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Symmetry properties, normal modes, and free energy of orientationally disordered crystals

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Symmetry-adapted functions are the appropriate coordinates for the description of orientational disorder in crystals. Here this approach is extended and orientational fluctuations are classified according to the irreducible representations of the space group of the crystal. As a counterpart to the theory of lattice vibrations, normal-mode coordinates are introduced for orientational fluctuations. The coupling of translational and rotational motion is studied. The nonequilibrium free energy for molecular crystals with translation-rotation coupling is derived. The results of the present work allow a systematic description of the symmetry reduction at phase transitions which involve orientational degrees of freedom.

I. INTRODUCTION

Orientationally disordered crystals are built up either from molecules or from molecular ions and single atoms. The equilibrium positions of the centers of mass of the molecules (or molecular ions) and of the individual single atoms form a crystalline lattice. The molecules (or molecular ions) are taken as rigid bodies. The centers of mass of the molecules and of the single atoms perform small oscillatory motions around their equilibrium lattice positions. These motions constitute the lattice vibrations or translational degrees of freedom. They will be called lattice vibrations or, even loosely speaking, translations. The elementary excitations which correspond to collective lattice vibrations are called phonons.

In addition to translations, molecular crystals usually possess rotational degrees of freedom. One distinguishes essentially two situations. Firstly, in strong potentials and at low temperature, the molecules are orientationally well localized. They can reorient among equivalent positions by quantum-mechanical tunneling. In addition the molecules carry out small oscillations around their equilibrium orientations. The corresponding elementary excitations, called librations, are very similar to optical phonons. Group-theoretical methods have been used[1,2] in their classification. Secondly, there is the case of orientational disorder, generally found at high temperature and relatively low potentials. Then the amplitudes of orientational motion are large. A description of the dynamics of these crystals on the basis of small angular displacements is in general not adequate. In fact no well-defined equilibrium positions exist in orientationally disordered phases. The full angular dependence of orientational motion can be dealt with by an analysis of physical quantities in terms of spherical harmonics (in the case of linear molecules) or in terms of Wigner D functions (in the general case of nonlinear molecules). This situation is also well known from molecular liquids.[3] In molecular solids, the symmetry of the crystalline state reduces the number of angular-dependent functions to certain linear combinations of these functions. These linear combinations are called symmetry-adapted functions.

In connection with orientational motion, this approach was used early by Devonshire.[4] He studied the rotation of a linear molecule in an octahedral field and expanded the single-particle orientational potential in terms of cubic harmonics. These symmetry-adapted functions had been introduced previously by Bethe for the study of electronic term splitting in crystals.[5] Later on, extensive use of symmetry-adapted functions was made by James and Keenan,[6] who gave a theoretical description of the phases in solid heavy methane. More recently symmetry-adapted functions have been used for the analysis of orientational disordered structures[7] as well as for the study of static[8] and dynamic[9] correlation functions. The main quantity which is measured by diffraction experiments in orientationally disordered crystals is the single-molecule (molecular-ion) orientational distribution function,[10] also called the probability density function. A systematic way of expanding the probability density function in terms of symmetry-adapted functions, made on the basis of group theory, was given in Ref. 11. This description takes into account the symmetry of the molecule and of the crystalline site.

In the present paper we extend the scope of previous work[10,11,6] and give a description of orientational fluctuations in solids which is based on the symmetry of the crystalline space group. In analogy with the classifications of the normal modes of lattice vibrations in crystals according to the irreducible representations of the space groups,[12,13] we shall present a systematic way of classification of orientational fluctuations according to the irreducible representations of the space group.

In Sec. II we start with a formulation of the single-molecule orientational distribution function in terms of site-adapted rotator functions. Subsequently (Secs. III and IV), we describe a group-theoretical method which allows us to find systematically the irreducible representations of orientational fluctuations. The method is based on the multiplier or ray representation[12–15] of the point group of the wave vector **k**. It was used previously for the classification of normal lattice vibrations. In Sec. V we show that the intermolecular potential, which is given as a sum over atom-atom potentials, can be formulated in terms of normal coordinates of rotations and translations. Next (Sec. VI), we derive the Helmholtz free energy which corresponds to orientation- and translation-dependent interactions. Contributions up to fourth order in the orientational order parameters are included. Thermodynamic consequences are discussed in the framework of a Landau theory, where all coefficients are explicitly derived from the interaction potential.

II. SYMMETRIES OF THE ORIENTATIONAL DISTRIBUTION

Here we give a general formulation of the orientational distribution function in terms of symmetry-adapted functions. Though our considerations are closely related to previous work,[10,11] a self-contained treatment was appropriate for the preparation of the subsequent sections.

Rotational properties of physical objects are conveniently expressed by means of spherical harmonics $Y_l^m(\Omega)$, where $\Omega \equiv (\theta,\varphi)$. (We shall follow closely the notations and conventions of Bradley and Cracknell.[16]) If in addition, the problem has a symmetry defined by a point group P, it is useful to combine the spherical harmonics to symmetry-adapted functions.[16–18] These functions, denoted by $S_{l(P)}^{\tau}(\Omega)$, are surface harmonics which form a basis of the irreducible representations of the point group P. A famous example is the Devonshire potential.[4] Generally speaking, the $2l+1$ functions Y_l^m for given l are related to the $2l+1$ symmetry-adapted functions S_l^{τ} by the unitary transformation

$$Y_l^m(\Omega) = \sum_{\tau} S_{l(P)}^{\tau}(\Omega)\beta_{l(P)}^{\tau m} , \tag{2.1a}$$

$$S_{l(P)}^{\tau}(\Omega) = \sum_{m=-l}^{l} Y_l^m(\Omega)\alpha_{l(P)}^{m\tau} . \tag{2.1b}$$

Here $\tau \equiv (\Gamma,\nu,\beta)$ stands for the irreducible representations Γ of the point group P under consideration, ν labels the independent Γ subspaces if the representation Γ occurs more than once in the decomposition at a given l, and β labels the components of Γ. The index τ takes $2l+1$ values. The transformation coefficients are unitary and satisfy

$$\sum_{\tau} \alpha_{l(P)}^{m\tau}\beta_{l(P)}^{\tau m'} = \delta_{m,m'}, \quad \sum_{m=-l}^{l} \beta_{l(P)}^{\tau m}\alpha_{l(P)}^{m\lambda} = \delta_{\tau\lambda} . \tag{2.2}$$

The matrices $\underline{\beta}_{l(P)}^{\dagger} = \underline{\alpha}_{l(P)}$ are Hermitian conjugates. (Here and in the following an underline indicates the matrix.) The values of the coefficients $\alpha_{l(P)}^{m\tau}$ are given in the tables of Ref. 16. The symmetry-adapted functions form a complete and orthonormal set.

Under rotation R with Euler angles $\omega \equiv (\alpha,\beta,\gamma)$, the spherical harmonics transform according to

$$R(\omega)Y_l^m(\Omega) = \sum_{n=-l}^{l} Y_l^n D_{nm}^l(\omega) , \tag{2.3a}$$

where D_{nm}^l denote the Wigner rotator functions. The latter functions form a orthonormal set

$$\int d\omega\, D_{nm}^l(\omega) D_{n'm'}^{l'*}(\omega) = \frac{8\pi^2}{2l+1}\delta_{ll'}\delta_{nn'}\delta_{mm'} . \tag{2.3b}$$

In analogy with Eq. (2.3a), the symmetry-adapted functions transform according to

$$R(\omega)S_{l(P)}^{\tau}(\Omega) = \sum_{\lambda} S_{l(P)}^{\lambda}(\Omega) U_{l(P)}^{\lambda\tau}(\omega) , \tag{2.4a}$$

where the quantities

$$U_{l(P)}^{\lambda\tau}(\omega) = \sum_{n,m=-l}^{l} \beta_{l(P)}^{\lambda n} D_{nm}^l(\omega)\alpha_{l(P)}^{m\tau} \tag{2.4b}$$

are called rotator functions. They have been introduced in Ref. 6 for the particular example of tetrahedral rotator functions and used more generally in Refs. 10 and 11. For operations R, which belong to the symmetry elements h of the point group P, including the elements which are given by the product of a proper rotation and an inversion, the transformation law (2.4a) simplifies to

$$R(h)S_{l(P)}^{\Gamma\nu\beta}(\Omega) = \sum_{\beta'} S_{l(P)}^{\Gamma\nu\beta'}(\Omega)\rho_{l(P)}^{\Gamma\nu\beta'\beta}(h) , \tag{2.5a}$$

with

$$\rho_{l(P)}^{\Gamma\nu\beta'\beta}(h) = \sum_{n,m=-l}^{l} \beta_{l(P)}^{\Gamma\nu\beta' n} D_{nm}^l(h)\alpha_{l(P)}^{m\Gamma\nu\beta} . \tag{2.5b}$$

In Eq. (2.5a) summation is reduced to components β' of one irreducible representation Γ. The matrices $\underline{\rho}_{l(P)}^{\Gamma}(h)$ form an irreducible representation of the point group P. If Γ corresponds to the unit representation Γ_0, the matrix $\underline{\rho}_l$ reduces to unity:

$$\underline{\rho}_{l(P)}^{\Gamma_0}(h) = 1 . \tag{2.6}$$

We now consider a molecule which is taken as rigid body and resides in a crystal site of point-group symmetry S_0. We define an orthonormal system of axes $(\mathbf{X},\mathbf{Y},\mathbf{Z})$ attached to the crystal site and another one $(\mathbf{x},\mathbf{y},\mathbf{z})$ attached to the molecule. The origins of both systems of axes coincide with the center of mass of the molecule. The molecular symmetry is described by a point group M_0, the operations of which are defined in the molecular system of axes. The molecular orientation is described by the Euler angles $\omega \equiv (\alpha,\beta,\gamma)$. A rotation by ω brings the system of axes $(\mathbf{x},\mathbf{y},\mathbf{z})$ in coincidence with the crystal site system $(\mathbf{X},\mathbf{Y},\mathbf{Z})$. As has been discussed in Ref. 11, one has to discriminate among the operations of S_0 and M_0, which are proper rotations, from those which are improper ones (inversion rotations). By writing $S_0 = S + h_i hS$, $M_0 = M + h_i h'M$, where h and h' are proper rotations and h_i is the inversion, we see that S and M are the subgroups of S_0 and M_0, respectively. Yvinec and Pick[11] have shown that all orientational properties of the molecules should be analyzed with the aid of rotational subgroups S and M instead of the full point groups S_0 and M_0. Therefore, below, in referring to the molecular or site symmetry groups we shall mean their subgroups S and M of proper rotations.

