpha(q)$ corresponds to $Y^e_\nu(q)$, and $s(q)$ to $s^e(q)$. We note that these nonequilibrium variables are also time dependent. An index 0 has been added to C to designate the bare elastic constants, i.e., C in Ref. 6 means C^0 here. For reasons of notational simplicity, the explicit tensorial nature of C^0, B, and D will not be indicated. Furthermore, explicit mention of the wave-vector dependence will be omitted, except where confusion could arise.

In Ref. 6, the quantity α stands for the polarizability-tensor field. In order to make the connection with the orientational dynamic variables used in Ref. 12, we define a polarizability field that is orthogonalized to the displacement field:

$$\theta(q) \equiv \alpha(q) + iq\frac{D}{B}s(q) . \tag{3.2}$$

Then, Eq. (3.1) becomes

$$\mathcal{R} = \mathcal{T} + \tfrac{1}{2}q^2Cs^*s + \tfrac{1}{2}B\theta^*\theta , \tag{3.3}$$

where C now denotes the dressed elastic constants (denoted by C_{eff} in Ref. 6),

$$C \equiv C^0 - D^2/B . \tag{3.4}$$

The static correlation functions are calculated with the probability distribution function $\exp(-\beta\mathcal{R})$.[14] It immediately follows from (3.3) that

$$\langle p^*p\rangle = m/\beta , \tag{3.5a}$$

$$\langle s^*s\rangle = 1/Cq^2\beta , \tag{3.5b}$$

$$\langle \theta^*\theta\rangle = 1/B\beta . \tag{3.5c}$$

Furthermore, using (3.2) and $\langle s^* \theta\rangle = 0$, one finds

$$\langle \alpha^* \alpha\rangle = C^0/\beta BC\,, \tag{3.5d}$$

$$\langle s(q)\alpha^*(q)\rangle = -\langle \alpha(q) s^*(q)\rangle = iD/\beta qBC\,. \tag{3.5e}$$

We now rewrite the equations of motion (4) of Ref. 6, using (3.2) and transforming to reciprocal space:

$$m\dot{s} = p\,, \tag{3.6a}$$

$$\dot{p} + \frac{q^2}{m}\left(\Gamma^{\epsilon} - \frac{D}{B}\,\Gamma^{\alpha\epsilon}\right)p + q^2Cs - iqD\theta - iq\,\Gamma^{\alpha\epsilon}\dot{\theta} = 0\,, \tag{3.6b}$$

$$B\theta + \Gamma^{\alpha}\dot{\theta} + \frac{iq}{m}\left(\Gamma^{\alpha\epsilon} - \frac{D}{B}\,\Gamma^{\alpha}\right)p = 0\,. \tag{3.6c}$$

Here the dots denote first derivative with respect to time, e.g., $\dot{s} \equiv (d/dt)s$, etc. We now eliminate $\dot{\theta}$ on the left-hand side of (3.6b) using (3.6c). Defining a column vector $\vec{a}$,

$$\vec{a} \equiv (s, p, \theta)\,, \tag{3.7}$$

a restoring-force matrix $\tilde{\Omega}$

$$\tilde{\Omega} \equiv i\begin{pmatrix} 0 & \dfrac{1}{m} & 0 \\ -q^2C & 0 & iqD \\ 0 & \dfrac{iqD}{mB} & 0 \end{pmatrix}\,, \tag{3.8}$$

and a dissipation matrix $\tilde{\Sigma}$,

$$\tilde{\Sigma} \equiv i\begin{pmatrix} 0 & 0 & 0 \\ 0 & q^2\Gamma/m & iqB\,\Gamma^{\alpha\epsilon}/\Gamma^{\alpha} \\ 0 & iq\,\Gamma^{\alpha\epsilon}/m\,\Gamma^{\alpha} & B/\Gamma^{\alpha} \end{pmatrix}\,, \tag{3.9a}$$

with

$$\Gamma \equiv \Gamma^{\epsilon} - (\Gamma^{\alpha\epsilon})^2/\Gamma^{\alpha}\,, \tag{3.9b}$$

system (3.7) is rewritten as

$$\left(\tilde{1}\,\frac{d}{dt} + i\tilde{\Omega} - i\tilde{\Sigma}\right)\vec{a}(t) = 0\,. \tag{3.10}$$

