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Orientational disorder in plastic molecular crystals
II. — Neutron scattering and orientational dynamics

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Abstract. — In this paper, it is shown how the formalism of the canonical symmetry adapted functions can be used to analyse neutron scattering data related to orientationally disordered molecular crystals when the rotational dynamics of the molecule is assumed to be independent of the lattice dynamics. In this approximation, the rotational contribution to the intermediate scattering function is expanded in terms of correlations between the symmetry adapted functions of the molecular orientations. The site and molecular symmetry are taken into account to derive the complete set of independent correlation functions and to find which of them can be measured through neutron coherent and incoherent scattering experiments performed on single crystals or powder sample. Besides, it is shown that the orientational probability density function can be fully determined from the elastic part of incoherent neutron scattering.

1. Introduction. — 1.1. — A great interest has recently been devoted to neutron scattering experiments performed on plastic phases (see e.g. Refs. [1-3]). Neutron scattering is indeed a powerful tool for the study of orientational disorder in those phases: while elastic scattering, depending on the mean position of the molecules, reflects the static aspect of orientational disorder, quasi-elastic and inelastic scattering are concerned with the whole dynamics of external modes, which besides translational phonons, include librational and reorientational motions.

In the first paper of this series [4], hereafter referred to as I, we proposed a formal description of the static aspect of orientational disorder, when molecules, with a symmetry group $\mathcal{M}$, lie on lattice sites which have the symmetry of the point group $\mathcal{S}$. For this purpose, we set up a symmetry adapted canonical basis of functions \{ $A_{\xi}^{m}(\Omega)$ \}, where $\Omega$ is a short notation for the set of the three Euler angles $\{ \alpha, \beta, \gamma \}$ describing the molecular orientation in the crystal axis. Following the definitions adopted in I, the symmetry operations of the site and molecular groups transform the basis functions $A_{\xi}^{m}(\Omega)$ according to the irreducible representations of the product $\mathcal{S} \mathcal{M}$. In this notation, the index $l$ means that $A_{\xi}^{m}(\Omega)$ is a linear combination of Wigner function $W_{\xi,mm'}(\Omega)$ belonging to the same representation $l$ of the full rotational group; the label $\lambda$ (resp. $\lambda'$) is a short hand notation for the composite index $(l, \mu, n)$ (resp. $(l', \mu', n')$) where $\Gamma$ (resp. $\Gamma'$) is the name of an irreducible representation of the group $\mathcal{S}$ (resp. $\mathcal{M}$). $\mu$ (resp. $\mu'$) labels independent subspaces transforming according to the same $\Gamma$ (resp. $\Gamma'$) representation (if this representation is included more than once in the $l$ representation of the full rotational group). $n$ (resp. $n'$) labels the different basis vectors for multidimensional representations.

(1) In this paper, we shall, for simplicity, adopt the same notation $\Omega$ for the rotation which brings the crystal axis in coincidence with the molecular axis and for the set of Euler angles $\{ \alpha, \beta, \gamma \}$ associated with this rotation in the crystal axis.

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In this paper, we intend to use the formalism of this canonical basis to analyse neutron scattering data related to orientationally disordered phases. The relationship between neutron cross sections and molecular orientations can, indeed, be expanded in terms of symmetry adapted functions. This procedure allows to take fully into account the molecular and site symmetry in deriving which informations on orientational disorder and rotational dynamics are actually obtainable from the various neutron scattering experiments.

1.2. — We shall deal here with the elastic and quasi-elastic parts of neutron spectra. Inelastic neutron scattering is in fact concerned with the whole dynamics of the molecules involving together translational, rotational and vibrational motions. The approximation of rigid molecules is usually quite justified when looking at the quasi-elastic scattering because the frequencies of the vibrational modes are generally much higher than those of external modes. On the contrary, translational and rotational motions fall in the same frequency range and the hypothesis according to which the translational phonons do not couple with the rotational (librational and reorientational) dynamics is much less obvious, especially in the cases where there is a steric hindrance to molecular reorientations. The independence between translational and rotational dynamics is certainly more likely in the case of small globular molecules (such as neopentane or tertbutylchlorine) and this independence will be the basic assumption used throughout this paper. Under this assumption, the rotational contribution to neutron scattering appears as a linear combination of basic correlation functions such as 

\[ \langle \Delta^{i_1,j_1}(\Omega_1) \Delta^{i_2,j_2}(\Omega_2(t)) \rangle \]

involving the canonical functions of molecular orientations \( \{ \Omega_1, \Omega_2 \} \). As we shall see in this paper, symmetry considerations allow then to predict which of those correlation functions are a priori non zero and which are relevant for neutron scattering.

