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We have developed a new lattice dynamics scheme for handling large amplitude librational motions or hindered rotations, anharmonic translational vibrations and translation-rotation coupling in molecular crystals. This formalism is based on expanding the intermolecular potential in the molecular displacements and including the cubic and higher terms, while retaining its exact anisotropy. This potential is first used to construct mean field states for the molecular translations and hindered rotations, and next to solve the equations of motion for the crystal in the random phase approximation (RPA), which takes into account the correlations between the molecular motions as well as translation-rotation coupling. It is illustrated that this scheme gives very accurate results for the ordered $\alpha$ and $\gamma$ phases of solid nitrogen, while it also yields, for the first time, a quantum dynamical description of the molecular motions in the plastic $\beta$ phase and a fairly accurate $\alpha-\beta$ transition temperature.

**1. Introduction**

In many molecular crystals, especially in those composed of light molecules or in those in a thermodynamic state near to a phase transition, the molecules perform oscillatory motions with very large amplitudes, or, in the case of plastic crystals, even hindered rotations. As opposed to the pure harmonic motions (1) the oscillatory motions with large amplitudes are relatively poorly understood. The traditional method (1) of perturbation expansion around a harmonic approximation very soon runs into calculational problems because large order perturbation terms are needed. Moreover, in view of the fact that the perturbation series for a quartic anharmonic oscillator has vanishing range of convergence (2), one should be very careful with the interpretation of the results of perturbation calculations.

In the case the molecules perform hindered rotations, with their centres of mass fixed to a lattice point, fairly good results have been obtained (3-9). In many cases this model will not be very realistic, however. Most molecular crystals are rather closely packed, which urges the molecules to separate before large changes in their orientations can occur. This means that there will be a considerable coupling between the translational and the rotational motions of the molecules. It is just this coupling which has attracted a lot of attention (9-15) during the last years, and which will be the subject of the present paper.

A striking property of almost all theories dealing with rotation-translation coupling in molecular crystals is that the translations and rotations are first treated separately, most often in completely different ways, and that the coupling is introduced afterwards. Although this seems physically appealing, it brings with it a lot of computational problems if one wishes to perform actual dynamics calculations, rather than to give a more or less phenomenological description. Our formalism (16-18) avoids these problems by introducing the rotation-translation coupling simultaneously with the correlation between the translational and the rotational vibrations of the individual molecules, while using the full space group symmetry of the system.

We have chosen to illustrate the results of this formalism by applying it to solid nitrogen, for two reasons. The first reason is that nitrogen occurs in different modifications, ordered as well as orientationally disordered, and that many experimental data are available (19-20). Even in the ordered phases, especially in the neighbourhood of the $\alpha-\beta$ order-disorder phase transition, but also at lower temperatures, the amplitudes of the orientational oscillations of the molecules are rather large and their motions will be strongly anharmonic. The second reason is the availability of an ab initio intermolecular potential (21) which has been given in the desired analytic form, and which has already proved its quality on several bulk properties (22-24).

**2. The Hamiltonian**

In order to model the crystal we associate a position vector with each point $P = (\vec{r}, j)$ of a lattice. The position vector of the point $P$ is given by $\vec{R}_P = \vec{R}_n^P + \vec{r}_j$, where $\vec{R}_n^P$ is the position vector of the origin of the
unit cell to which \( P \) belongs, and \( \overrightarrow{R}_p \) the position vector of \( P \) relative to this origin. The molecules are supposed to librate and oscillate in the neighbour-hood of the points they are associated with. The position vector of the centre of mass of the molecule at \( P \) relative to \( \overrightarrow{R}_p \) will be denoted by \( \overrightarrow{u}_p \). In order to describe the orientation of a given molecule we attach a rectangular coordinate frame to it, and give the Euler angles \( \omega_p = (\alpha_p, \beta_p, \gamma_p) \) of this frame relative to a fixed lattice frame.

The potential energy of two molecules, at \( P \) and \( P' \) respectively, is expanded (25-30) in a complete set of functions of the variables \( \omega_p, \omega_{p'} \) and \( \overrightarrow{u}_{pp'} \), where \( \overrightarrow{u}_{pp'} \) is the unit vector in the direction of \( \overrightarrow{u}_{pp'} \). Euler angles relative to the new and the old lattice frame, respectively.

Using the second of these relations we construct linear combinations \( G^{(1)}_m (\omega) = \sum_n A^{(1)}_n D^{(1)}_{mn} (\omega) \), which transform according to the totally symmetric representation of the molecular point group. Only these combinations will occur in the expansion of the potential energy. Using the first of the above relations we can impose the condition that the expansion should be invariant under any rotation of the lattice frame. The final result then is

\[
\begin{align*}
\Phi (\overrightarrow{u}_{pp'}, \omega_p, \omega_{p'}) &= \sum_{\xi} \varphi_{\xi} (\overrightarrow{u}_{pp'}) \sum_m \left( \begin{array}{ccc}
\alpha & \beta & \gamma \\
m_1 & m_2 & m_3
\end{array} \right) \\
& \times G^{(1)}_{m_1} (\omega_p) G^{(2)}_{m_2} (\omega_{p'}) G^{(3)}_{m_3} (\overrightarrow{u}_{pp'})
\end{align*}
\]  

Here the first symbol after the second summation sign is a 3-\( j \) coefficient; the labels are defined as \( \xi = (\xi_1, \xi_2, \xi_3) \) and \( m = (m_1, m_2, m_3) \). In case the intermolecular potential is given in terms of atom-atom potentials, the coefficients \( \varphi_{\xi} (\overrightarrow{u}_{pp'}) \) can be analytically evaluated (29,30). When the potential is numerically known, for instance, from ab initio calculations, the coefficients can be obtained (21) by a numerical integration for several values of \( \overrightarrow{u}_{pp'} \), and then fitted to analytical expressions.