We shall apply symmetry considerations in order to describe the mass distribution of one kind of atoms on a spherical shell in the molecule. We start with a molecular orientation such that the axes $(\mathbf{x},\mathbf{y},\mathbf{z})$ of the molecular system coincide with those of the site $(\mathbf{X},\mathbf{Y},\mathbf{Z})$. Then the location of one kind of atoms on a spherical shell with fixed radius can be represented by the distribution function

$$\begin{aligned}\sum_{\nu}\delta(\Omega-\Omega'_{\nu}) &= \sum_{l,\tau}\sum_{\nu} S^{\tau}_{l(S)}(\Omega'_{\nu})S^{\tau}_{l(S)}(\Omega) \\ &= \sum_{l}\sum_{\tau,\tau'}\left[\sum_{\nu} S^{\tau}_{l(M)}(\Omega'_{\nu})\right] \\ &\quad\times\left[\sum_{m}\beta^{\tau m}_{l(M)}\alpha^{m\tau'}_{l(S)}\right] S^{\tau'}_{l(S)}(\Omega) , \qquad (2.7)\end{aligned}$$

where we have used relations (2.1a) and (2.2). Here $\Omega'_{\nu}\equiv(\theta'_{\nu},\varphi'_{\nu})$ determines the position of the atom ν on the spherical shell in the molecular system of axes and the prime at Ω_{ν} indicates that both systems of axes coincide. The angle $\Omega\equiv(\theta,\varphi)$ is defined in the site system of axes $(\mathbf{X},\mathbf{Y},\mathbf{Z})$. So far the orientation of the molecule is fixed in the site system of axes. In course of time, the molecule changes its orientation. We want to write down the distributions of atoms (2.7) if the molecule has been rotated from the initial position Ω'_{ν} to the final position Ω_{ν} by the Euler angles $\omega\equiv(\alpha,\beta,\gamma)$, i.e.,

$$\Omega_{\nu}=R(\omega)\Omega'_{\nu} . \qquad (2.8)$$

Defining the distribution of mass of the rotated molecule as

$$f(\Omega;\omega)\equiv R(\omega)\sum_{\nu}\delta(\Omega-\Omega'_{\nu})=\sum_{\nu}\delta(\Omega-R(\omega)\Omega'_{\nu}) , \qquad (2.9)$$

and using Eqs. (2.4a), (2.4b), and (2.7), we find

$$\begin{aligned}f(\Omega;\omega) &= \sum_{l,\tau}\left[\sum_{\nu} S^{\tau}_{l(S)}(R(\omega)\Omega'_{\nu})\right] S^{\tau}_{l(S)}(\Omega) \\ &= \sum_{l}^{\Gamma_0}\left[\sum_{\tau} b^{\tau}_{l}(\omega)S^{\tau}_{l(S)}(\Omega)\right] , \qquad (2.10)\end{aligned}$$

where

$$b^{\tau}_{l}(\omega)=\sum_{\nu} S^{\tau}_{l(S)}(\Omega_{\nu})=\sum_{\lambda} g^{\lambda}_{l} U^{\lambda\tau}_{l(M,S)}(\omega) , \qquad (2.11a)$$

with

$$g^{\lambda}_{l}=\sum_{\nu} S^{\lambda}_{l(M)}(\Omega'_{\nu}) , \qquad (2.11b)$$

and

$$U^{\lambda\tau}_{l(M,S)}(\omega)=\sum_{n,m}\beta^{\lambda n}_{l(M)}D^{l}_{nm}(\omega)\alpha^{m\tau}_{l(s)} . \qquad (2.11c)$$

The rotator function (2.11c) depends simultaneously on the representations λ and τ of the molecular symmetry point group M and the site point group S, respectively. Both representations belong to the same l. The function $U^{\lambda\tau}_{l(M,S)}$ has been previously introduced in Ref. 11, Eq. (3.5), where it is denoted by $\Delta^{\lambda\lambda'}_{l}$. In Ref. 11 the functions $\Delta^{\lambda\lambda'}_{l}$ are used as relevant basis function for the expansion of physical quantities. We prefer to use the functions $b^{\tau}_{l}(\omega)$ which are related to the rotator functions U by Eq. (2.11a). The coefficients g^{λ}_{l} account for the structure of the molecules, Eq. (2.11b); they are nonzero only if λ refers to the identity representation $\Gamma_0(M)$. Otherwise $g^{\lambda}_{l}=0$. Therefore the sum over l in Eq. (2.10) is restricted to such values of l for which the list of irreducible representations of the molecular group M contains the identity representation $\Gamma_0(M)$.

The functions $b^{\tau}_{l}(\omega)$ with $\tau\equiv(\Gamma,\nu,\beta)$ will be called *site-adapted rotator functions*. They transform according to the same laws as the basis functions $S^{\tau}_{l(S)}$ of the irreducible representation Γ of the site rotational point group S. Indeed, from Eqs. (2.11a) and (2.5a) one finds

$$R(h)b^{\Gamma\nu\beta}_{l}(\omega)=\sum_{\beta'} b^{\Gamma\nu\beta'}_{l}(\omega)\rho^{\Gamma\nu\beta'\beta}_{l(S)}(h) , \qquad (2.12)$$

where the symmetry element h belongs to the point group S, and the matrices $\rho^{\Gamma}_{l(S)}$ form an irreducible representation Γ of S. For an arbitrary rotational motion only those site-adapted rotator functions of a given l do not vanish for which at least one geometrical factor [Eqs. (2.11b) and (2.12)] of the same l is nonzero. Otherwise

$$b^{\tau}_{l}(\omega)=0 \text{ if all } g^{\lambda}_{l}=0 , \qquad (2.13)$$

for a specific l.

The site-adapted rotator functions form an orthogonal set. Using Eqs. (2.11a), (2.2), and (2.3b), one finds

$$\int d\omega\, b^{\tau}_{l}(\omega)[b^{\tau'}_{l'}(\omega)]^{*}=\eta_l\delta_{ll'}\delta_{\tau\tau'} , \qquad (2.14a)$$

where

$$\eta_l=\frac{8\pi^2}{2l+1}\sum_{\lambda}(g^{\lambda}_{l})^2 . \qquad (2.14b)$$

III. REPRESENTATIONS OF PHONONS AND OF ORIENTATIONAL FLUCTUATIONS

So far we have shown how to assign to the leading orientational fluctuations the irreducible representations of the rotational site point group S. That approach is adequate if we restrict ourselves to local properties as the single-particle orientational distribution function. The situation is then comparable to the crystal-field-splitting problem where one considers the atomic orbitals at an isolated site.[5,19] On the other hand, in order to study collective phenomena as orientational phase transitions and the interaction of orientational fluctuations with lattice vibrations, one should know the representations of the leading orientational fluctuations in the space group of the crystal. In fact the last problem has analogy with the study of electronic band structure in crystals, where both the point-group symmetry of the atomic sites and the translational symmetry of the lattice are relevant.

We start with reminding some basic concepts of the symmetry of crystals.[13,16,15,19,20] As is well known, the space group F of the crystal can be decomposed into left cosets with respect to the invariant subgroup of translations:

$$F=\{f_1\,|\,\beta_1\}T+\{f_2\,|\,\beta_2\}T+\cdots+\{f_j\,|\,\beta_j\}T\;. \qquad (3.1)$$

Here we have used the Seitz notation for the symmetry element $\{f\,|\,\beta\}$ which consists of proper or improper rotations f_i and partial translations β_i. Note that $\beta_i\neq 0$ in the case of nonsymmorphic groups. The index j is an integer with value equal to the number of symmetry elements of the corresponding crystal class.

The space group $G(\mathbf{k})$ of the wave vector $\mathbf{k}$ (called also[16] little group of $\mathbf{k}$) is a subgroup of F and can also be decomposed into cosets of T:

$$G(\mathbf{k})=\{g_1\,|\,\alpha_1\}T+\cdots+\{g_q\,|\,\alpha_q\}T\;, \qquad (3.2)$$

such that

$$F=\{p_1\,|\,\gamma_1\}G(\mathbf{k})+\cdots+\{p_t\,|\,\gamma_t\}G(\mathbf{k})\;, \qquad (3.3)$$

where $t=j/q$ is the number of arms in the star of $\mathbf{k}$. All elements $\{g_i\,|\,\alpha_i\}$ and the generators $\{p_i\,|\,\gamma_i\}$ occur in the set of elements $\{f_i\,|\,\beta_i\}$. All point-group symmetry elements of the space group $G(\mathbf{k})$ leave the wave vector $\mathbf{k}$ invariant, i.e.,

$$g_i\mathbf{k}=\mathbf{k}+\mathbf{b}\;, \qquad (3.4)$$

where $\mathbf{b}$ is equal to zero or to a reciprocal-lattice vector. The point-group symmetry elements p_i of the generators $\{p_i\,|\,\gamma_i\}$ define all different arms of the irreducible star $\{k_i\}$, such that

$$\mathbf{k}_1=p_1\mathbf{k},\ \mathbf{k}_2=p_2\mathbf{k},\ldots,k_t=p_t\mathbf{k}\;, \qquad (3.5)$$

with $t=j/q$.

The point group

$$\hat{G}(\mathbf{k})=\{g_1,g_2,\ldots,g_q\}\;, \qquad (3.6)$$

which consists of all point-group symmetry elements of the space group $G(\mathbf{k})$, expression (3.2), is usually called the group of the wave vector $\mathbf{k}$. The representation $\Gamma(k;\{g\,|\,\boldsymbol{\alpha}\})$ of the space group $G(\mathbf{k})$ and the representation $\hat{\Gamma}(k;g)$ of the point group $\hat{G}(k)$ are related by

$$\hat{\Gamma}(\mathbf{k};g)=\Gamma(\mathbf{k};\{g\,|\,\alpha\})\exp(i\mathbf{k}\cdot\boldsymbol{\alpha})\;. \qquad (3.7)$$

$\hat{\Gamma}(\mathbf{k};g)$ is called multiplier or ray representation.[12–15]

The position of the center of mass of the κth object in the $\mathbf{n}$th unit cell of the crystal is denoted by

$$\mathbf{R}(\mathbf{n},\kappa)=\mathbf{X}(\mathbf{n},\kappa)+\mathbf{u}(\mathbf{n},\kappa)\;, \qquad (3.8a)$$

where $\mathbf{X}(\mathbf{n},\kappa)$ denotes the equilibrium position

$$\mathbf{X}(\mathbf{n},\kappa)=\mathbf{X}(\mathbf{n})+\mathbf{x}(\kappa)\;. \qquad (3.8b)$$

Here $\mathbf{X}(\mathbf{n})=n_1\mathbf{a}+n_2\mathbf{b}+n_3\mathbf{c}$; $\mathbf{n}=(n_1,n_2,n_3)$ are integers and $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ primitive lattice translation vectors. The vector $\mathbf{x}(\kappa)$ fixes the equilibrium position of the κth object in the unit cell, with $\kappa=1,2,\ldots,s$ or $\kappa=1,2,\ldots,m$, where s and m are the numbers of individual atoms and molecules in the unit cell, respectively.

The lattice displacements $\mathbf{u}(\mathbf{n},\kappa)$ can be expanded in new coordinates:

$$u_i(\mathbf{n},\kappa)=\frac{1}{(NM_\kappa)^{1/2}}\sum_{\mathbf{k}}\sum_{j,\mu,a}Q(\mathbf{k},j,\mu,a)\exp[i\mathbf{k}\cdot\mathbf{X}(\mathbf{n},\kappa)]\times e_i(\kappa\,|\,\mathbf{k},j,\mu,a)\;, \qquad (3.9)$$

where $Q(\mathbf{k},j,\mu,a)$ refers to the amplitude of the new coordinate. Here $\mathbf{k}$ and j denote the wave vector and the index of the irreducible representation $D^{(j)}(\mathbf{k})$ of the space group of the wave vector $G(\mathbf{k})$ and μ labels the components of the irreducible representation $D^{(j)}(\mathbf{k})$, $\mu=1,2,\ldots,d_j$, where d_j is the dimension of $D^{(j)}(\mathbf{k})$.[12,13] A given representation $D^{(j)}(\mathbf{k})$ can occur in the expansion (3.9) $a_j(\mathbf{k})$ times. To account for that we have introduced the index a, which takes on the values $1,2,\ldots,a_j(\mathbf{k})$. The triplet of indices (j,μ,a) takes $3(s+m)$ values. M_κ is the mass of the object κ and N is the number of unit cells in the crystal. The quantities $e_i(\kappa\,|\,k,j,\mu,a)$ are the polarization vectors which bring the phonon dynamical matrix to the block form.

A specific instantaneous orientational configuration can be analyzed in terms of Fourier coordinates:

$$b_l^\tau(\mathbf{n},\kappa)=\frac{1}{\sqrt{N}}\sum_{\mathbf{k}}\sum_{j,\mu,c}b_l(\mathbf{k},j,\mu,c)\exp[i\mathbf{k}\cdot\mathbf{X}(\mathbf{n},\kappa)]\times h_l^\tau(\kappa\,|\,\mathbf{k},j,\mu,c)\;. \qquad (3.10)$$

Here and in the following we write $b_l^\tau(\mathbf{n},\kappa)$ instead of $b_l^\tau(\omega(\mathbf{n},\kappa))$. Equation (3.10) is the orientational analog of expression (3.9) for the center-of-mass displacements. Here again j is the index of the irreducible representation $D^{(j)}(\mathbf{k})$ of $G(\mathbf{k})$ and $\mu=1,2,\ldots,d_j$ labels the components of $D^{(j)}(\mathbf{k})$. The site-adapted rotator functions $b_l^\tau(\mathbf{n},\kappa)$ form an infinite set with respect to l. The usual approximation, however, will be to confine the treatment to a small finite set of such l which are allowed by the symmetry of molecules and sites. Each l, however, constitutes a subsystem in the sense that no symmetry operation can transfer any quantity indexed by l to the subsystem of l' when $l'\neq l$. A given irreducible representation $D^{(j)}(\mathbf{k})$ can occur in the expansion (3.10) for a specific l, $c_j^{(l)}(\mathbf{k})$ times. In Eq. (3.10) the index c takes the values $c=1,2,\ldots,c_j^{(l)}(\mathbf{k})$. The index triplet (j,μ,c) for a given l takes $\sum_{\kappa=1}^{m}\gamma_\kappa(2l+1)$ values, where $\gamma_\kappa=1$ if the l is allowed by the symmetry of the molecule at site κ, and $\gamma_\kappa=0$ otherwise.