Both cases of coherent and incoherent scattering will be discussed. In fact, incoherent scattering is always dominant in plastic crystals containing hydrogen atoms and coherent scattering can be obtained from deuterated phases. In particular, we shall stress that the neutron selection rules arising from group theoretical arguments are not the same for coherent and incoherent scattering; this, indeed, comes from the fact that the coherent scattering amplitude of each molecule reflects the molecular symmetry while this symmetry appears only in the scattered incoherent intensity.

1.3. — The next part (part 2) of this paper is devoted to generalities about neutron scattering in molecular crystals. The neutron coherent and incoherent cross section are then derived in terms of symmetry adapted function.

Part 3 deals with the elastic part of coherent and incoherent scattering. The elastic scattering arises from the limit, for infinite time, of the correlation functions, which involve the static orientational probability density function \( P_o(\Omega) \). In I, this function was developed on the canonical basis. In particular it was shown that, when both the molecular group \( \mathcal{M} \) and the site group \( S \) contain improper rotations, the symmetry group of \( P_o(\Omega) \) is not the full product \( S \cdot \mathcal{M} \), but only the reduced subgroup \( S_\mathcal{M} \), containing only those operations of \( S \cdot \mathcal{M} \) which involve an even number of improper rotations. As a result, the canonical development of \( P_o(\Omega) \) included two kinds of basis functions:

- the functions \( A^{l_1,j_1}(\Omega) \), the indices of which belong to the identity representations of the molecular and site group \( (\Gamma_0^S \text{ for } S \text{ and } \Gamma_0^\mathcal{M} \text{ for } \mathcal{M}) \);
- the functions \( A^{l_1,j_1}(\Omega) \), the indices of which belong to the other one dimensional representation of \( S \) and \( \mathcal{M} \) (called \( \Gamma_0^S \text{ for } S \text{ and } \Gamma_0^\mathcal{M} \text{ for } \mathcal{M} \)) which induces the identity representation of the reduced subgroups \( S_\mathcal{M} \).

\[
P_o(\Omega) = \sum_{l_1,l_2,j_1,j_2} A^{l_1,j_1}(\Omega) A^{l_2,j_2}(\Omega) + \sum_{l_1,l_2,j_1,j_2} A^{l_1,j_1}(\Omega) A^{l_2,j_2}(\Omega)
\]

Hüller and Press (Ref. [1-2]) already used such a development of the pdf \( P_o(\Omega) \) to analyse elastic coherent scattering. These authors showed that elastic coherent scattering provides a measurement of the coefficients \( A^{l_1,j_1}(\Omega) \), called coefficients of the first kind (at least for small value of \( l \)). These coefficients have been measured e.g. in the plastic phases of CD\(_4\) (Hüller and Press, Ref. [1]), CB\(_4\) (More et al., Ref. [6]) and adamantane (Amoureux and Bee, Ref. [10]).

In this paper, it is shown that the pdf \( P_o(\Omega) \) can be totally determined, including the coefficients of the second kind, \( A^{l_1,j_1}(\Omega) \) (or, at least, the square of their value), from the elastic part of incoherent neutron scattering, even in a powder experiment, a technique which is frequently used as generally single crystals are not available.