In order to obtain the translational dependence of the potential energy in a more tractable form we expand the translationally dependent part of eq. (2.3) in a Taylor series.
trical top expression \((32,33)\). The double sum in eq. (2.6) represents the potential energy of the whole crystal. This term is sometimes written \((3)\) as a sum of one-particle contributions plus a sum of two-particle contributions, or one \((9-11)\) has distinguished between pure translational, pure rotational and coupled translational-rotational terms. Although such partitionings might contribute to an understanding of the physical contents of the theory, we shall not introduce them here, because they are not essential for the application of the method described in the next section. A second remark: it is natural \((34)\), especially in a mean field treatment of the Hamiltonian \((2.6)\), to use the basis functions of the representations of the site group of the point \(P\), instead of the spherical harmonics \(c_{\alpha m}^{(s)}(\gamma_p)\). We shall not follow this convention, because we find it easier to write the formulas (and implement them in a computer program) in terms of spherical harmonics. Of course, the results can always be re-expressed in terms of basis functions adapted to the site group.

3. Lattice dynamics

The essential aspect of our lattice dynamics calculation is that we first treat the complete hamiltonian \((2.6)\) in a mean field approximation, and then use the resulting mean field states in an RPA treatment, again of the complete hamiltonian \((2.6)\). An important property of our method is that it yields the exact results for a harmonic hamiltonian, including the translation-rotation coupling which is present at the harmonic level. Moreover, in the general case, it gives good results for pure rotational as well as for pure translational systems.

A. The mean field approximation

The mean field approximation is based on the thermodynamic variation principle \((35,36)\)

\[
A_{\text{var}} = A_0 + \langle H - H_0 \rangle_\gamma P \geq A_0,
\]

(3.1)

where \(H_0\) can be any hamiltonian, and \(\langle X \rangle_\gamma P\) is the thermodynamic average of an operator \(X\) over the states of \(H_0\), i.e. \(\langle X \rangle_\gamma P = Z_0^{-1} \text{Tr} X \exp (- \beta H_0)\) with \(Z_0 = \text{Tr} \exp (- \beta H_0)\) and \(\beta = (k_B T)^{-1}\). The Helmholtz free energy corresponding with \(H_0\) is \(A_0 = -k_B T \ln Z_0\) and \(A\) is the free energy corresponding with the exact hamiltonian \(H\). The mean field approximation consists in choosing \(H_0\) as a sum of one-particle operators

\[
H_0 = \sum_p H_p^{MF}(\uparrow_p, \omega_p),
\]

(3.2)

such that \(A_{\text{var}}\) is stable against all first order variations of \(H_p^{MF}\). As is well known, this leads to a set of coupled equations

\[
H_p^{MF}(\uparrow_p, \omega_p) = T(\uparrow_p) + L(\omega_p) + \sum_{p' \neq p} \langle \Phi^{MF}(\uparrow_p, \omega_p; \uparrow_{p'}, \omega_{p'}) \rangle_{p'p},
\]

(3.3)

which have to be solved for \(H_p^{MF}\). Here \(\langle X \rangle_{p'}^{MF}\) denotes the thermodynamic average of \(X\) over the states of \(H_p^{MF}(\uparrow_p, \omega_p)\). Once the \(H_p^{MF}\) are known, the approximate thermodynamic properties of the system are given by

\[
A = -k_B T \ln Z_p^{MF} - \frac{1}{2} \sum_p \langle \Phi^{MF} \rangle_p.
\]

(3.4)

\[
S = -\frac{\partial A}{\partial T} = k_B \sum_p \ln Z_p^{MF} + T \sum_p \langle H_p^{MF} \rangle_p
\]

(3.5)

\[
E = A + TS = \sum_p \langle H_p^{MF} \rangle_p - \frac{1}{2} \sum_p \langle \Phi^{MF} \rangle_p.
\]

(3.6)

Here \(z_p^{MF} = \text{Tr} \exp (- \beta H_p^{MF})\).