A configuration of orientations $\{\omega(\mathbf{n},\kappa)\}$ can be specified by a set of amplitudes $b_l(\mathbf{k},j,\mu,c)$ of the site-adapted rotator functions. Different configurations $\{\omega(\mathbf{n},\kappa)\}$ are characterized by different sets of amplitudes $b_l(\mathbf{k},j,\mu,c)$. The polarization vectors $h_l^\tau(\kappa\,|\,\mathbf{k},j,\mu,c)$ describe the pattern of molecular orientations in the crystal, and they bring the orientational coupling matrix of the specific l, which is an analog of the dynamical matrix for phonons, to the block form. Each block contains elements labeled by the same irreducible representation $D^{(j)}(\mathbf{k})$, and has dimension $d_jc_j^{(l)}(\mathbf{k})\times d_jc_j^{(l)}(\mathbf{k})$. The orientational coupling block matrix can be completely diagonalized by additional transformation of the polarization vectors $h_l^\tau(\kappa\,|\,\mathbf{k},j,\mu,c)$. Two polarization vectors which belong to two subsystems indexed by different l and l' cannot be transformed to each other by any symmetry element. The polarization vectors $e_i(\kappa\,|\,\mathbf{k},j,\mu,a)$ of the lattice vibrations and $h_l^\tau(\kappa\,|\,\mathbf{k},j,\mu,c)$ of the orientational fluctuations generate the physical representations of lattice displacements and orientations, respectively. In order to specify those representations, one has to know the transformation laws under a symmetry operation $\{g\,|\,\boldsymbol{\alpha}\}$ which belongs to the space groups of the wave vector $G(\mathbf{k})$. We first consider a lattice displacement related with a mode $(\mathbf{k},j,\mu,a)$

$$u_i(\mathbf{n},\kappa)=\frac{1}{(NM_\kappa)^{1/2}}E_i(\kappa\,|\,\mathbf{k},j,\mu,a)\exp[i\mathbf{k}\cdot\mathbf{X}(\mathbf{n})]\ , \tag{3.11a}$$

where we have denoted

$$E_i(\kappa\,|\,\mathbf{k},j,\mu,a)=Q(\mathbf{k},j,\mu,a)\exp[i\mathbf{k}\cdot\mathbf{x}(\mathbf{k})] \times e_i(\kappa\,|\,\mathbf{k},j,\mu,a)\ . \tag{3.11b}$$

We shall see later that the form of the polarization vector $E_i(\kappa\,|\,\mathbf{k},j,\mu,a)$ which follows from the symmetry requirement is independent at the index a. Under an operation $\{g\,|\,\alpha\}$, the displacement $\mathbf{u}(n,\kappa)$ transforms as a vector, and in addition the site $\mathbf{X}(\mathbf{n},\kappa)$ is transferred to position

$$\mathbf{X}(\mathbf{n}',\kappa')=\{g\,|\,\boldsymbol{\alpha}\}^{-1}\mathbf{X}(\mathbf{n},\kappa)\ .$$

Consequently one obtains[20,12]

$$R\{g\,|\,\alpha\}u_i(\mathbf{n},\kappa)=\sum_{i'=1}^{3}u_{i'}(\mathbf{n}',\kappa')R_{i'i}(g)\ , \tag{3.12}$$

where $R\{g\,|\,\alpha\}$ is the linear functional operator associated with the operation $\{g\,|\,\boldsymbol{\alpha}\}$ and where $\underline{\mathbf{R}}(g)$ is the corresponding 3×3 vector representation of the point-group symmetry g.

In analogy with the considerations on lattice displacements, we write for an orientational fluctuation

$$b_l^\tau(\mathbf{n},\kappa)=\frac{1}{\sqrt{N}}H_l^\tau(\kappa\,|\,\mathbf{k},j,\mu,c)\exp[i\mathbf{k}\cdot\mathbf{X}(\mathbf{n})]\ , \tag{3.13a}$$

with

$$H_l^\tau(\kappa\,|\,\mathbf{k},j,\mu,c)=b_l(\mathbf{k},j,\mu,c)\exp[i\mathbf{k}\cdot\mathbf{x}(\kappa)] \times h_l^\tau(\kappa\,|\,\mathbf{k},j,\mu,c)\ . \tag{3.13b}$$

The transformation properties of the site-adapted rotator functions have been established in Eq. (2.12) for symmetry operations of the site point group $S^{(\kappa)}$. It is easy to extend the transformation properties of $b_l^\tau(\mathbf{n},\kappa)$ to all symmetry elements of the space group $G(\mathbf{k})$ of the wave vector. Using relations (2.11a), (2.1a), (2.1b), (2.5a), and (2.5b), and replacing the symmetry-adapted functions of the rotational point group $S^{(\kappa)}$ by those of the point group $\hat{G}(\mathbf{k})$, one obtains

$$R\{g\,|\,\alpha\}b_l^\tau(\mathbf{n},\kappa)=\sum_{\tau'}b_l^{\tau'}(\mathbf{n}',\kappa')C^{\tau'\tau}_{l(\hat{G},S^{(\kappa)})}(g)\ , \tag{3.14a}$$

with the definitions

$$C^{\tau'\tau}_{l(\hat{G},S^{(\kappa)})}(g)=\sum_{\pi,\alpha}\sum_{\beta}\gamma^{\tau',\pi\alpha}_{l(S^{(\kappa)},\hat{G})}\rho^{\pi\alpha\beta}_{l(\hat{G})}(g)(\gamma^{\pi\beta,\tau}_{l(S^{(\kappa)},\hat{G})})^\dagger\ , \tag{3.14b}$$

and

$$\gamma^{\tau\sigma}_{l(S^{(\kappa)},\hat{G})}=\sum_{m=-l}^{l}\beta^{\tau m}_{l(S^{(\kappa)})}\alpha^{m\sigma}_{l(G)}\ . \tag{3.14c}$$

Here τ,τ' label the irreducible representations and their components of the site rotator point group $S^{(\kappa)}$, and $\sigma\equiv(\pi,\alpha)$ or (π,β) refer to the irreducible representations of the point group $\hat{G}(\mathbf{k})$ of the wave vector. The matrix $\underline{\rho}_l$ is defined by expression (2.5b). Since the matrix (3.14c) is unitary, the representations $\underline{C}_{l(\hat{G},S^{(\kappa)})}$ and $\underline{\rho}_{l(\hat{G})}$ are equivalent and have the same characters.

The symmetry element $\{g\,|\,\alpha\}$ transfers the molecule from site $(\mathbf{n}',\kappa')$ to site $(\mathbf{n},\kappa)$:

$$\mathbf{X}(\mathbf{n},\kappa)=\{g\,|\,\boldsymbol{\alpha}\}\mathbf{X}(\mathbf{n}',\kappa')=\underline{\mathbf{R}}(g)\mathbf{X}(\mathbf{n}',\kappa')+\boldsymbol{\alpha}\ . \tag{3.15}$$

In order to handle this operation, one introduces the symbol[12,13]

$$\delta_{\kappa'\kappa}\{g\,|\,\boldsymbol{\alpha}\}=1 \text{ or } 0\ . \tag{3.16}$$

The value 1 is taken if the molecule at site $(\mathbf{n}',\kappa')$ is transferred by the operation $\{g\,|\,\boldsymbol{\alpha}\}$ to the site $(\mathbf{n},\kappa)$ and there one finds the same kind of molecule κ. Otherwise the value is 0.

Comparing now Eqs. (3.11a), (3.11b) with (3.12), and (3.13a), (3.13b) with (3.14a), respectively, we obtain the transformation laws for the polarization vectors:

$$R\{g\,|\,\alpha\}E_i(\kappa\,|\,\mathbf{k},j,\mu,a) =\sum_{i',\kappa'}E_{i'}(\kappa'\,|\,\mathbf{k},j,\mu,a)R_{i'i}(g)\delta_{\kappa'\kappa}\{g\,|\,\alpha\} \times\exp[i\mathbf{k}\cdot\mathbf{X}(\mathbf{n}')]\ , \tag{3.17a}$$

and

$$R\{g\,|\,\alpha\}H_l^\tau(\kappa\,|\,\mathbf{k},j,\mu,c) =\sum_{\tau',\kappa'}H_l^{\tau'}(\kappa'\,|\,\mathbf{k},j,\mu,c)C^{\tau'\tau}_{l(\hat{G},S^{(\kappa)})}(g)\delta_{\kappa'\kappa}\{g\,|\,\alpha\} \times\exp[i\mathbf{k}\cdot\mathbf{X}(\mathbf{n}')]\ . \tag{3.17b}$$

Without loss of generality we have here assumed $\mathbf{X}(\mathbf{n})=0$. Note that in Eq. (3.17a), the indices κ and κ' refer to all objects (i.e., individual atoms and molecules) in the units cell, while in Eq. (3.17b) they refer only to the molecules in the unit cell.

Using Eqs. (3.16) and (3.4), one finds

$$\mathbf{k}\cdot\mathbf{X}(n')=\mathbf{k}\cdot[\mathbf{x}(\kappa)-\{g\,|\,\alpha\}\mathbf{x}(\kappa')]\ . \tag{3.18}$$

Combining Eqs. (3.17a), (3.18), and (3.7), one arrives at the physical ray representation of displacements (phonons),

$$[\hat{\Gamma}^E(\mathbf{k};g)]_{\kappa'i',\kappa i}=R_{i'i}(g)\delta_{\kappa'\kappa}\{g\,|\,\alpha\} \times\exp\{i\mathbf{k}\cdot[\mathbf{x}(\kappa)-g\mathbf{x}(\kappa')]\}\ , \tag{3.19a}$$

and at the physical ray representation of orientations,

$$[\hat{\Gamma}_l^H(\mathbf{k};g)]_{\kappa'\tau',\kappa\tau}=C^{\tau'\tau}_{l(\hat{G},S^{(\kappa)})}(g)\delta_{\kappa'\kappa}\{g\,|\,\alpha\} \times\exp\{i\mathbf{k}\cdot[\mathbf{x}(\kappa)-g\mathbf{x}(\kappa')]\}\ . \tag{3.19b}$$

The physical representation of orientations shows that the polarization vectors $h_l^\tau(\kappa\,|\,\mathbf{k},j,\mu,c)$ for different l can be treated as independent quantities, which means that the symmetry operations of the space group $G(\mathbf{k})$ do not mix the polarization vectors $h_l^\tau(\kappa\,|\,\mathbf{k},j,\mu,c)$ and $h_{l'}^\tau(\kappa\,|\,\mathbf{k},j,\mu,c)$ provided $l\neq l'$, although they may belong to the same representation τ or (j,μ). In the form of direct products, Eqs. (3.19a) and (3.19b) read

$$\hat{\Gamma}^{E}(\mathbf{k};g)=\underline{\boldsymbol{R}}(g)\otimes\underline{\boldsymbol{\Delta}}(k,\{g\,|\,\boldsymbol{\alpha}\})\;, \tag{3.20a}$$

$$\hat{\Gamma}_{l}^{H}(\mathbf{k};g)=\underline{\boldsymbol{C}}_{l(G,S)}\otimes\underline{\boldsymbol{\Delta}}(k,\{g\,|\,\boldsymbol{\alpha}\})\;, \tag{3.20b}$$

where

$$[\underline{\boldsymbol{\Delta}}(k,\{g\,|\,\boldsymbol{\alpha}\})]_{\kappa'\kappa}=\delta_{\kappa'\kappa}\{g\,|\,\boldsymbol{\alpha}'\}\exp\{i\mathbf{k}\cdot[\mathbf{x}(\kappa)-g\mathbf{x}(\kappa')]\}\;. \tag{3.21}$$

The lattice displacements form a basis of the ray representation $\hat{\Gamma}^{E}(\mathbf{k};g)$ of the point group of the wave vector.[13,12] Here we have shown also that the orientational fluctuations, described by site-adapted rotator functions, provide a basis of the ray representation $\hat{\Gamma}_{l}^{H}(\mathbf{k};g)$ of the point group of the wave vector.