To allow a direct comparison with Refs. 12 and 13, it is simplest to build from (3.10) the equation of motion for the Laplace transform of the correlation matrix [Eq. (33) of Ref. 13)] or, what is equivalent, the equation for the Kubo relaxation function $\tilde{\Phi}(z)$ [Eq. (3.28) of Ref. 12]. One can proceed in two equivalent ways. A first route is to Laplace-transform (3.10), to take the outer product with the initial-value vector $\vec{a}(t=0)$, and to calculate the average over those initial values using their distribution function $\exp(-\beta\mathcal{R})$. In this manner, the Laplace-transformed dynamic correlation functions are expressed in terms of the static averages (3.5). This well known procedure[19] was also used in Ref. 6. An alternate route is to use results of linear response theory.[20] To make connection with those references, the Laplace-transform operation is defined

$$\vec{a}(z) = -i\int_0^{\infty} \exp(izt)\vec{a}(t)dt\,, \tag{3.11}$$

where $\operatorname{Im} z > 0$. After this transformation, (3.10) reads

$$(\tilde{1}z - \tilde{\Omega} + \tilde{\Sigma})\vec{a}(z) = \vec{a}(t=0)\,. \tag{3.12}$$

Using the relation[21]

$$a_{\alpha}(z) = \Phi_{\alpha\beta}(z)\chi^{-1}_{\beta\gamma}(0)a_{\gamma}(t=0)\,, \tag{3.13}$$

where $\tilde{\Phi}$ is Kubo's relaxation function and $\tilde{\chi}(0)$ is the static susceptibility, Eq. (3.12) gives

$$(\tilde{1}z - \tilde{\Omega} + \tilde{\Sigma})\tilde{\Phi}(z) = \tilde{\chi}(0)\,, \tag{3.14}$$

which is Mori's equation for the relaxation function. In the classical limit, $\chi_{\alpha\beta}(0) = \beta\langle a_{\alpha}a^*_{\beta}\rangle$, so that, using (3.5),

$$\chi(0,q) = \begin{pmatrix} 1/Cq^2 & 0 & 0 \\ 0 & m & 0 \\ 0 & 0 & 1/B \end{pmatrix}\,. \tag{3.15}$$

Equation (3.14) has to be compared with Eq. (3.28) of Ref. 12. Since the latter has been written down under the assumption that anharmonic translational displacements are negligible, we must take $\Gamma^{\epsilon} = 0$ and $\Gamma^{\alpha\epsilon} = 0$ in (3.9). Under that condition, there is complete agreement between Eq. (3.14), with $\tilde{\Omega}$, $\tilde{\Sigma}$, and $\tilde{\chi}(0)$ specified as before, and Eq. (3.28) of Ref. 12. This leads to the following identification (with $m = 1$):

$$\tilde{D} \equiv (s,s)^{-1} \longleftrightarrow q^2C\,, \tag{3.16a}$$

$$\tilde{\beta} \equiv (\bar{Y}, \mathcal{L}p) \longleftrightarrow q\,\frac{D}{B}\,, \tag{3.16b}$$

$$\tilde{\lambda} \longleftrightarrow \frac{B}{\Gamma^{\alpha}}\,, \tag{3.16c}$$

$$(\bar{Y}, \bar{Y})^{-1} \equiv X \longleftrightarrow B\,. \tag{3.16d}$$

On the left-hand side (lhs) are the quantities of Ref. 12, and on the rhs, the corresponding quantities of Ref. 6. This identification is also fully compatible with (2.43) if we observe that $\alpha \to Y_{\alpha}$ of Ref. 12 and that the present variable θ corresponds to $\bar{Y}$ of Ref. 12.