Regarding the solution of the system of equations \((3.3)\) let us make two remarks. First, in order to calculate the thermodynamic averages we diagonalize \(H_p^{MF}\), i.e. we construct eigenfunctions of \(H_p^{MF}\), and then perform the averaging in the obvious way. The mean field eigenstates can be constructed as linear combinations of the products \(\psi_L^{(n)}(\uparrow_p) D_{nm}^{(1)}(\omega_p)\), where the translational basisfunctions \(\psi_L^{(n)}(\uparrow_p) = r_L^{(n)}(\uparrow_p) C_{Lm}^{(s)}(\omega_p)\) are 3-dimensional harmonic oscillator expressed in spherical coordinates; the radial functions \(r_L^{(n)}(\uparrow_p)\) are essentially Laguerre functions \((18,37)\). The problem with this approach, however, is that the size of the product basis required to approach the mean-field states will be very large. Therefore, we choose to further separate the mean-field hamiltonian \((3.2)\) into a translational and a rotational part:

\[
H_0 = \sum_p \{ H_T^{MF}(\uparrow_p^T) + H_R(\omega_p) \}.
\]

(3.7)

The mean field formalism given above then remains essentially the same, the main change being that \(P\) must be replaced by the pair \((P,K)\), where \(K = T, L\) distinguishes the translational from the rotational degrees of freedom. One can envisage the crystal now as consisting of two "particles" at every lattice point \(P\), one librating and one oscillating particle. The mean field eigenstates of \(H_T^{MF}(\uparrow_p^T)\) will be linear combinations of \(\psi_L^{(n)}(\uparrow_p)\), and those of \(H_R(\omega_p)\) will be linear combinations of \(D_{nm}^{(1)}(\omega_p)\). Matrix elements over such basis functions with the potential \((2.5)\) are not difficult to evaluate; the angular integrals over \(D_{nm}^{(1)}(\omega)\) and \(C_{Lm}^{(s)}(\omega)\) functions reduce to products of 3-j symbols \((31,33)\) and the radial integrals can be calculated from the formulas given in ref. \((18,38)\). The mean-field equations for \(H_T^{MF}(\uparrow_p^T)\) and \(H_R(\omega_p)\) are coupled, but this coupling can be treated along with the coupling contained in the translational and librational mean-field equations themselves by following the usual iterative procedure to find the self-consistent solutions.

As a second remark we mention that, in order to solve the mean field equations we must impose symmetry relations on the \(H_p^{MF}\). We mostly use the experimentally observed symmetry. In some cases (see section 4), we find that the mean field solution with the experimental symmetry is not stable, however, (see section 3.C) and we look for solutions of lower symmetry. As a result of the translational symmetry, it follows that \(H_P^{MF} = H_P^{MF}\), when \(P_pp^*\) is equal to a primitive lattice vector. Moreover, as a result of the point group symmetry, only the \(H_p^{MF}\) of the molecules in the asymmetric part of the unit cell are independent. For the other molecules in the unit cell, generically labeled by \(P^i\), there exist Euler angles \(\omega_{p'p}\) such that the transformed mean field field \(R(\omega_{p'p})\Phi_P^{MF}\) (see section 2) is equal to \(\Phi_{P^{i*}}^{MF}\), where \(P\) labels the molecule to which the molecule at \(P^i\) is connected by a symmetry operation. Using eq. \((2.1)\) and the definition of \(G_m^{(s)}\) we then derive

\[
\langle G_m^{(s)} \rangle_{p'P} = \sum_m \langle G_m^{(s)} \rangle_{pL} \delta_{m_m} \langle \omega_p \rangle.
\]

(3.8)
We obtain the excited states by use of the excitation state
that represents the mean field ground state of the crystal.

The mean field treatment of the preceding subsection has provided a set of single-particle states $|\psi_{PT}(a)\rangle$ and $|\psi_{PL}(a)\rangle$. From these we construct a crystal state

$$|\psi_{MF}(a),\delta\rangle = \prod_p |\psi_{PT}(a_p)\rangle |\psi_{PL}(a_p')\rangle$$

(3.10)

In case all the $\alpha_p$ and $\beta_p$ are equal to zero, eq. (3.10) represents the mean field ground state of the crystal. We obtain the excited states by use of the excitation operators $(E_{PK})^\dagger$, which replace $|\psi_{PT}(a)\rangle$ by $|\psi_{PT}(a')\rangle$, when applied to the mean field ground state. The random phase formalism consists of two approximations. First, we write the Hamiltonian eq. (2.6) as a quadratic form in the excitation operators $(E_{PK})^\dagger$ and their hermitian conjugates $E_{PK}^\dagger$:

$$H = \sum_{P,K,P',K'} \sum_{\alpha,\beta} \left[ A_{\alpha K}^{\beta K'} (E_{PK})^\dagger E_{P'K'}^\dagger \right] + B_{\alpha K}^{\beta K'} (E_{PK})^\dagger (E_{P'K'})^\dagger + \text{hermitian conjugate}$$

(3.11)

Here, the prime on the first summation sign indicates that $P = P'$ together with $K = K'$ should be excluded. Linear terms are absent in eq. (3.11) because of the Brillouin theorem. The coefficients $A_{\alpha K}^{\beta K'}$ and $B_{\alpha K}^{\beta K'}$ can be calculated by equating the nonzero matrix elements of eq. (3.11) in the basis given by eq. (3.10) to the corresponding matrix elements of eq. (2.6) in the same basis. The translational symmetry of the mean field states can be used to show that the A and B coefficients do not depend on the position labels $P = (q_i,i)$ and $P' = (q_{i'},i')$ but only on the sublattice labels $i$ and $i'$. The second step in the RPA formalism is that we assume boson commutation rules for the excitation and de-excitation operators. It is not difficult to see that this is only approximately true (39,40).