IV. DECOMPOSITION INTO IRREDUCIBLE REPRESENTATIONS

It is possible to decompose the reducible representations $\hat{\Gamma}^{E}$ and $\hat{\Gamma}^{H}$ by projecting them onto the irreducible ray representations $\hat{D}^{(j)}(\mathbf{k};g)$ of the point group $\hat{G}(\mathbf{k})$. The corresponding projection operators can be obtained by known methods.[21] They are given by

$$\underline{\boldsymbol{P}}_{\mu\mu'}^{E,(j)}(\mathbf{k})=\frac{d_j}{N_g}\sum_{g}[\hat{D}^{(j)}(\mathbf{k};g)]_{\mu'\mu}^{*}\hat{\Gamma}^{E}(\mathbf{k};g)\;, \tag{4.1a}$$

$$\underline{\boldsymbol{P}}_{l,\mu\mu'}^{H,(j)}(\mathbf{k})=\frac{d_j}{N_g}\sum_{g}[\hat{D}^{(j)}(\mathbf{k};g)]_{\mu'\mu}^{*}\hat{\Gamma}_{l}^{H}(\mathbf{k};g)\;, \tag{4.1b}$$

where $g\in\hat{G}(\mathbf{k})$, where d_j is the dimension of the irreducible representation $\hat{D}^{(j)}(\mathbf{k})$ and N_g is the number of the symmetry elements in the point group $\hat{G}(\mathbf{k})$. Hence, the polarization vectors which correspond to the same irreducible representation $\hat{D}^{(j)}(\mathbf{k})$ and the same index a or c, are related by

$$\mathbf{E}(\mathbf{k},j,\mu,a)=\underline{\boldsymbol{P}}_{\mu\mu'}^{E(j)}(\mathbf{k})\mathbf{E}(\mathbf{k},j,\mu',a)\;, \tag{4.2a}$$

$$H_l(\mathbf{k},j,\mu,c)=\underline{\boldsymbol{P}}_{\mu\mu'}^{H(j)}(\mathbf{k})\mathbf{H}_l(\mathbf{k},j,\mu',c)\;. \tag{4.2b}$$

Here the $\mathbf{E}(\mathbf{k},j,\mu,a)$ and $\mathbf{H}_l(\mathbf{k},j,\mu,c)$ are the column vectors having $3(s+m)$ and $\sum_{\kappa=1}^{m}\gamma_\kappa(2l+1)$ components, respectively. The projection operators [Eqs. (4.1a) and (4.1b)] are square matrices of the corresponding dimensions. By applying the projection operators of the same components $\mu\mu$, i.e., $\underline{\boldsymbol{P}}_{\mu\mu}^{E(j)}(\mathbf{k})$ or $\underline{\boldsymbol{P}}_{\mu\mu}^{H(j)}(\mathbf{k})$ to an arbitrary vector, it is possible to find from Eqs. (4.2a) and (4.2b) the general form of the polarization vectors $E_i(\kappa\,|\,\mathbf{k},j,\mu,a)$ and $H_l^{\tau}(\kappa\,|\,\mathbf{k},j,\mu,c)$. The symmetry implies some restrictions on the components of the polarization vectors. The coordinates $Q(\mathbf{k},j,\mu,a)$ and $b_l(\mathbf{k},j,\mu,c)$, for fixed values of a and l,c, do not depend on the components (i,κ) and (τ,κ), respectively; therefore, they transform as the bases for the irreducible ray representation of the point group $\hat{G}(\mathbf{k})$. Thus

$$P(g)Q(\mathbf{k},j,\mu,a)=\sum_{\mu'}Q(\mathbf{k},j,\mu',a)[\hat{D}^{(j)}(\mathbf{k};g)]_{\mu'\mu}\;, \tag{4.3a}$$

$$P(g)b_l(\mathbf{k},j,\mu,c)=\sum_{\mu'}b_l(\mathbf{k},j,\mu',c)[\hat{D}^{(j)}(\mathbf{k};g)]_{\mu'\mu}\;. \tag{4.3b}$$

In general the ray representations of displacements (3.19a) and orientations (3.19b) are reducible, and can be decomposed into irreducible ray representations. The irreducible ray representations $\hat{D}^{(j)}(\mathbf{k};g)$ of all point groups $\hat{G}(\mathbf{k})$ for the wave vectors of the Brillouin zone of all space groups are listed in the tables by Kovalev.[14] The knowledge of the representations of lattice translations and orientational fluctuations (rotations), enables us to study the order of coupling between these degrees of freedom. Generally speaking, a linear coupling exists if the direct product representation contains the identical or unit representation $\hat{\Gamma}_0$:

$$\hat{\Gamma}^{E}(\mathbf{k};g)\otimes\hat{\Gamma}^{H}(\mathbf{k};g)=\hat{\Gamma}_0(\mathbf{k};g)+\cdots\;. \tag{4.4}$$

This statement follows from the fact that the linear coupling term in the Hamiltonian should have the full symmetry of the molecular crystal. In general the representations $\hat{\Gamma}^{E}$ and $\hat{\Gamma}^{H}$ are reducible. In order to investigate whether their product contains the identical representation, one should decompose $\hat{\Gamma}^{E}$ and $\hat{\Gamma}^{H}$ into irreducible ray representations. If both decompositions have at least one irreducible representation in common, Eq. (4.4) holds.

Without further calculations, the preceding considerations allow us to draw a series of useful conclusions. Molecules, for which the orientational behavior is well described by symmetry-adapted functions with $l=1$, can be treated as mass distributed dipoles. The corresponding dipole representation is the vector representation. We observe that the permutation representation $\underline{\boldsymbol{\delta}}\{g\,|\,\boldsymbol{\alpha}\}$ in Eq. (3.19b), which refers to the centers of mass of rotating molecules, is also contained in the permutation representation of phonons $\underline{\boldsymbol{\delta}}\{g\,|\,\boldsymbol{\alpha}\}$ in Eq. (3.19a). From these two statements we conclude that for any wave vector $\mathbf{k}$, the decomposition of the representation of lattice vibrations $\hat{\Gamma}^{E}$ into irreducible representations of the space group contains all irreducible representations of orientations arising from the decomposition of $\hat{\Gamma}^{H}$ with $l=1$. (The reverse statement is not always true.) Therefore the bilinear coupling between translational and rotational degrees of freedom will always be present in crystals where the orientational behavior of molecules is described by representations with $l=1$.

On the other hand, if the orientational behavior of the molecules can be well described by symmetry-adapted rotator functions with $l=2$, then the corresponding representation is that of a quadrupole, a second-rank tensor. The strain of the crystal, being related to the wave vector $\mathbf{k}\rightarrow\mathbf{0}$, is also a second-rank tensor. Consequently, for crystals containing molecules of symmetry D_n and D_{nh}, one expects linear strain-rotation coupling, provided the permutation representation of the centers of mass of rotating molecules in Eq. (3.19b) contains the identical representation. The last requirement is fulfilled for instance in crystals described by symmorphic groups, and where the molecules are located at sites having the symmetry of the point group of the crystals. The strain-rotation coupling occurs at the center of the Brillouin zone, it is equivalent to a coupling of rotations and acoustic phonons in the long-wavelength limit. In each particular point of the Brillouin zone a bilinear translation-rotation coupling can occur due to the coincidence of representations of phonons and site-adapted rotator functions. However, each such case should be worked out separately. As an example of the coupling of an uneven ($l=1$) rotational mode to lattice vibrations,[22] we mention $NaNO_2$. On the other hand, the CN molecular ion in KCN can be approximated by a symmetric dumbbell. The corresponding $l=2$ orientational mode couples to acoustic phonons[23] or equivalently to elastic strain in the long-wavelength limit.[24]

The assignment of the representation to the orientational degrees of freedom can also be used to analyze the symmetry reduction at phase transitions of molecular crystals. As examples we mention KCN,[25] KND_2,[26] NaO_2,[27] and adamantane.[28]

V. ORIENTATION-DEPENDENT INTERACTIONS

Having established in the last two sections the symmetry properties of orientational and translational excitations in molecular crystals with orientational disorder, we will present now a systematic formulation of orientation-dependent interactions.

We consider a molecular crystal built up from objects, i.e., rigid molecules and individual atoms as specified in Sec. III. The center-of-mass positions of the objects are given by Eqs. (3.8a) and (3.8b). In order to condense the notation, we shall contract the two indices $\mathbf{n}$ and κ for the object κ in cell $\mathbf{n}$ by a single index $\mathbf{r}\equiv(\mathbf{n},\kappa)$. For instance, we write $\mathbf{X}(\mathbf{r})$ for $\mathbf{X}(\mathbf{n},\kappa)$. We start from the assumption that the potential between two molecules at center-of-mass positions $\mathbf{r}$ and $\mathbf{r}'$ can be written as a sum of atom-atom potentials:

$$\begin{aligned} V(\mathbf{r},\mathbf{r}') &= \sum_{\nu,\nu'} V(\mathbf{R}(\mathbf{r})-\mathbf{R}(\mathbf{r}');\Omega_\nu(\mathbf{r}),\Omega_{\nu'}(\mathbf{r}')) \\ &\equiv \sum_{\nu,\nu'} V(\mathbf{r},\mathbf{r}';\nu,\nu') \ . \end{aligned} \tag{5.1}$$

Here $\mathbf{R}(\mathbf{r})$ stands for the center-of-mass position (3.8a). The angular coordinates $\Omega_\nu(\mathbf{r})\equiv(\theta_\nu(\mathbf{r}),\varphi_\nu(\mathbf{r}))$ determine the orientational position of the νth atom of the molecule at $\mathbf{r}$ as a function of the molecular orientation with respect to the crystal fixed system of axes. In order to keep the notation tractable, we restrict ourselves to one spherical shell around the molecular center of mass. $\sum_\nu 1=A(\kappa)$ is the total number of atoms on the shell of the molecule κ. If the molecule κ is replaced by an individual atom, $A(\kappa)=1$.