Having shown the full equivalence of the hydrodynamic theory of Ref. 6 with the microscopic approach of Ref. 12, we now turn to a comparison with Ref. 13. It was pointed out in Ref. 12 that the anharmonicities in the translational lattice displacements lead to additional transport coefficients Γ^{ϵ}, $\Gamma^{\alpha\epsilon}$. These occur in the hydrodynamic approach which makes no restriction to a harmonic lattice; these anharmonicities have also been introduced in Ref. 13. Comparing (3.14) with Eq. (33) of Ref. 13, with $m=1$, one finds the correspondences

$$\alpha_W \longleftrightarrow \alpha\,, \tag{3.17a}$$

$$Q_W \longleftrightarrow s\,, \tag{3.17b}$$

$$P_W \longleftrightarrow p\,, \tag{3.17c}$$

$$\beta_W \longleftrightarrow \theta\,, \tag{3.17d}$$

where the symbols on the lhs are those of Ref. 13 (plus a subscript W). Comparing (3.15) with Eqs. (18) and (19) of Ref. 13, one gets

$$T^{-1}\langle AA^{+}\rangle_W \longleftrightarrow \tilde{\chi}(0)\,, \tag{3.18a}$$

$$TM_W \longleftrightarrow Cq^2\,, \tag{3.18b}$$

$$T^{-1}(\chi_\beta)_W \equiv T^{-1}\langle \beta\beta^{+}\rangle_W \longleftrightarrow B^{-1}\,. \tag{3.18c}$$

Comparing (3.8) with Eq. (23) of Ref. 13, one has

$$\Omega_W \longleftrightarrow -\tilde{\Omega}\,, \tag{3.19a}$$

which confirms (3.18b), (3.18c), and in addition gives

$$(\nu\chi_\beta^{-1})_W \longleftrightarrow qD\,, \tag{3.19b}$$

$$T^{-1}\nu_W^{+} \longleftrightarrow qD/B\,. \tag{3.19c}$$

Since $\nu^{+}=\nu^{\tau}$ (τ, transposed), and since the explicit tensorial character of D, B, and ν was neglected, we have here $\nu^{+}=\nu$. Note that (3.19b) and (3.19c) are in agreement with (3.18c). Finally, comparing (3.9a) with Eq. (27) of Ref. 13, one finds

$$iK_W \longleftrightarrow \tilde{\Sigma}\,, \tag{3.20a}$$

$$\eta_W \longleftrightarrow q^2\Gamma\,, \tag{3.20b}$$

$$\gamma'_W \longleftrightarrow iqB\,\Gamma^{\alpha\epsilon}/\Gamma^{\alpha}\,, \tag{3.20c}$$

$$\gamma''_W \longleftrightarrow iq\,\Gamma^{\alpha\epsilon}/\Gamma^{\alpha}\,, \tag{3.20d}$$

$$\lambda_W \longleftrightarrow B/\Gamma^{\alpha}\,. \tag{3.20e}$$

We recall that all elements of K_W have to be taken in the low-frequency limit. Considering (3.20c), (3.20d), and (3.18c), one finds $(\gamma'\chi_\beta)_W = -T(\gamma'')^{*}_W$ which is also a result of time-reversal symmetry in Eqs. (29) and (30) of Ref. 13. Finally, to complete the identification, we note that

$$[-iT^{-1}\tilde{C}(-iz,-q)]_W \longleftrightarrow \tilde{\Phi}(z,\vec{q})\,. \tag{3.21}$$

Consequently, the correlation-function matrix $\tilde{C}_W$ of Ref. 13 is equivalent to Kubo's relaxation function.[20, 21] Note that in Ref. 13 the spatial Fourier transformation is defined with a sign of $\vec{q}$ opposite to that used in Refs. 6 and 12, as well as here.

IV. CORRELATION FUNCTIONS AND SUM RULES

Given the identification made in Sec. III between the hydrodynamic and the Mori approaches, it is not possible for these theories to give incompatible results for the correlation function $C^{\alpha\alpha}(z)$ or equivalently $\Phi^{\alpha\alpha}(z)$. Such an incorrect conclusion was drawn using Eq. (64) of Ref. 13. In fact, that equation is incomplete since interference terms between translations and orientations have been omitted.[22] Using Eq. (32), one obtains

$$\begin{aligned} C^{\alpha\alpha}(q,z) &= \Big\langle\Big(\theta(q,z) + iq\,\frac{D}{B}\,s(q,z)\Big) \\ &\qquad\times\Big(\theta(q,0) - iq\,\frac{D}{B}\,s^{\dagger}(q,0)\Big)\Big\rangle \\ &= C^{\theta\theta}(q,z) + iq\,\frac{D}{B}C^{s\theta}(q,z) \\ &\qquad - iq\,\frac{D}{B}C^{\theta s}(q,z) + \Big(\frac{qD}{B}\Big)^2 C^{ss}(q,z)\,. \end{aligned} \tag{4.1}$$