Once we have made these approximations, it is easy to diagonalize the hamiltonian eq. (3.11). A partial diagonalization is of course obtained by adapting the problem to the translational symmetry of the crystal, i.e. by using operators

$$E_{IK}(\vec{q}) = \frac{1}{\sqrt{N}} \sum_{n} e^{i\vec{q} \cdot \vec{n}} E_{\{n,i\}}^\alpha K$$

(3.12)

where $N$ is the number of unit cells in the crystal and $\vec{q}$ is the wave vector. It is well known that the boson commutation rules are preserved under such a transformation. The next step is to define operators $a_{\alpha}(\vec{q})^\dagger$ which represent the exact excitation operators of the crystal and to express these operators as

$$a_{\alpha}(\vec{q})^\dagger = \sum_{\alpha IK} (^{(+)\alpha}_{\alpha IK} \omega_{\alpha}(\vec{q}) \mathbf{E}_{\{IK\}}(\vec{q})^\dagger +$$

$$+ (-)^{\alpha}_{\alpha IK} \omega_{\alpha}(\vec{q}) \mathbf{E}_{\{IK\}}(-\vec{q}) \mathbf{E}_{\{IK\}}(-\vec{q}))$$

(3.13)

These operators must satisfy the equations of motion

$$[H, a_{\alpha}(\vec{q})^\dagger] = \omega_{\alpha}(\vec{q}) a_{\alpha}(\vec{q}),$$

(3.14)

$$[H, a_{\alpha}(\vec{q})] = -\omega_{\alpha}(\vec{q}) a_{\alpha}(\vec{q}).$$

(3.15)

which leads to the RPA eigenvalue problem for the coefficients $(^{(+)\alpha}_{\alpha IK} C_{\alpha IK}$ and those of the matrix $\Phi$ are defined as

$$\chi_{\alpha IK,\alpha'I'K'} = \delta_{\alpha\alpha'} \delta_{ii'} \delta_{KK'} (e_{\alpha,K} - e_{0,K})$$

(3.17)

with $e_{\alpha,K} - e_{0,K}$ being the mean-field excitation energies and

$$\Phi_{\alpha IK,\alpha'I'K'} = \sum_{\eta} \langle \psi_{MF}^\alpha_{\eta PK} | \Phi_{PP'} | \psi_{MF}^\alpha_{\eta'P'K'} \rangle$$

(3.18)

with $P = \{q_i,i\}$, $P' = \{q_{i'},i'\}$, $P'' = \{q_{i''},i''\}$, $K = T$ or $L$, $K_\alpha = L$ or $T$, and $\Phi_{PP'}$ being the potential (2.5).

The mean-field states $\psi_{MF}^\alpha_{\eta PK}$ are given by eq. (3.10) ; they correspond to excitations $(\alpha_p > 0)$ of one translational, $K = T$, or librational, $K = L$, "particle". Accordingly, each matrix $\Phi(\vec{q})$ occurring in eq. (3.16) has diagonal submatrices, $\Phi^{TT}$, correlating the translational motions of the molecules in the lattice, and $\Phi^{LL}$, correlating their librational motions, and off-diagonal submatrices $\Phi^{LT}$ and $\Phi^{TL}$, which account for the translational-librational coupling. The eigenvectors of the RPA equations (3.16) may be conceived as generalized normal modes of the system, one for each $\vec{q}$ and $\alpha$, with fundamental frequencies $\omega_{\alpha}(\vec{q})$. In general, these modes will be mixed translational-librational, their translational components can be strongly anharmonic, and their rotational components may describe (anharmonic) librations as well as (hindered) rotations.
C. Stability conditions

The mean field equations (3.3) have been obtained by making the free energy $A_{\text{var}}$, eq. (3.1), stationary with respect to variations of the mean field hamiltonian $H_{p}^{MF}$ or variations of the corresponding density operator $\rho_{p}^{MF} = Z_{p} \exp (-\beta H_{p}^{MF})$. This amounts to setting the first order variation $A_{\text{var}}^{(1)}$ equal to zero. The resulting solution, i.e. the mean field solution, only corresponds to a minimum of $A_{\text{var}}$, however, if the second order variation, $A_{\text{var}}^{(2)}$, is positive for all variations of $\rho_{p}^{MF}$. This quantity $A_{\text{var}}^{(2)}$ can be written as a quadratic form with the matrix

$$N(\vec{q}) = \begin{pmatrix} \Phi(\vec{q}) - X & \Phi(\vec{q}) \\ \Phi(\vec{q}) & \Phi(\vec{q}) - X \end{pmatrix}$$

(3.19)

as Hessian. $A_{\text{var}}^{(2)}$ will be positive definite only if the (hermitian) matrix $N(\vec{q})$ is positive definite. This matrix $N(\vec{q})$ is closely related to the matrix

$$\begin{pmatrix} X - \Phi(\vec{q}) & -\Phi(\vec{q}) \\ \Phi(\vec{q}) & X + \Phi(\vec{q}) \end{pmatrix} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} N(\vec{q})$$

(3.20)

occurring in the RPA problem, eq. (3.16), and it can be demonstrated that the RPA eigenvalues $\omega_n(\vec{q})$ are indicators for the stability of the original mean field solution, which was used to construct the RPA matrices, via eqs. (3.17) and (3.18). The eigenvalues $\omega_n(\vec{q})$ are purely real or purely imaginary; if one or more of these eigenvalues is imaginary, then the mean field solution is not stable, i.e. it does not correspond to a minimum of $A_{\text{var}}$. Searching in the direction of the eigenvector(s) corresponding to the imaginary eigenvalue(s), can help us in finding a new, stable mean field solution.