We assume that the center-of-mass displacements of the molecules and of the individual atoms are small and expand expression (5.1) in terms of $\mathbf{u}(\mathbf{r})$:

$$V(\mathbf{r},\mathbf{r}')=\sum_p\sum_{\nu,\nu'}\frac{1}{p!}V^{(p)}_{i_1\cdots i_p}(\mathbf{r},\mathbf{r}';\nu,\nu')[u_{i_1}(\mathbf{r})-u_{i_1}(\mathbf{r}')]\cdots[u_{i_p}(\mathbf{r})-u_{i_p}(\mathbf{r}')] \ , \tag{5.2a}$$

where

$$V^{(p)}_{i_1\cdots i_p}(\mathbf{r},\mathbf{r}';\nu,\nu')=\left.\frac{\partial^p V(\mathbf{r},\mathbf{r}';\nu,\nu')}{\partial X_{i_1}(\mathbf{r})\cdots\partial X_{i_p}(\mathbf{r})}\right|_{u=0} , \tag{5.2b}$$

with $p=0,1,2,\ldots$. In particular $V^{(0)}(\mathbf{r},\mathbf{r}';\nu,\nu')$ is the intermolecular potential of two molecules with center-of-mass positions at the equilibrium lattice sites $\mathbf{X}(\mathbf{r})$ and $\mathbf{X}(\mathbf{r}')$. In Eq. (5.2a), summation is understood over the repeated Cartesian indices $i_1,\ldots,i_p$. The coefficients $V^{(p)}$ still contain the full orientational dependence of the molecules at sites $\mathbf{r}$ and $\mathbf{r}'$. We therefore expand $V^{(p)}$ in terms of site symmetry-adapted functions:

$$V^{(p)}_{i_1\cdots i_p}(\mathbf{r},\mathbf{r}';\nu,\nu')=\sum_{L,L'}v^{(p)}_{i_1\cdots i_p}\begin{bmatrix} L & L' \\ \mathbf{r} & \mathbf{r}' \end{bmatrix}S^{L}_{(S)}(\Omega_\nu(\mathbf{r}))S^{L'}_{(S)}(\Omega_{\nu'}(\mathbf{r})) \ . \tag{5.3a}$$

Here we have condensed the two indices (τ,l) of the symmetry-adapted function S_l^τ into L; therefore, summation over L stands for a sum over τ and l (see Sec. II). In Eq. (5.3a) we have defined

$$v^{(p)}_{i_1\cdots i_p}\begin{bmatrix} L & L' \\ \mathbf{r} & \mathbf{r}' \end{bmatrix}=\int d\Omega_\nu(\mathbf{r})\int d\Omega_{\nu'}(\mathbf{r}')V^{(p)}_{i_1\cdots i_p}(\mathbf{r},\mathbf{r}';\nu,\nu')S^{L}_{(S)}(\Omega_\nu(\mathbf{r}))S^{L'}_{(S)}(\Omega\nu'(\mathbf{r}')) \ . \tag{5.3b}$$

Translational invariance of the rigid lattice implies

$$v^{(p)}_{i_1\cdots i_p}\begin{bmatrix} L & L' \\ \mathbf{n},\kappa & \mathbf{n}',\kappa' \end{bmatrix}=v^{(p)}_{i_1\cdots i_p}\begin{bmatrix} L & L' \\ \mathbf{n}-\mathbf{n}',\kappa & \kappa \end{bmatrix}=v^{(p)}_{i_1\cdots i_p}\begin{bmatrix} L & L' \\ \kappa & \mathbf{n}'-\mathbf{n},\kappa \end{bmatrix} . \tag{5.4}$$

Inserting expression (5.3a) into the right-hand side (rhs) of Eq. (5.2a) and making use of relations (2.11a)–(2.11c), we obtain

$$V(\mathbf{r},\mathbf{r}')=V^{(0)}(\mathbf{r},\mathbf{r}')+V^{(1)}(\mathbf{r},\mathbf{r}')+V^{(2)}(\mathbf{r},\mathbf{r}')+\cdots \ . \tag{5.5a}$$

The zeroth-order term on the right-hand side represents the orientational interaction between two molecules on a rigid lattice[6,29]

$$V^{(0)}(\mathbf{r},\mathbf{r}')=\sum_{L,L'}v^{(0)}\begin{bmatrix} L & L' \\ \mathbf{r} & \mathbf{r}' \end{bmatrix}b^{L}(\mathbf{r})b^{L'}(\mathbf{r}') \ . \tag{5.5b}$$

[Here $b^L(\mathbf{r})$ stands for $b^L(\mathbf{n},\kappa)\equiv b^L(\omega(\mathbf{n},\kappa))$.] The contributions of the deformed lattice to the orientational interaction are given by

$$V^{(p)}(\mathbf{r},\mathbf{r}')=\sum_{L,L'} v^{(p)}_{i_1\cdots i_p}\begin{bmatrix} L & L' \\ \mathbf{r} & \mathbf{r}'\end{bmatrix} b^L(\mathbf{r})b^{L'}(\mathbf{r}')[u_{i_1}(\mathbf{r})-u_{i_1}(\mathbf{r}')]\cdots[u_{i_p}(\mathbf{r})-u_{i_p}(\mathbf{r}')] , \tag{5.5c}$$

for $p=1,2,\ldots$. We see that in expressions (5.5a) and (5.5b) the orientational dependence of the interaction is taken into account by the symmetry-adapted rotator functions b^L.

So far our considerations have been quite general, in particular no restriction has been made with respect to the value of $L\equiv(l,\tau)$. It is useful to consider the case where either one or both of the indices L and L' have value (0,0). In that situation the corresponding molecule is replaced by a spherical distribution of mass. We quote

$$S^{L=0}=S^0_0=1/\sqrt{4\pi},\quad b^{L=0}(\mathbf{n},\kappa)=A(\kappa)/\sqrt{4\pi} , \tag{5.6}$$

where $A(\kappa)$ is the total number of atoms on the molecular shell. If the molecule at κ is replaced by an individual atom, $A(\kappa)=1$. We now consider the various possibilities: (1) $L=(0,0)$, $L'=(0,0)$; (2) $L=(0,0)$, $L'\neq(0,0)$; and (3) $L\neq(0,0)$, $L'\neq(0,0)$.

In the first case the intermolecular interaction (5.5b) reduces to a constant which contributes only to the rigid-lattice ground-state energy. The term $V^{(1)}$ is then also orientation independent, and since it is of first order in the lattice displacements, it can be absorbed in the equilibrium conditions of the crystal. Of interest here is the term $V^{(2)}$ which for $L=(0,0)$, $L'=(0,0)$ reduces to a genuine translation-translation interaction:

$$V^{\mathrm{TT}}(\mathbf{r},\mathbf{r}')=\tfrac{1}{2}v^{(2)}_{ij}(\mathbf{r},\mathbf{r}')[u_i(\mathbf{r})-u_i(\mathbf{r}')][u_j(\mathbf{r})-u_j(\mathbf{r}')] , \tag{5.7a}$$

with

$$v^{(2)}_{ij}(\mathbf{r},\mathbf{r}')\equiv\frac{A(\kappa)A(\kappa')}{4\pi}v^{(2)}_{ij}\begin{bmatrix} 0 & 0 \\ \mathbf{r} & \mathbf{r}'\end{bmatrix} . \tag{5.7b}$$

By summing over all objects in the crystals, we obtain

$$V^{\mathrm{TT}}=\tfrac{1}{2}\sum_{\mathbf{r},\mathbf{r}'}V^{\mathrm{TT}}(\mathbf{r},\mathbf{r}') . \tag{5.7c}$$

Next we consider case (2), $L'=(0,0)$, $L\neq(0,0)$. The first term on the rhs of Eq. (5.5a), or equivalently Eq. (5.5b), now reads

$$V^R(\mathbf{r},\mathbf{r}')=V^{(0)}(\mathbf{r},\mathbf{r}')\,|_{L'=0}=\sum_L\frac{A(\kappa')}{\sqrt{4\pi}}v^{(0)}\begin{bmatrix} L & 0 \\ \mathbf{r} & \mathbf{r}'\end{bmatrix} b^L(\mathbf{r}) . \tag{5.8}$$

Summing over all "spheres" $\mathbf{r}'$, we obtain the total single-particle potential or crystal-field potential acting on molecule $\mathbf{r}=(\mathbf{n},\kappa)$ in a rigid lattice:

$$V^R(\mathbf{r})\equiv\sum_{\mathbf{r}'}V^R(\mathbf{r},\mathbf{r}')=\sum_L v^{(0)}\begin{bmatrix} L \\ \kappa\end{bmatrix} b^L(\mathbf{r}) , \tag{5.9a}$$

with

$$v^{(0)}\begin{bmatrix} L \\ \kappa\end{bmatrix}=\sum_{\mathbf{r}'}\frac{A(\kappa)}{4}v^{(0)}\begin{bmatrix} L & 0 \\ \mathbf{r} & \mathbf{r}'\end{bmatrix}(1-\delta_{L,0}) . \tag{5.9b}$$

In the last expression translational invariance implies that $v^{(0)}\binom{L}{\kappa}$ does not depend on the cell index $\mathbf{n}$ but only on the site index κ. Summing over all molecules in the crystal, we obtain the total single-particle potential

$$V^R\equiv\sum_{\mathbf{r}}V^R(\mathbf{r})=\sum_{\mathbf{n}}\sum_{\kappa}\sum_{L}v^{(0)}\begin{bmatrix} L \\ \kappa\end{bmatrix} b^L(\mathbf{n},\kappa) . \tag{5.10}$$

This expression should have the full symmetry of the space group, and therefore the values of L are restricted. To find the allowed values, one uses expression (3.13a), carries out the sum over $\mathbf{n}$ in Eq. (5.10), and obtains

$$V^R=\sqrt{N}\sum_{\kappa}\sum_{L}v^{(0)}\begin{bmatrix} L \\ \kappa\end{bmatrix} H^L(\kappa\,|\,\mathbf{k}=\mathbf{0},j,\mu,c) , \tag{5.11}$$

where $L\equiv(l,\tau)$. The polarization vector $H^\tau_l(\kappa\,|\,\mathbf{k}=\mathbf{0},j,\mu,c)$ transforms according to the μth component of the jth irreducible representation $\hat{D}^j(\mathbf{k}=\mathbf{0};g)$ of the group $\hat{G}(\mathbf{k}=\mathbf{0})$. To satisfy the symmetry requirement, only those values of j in expression (5.11) remain which correspond to the identical representation. We write $j=j_0$ and since $\mu=1$, drop the index μ. This requirement due to the symmetry of the space group automatically restricts the allowed values of l and insures that the symmetry of the site is realized.

Under the assumption $L'=(0,0)$, $L\neq0$, we obtain for the second term on the rhs of Eq. (5.5a)

$$\begin{aligned} V^{\mathrm{TR}}(\mathbf{r},\mathbf{r}')&\equiv V^{(1)}(\mathbf{r},\mathbf{r}')\,|_{L'=0}\\ &=\sum_L v^{(1)}_{iL}(\mathbf{r},\mathbf{r}')b^L(\mathbf{r})[u_i(\mathbf{r})-u_i(\mathbf{r}')] , \end{aligned}\tag{5.12a}$$

where

$$v^{(1)}_{iL}(\mathbf{r},\mathbf{r}')=\frac{A(\kappa')}{\sqrt{4\pi}}v^{(1)}_i\begin{bmatrix} L & 0 \\ \mathbf{r} & \mathbf{r}'\end{bmatrix}(1-\delta_{L,0}) . \tag{5.12b}$$

Expression (5.12a) represents the bilinear translation-rotation coupling. By summing over all objects in the crystal, the total bilinear coupling reads

$$V^{\mathrm{TR}}=\sum_{\mathbf{r},\mathbf{r}'}\sum_{L,i}v^{(1)}_{iL}(\mathbf{r},\mathbf{r}')b^L(\mathbf{r})[u_i(\mathbf{r})-u_i(\mathbf{r}')] . \tag{5.13}$$

Substituting Eqs. (3.11a) and (3.13a) in Eq. (5.13), one is able to express the translation-rotation coupling in terms of the polarization vectors $E_i(\kappa\,|\,\mathbf{k},j,\mu,c)$ and $H^\tau_l(\kappa\,|\,\mathbf{k},j',\mu',c)$. The coupling does not vanish, provided that both these polarization vectors belong to the same irreducible representation of the crystal space group.