Space and time-reversal symmetries imply

$$C^{s\theta}(q,z) = -C^{\theta s}(q,z)\,, \tag{4.2}$$

similar to Eq. (60) of Ref. 13. Equation (4.1) then becomes

$$\begin{aligned} C^{\alpha\alpha}(q,z) &= C^{\theta\theta}(q,z) + \Big(\frac{qD}{B}\Big)^2 C^{ss}(q,z) \\ &\qquad + 2iq\,\frac{D}{B}\,C^{s\theta}(q,z)\,. \end{aligned} \tag{4.3}$$

The last term on the rhs of this expression is due to interference between translational and orientational motions. These interference terms have already been introduced in Ref. 12, where they correspond to the functions $\Phi_{s\overline{Y}}(\vec{q},z)$ and $\Phi_{\overline{Y}s}(\vec{q},z)$. They are obtained from the equation of motion (3.34) of Ref. 12. In the notation of Ref. 13, (4.3) reads

$$\begin{aligned} C_{\alpha\alpha}(q,z) &= C_{\beta\beta}(q,z) + \Big(\frac{\langle\alpha Q^{+}\rangle}{\langle QQ^{+}\rangle}\Big)^2 C_{QQ}(q,z) \\ &\qquad + 2\,\frac{\langle\alpha Q^{+}\rangle}{\langle QQ^{+}\rangle}\,C_{Q\beta}(q,z)\,, \end{aligned} \tag{4.4}$$

which is immediately obtained from Eq. (9) of Ref. 13. The correspondence of (4.4) and (4.3) can be shown using the relations (3.5b), (3.5e), and (3.17)–(3.19).[23] Using (4.4) instead of Eqs. (64) or (75) of Ref. 13, it is rather straightforward to verify full equivalence with Eq. (80) of Ref. 13. In view of the previous sections, this comes as no surprise. In particular, this equivalence entails no restrictive condition; note that Eq. (86) of Ref. 13 is indeed an exact relation between static correlation functions that follows directly from (3.5e) and (3.5b).

Equations (3.5) contain all the sum rules needed. It is of interest to note, however, that identical relations can also be obtained using familiar concepts of linear-response theory.[20] Given two operators A and B, the dynamic susceptibility is defined as[24]

$$\chi_{AB}(z) \equiv -\langle\langle A;B^\dagger\rangle\rangle = i\int_{-\infty}^{+\infty} dt\Theta(t)e^{izt}\langle[A(t),B^\dagger(0)]\rangle\,, \tag{4.5}$$

with $\mathrm{Im}z > 0$. Note that $\langle\langle A;B^\dagger\rangle\rangle$ is the well known retarded Green's function. The function $\chi_{AB}(z)$, which is holomorphic for $\mathrm{Im}z \neq 0$, is written as a spectral integral

$$\chi(z) = \int_{-\infty}^{+\infty} \frac{d\omega}{\pi}\frac{\chi''(\omega)}{\omega - z}\,. \tag{4.6}$$

Here, $\chi''(\omega)$ is the discontinuity of $\chi(z)$ across the real axis

$$\chi(\omega \pm i0) = \chi'(\omega) \pm i\chi''(\omega)\,. \tag{4.7}$$

The static susceptibility $\chi_{AB}(z=0) \equiv (A,B)$, is then given by

$$(A,B) \equiv \chi_{AB}(0) = \int_{-\infty}^{+\infty} \frac{d\omega}{\pi}\frac{\chi''_{AB}(\omega)}{\omega}\,, \quad \omega \in \mathrm{Re}\,. \tag{4.8}$$