4. Application to solid nitrogen

As mentioned in the introduction, solid nitrogen is an interesting system to illustrate the possibilities of our formalism. We have not yet studied the very high pressure phases, which have recently been discovered (42,43), but we have restricted ourselves to the ordered $\alpha$ and $\gamma$ phases and the orientationally disordered $\beta$ phase, since most of the experimental data refer to these phases. Figure 1 shows the structures of these modifications.

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Fig. 1. - Crystal structures of $\alpha$, $\beta$ and $\gamma$ nitrogen, according to ref. [19]
The pairwise additive, intermolecular potential which we have adopted is the ab initio potential of Berns and Van der Avoird \((21)\). This potential has been given in the appropriate form, eq. (2.3), but since the nitrogen molecule is linear we need only two Euler angles, \(\omega_p = (\theta_p, \phi_p)\), to define its orientation. The symmetry adapted functions \(C^m_l(\omega_p)\) in the potential (2.3) and (2.5) can be replaced by Racah spherical harmonics \(\tilde{C}^m_l(\omega_p)\), with even \(\ell\) only (if we disregard the occurrence of mixed isotrope \(^{14}\)N \(^{15}\)N molecules, the natural abundance of \(^{15}\)N being only 0.37%). The rotational kinetic energy in the Hamiltonian (2.6) becomes simply

\[
\mathcal{L}(\omega_p) = B J^2
\]

with the rotational constant \(B = 2.013 \text{ cm}^{-1}\) for \(^{14}\)N \(^{14}\)N. The Wigner \(D^m_l(\omega_p)\) functions in the orientational mean field basis can also be replaced by spherical harmonics \(C^m_l(\omega_p)\), with even \(\ell\) for ortho-nitrogen \((l = 0, 2)\) and odd \(\ell\) for para-nitrogen \((l = 1)\). We have noticed that the results of our calculations are mostly very similar for the ortho and para species, due to the quenching of the \(N_2\) rotations, i.e. the orientational localization, caused by the anisotropic potential.

In order to check the accuracy of our calculations, we have tested for the various truncation errors. The lattice summations over the potential were finally taken over all neighbouring molecules within a range of approximately 10 Å, i.e. about 86 molecules in \(\alpha\), \(\beta\) and \(\gamma\) nitrogen. The expansion of the potential in terms of the molecular displacements, eqs. (2.4) and (2.5), was truncated after \(\ell_{\text{max}} = 4\) (taking \(\ell_{\text{max}} = 2\) would make the potential harmonic in the translational vibrations). This value \(\ell_{\text{max}} = 4\) corresponds to 1% accuracy of the expanded potential for displacements as large as 0.3 Å; the actual root mean square displacements emerging from the calculations are only about 0.1 Å (see below). The orientational dependence of the ab initio potential \((21)\), which contains terms up to \(\ell_{\text{max}} = 6\), was fully retained in the dynamics calculations. The basis for the translational vibrations contained all 3-d harmonic oscillator functions up to \(\ell_{\text{max}} = 5\) inclusive, and the basis for the orientational motions all spherical harmonics up to \(\ell_{\text{max}} = 10\) for \(\alpha\) and \(\beta\) nitrogen and \(\ell_{\text{max}} = 12\) for \(\gamma\) nitrogen. For convenience, the latter basis was actually used in the form of real tesseral harmonics.

A. The ordered \(\alpha\)-and \(\gamma\)-phases

The \(\alpha\)- and \(\gamma\)-phases are both stable at low temperature. The \(\alpha\)-phase exists in equilibrium with nitrogen vapour of very low pressure (practically \(p = 0\)). The \(\gamma\)-phase is stable above \(p = 4\) kbar. While studying the dynamics of the crystal we also optimized the cell parameters, as follows. For the \(\alpha\)-phase we calculated the minimum of the free energy \(A\) in the mean field approximation, eq. (3.4), as a function of the cubic cell parameter \(a\). This yielded the optimum cell parameter \(a = 5.699\) Å (experimentally \(19\) \(a = 5.644\) Å) and the mean field lattice cohesion energy at \(T = 0\) K of \(\Delta E = 5.92\) kJ/mol (experimentally \(\Delta E = 6.92\) kJ/mol).