Finally, in case (3), $L\neq(0,0)$, $L'\neq(0,0)$, we rewrite $V^{(0)}(\mathbf{r},\mathbf{r}')$, Eq. (5.5b), as

$$V^{\mathrm{RR}}(\mathbf{r},\mathbf{r}')\equiv V^{(0)}(\mathbf{r},\mathbf{r}')=\sum_{L,L'}v^{(0)}_{LL'}(\mathbf{r},\mathbf{r}')b^L(\mathbf{r})b^{L'}(\mathbf{r}') , \tag{5.14a}$$

with

$$v^{(0)}_{LL'}(\mathbf{r},\mathbf{r}')=v^{(0)}\begin{bmatrix} L & L' \\ \mathbf{r} & \mathbf{r}'\end{bmatrix}(1-\delta_{L,0})(1-\delta_{L',0}) . \tag{5.14b}$$

The total rotation-rotation interaction[6] on a rigid lattice is then obtained by summing over all molecules:

$$V^{\mathrm{RR}}=\tfrac{1}{2}\sum_{\mathbf{r},\mathbf{r}'}\sum_{L,L'} v^{(0)}(\mathbf{r},\mathbf{r}')b^{L}(\mathbf{r})b^{L'}(\mathbf{r}') \ , \tag{5.15}$$

where $\mathbf{r}$ and $\mathbf{r}'$ run over all molecular sites. Here again the relevant polarization vectors $H(\kappa\,|\,k,j,c)$, which occur in the site-adapted rotator functions by virtue of Eq. (3.13a), should belong to the same representation of the space group. Under the same assumption, case (3), $V^{(1)}$ in Eq. (5.5a) gives rise to terms of the structure V^{RRT} and $V^{(2)}$ yields terms V^{RRTT}. They follow as particular results from our general expression (5.5c). Since in this paper we deliberately restrict ourselves to second order in either translational or rotational coordinates, we shall neglect terms such as V^{RRT}, V^{RRTT}, etc. Within that assumption, the total translation and rotation-dependent crystal potential reads

$$V=V^{\mathrm{TT}}+V^{\mathrm{TR}}+V^{\mathrm{RR}}+V^{R} \ , \tag{5.16}$$

where the various terms on the rhs are given respectively by expressions (5.7), (5.13), (5.15), and (5.10). We rewrite the potentials (5.7), (5.13), (5.15), and (5.10) in terms of normal coordinates by making use of expressions (3.9) and (3.10). The results read

$$V^{\mathrm{TT}}=\tfrac{1}{2}\sum_{\mathbf{k}}\sum_{j,\mu}\sum_{a,a'} M(\mathbf{k},j,a,a')Q(-\mathbf{k},j,\mu,a)Q(\mathbf{k},j,\mu,a') \ , \tag{5.17a}$$

$$V^{\mathrm{TR}}=\sum_{k}\sum_{l}\sum_{j}\sum_{a,c} v_l^{(1)}(\mathbf{k},j,c,a)b_l(-\mathbf{k},j,\mu,c)Q(\mathbf{k},j,\mu,a) \ , \tag{5.17b}$$

$$V^{\mathrm{RR}}=\tfrac{1}{2}\sum_{\mathbf{k}}\sum_{l,l'}\sum_{j,\mu}\sum_{c,c'} J_{ll'}(\mathbf{k},j,c,c')b_l(-\mathbf{k},j,\mu,c) \times b_{l'}(\mathbf{k},j,\mu,c') \ , \tag{5.17c}$$

$$V^{R}=\sum_{l_0}\sum_{j_0} v_{l_0}^{(0)}(j_0,c)b_{l_0}(\mathbf{k}=\mathbf{0},j_0,c) \ . \tag{5.17d}$$

Here we have defined the translational block matrix $M(\mathbf{k},j,a,a')$ by

$$\sum_{\kappa,\kappa'}\sum_{i,i'} e_i(\kappa\,|\,-\mathbf{k},j,\mu,a)M_{ii'}^{\kappa\kappa'}(\mathbf{k})e_{i'}(\kappa'\,|\,\mathbf{k},j',\mu',a') =M(\mathbf{k},j,a,a')\delta_{jj'}\delta_{\mu\mu'} \ , \tag{5.18a}$$

with the dynamical matrix given by

$$M_{ii'}^{\kappa\kappa'}(\mathbf{k})=\frac{1}{(M_\kappa M_{\kappa'})^{1/2}}\sum_{\mathbf{n}}\left[\sum_{\nu} v_{ii'}^{(2)}(\mathbf{0},\kappa;\mathbf{n},\nu)\delta_{\kappa\kappa'}-v_{ii'}^{(2)}(\mathbf{0},\kappa;\mathbf{n},\kappa')\cos[\mathbf{X}(\mathbf{n})+\mathbf{x}(\kappa)-\mathbf{x}(\kappa')]\right] . \tag{5.18b}$$

The matrix $\underline{M}$ is Hermitian. The coupling matrix $\underline{v}_l$ in Eq. (5.17b) is given by

$$\sum_{\kappa,\kappa'}\sum_{\tau,i} h_l^{\tau}(\kappa\,|\,-\mathbf{k},j,\mu,c)v_{\tau li}^{\kappa\kappa'}(\mathbf{k})e_i(\kappa'\,|\,\mathbf{k},j',\mu',a)=v_l^{(1)}(\mathbf{k},j,c,a)\delta_{jj'}\delta_{\mu\mu'} \ , \tag{5.19a}$$

with

$$v_{Li}^{\kappa\kappa'}(\mathbf{k})=\frac{1}{(M_{\kappa'})^{1/2}}\sum_{\mathbf{n}}\left[\sum_{\nu} v_{Li}^{(1)}(\mathbf{0},\kappa;\mathbf{n},\nu)\delta_{\kappa\kappa'}-v_{Li}^{(1)}(\mathbf{0},\kappa;\mathbf{n},\kappa')\exp\{i\mathbf{k}\cdot[\mathbf{X}(\mathbf{n})+\mathbf{x}(\kappa')-\mathbf{x}(\kappa)]\}\right] , \tag{5.19b}$$

where $L\equiv(l,\tau)$. The orientational block matrix $J_{ll'}(\mathbf{k},j,c,c')$ in Eq. (5.17c) is obtained as

$$\sum_{\kappa,\kappa'}\sum_{\tau,\tau'} h_l^{\tau}(\kappa\,|\,-\mathbf{k},j,\mu,c)J_{l\tau l'\tau'}^{\kappa\kappa'}(\mathbf{k})h_{l'}^{\tau'}(\kappa'\,|\,\mathbf{k},j',\mu',c')=J_{ll'}(\mathbf{k},j,c,c')\delta_{jj'}\delta_{\mu\mu'} \ , \tag{5.20a}$$

with the orientational coupling matrix given by

$$J_{LL'}^{\kappa\kappa'}(\mathbf{k})=\sum_{\mathbf{n}} v_{LL'}^{(0)}(\mathbf{0},\kappa;\mathbf{n},\kappa') \times\exp\{-i\mathbf{k}\cdot[\mathbf{X}(\mathbf{n})+\mathbf{x}(\kappa')-\mathbf{x}(\kappa)]\} \ , \tag{5.20b}$$

where $L\equiv(l,\tau)$ and $L'\equiv(l',\tau')$. The single-particle coefficient $v_{l_0}^{(0)}$ in Eq. (5.17d) is obtained from

$$\sum_{\kappa} h_{l_0}^{\tau_0}(\kappa\,|\,\mathbf{k}=\mathbf{0},j_0,1,c)\sqrt{N}v^{(0)}\begin{bmatrix} l_0\ \tau_0 \\ \kappa \end{bmatrix}=v_{l_0}^{(0)}(j_0,c) \ , \tag{5.21}$$

with $v^{(0)}\binom{L}{\kappa}$, $L\equiv(l,\tau)$, given by Eq. (5.9b).

For practical reasons it is sometimes useful to introduce intermediate coordinates defined by

$$u_i^{\kappa}(\mathbf{k})=\sum_{j,\mu,a} Q(\mathbf{k},j,\mu,a)e_i(\kappa\,|\,\mathbf{k},j,\mu,a) \ , \tag{5.22a}$$

$$b_l^{\tau,\kappa}(\mathbf{k})=\sum_{j,\mu,c} b_l(\mathbf{k},j,\mu,c)h_l^{\tau}(\kappa\,|\,\mathbf{k},j,\mu,c) \ . \tag{5.22b}$$

Recalling that the polarization vectors $\mathbf{e}$ and $\mathbf{h}$ form orthonormal and complete sets, we rewrite the interaction potentials (5.17a)—(5.17d) in the form:

$$V^{\mathrm{TT}}=\tfrac{1}{2}\sum_{\mathbf{k}}\sum_{\kappa,\kappa'}\sum_{i,i'} M_{ii'}^{\kappa\kappa'}(\mathbf{k})u_i(\mathbf{k})u_{i'}^{\kappa'}(-\mathbf{k}) \ , \tag{5.23a}$$

$$V^{\mathrm{TR}}=\sum_{\mathbf{k}}\sum_{\kappa,\kappa'}\sum_{L} v_{Li}^{\kappa\kappa'}(\mathbf{k})b_L^{\kappa}(-\mathbf{k})u_i^{\kappa'}(\mathbf{k}) \ , \tag{5.23b}$$

$$V^{\mathrm{RR}}=\tfrac{1}{2}\sum_{\mathbf{k}}\sum_{\kappa,\kappa'}\sum_{L,L'} J_{LL'}^{\kappa\kappa'}(\mathbf{k})b_L^{\kappa}(-\mathbf{k})b_{L'}^{\kappa'}(\mathbf{k}) \ , \tag{5.23c}$$

$$V^{R}=\sum_{L_0}\sum_{\kappa}\sqrt{N}v^{(0)}\begin{bmatrix} L_0 \\ \kappa \end{bmatrix}b_{L_0}^{\kappa}(\mathbf{k}=\mathbf{0}) \ . \tag{5.23d}$$

In the next section we shall calculate the free energy, starting from the potentials (5.23a)–(5.23d).

VI. FREE ENERGY

The main thermodynamic quantity which characterizes the state of a system is the free energy. The Landau theory of phase transitions is based on an expansion of the free energy in terms of powers of the order-parameter variables.[30] Since we consider crystals with translational and rotational degrees of freedom, we want to construct an expression of the instantaneous nonequilibrium free energy in terms of nonequilibrium expectation values of translational and rotational coordinates. We shall apply a method which has been used previously for pseudospin systems coupled to phonons.[31] Subsequently it has been applied to derive the free energy for a system of linear molecules on a cubic lattice by retaining terms up to second order in the order-parameter variables.[32] Here we want to extend that work in several respects. Firstly, we start from the general interaction potential (5.16) which has been considered in the preceding section. The derivation will be general as far as molecular and lattice symmetry is concerned. Secondly, we include third- and fourth-order contributions. Thirdly, the self-interaction of the molecules with the surrounding lattice deformations will be derived in a systematic way.

Since we are interested in static phenomena near structural phase transitions, we can omit the kinetic energy of translational and rotational motion. The Helmholtz free energy is given by

$$F=\mathrm{Tr}(\rho V+T\rho\ln\rho)\ . \tag{6.1}$$

Here Tr denotes the trace, ρ is the density matrix, and V is the potential energy (5.16). $T=\beta^{-1}$ stands for the temperature, units are taken such that $k_B=1$. The density matrix satisfies the condition

$$\mathrm{Tr}\rho=1\ . \tag{6.2}$$

At present we want to formulate the free energy in terms of instantaneous expectation values of the order-parameter variables which belong to the active irreducible representation of the space group of the crystal. These expectation values are given by

$$u_I^e(\mathbf{k})=\mathrm{Tr}[\rho u_I(\mathbf{k})]\ , \tag{6.3a}$$

$$b_\Lambda^e(\mathbf{k})=\mathrm{Tr}[\rho b_\Lambda(\mathbf{k})]\ . \tag{6.3b}$$

Here $u_I(k)$ and $b_\Lambda(k)$ stand for the "intermediate" coordinates, (5.22a) and (5.22b), respectively. Here, and in most of the subsequent considerations, we use the abbreviations $I\equiv(\kappa,i)$, $\Lambda\equiv(l,\tau,\kappa)=(L,\kappa)$.

We want to find an expression of the free energy as a functional of the expectation values [Eqs. (6.3a) and (6.3b)]:

$$F=F\{u_I^e,b_\Lambda^e\}\ . \tag{6.4}$$

We use the method of Lagrange multipliers to minimize Eq. (6.1) under the conditions (6.2)–(6.3b). The density matrix is found to be

$$\rho=(1/Z)\mathrm{Tr}\exp(-\beta\mathscr{V})\ , \tag{6.5a}$$

with

$$Z=\mathrm{Tr}\exp(-\beta\mathscr{V})\ , \tag{6.5b}$$

and where

$$\mathscr{V}=V-\sum_{\mathbf{k}}[\boldsymbol{\lambda}^\dagger(\mathbf{k})\mathbf{u}(\mathbf{k})+\boldsymbol{\gamma}^\dagger(\mathbf{k})\mathbf{b}(k)]\ . \tag{6.6}$$

Here we have used a vector notation to account for the values of the components I and Λ of $u_I(\mathbf{k})$ and $b_\Lambda(\mathbf{k})$, respectively. The Lagrange multipliers $\boldsymbol{\lambda}(\mathbf{k})$ and $\gamma(k)$ play the role of external fields. They are determined by the conditions (6.3a) and (6.3b).