The thermal average $\langle A^\dagger B\rangle$ is then related to χ''_{AB} by the fluctuation-dissipation theorem

$$\langle AB^\dagger\rangle = \int_{-\infty}^{+\infty} \frac{d\omega}{\pi}\left[1 - \exp\left(\frac{-\omega}{T}\right)\right]^{-1} \chi''_{AB}(\omega)\,. \tag{4.9}$$

In the classical limit, Eqs. (4.8) and (4.9) combine to

$$(A,B) = \frac{\langle AB^\dagger\rangle}{T}\,. \tag{4.10}$$

Kubo's relaxation function $\Phi(z)$, introduced in Sec. III, Eq. (3.13), is related to the dynamic susceptibility by

$$\Phi(z) = \frac{\chi(0) - \chi(z)}{z}\,. \tag{4.11}$$

This last equation implies $\chi''(\omega) = -\omega\Phi''(\omega)$. We now apply the general equation (4.8) to the variables s, α, and θ. We first calculate the relaxation functions $\Phi_{ss}(z)$, $\Phi_{s\theta}(z)$, and $\Phi_{\theta\theta}(z)$ by inverting the matrix equation (3.13). Then, we calculate $\Phi''(\omega)$ and carry out the integral over ω in Eq. (4.8). As a result we find

$$(s,s) = \int_{-\infty}^{+\infty} \frac{d\omega}{\pi\omega}\,\chi''_{ss}(\omega,q) = \frac{1}{Cq^2}\,, \tag{4.12a}$$

$$(s,\alpha) = \int_{-\infty}^{+\infty} \frac{d\omega}{\pi\omega}\,\chi''_{s\alpha}(\omega,q) = \frac{iD}{BqC}\,, \tag{4.12b}$$

$$(\alpha,\alpha) = \int \frac{d\omega}{\pi\omega}\,\chi''_{\alpha\alpha}(\omega,q) = \frac{C^0}{CB}\,, \tag{4.12c}$$

$$(\theta,\theta) = \int \frac{d\omega}{\pi\omega}\,\chi''_{\theta\theta}(\omega,q) = 1/B\,, \tag{4.12d}$$

$$(s,\theta) = \int \frac{d\omega}{\pi\omega}\,\chi''_{s\theta}(\omega,q) = 0\,. \tag{4.12e}$$

Using (4.10), these are just the same as the static correlation functions (3.5) calculated with the probability distribution $\exp(-\beta\mathcal{H})$. It is also easy to check that, with these expressions, the sum rule applied to (4.3) just reproduces (3.4). Finally, in the absence of translation-orientation coupling, $D=0$ and $C^0=C$, where C^0 is the isothermal elastic tensor of the phonon system; (4.12a) then reduces to a well known isothermal sum rule for phonons.[25]

V. CONCLUDING REMARKS

Using a molecular-field-type approach, we have derived the nonequilibrium free energy from a Hamiltonian with bilinear translational-orientational coupling. This free energy is the starting point for deriving macroscopic hydrodynamic equations. The approach formulated in Sec. II is very general; it is not restricted to a particular molecular crystal. In fact, the details of a given system are taken into account by the structure of the matrix of bilinear coupling, by the single-particle orientational potential, by the symmetry of the orientational dynamic variables, and by the bare elastic constants. The transport coefficients entering the dynamic equations are assumed to be independent of frequency. The hydrodynamic equations for translations and rotations thus obtained are compared with transport equations derived by means of the Mori-Zwanzig projection-operator technique.

The latter method has the *a priori* advantage that the matrix of restoring forces as well as the matrix of memory functions are formulated in terms of closed mathematical expressions. In principle, these expressions can be evaluated from the knowledge of a microscopic Hamiltonian. However, in practice, one has to use approximations in carrying out such an evaluation. Essentially two approximations are made: firstly, the use of molecular-field theory in calculating the static susceptbilities, and secondly, the omission of memory effects by assuming constant transport coefficients. Then, it is found that the dynamic equations derived by means of the macroscopic method are equivalent to those derived by means of the projection-operator method.