For the \(\gamma\)-phase we calculated the free energy \(A\) for several values of the tetragonal cell parameters \(a\) and \(c\), and fitted \(A\) \((a, c)\) by a quadratic function. On each curve of constant molar volume \(v = N a^2 c/2\) we determined the optimum \(a\) and \(c\) by minimizing \(A\). Using the optimum points and the corresponding free energies \(\partial A/\partial v\), we calculated the pressure as \(p = -\partial A/\partial v\). Thus we found

\[
T = 0\text{K}
\]

\(\gamma-N_2\) groundstate \(|\psi|^2\)

\(\alpha-N_2\) groundstate \(|\psi|^2\)

Fig. 2. — Orientational probability distributions of the molecular axes in \(\alpha\) (Fig. 2a) and \(\gamma\) (Fig. 2b) nitrogen. Contours of constant probability for the molecule in origin, calculated in the mean field model, are plotted as functions of the polar angles \((\theta, \phi)\) with respect to the crystal axes (Fig. 1). The angle \(\phi\) increases linearly with the radius of the plots from 0 (in the center) to \(\pi/2\) (at the boundary), \(\phi\) is the phase angle.
### TABLE I

Translational and librational amplitudes from mean field calculations

<table>
<thead>
<tr>
<th>( \alpha-N_2 )</th>
<th>( T = 0 \text{ K} )</th>
<th>( p = 0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle u^2 \rangle )</td>
<td>0.112 ( \AA )</td>
<td>( u_r = u_{[1,1,1]} )</td>
</tr>
<tr>
<td>( \langle u_2^2 \rangle )</td>
<td>0.107 ( \AA )</td>
<td></td>
</tr>
<tr>
<td>( \langle u_3^2 \rangle )</td>
<td>0.189 ( \AA )</td>
<td></td>
</tr>
<tr>
<td>( \arccos(\langle \cos^2 \theta \rangle) )</td>
<td>16.1°</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( \gamma-N_2 )</th>
<th>( T = 0 \text{ K} )</th>
<th>( p = 4 \text{ kbar} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle u^2 \rangle )</td>
<td>0.100 ( \AA )</td>
<td>( u_{[1,1,0]} )</td>
</tr>
<tr>
<td>( \langle u_{lab}^2 \rangle )</td>
<td>0.086 ( \AA )</td>
<td>( u_{[1,-1,0]} )</td>
</tr>
<tr>
<td>( \langle u_{lc}^2 \rangle )</td>
<td>0.087 ( \AA )</td>
<td>( u_{[0,0,1]} )</td>
</tr>
<tr>
<td>( \arccos(\langle \cos^2 \theta \rangle) )</td>
<td>12.9°</td>
<td></td>
</tr>
</tbody>
</table>

Asymmetry parameter (rotation out of ab-plane - rotation in ab-plane): \( \frac{\sin^2(\varphi) \cos^2 \omega}{\sin^2 \omega} = 0.05 \)

### TABLE II

\( \alpha_{\text{max}} \) dependence of some RPA lattice frequencies for \( \alpha-N_2 \) \( (a = 5.644 \AA, T = 0 \text{ K}) \)

<table>
<thead>
<tr>
<th>( \alpha_{\text{max}} )</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (0,0,0) )</td>
<td>( \Gamma )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_B )</td>
<td>32.8</td>
<td>32.8</td>
<td>32.8</td>
</tr>
<tr>
<td>( T_B )</td>
<td>43.4</td>
<td>43.4</td>
<td>43.4</td>
</tr>
<tr>
<td>( T_B )</td>
<td>71.6</td>
<td>71.6</td>
<td>71.6</td>
</tr>
<tr>
<td>( A_u )</td>
<td>42.3</td>
<td>42.3</td>
<td>50.6</td>
</tr>
<tr>
<td>( T_u )</td>
<td>48.7</td>
<td>48.7</td>
<td>52.7</td>
</tr>
<tr>
<td>( E_u )</td>
<td>55.7</td>
<td>55.7</td>
<td>60.2</td>
</tr>
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<td>73.0</td>
<td>79.4</td>
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\( M(0,0,0) \)

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<td>( N_{12} )</td>
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TABLE III
Lattice frequencies in α-N₂ (in cm⁻¹) T = 0 K, ρ = 0

<table>
<thead>
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<th></th>
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<tbody>
<tr>
<td>α(Å)</td>
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<td>5.644</td>
<td>5.796</td>
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<td>Γ(0,0,0)</td>
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<tr>
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</tr>
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<td>E₂₃</td>
<td>33.9</td>
<td>34.4</td>
<td>34.2</td>
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<td>35.7</td>
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<td>47.2</td>
<td>57.8</td>
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<td>50.8</td>
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r.m.s. deviation of librational frequencies 10.6 9.7 5.0
r.m.s. deviation of translational frequencies 0.6 1.6 2.1
r.m.s. deviation of all lattice frequencies 6.1 6.0 3.4

TABLE IV
Lattice frequencies in γ-N₂ (in cm⁻¹) T = 0 K, ρ = 4 kbar

<table>
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<tr>
<td>α(Å)</td>
<td>3.957</td>
<td>3.940</td>
<td>4.100</td>
<td>3.961</td>
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<td>c(Å)</td>
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<td>5.086</td>
<td>5.188</td>
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<tr>
<td>Γ(0,0,0)</td>
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<tr>
<td>librations</td>
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<td></td>
</tr>
<tr>
<td>Eₛ</td>
<td>55.0</td>
<td>50.5</td>
<td>56.5</td>
<td>67.6</td>
</tr>
<tr>
<td>Eₛ</td>
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<td>103.3</td>
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<td>A₂₃</td>
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<td>107.1</td>
<td>124.4</td>
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<tr>
<td>translational vibrations</td>
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<td></td>
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</tr>
<tr>
<td>Eᵤ</td>
<td>65.0</td>
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<td>69.3</td>
<td>65.2</td>
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<td>Bᵤ</td>
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<td>r.m.s. deviation</td>
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<td>7.9</td>
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</table>