It is convenient to define an auxiliary thermodynamic potential[31]

$$F^e=-T\ln Z\ . \tag{6.7a}$$

Taking into account the explicit form of the density matrix ρ, one notices that the free energy F^e is a functional of the "external" fields:

$$F^e=F^e\{\boldsymbol{\lambda}(\mathbf{k}),\gamma(\mathbf{k})\}\ . \tag{6.7b}$$

The corresponding derivatives are equal to the expectation values of the order parameters:

$$\frac{\partial F^e}{\partial\boldsymbol{\lambda}^\dagger(\mathbf{k})}=-\mathbf{u}^e(\mathbf{k}),\quad \frac{\partial F^e}{\partial\gamma^\dagger(\mathbf{k})}=-\mathbf{b}^e(\mathbf{k})\ . \tag{6.8}$$

The free energy F is related to the thermodynamic potential F^e by

$$\begin{aligned}F&=F^e+\mathrm{Tr}[\rho(V-\mathscr{V})]\\&=F^e+\sum_{\mathbf{k}}[\boldsymbol{\lambda}^\dagger(\mathbf{k})\mathbf{u}^e(\mathbf{k})+\boldsymbol{\gamma}^\dagger(\mathbf{k})\mathbf{b}^e(\mathbf{k})]\ .\end{aligned} \tag{6.9}$$

We want to obtain an expression for F^e which can be evaluated by molecular-field theory. Therefore we first separate phonons and orientational variables by means of a canonical transformation. Defining

$$\hat{u}(\mathbf{k})=\mathbf{u}(\mathbf{k})+\underline{\boldsymbol{M}}^{-1}[\underline{v}(\mathbf{k})\mathbf{b}(\mathbf{k})-\boldsymbol{\lambda}(\mathbf{k})]\ , \tag{6.10}$$

we rewrite the potential (6.6) as

$$\mathscr{V}=V_{\mathrm{ph}}+V^{\mathrm{RR}}(\mathbf{B})-\tfrac{1}{2}\sum_{\mathbf{k}}\boldsymbol{\lambda}^\dagger(\mathbf{k})\underline{\boldsymbol{M}}^{-1}\boldsymbol{\lambda}(\mathbf{k})+V^R\ . \tag{6.11}$$

Here V_{ph} stands for the phonon potential

$$V_{\mathrm{ph}}=\tfrac{1}{2}\sum_{\mathbf{k}}\hat{\mathbf{u}}^\dagger(\mathbf{k})\underline{\boldsymbol{M}}\hat{u}(\mathbf{k})\ , \tag{6.12}$$

and $V^{\mathrm{RR}}(\mathbf{B})$ represents the effective orientational interaction:

$$V^{\mathrm{RR}}(\mathbf{B})=\tfrac{1}{2}\sum_{\mathbf{k}}[\mathbf{b}^\dagger(\mathbf{k})\underline{\boldsymbol{K}}(\mathbf{k})\mathbf{b}(\mathbf{k})+\mathbf{B}^\dagger(\mathbf{k})\mathbf{b}(\mathbf{k})]\ . \tag{6.13}$$

The auxiliary field $\mathbf{B}$ is defined by

$$\mathbf{B}(\mathbf{k})=\gamma(\mathbf{k})-\boldsymbol{\lambda}^\dagger(k)\underline{\boldsymbol{M}}^{-1}\underline{v}(\mathbf{k})\ . \tag{6.14}$$

The interaction

$$\underline{\boldsymbol{K}}(\mathbf{k})=\underline{\boldsymbol{J}}(\mathbf{k})-\underline{\boldsymbol{C}}(\mathbf{k}) \tag{6.15}$$

is a sum of the direct interaction J, Eq. (5.20b), and a lattice mediated interaction:

$$\underline{C}(\mathbf{k})=\underline{v}(\mathbf{k})\underline{M}^{-1}v^{\dagger}(\mathbf{k}) \ . \qquad (6.16)$$

Finally V^R in Eq. (6.11) stands for the single-particle potential (5.23d). It is necessary to separate in Eq. (6.13) the interaction between different molecules from the self-energy of each molecule in the vibrating crystal. The last one corresponds to the Onsager reaction field,[33] the importance of which has also been realized in Jahn-Teller systems.[34] We subtract from the first term on the rhs of Eq. (6.13) a contribution

$$W^0=-\tfrac{1}{2}\sum_{\mathbf{k}}\mathbf{b}^{\dagger}(k)\underline{C}^0\mathbf{b}(\mathbf{k}) \ , \qquad (6.17\text{a})$$

with

$$\underline{C}^0=\frac{1}{N}\sum_{\mathbf{k}}\underline{C}(\mathbf{k}) \ , \qquad (6.17\text{b})$$

and add it to the single-particle potential. Hence the effective single-particle potential reads[35]

$$W^R=V^R+W^0 \ . \qquad (6.18)$$

In real space W^0 is given by

$$W^0=-\sum_{\mathbf{n}}\left[\sum_{L,\kappa}C^0_{L\kappa,L\kappa}[b^L(\mathbf{n},\kappa)]^2\right] \ . \qquad (6.19)$$

Here each term of the sum transforms as a unit representation of the corresponding site point group. It represents the single-particle potential produced by the deformation of the lattice. The deformation itself, in turn, is induced by a specific orientation of the molecule under consideration. By taking into account Eqs. (6.18), (6.19), and (6.13), the potential (6.11) reads

$$\mathscr{V}=V_{\text{ph}}+W^{\text{RR}}(\mathbf{B})-\tfrac{1}{2}\sum_{\mathbf{k}}\lambda^{\dagger}(\mathbf{k})\underline{M}^{-1}(\mathbf{k})\lambda(\mathbf{k})+W^R \ , \qquad (6.20)$$

with

$$W^{\text{RR}}(\mathbf{B})=\tfrac{1}{2}\sum_{\mathbf{k}}[\mathbf{b}^{\dagger}(\mathbf{k})\underline{L}(\mathbf{k})\mathbf{b}(\mathbf{k})+\mathbf{B}^{\dagger}(\mathbf{k})\mathbf{b}(\mathbf{k})] \ , \qquad (6.21\text{a})$$

where the genuine interaction part is given by

$$\underline{L}(\mathbf{k})=\underline{K}(\mathbf{k})+\underline{C}^0 \ . \qquad (6.21\text{b})$$

We now return to the auxiliary thermodynamic potential (6.7a), and by using Eq. (6.20), we obtain

$$F^e=F_{\text{ph}}+F_R(\mathbf{B})-\tfrac{1}{2}\sum_{\mathbf{k}}\lambda^{\dagger}(\mathbf{k})\underline{M}^{-1}(\mathbf{k})\lambda(\mathbf{k}) \ , \qquad (6.22\text{a})$$

with

$$F_{\text{ph}}=-\beta^{-1}\ln \operatorname{Tr}\exp(-\beta V_{\text{ph}}) \ , \qquad (6.22\text{b})$$

and

$$F_R(\mathbf{B})=-\beta^{-1}\ln \operatorname{Tr}\exp[-\beta W^{\text{RR}}(\mathbf{B})-\beta W^R] \ . \qquad (6.22\text{c})$$

Here we have taken advantage of the fact that the third term in Eq. (6.20) is a *c*-number. The separation of terms in Eq. (6.22) means that the subsystem of lattice distortions $\{\lambda(\mathbf{k})\}$ contributes exclusively to the internal energy of the crystal and not to the entropy. That property is well known for displacive phase transitions. In molecular crystals the orientational disorder, accounted for by the second term on the rhs of Eq. (6.22a), gives the essential contribution to the entropy. Finally F_{ph}, Eq. (6.22b), represents the fast fluctuating lattice contributions which arise from the harmonic phonon potential (6.12). This thermal phonon part can be evaluated by conventional lattice dynamics; it is of no importance for the occurence of structural phase transitions.

The remaining problem consists in the evaluation of the orientational free energy $F_R(\mathbf{B})$ and in the determination of the Lagrange multipliers. This will be done within molecular-field approximation.[32] We separate the site-adapted rotator function into two parts

$$\mathbf{b}(\mathbf{k})=\mathbf{b}^e(\mathbf{k})-\Delta(\mathbf{k}) \ , \qquad (6.23)$$

where $\mathbf{b}^e(\mathbf{k})$ is the expectation value (6.3b), and where $\Delta(\mathbf{k})$ accounts for fluctuations. The average value (6.3b) of $\mathbf{b}(\mathbf{k})$ with the full density matrix (6.5a) is equal to $\mathbf{b}^e(\mathbf{k})$. Hence

$$\langle \Delta(\mathbf{k})\rangle=\operatorname{Tr}[\rho\Delta(\mathbf{k})]=\mathbf{0} \ . \qquad (6.24)$$

However, if one calculates the average of $\mathbf{b}(\mathbf{k})$ in the undistorted local-field potential (6.18) with the density matrix

$$\rho_R=[\exp(-\beta W^R)]/\operatorname{Tr}\exp(-\beta W^R) \ , \qquad (6.25\text{a})$$

one finds

$$\langle \mathbf{b}(\mathbf{k})\rangle_W=\operatorname{Tr}[\rho_R\mathbf{b}(\mathbf{k})]=\mathbf{0} \ , \qquad (6.25\text{b})$$

provided the irreducible representation L of the relevant components of the vector $\mathbf{b}(\mathbf{k})$ does not belong to the fully symmetric representation of the site point group, i.e., $L\neq L_0$. We recall that the single-particle potential has the full site symmetry L_0. Consequently, the average fluctuation in the single-particle potential has to be equal to the expectation value $\mathbf{b}^e(\mathbf{k})$:

$$\langle \Delta(\mathbf{k})\rangle_W=\operatorname{Tr}[\rho_R\Delta(\mathbf{k})]=\mathbf{b}^e(\mathbf{k}) \ . \qquad (6.26)$$

Introducing the rhs of Eq. (6.23) into the rotation-rotation free energy $F_R(\mathbf{B})$ and neglecting second-order terms in $\Delta(\mathbf{k})$, we find within the mean-field approximation:

$$F_R^{\text{MF}}(\mathbf{B})=\sum_{\mathbf{k}}\{\tfrac{1}{2}[\mathbf{b}^e(\mathbf{k})]^{\dagger}\underline{L}(\mathbf{k})\mathbf{b}^e(\mathbf{k})-\mathbf{B}^{\dagger}(\mathbf{k})\mathbf{b}^e(\mathbf{k})\} +F_R^W+F_R^{\Delta} \ . \qquad (6.27\text{a})$$

Here F_R^W is the single-particle free energy

$$F_R^W=-\beta^{-1}\ln \operatorname{Tr}[\exp(-bW^R)] \ , \qquad (6.27\text{b})$$

and F_R^{Δ} is given by

$$F_R^{\Delta}=-\beta^{-1}\ln\left\langle \exp\left[-\beta\sum_{\mathbf{k}}\mathbf{a}^{\dagger}(k)\Delta(\mathbf{k})\right]\right\rangle_W \ , \qquad (6.27\text{c})$$

with

$$\mathbf{a}(\mathbf{k})=-[\mathbf{b}^e(\mathbf{k})]^{\dagger}\underline{L}(\mathbf{k})+\mathbf{B}^{\dagger}(\mathbf{k}) \ . \qquad (6.28)$$

In Eq. (6.27c) the large angular brackets $\langle \cdots \rangle_W$ denote a thermal average, calculated with the density matrix ρ_R. The trace there stands for a multiple integration over the orientational coordinates of the single-particle potential.