If one wants to go beyond the framework of

Markoffian response, the microscopic method offers a well established procedure for doing so. In particular, it is possible to give explicit expressions for the frequency-dependent memory kernels by using a self-consistent reasoning. Such a calculation was performed recently for a Hamiltonian with bilinear translation-orientation coupling.[26]

On the other hand, in many cases, molecular crystals are of such complexity that a microscopic Hamiltonian is not available. The hydrodynamic approach then still allows meaningful dynamic equations to be written down and allows the explanation of experiments. The relevant parameters are then the coefficients of the nonequilibrium free energy and the kinetic coefficients of the dissipation function.

ACKNOWLEDGMENTS

The authors acknowledge useful discussions with Jan Fivez and Bart De Raedt. This paper is partially supported by the Belgian project Neutron Scattering, Interuniversitary Institute for Nuclear Research, Belgium.

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[1] L. Onsager, Phys. Rev. 37, 1105 (1931); 38, 2265 (1931).

[2] S. Machlup and L. Onsager, Phys. Rev. 91, 1512 (1953).

[3] J. Feder and E. Pytte, Phys. Rev. B 8, 3978 (1973).

[4] Y. Yamada, H. Takatera, and D. L. Huber, J. Phys. Soc. Jpn. 36, 641 (1974).

[5] See, for example, N. D. Gershon and I. Oppenheim, Physica (Utrecht) 64, 247 (1973), and references quoted therein.

[6] E. Courtens, J. Phys. (Paris) Lett. 37, L-21 (1976).

[7] T. Bischofberger and E. Courtens, Phys. Rev. Lett. 35, 1451 (1975).

[8] H. Mori, Prog. Theor. Phys. 23, 423 (1965); R. W. Zwanzig, J. Chem. Phys. 33, 1388 (1960).

[9] See, for example, C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids* (Clarendon, Oxford, 1972).

[10] K. H. Michel and Hans De Raedt, J. Chem. Phys. 65, 977 (1976).

[11] K. H. Michel and J. Naudts, Phys. Rev. Lett. 39, 212 (1977); J. Chem. Phys. 67, 547 (1977).

[12] K. H. Michel and J. Naudts, J. Chem. Phys. 68, 216 (1978).

[13] C. H. Wang, J. Chem. Phys. 70, 3796 (1979).

[14] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1958), §111 and §118 to 121.

[15] For an extensive group-theoretical treatment, we refer to M. Yvinec and R. Pick, J. Phys. (Paris) 41, 1045 (1980). The assumption that the nonequilibrium free energy should be expandable in terms of symmetry-adapted functions was made by M. Boissier, R. Vacher, D. Fontaine, and R. Pick, J. Phys. 39, 205 (1978).

[16] A. F. Devonshire, Proc. R. Soc. London Ser. A 153, 601 (1936).

[17] L. D. Landau and E. M. Lifshitz, Ref. 14, Chap. VI.

[18] R. Brout and H. Thomas, Physics (N.Y.) 3, 317 (1967); H. Thomas and R. Brout, J. Appl. Phys. 39, 624 (1968).

[19] See, for example, R. D. Mountain, J. Res. Nat. Bur. Stand. Sec. A 70A, 207 (1966).

[20] R. Kubo, J. Phys. Soc. Jpn. 12, 570 (1957); L. P. Kadanoff and P. C. Martin, Ann. Phys. (N.Y.) 24, 419 (1963).

[21] W. Götze and K. H. Michel, in *Dynamical Properties of Solids*, edited by G. K. Horton and A. A. Maradudin (North-Holland, Amsterdam, 1974), p. 509, Eq. (1.56b).

[22] A corresponding omission appeared accidentally in the previous work on this subject, Eq. (6.24) of Ref. 12, where, however, it did not lead to any particular consequences.

[23] In doing so, it is important to replace $\vec{q}$ by $-\vec{q}$ in Ref. 13 and to correct a misprint in Eq. (59) of Ref. 13 that should read $C_{\beta Q}(z) = (-i\nu^{+} + kT\gamma'')/\Delta$.

[24] D. N. Zubarev, Usp. Fiz. Nauk 71, 71 (1960) [Sov. Phys.–Usp. 3, 320 (1960)].

[25] W. Götze, Phys. Rev. 156, 951 (1967).

[26] B. de Raedt and K. H. Michel, Discuss. Faraday Soc., in press.