Part 4 deals first with the rotational contribution to quasi-elastic incoherent scattering. In the formalism of symmetry adapted functions, the rotational dynamics appears in the incoherent scattering law through self-correlation functions such as

\[
\langle \Delta^{l_1,j_1}(\Omega_1(0)) \Delta^{l_2,j_2}(\Omega_1(t)) \rangle.
\]

These correlation functions imply an averaging process over molecular orientations using the self orientational density function \( P(\Omega_1, \Omega_2, t) \) which is the density of probability for a molecule to have the orientation \( \Omega_1 \) at a time \( t_1 \) and the orientation \( \Omega_2 \) at a later time \( t_2 = t_1 + t \). This function which characterizes the individual rotational dynamics of the molecules is first studied from the symmetrical point...
of view, using the group theory method described in I. This method provides the number of independent, non-zero, self-correlation functions which are consistent with the molecular and site symmetry. It is to be stressed that the analysis presented here, lies only on symmetry considerations and assumes nothing about the actual rotational dynamics of the molecules. A few examples are given to illustrate the general method. From the neutron selection rules, made explicit in part 2, we then derive which of those correlations functions are actually measured through incoherent neutron scattering experiments performed on single crystal or powder sample. At last, the case of coherent scattering is discussed in the simple approximation where the rotational motions of neighbouring molecules are assumed to be independent.

2. Generalities: neutron cross section in terms of symmetry adapted functions. — 2.1. — As it is well-known the partial differential cross sections for neutron scattering with energy change $\hbar \omega$ and momentum transfer $\hbar k$ is directly related to the space-time Fourier transform of a nuclear density-density correlation function.

For simplicity, we shall consider a plastic phase with one molecule per unit cell. In this study, we consider only heavy molecules and sufficiently high temperature to make negligible quantum rotational tunnelling effects. Therefore, the nuclear spins within a molecule are assumed to be uncorrelated and each nucleus $L_j$ contributes to coherent scattering with a coherent scattering length $b^{cL_j}$ and to incoherent scattering with an incoherent scattering length $b^{incL_j}$. The coherent cross section (which results from a summation of the nuclear scattering amplitudes) is proportional to the coherent scattering function $I_c(k, \omega)$:

$$I_c(k, \omega) = \int_{-\infty}^{+\infty} e^{-i\omega t} I_c(k, t) \, dt$$ (2.1a)

with

$$I_c(k, t) = \left\langle \sum_{L_j} \overline{b^{cL_j}}^* b^{cL_j} e^{-i\overline{R}_{L_j}(0) \cdot \overline{r}_{L_j}(t)} \right\rangle.$$ (2.1b)

On the other hand, the incoherent contributions of the different nuclei do not interfere and the incoherent cross section is proportional to

$$I_{inc}(k, \omega) = \int_{-\infty}^{+\infty} e^{-i\omega t} I_{inc}(k, t) \, dt$$ (2.2a)

with

$$I_{inc}(k, t) = \left\langle \sum_{L_j} b^{incL_j} |^2 e^{-i\overline{R}_{L_j}(0) \cdot \overline{r}_{L_j}(t)} \right\rangle.$$ (2.2b)

The brackets (2.1b) and (2.2b) stand for a thermal averaging over the position vector $\overline{R}_{L_j}(t)$ of the different nuclei. The translational and rotational contributions to $\overline{R}_{L_j}(t)$ can be explicitly written under the form:

$$\overline{R}_{L_j}(t) = \overline{R}_L + \overline{u}_L(t) + \overline{r}_{L_j}(t)$$ (2.3a)

where

$\overline{R}_L$ is the equilibrium position of the molecular centre of mass,
$\overline{u}_L(t)$ is the translational displacement of this centre of mass and
$\overline{r}_{L_j}(t)$ the position vector of the $(L_j)$ nucleus relative to the molecular centre.

As previously stressed, we shall ignore here the internal degrees of freedom and treat each molecule as a rigid body. Thus, the position vectors $\overline{r}_{L_j}(t)$ have constant lengths and depend on time only through the molecular orientations $\Omega_L(t)$.

$$\overline{r}_{L_j}(t) = r_j \tilde{r}_{L_j}(\Omega_L(t))$$ (2.3b)

($r_j$ is a unit vector along the $\tilde{r}_{L_j}$ direction).

In the following we shall focus our interest on

a) the strictly elastic scattering which arises from the limit at infinite time of the intermediate scattering functions $I_{c}(k, t)$ and $I_{inc}(k, t)$ and thus only reflects the static aspect of the molecular disorder;

b) the contribution of the rotational dynamics to the quasi-elastic scattering. For this, as already stressed, we shall assume that we are dealing with a plastic phase where the molecular rotational motions are totally independent from the translational dynamics.