In order to evaluate the rhs of Eq. (6.27c), we make use of a cumulant expansion.[36] Retaining contributions up to fourth order in b^e and taking into account that $\mathbf{a}(\mathbf{k})$ is of first order in b^e, we obtain

$$
\begin{aligned}
F_R^{\Delta} = {} & \sum_{\mathbf{k}} a_\Lambda^*(\mathbf{k}) b_\Lambda^e(k) - \frac{\beta}{2!} \sum_{\mathbf{k}_1,\mathbf{k}_2} a_{\Lambda_1}^*(\mathbf{k}_1) a_{\Lambda_2}^*(\mathbf{k}_2) \langle b_{\Lambda_1}(\mathbf{k}_1) b_{\Lambda_2}(\mathbf{k}_2)\rangle_W \\
& - \frac{\beta^2}{3!} \sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3} a_{\Lambda_1}^*(\mathbf{k}_1) a_{\Lambda_2}^*(\mathbf{k}_2) a_{\Lambda_3}^*(\mathbf{k}_3) \langle b_{\Lambda_1}(\mathbf{k}_1) b_{\Lambda_2}(\mathbf{k}_2) b_{\Lambda_3}(\mathbf{k}_3)\rangle_W \\
& - \frac{\beta^3}{4!} \sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} a_{\Lambda_1}^*(\mathbf{k}_1) a_{\Lambda_2}^*(\mathbf{k}_2) a_{\Lambda_3}^*(\mathbf{k}_3) a_{\Lambda_4}^*(\mathbf{k}_4) [\, \langle b_{\Lambda_1}(\mathbf{k}_1) b_{\Lambda_2}(\mathbf{k}_2) b_{\Lambda_3}(\mathbf{k}_3) b_{\Lambda_4}(\mathbf{k}_4)\rangle_W \\
& \qquad - 3\langle b_{\Lambda_1}(\mathbf{k}_1) b_{\Lambda_2}(\mathbf{k}_2)\rangle \langle b_{\Lambda_3}(\mathbf{k}_3) b_{\Lambda_4}(k_4)\rangle_W] \,.
\end{aligned}
\tag{6.29}
$$

In obtaining this result, we have taken into account the fact that $a_\Lambda(\mathbf{k})$ are c-numbers. The summation convention is used for all repeated indices $\Lambda, \Lambda_1, \ldots, \Lambda_4$. We recall that Λ refers to the triplet of indices (l,τ,κ). In order to simplify the thermal averages in Eq. (6.29), one uses the translational invariance of the lattice and the single-particle nature of the potential W^R. Only products of $b_\Lambda(\mathbf{n}) = b_l^{\tau\kappa}(\mathbf{n})$, which belong to the same site, contribute to the thermal averages.

Finally, the free energy F_R^Δ, Eq. (6.29), is rewritten as

$$
\begin{aligned}
F_R^{\Delta} = {} & \sum_{\mathbf{k}} \sum_{\Lambda} a_\Lambda^*(\mathbf{k}) b_\Lambda^e(\mathbf{k}) - \frac{\beta}{2!} \sum_{\mathbf{k}} \sum_{\Lambda} a_\Lambda^*(\mathbf{k}) a_\Lambda(\mathbf{k}) \langle (b_\Lambda)^2\rangle_W \\
& - \frac{\beta^2}{3!\sqrt{N}} \sum_{\mathbf{k},\mathbf{p}} \sum_{\Lambda_1,\Lambda_2,\Lambda_3} a_{\Lambda_1}^*(\mathbf{k}) a_{\Lambda_2}^*(\mathbf{p}) a_{\Lambda_3}(\mathbf{k}+\mathbf{p}) \langle b_{\Lambda_1} b_{\Lambda_2} b_{\Lambda_3}\rangle_W \delta_{\kappa_1\kappa_2} \delta_{\kappa_2\kappa_3} \\
& - \frac{\beta^3}{4!N} \sum_{\mathbf{k},\mathbf{p},\mathbf{q}} \sum_{\Lambda} a_\Lambda^*(\mathbf{k}) a_\Lambda^*(\mathbf{p}) a_\Lambda^*(\mathbf{q}) a_\Lambda(\mathbf{p}+\mathbf{k}+\mathbf{q}) [\langle (b_\Lambda)^4\rangle_W - 3\langle (b_\Lambda)^2\rangle_W^2] \,.
\end{aligned}
\tag{6.30}
$$

In order to determine the external fields $\boldsymbol{\lambda}$ and $\boldsymbol{\gamma}$ which occur in Eq. (6.14), we use the conditions (6.8) with F^e and $F_R(\mathbf{B})$ given by (6.22a) and (6.27a), respectively. One finds

$$
\boldsymbol{\lambda}(\mathbf{k}) = \underline{\boldsymbol{M}} \mathbf{u}^e(\mathbf{k}) + \underline{\boldsymbol{v}}^{\dagger}(\mathbf{k}) \mathbf{b}^e(\mathbf{k}) \,, \tag{6.31}
$$

and

$$
\frac{\partial F_R^\Delta}{\partial \boldsymbol{\gamma}^\dagger(\mathbf{k})} = \frac{\partial F}{\partial \mathbf{a}^\dagger(k)} = \mathbf{0} \,. \tag{6.32}
$$

Combining the two last equations, we obtain

$$
\begin{aligned}
a_\Lambda(\mathbf{k}) = \frac{\beta^{-1}}{\langle (b_\Lambda)^2\rangle_W} \Bigg[& b_\Lambda^e(\mathbf{k}) - \frac{\beta^2}{2\sqrt{N}} \sum_{\mathbf{p}} \sum_{\Lambda_2} \sum_{\Lambda_3} a_{\Lambda_2}^*(\mathbf{p}) a_{\Lambda_3}^*(-\mathbf{k}-\mathbf{p}) \langle b_\Lambda b_{\Lambda_2} b_{\Lambda_3}\rangle_W \delta_{\kappa_1\kappa_2} \delta_{\kappa_1\kappa_3} \\
& - \frac{\beta^3}{3!} \sum_{\mathbf{pq}} a_\Lambda^*(\mathbf{p}) a_\Lambda^*(\mathbf{q}) a_\Lambda(\mathbf{k}+\mathbf{p}+\mathbf{q}) [\langle (b_\Lambda)^4\rangle_W - 3\langle (b_\Lambda)^2\rangle^2] \Bigg] \,.
\end{aligned}
\tag{6.33}
$$

Making use of Eq. (6.31), solving Eq. (6.33) by iteration, and substituting into Eq. (6.29), we obtain by means of Eqs. (6.27a), (6.22), (6.28), (6.14), and (6.9):

$$
\begin{aligned}
F = F_{\mathrm{ph}} + F_R^W + \tfrac{1}{2} \sum_{\mathbf{k}} \Bigg[& [\mathbf{u}^e(\mathbf{k})]^\dagger \underline{\boldsymbol{M}}(\mathbf{k}) \mathbf{u}^e(\mathbf{k}) + [\mathbf{b}^e(\mathbf{k})]^\dagger \underline{\boldsymbol{v}}(k) \mathbf{u}^e(k) + [\mathbf{u}^e(\mathbf{k})]^\dagger \underline{\boldsymbol{v}}^\dagger(\mathbf{k}) \mathbf{b}^e(\mathbf{k}) \\
& + \sum_{\Lambda_1,\Lambda_2} [J_{\Lambda_1\Lambda_2}(\mathbf{k}) + (\beta^{-1} x_{\Lambda_1}^{(2)} + C_{\Lambda_1\Lambda_2}^0) \delta_{\Lambda_1\Lambda_2}] [b_{\Lambda_1}^e(\mathbf{k})]^* b_{\Lambda_2}^e(\mathbf{k}) \Bigg] \\
& - \frac{\beta^{-1}}{3!\sqrt{N}} \sum_{\mathbf{k},\mathbf{p}} \sum_{\Lambda_1,\Lambda_2,\Lambda_3} x_{\Lambda_1\Lambda_2\Lambda_3}^{(3)} [b_{\Lambda_1}^e(\mathbf{k})]^* [b_{\Lambda_2}^e(\mathbf{p})]^* b_{\Lambda_3}^e(\mathbf{k}+\mathbf{p}) \\
& + \frac{\beta^{-1}}{4!N} \sum_{\mathbf{k},\mathbf{p},\mathbf{q}} \sum_{\Lambda} x_\Lambda^{(4)} [b_\Lambda^e(\mathbf{k})]^* [b_\Lambda^{(e)}(\mathbf{p})]^* [b_\Lambda^e(\mathbf{q})]^* b_\Lambda^e(\mathbf{k}+\mathbf{p}+\mathbf{q}) \,.
\end{aligned}
\tag{6.34}
$$

Here we have defined

$$x_{\Lambda}^{(2)}=(\langle b_{\Lambda}^{2}\rangle_W)^{-1}\,, \tag{6.35a}$$

$$x_{\Lambda_1\Lambda_2\Lambda_3}^{(3)}=\frac{\langle b_{\Lambda_1}b_{\Lambda_2}b_{\Lambda_3}\rangle_W\delta_{\kappa_1\kappa_2}\delta_{\kappa_1\kappa_3}}{\langle(b_{\Lambda_1})^2\rangle_W\langle(b_{\Lambda_2})^2\rangle_W\langle(b_{\Lambda_3})^2\rangle_W}\,, \tag{6.35b}$$

$$x_{\Lambda}^{(4)}=\frac{3\langle b_{\Lambda}^{2}\rangle_W^2-\langle b_{\Lambda}^{4}\rangle_W}{\langle b_{\Lambda}^{2}\rangle_W^4}\,. \tag{6.35c}$$

Obviously the coefficients $x_{\Lambda}^{(n)}\ldots$ depend on temperature and on the strength of the single-particle potential. In the case of a very strong single-particle potential which leads to two sterically different orientations, the orientational variable $\mathbf{b}_{\Lambda}$ is replaced by an Ising spin variable with values ±1. Then the single-particle expectation values reduce to $x^{(2)}=1$, $x^{(3)}=0$, $x^{(4)}=2$. Our formula (6.34) for the free energy then reduces to a simpler expression which has been derived previously[37] for the description of $NaNO_2$.

We remark that the occurence of the third-order terms in the free-energy expansion (6.34) can lead to a phase transition of first order. Actually the transition takes place at the intersection of the free energies of the disordered, $b_{\Lambda}^{e}(\mathbf{k})=0$, and ordered, $b_{\Lambda}^{e}(k)\neq 0$, phases. That intersection determines a transition temperature T_0.

Due to the bilinear interaction between translations and rotations, a given instantaneous configuration $\{b_{\Lambda}^{e}(\mathbf{k})\}$ of orientations entails a configuration $\{u_J^{e}(\mathbf{k})\}$ of lattice distortions. The latter are obtained by minimizing the quadratic term of the free energy (6.34), for fixed constraints $\{b_{\Lambda}^{e}(\mathbf{k})\}$, with respect to $u_J^{e}(\mathbf{k})$. One obtains

$$\mathbf{u}^e(\mathbf{k})=-\underline{M}^{-1}(\mathbf{k})\underline{v}(\mathbf{k})\mathbf{b}^e(\mathbf{k})\,. \tag{6.36}$$

We use this result to eliminate $\mathbf{u}^e(k)$ in the free energy (6.34) and obtain

$$F=F_{\text{ph}}+F_R^W+\tfrac{1}{2}\sum_{\mathbf{k}}\sum_{\Lambda_1,\Lambda}b_{\Lambda_1}^{e*}(\mathbf{k})[Tx_{\Lambda_1}^{(2)}\delta_{\Lambda_1\Lambda_2}+L_{\Lambda_1\Lambda_2}(\mathbf{k})]\times b_{\Lambda_2}^{e}(\mathbf{k})+O(\mathbf{b}^e(\mathbf{k}))\,. \tag{6.37}$$

Here $T=\beta^{-1}$ and $\underline{L}$ is the interaction matrix, defined by Eq. (6.21b). The last term on the rhs in Eq. (6.37) refers to third- and higher-order terms. According to the Landau theory of second-order phase transitions, the high-temperature phase becomes unstable at a temperature T_c and wave vector $\mathbf{k}_c$ where the rotational susceptibility matrix with elements

$$\chi_{\Lambda_1\Lambda_2}(\mathbf{k})=\left[\frac{\delta^2F}{\delta[b^e(\mathbf{k})]^*\delta b^e(\mathbf{k})}\right]_{\Lambda_1\Lambda_2}^{-1} \tag{6.38}$$

diverges.

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