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axes, again in agreement with experimental data. Analogous figures for temperatures up to 40 K are qualitatively similar. The amount of delocalization is measured by the order parameter \( S = \langle \rho_2 \cos \theta \rangle \) where \( \theta \) is now defined relative to the ground state. At \( T = 0 \) K we find \( S = 0.885 \) and \( S = 0.925 \) for the \( \alpha \) and \( \gamma \) phase respectively. Experimentally one finds \( S = 0.863 \) for the \( \alpha \)-phase. The agreement is fair, as usual the mean field calculations slightly overestimate the order parameters. Similar parameters are given in Table I for the translational vibrations. As indicated already by the librational order parameter \( S \), we observe that the molecular motions in the \( \gamma \)-phase are slightly more restricted than in the \( \alpha \)-phase.

Having calculated the ground and excited mean field states of \( \alpha \)- and \( \gamma \)-nitrogen, we included the correlations between the molecular motions as well as the translational-rotational coupling by determining the eigenvalues of the RPA matrix \( \hat{M}(q) \), Eq. (3.16). Both calculations (mean field and RPA) were performed for \( \alpha_{\text{max}} = 2 \) (i.e. harmonic translational vibrations), \( \alpha_{\text{max}} = 3 \) and 4. Looking at Table II we observe that the size of the anharmonic corrections to the translational frequencies is comparable to the self-consistent phonon (SCP) corrections. This is a favourable result since the SCP method appears to work very well for the translational lattice modes in solid nitrogen. There is an important difference, however, between our formalism and the SCP method. The latter neglects those terms in the potential that depend on odd powers of the molecular displacements. The cubic terms are sometimes added perturbationally. Our formalism includes the cubic terms directly. In the pure translational modes of Table II they have no effect, however, because of the inversion symmetry in \( \alpha \)-nitrogen.

The frequencies from the RPA calculations are given in Tables III and IV for different wave vectors \( q \). The agreement with the experimental data is very satisfactory, especially if we remember that the ab initio potential has not been adjusted to improve this agreement (in contrast with most semi-empirical calculations). Particularly the pure libron frequencies are substantially improved with respect to earlier harmonic and SCP calculations using the same ab initio potential, and also with respect to semi-empirical harmonic calculations. Also the mixed phonon-libron modes, which describe explicitly the translational-rotational coupling, are represented very accurately by our formalism. All points in the Brillouin zone, except some points of high symmetry, actually yield such mixed modes and, therefore, the translational-rotational coupling can have important effects on the properties of the crystal. We intend to study such effects in the near future.

### B. The plastic \( \beta \)-phase

The \( \beta \)-phase is stable above \( T = 35.6 \) K. We started our calculations on this phase by assuming the experimentally observed symmetry. Thus, the two molecules in the hexagonal unit cell were given translationally equivalent mean field solutions. The probability density of the ground state wave function that resulted for the ortho-species is shown in Figure 3a. (The ground state of the para-species is twofold degenerate. The average probability density \( \frac{1}{2} (|\psi_1|^2 + |\psi_2|^2) \) is similar to Fig. 3a). We observe that the orientations of the molecular axes are delocalized. The motions can be described as precessions around the crystal c-axis which are hindered by small sixfold barriers. In accordance with the picture of Press and Hüller the angle \( \theta \) between the molecular axes and the c-axis shows a rather broad distribution. The maximum of this distribution lies at the "experimental" precession angle: about 56°.

Starting from this ground state and a number of excited states we wanted to calculate the libron frequencies. The relevant formulas are obtained by restricting Eqs. (3.16) to (3.18) to the librational "particles" only: \( K = L \). Some of the frequencies for \( q = 0 \) came out imaginary. According to section 2.C this implies...
that the delocalized mean field states do not correspond with a (local) minimum of the free energy. Inspecting the eigenvectors of the RPA problem belonging to the imaginary frequencies taught us that the free energy could be lowered by out-of-phase motions of the two neighbouring molecules in the unit cell.

Indeed, we found that there exists a mean field solution which is lower in free energy than the delocalized solution by 0.87 kJ/mol at zero temperature. In this new solution the orientations of the molecular axes are clearly localized (see Fig. 3b). The states for the two neighbouring molecules in the unit cell are equivalent, but rotated over 180° around the c-axis. This 180° rotation avoids the hindrance which occurs between neighbouring molecules when they process freely (51). The angle \( \theta \approx 52° \) between the molecular axes and the crystal c-axis is slightly smaller than for the delocalized case.

The most remarkable feature of the localized state is that the experimentally observed hexagonal symmetry is lost. This symmetry will be restored if we assume that for each molecule six equivalent mean field solutions are available, which are related to each other by rotations of 60° around the c-axis, and that the molecules can jump from one localized solution to another within the time that is characteristic for the observation process, i.e. the inverse NMR or NQR frequency (19), for example. We shall digress on this hypothesis in the next section.

We calculated the libron frequencies by the RPA method with two excited localized mean field states on each molecule. All frequencies came out real now, as they should be for a stable mean field solution (see Table VI). The experimental spectra (47,82) show two very broad peaks of which the higher one around 50 cm\(^{-1}\) (depending on the temperature and pressure) has been interpreted as a libron band and the lower one around 25 cm\(^{-1}\) as a translational phonon band. The higher libron frequency agrees reasonably well with our results, but according to our calculated frequencies, the libron modes might cause some absorption in the lower band as well (apart from symmetry and intensity considerations which we have not looked at). Our results indicate that the broadening of the observed libron band is caused by coupling of localized librational modes with more or less random jumps in the orientations of the molecules by multiples of 60° around the crystal c-axis.

The localized mean field solution poses yet another problem. Although we expect that the experimentally observed lattice symmetry can be restored by allowing rapid jumps between the six localized librational solutions, the lower symmetry of the actual solution makes it impossible to use our libron-phonon formalism as such. Indeed, we found that in the mean field of the "broken symmetry" librations the equilibrium positions of the molecules tend to shift away from the hexagonal lattice sites. In order to solve this problem one would have to extend our formalism with a dynamical model for the symmetry-restoring jumps.

C. The \( \alpha-\beta \) phase transition

In Figure 4 we have plotted the free energy A calculated for the different mean field solutions of \( \alpha \)- and \( \beta \)-nitrogen. The contribution from the translational vibrations is not included in this picture, for the reason mentioned in the previous section. However, we do not expect a great difference in this contribution between the \( \alpha \)- and \( \beta \)-phase. The curve for the delocalized mean field solution of \( \beta \)-nitrogen declines much steeper, with increasing temperature, than the localized \( \beta \)-N\(_2\) curve and the \( \alpha \)-N\(_2\) curve. This is caused by the considerably lower excitation energies for the delocalized states, which look like hindered rotor states rather than librational oscillators. It is characteristic that a free rotor model produces almost the same free energy curve as the delocalized model. However, the free energy at zero temperature for the delocalized model is too high to make its curve cross the \( \alpha \)-N\(_2\) curve at any reasonable temperature. So this model fails to explain the \( \alpha-\beta \) phase transition.

For the localized \( \beta \)-N\(_2\) model the energy is substantially lowered due to a more favorable packing of nearest neighbours. But its free energy curve runs almost parallel to the \( \alpha \)-N\(_2\) curve, because of the similar size of the mean field excitation energies. So we still find no crossing between the \( \alpha \)- and \( \beta \)-curve.

Let us consider, however, the jump model of the previous section. Because of important energy effects, the orientations of the molecules will not be completely

**TABLE V**

<table>
<thead>
<tr>
<th>calculated (libron)</th>
<th>experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RPA</td>
</tr>
<tr>
<td>temperature (K)</td>
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</tr>
<tr>
<td>molar volume (cm(^3).mol(^{-1}))</td>
<td>28.26</td>
</tr>
<tr>
<td>frequencies (cm(^{-1}))</td>
<td>35\pm3</td>
</tr>
<tr>
<td></td>
<td>34.9</td>
</tr>
<tr>
<td></td>
<td>65.7</td>
</tr>
<tr>
<td></td>
<td>73.3</td>
</tr>
</tbody>
</table>

\(^a\) as quoted in ref.[52]

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randomly distributed over the six possible localized librational solutions. On the contrary, they will show a strong short range correlation. The effect of this correlation is to lower the energy of the crystal and make it approximately equal to the energy of the localized model. The entropy of the crystal can be assessed to be the sum of two contributions. The first part originates from the librations of the molecules around their equilibrium orientations, and this is approximately the entropy of the localized model. The second part is due to the distribution of the molecules over the six positions. Although there is a strong short range correlation, it is in the spirit of the present mean field approach to set the corresponding entropy equal to \(-k_B T\) in \(6\) (see text).

5. Conclusions

The results which we have obtained for solid nitrogen demonstrate that the formalism which we have developed yields a realistic description of the anharmonic translational vibrations, the large amplitude librations, which are much more strongly anharmonic, and the translation-rotation coupling in molecular crystals. Using an ab initio intermolecular potential, the results for the ordered \(\alpha\) and \(\gamma\) phases are quantitatively very accurate. For the plastic \(\beta\) phase we predict that the experimentally observed orientational disorder is caused by rapid \(60^\circ\) jumps of the molecules around the crystal \(c\)-axis, between localized librational states. The two neighbouring molecules in the hexagonal unit cell tend to remain \(180^\circ\) out of phase, in order to obtain a considerably lower packing energy of the crystal than for the free precession model, which has also been invoked to explain the orientational disorder. Although we have not yet developed a dynamical model for the correlated jumps of the molecules, we find that the jump model for the \(\beta\)-phase can yield a fairly accurate transition temperature for the \(\alpha-\beta\) order-disorder phase transition.

References