With this last assumption, the validity of which we shall not discuss, the thermal averaging appearing in the scattering laws (2.2) can be splitted, even at finite time $t$, into an averaging over the translational coordinates $\{\overline{u}_L\}$ and another one involving only the rotational coordinates $\{\Omega_L\}$ which leads to:

$I_{c}(k, t) = \sum_{L'} \sum_{L_j} e^{-i\overline{k}L'}(t) e^{i\overline{k}L}(t) \times$

$I_{c}(k', t, L, L') \times$

$I_{c}(k', t, L, L') = \langle e^{-i\overline{k}_LL_j(t)} e^{i\overline{k}_L L_j(t)} \rangle$ (2.4a)

$I_{c}(k, t, L, L') = \sum_{L_j} \langle b^{cL_j}^* b^{cL_j} e^{-i\overline{k}_L L_j(t)} e^{i\overline{k}_L L_j(t)} \rangle$ (2.4b)

and

$I_{inc}(k, t) = I_{inc}(k, t) I_{inc}(k, t)$ (2.5)

with

$I_{inc}(k, t) = \sum_{L} \overline{b}^{incL} |^2 e^{-i\overline{k}_L L_j(t)} e^{i\overline{k}_L L_j(t)}$ (2.5a)

$I_{inc}(k, t) = \sum_{L} \overline{b}^{incL} |^2 e^{-i\overline{k}_L L_j(t)} e^{i\overline{k}_L L_j(t)}$ (2.5b)
Evaluation of the translational part (2.4a) is a well-known problem (see e.g. Ref. [5]) and yields:

\[
F_{\text{trans}}(k, t, L, L') = e^{-2w(k)} (1 + e^{i k \bar{w}_k(t) + i k \bar{L}(t)})
\]

(2.6)

where \(w(k)\) is the Debye-Waller factor.

The first term in (2.6) leads to the elastic translational scattering, and the expansion of the second term up to the first order yields the one phonon cross section, up to the second order the two phonon cross section, etc.

Let us rather focus our attention on the rotational terms (2.4b) and (2.5b). These can be expanded on the basis of the symmetry adapted functions introduced in I.

Let us first, following the work of V. F. Sears on molecular liquids (Ref. [14]) use the expansion of \(e^{ikrL_j}\) in terms of spherical harmonics

\[
e^{i k r L_j} = 4 \pi \sum_j j_i j_k \eta_i^m(\hat{k}) Y_j^m(\hat{r}_L)
\]

(2.7)

where \(j_i\) is the spherical Bessel function of order \(l\).

The direction \(\hat{r}_L\) for the \(j\) atom in crystal axis, can be deduced from the same direction \(\hat{r}_j\) in the molecular axis through the rotation \(Q_L\) characterizing the orientation of the molecule \(L\). (Following the definition adopted in I, \(Q_L\) is the rotation which brings the crystal axis in coincidence with the molecular axis.) Thus

\[
Y_j^m(\hat{r}_L) = Y_j^m(\Omega_L \hat{r}_j)
\]

(2.8)

and

\[
e^{i k r L_j} = 4 \pi \sum_{lmm'} \eta_l j_l(kr_j) Y_l^m(\hat{k}) D_{mm'}^{l}((\Omega_L)) Y_l^{m'}(\hat{r}_j)
\]

(2.9)

If we use the definitions of the surface harmonics \(S_{ij}^a\) relative to the site group, of the surface harmonics \(M_{ij}^a\) relative to the molecular group and, at last, of the canonical basis functions \(A_{ij}^{a\beta}\), it appears that \(e^{i k r L_j}\) can be written as

\[
e^{i k r L_j} = 4 \pi \sum_{lmm'} \eta_l j_l(kr_j) Y_l^m(\hat{k}) D_{mm'}^{l}((\Omega_L)) A_{lmm'}^{a\beta}(\Omega_L(t)).
\]

(2.10)

The indexes \(a\) and \(\beta\) in (2.10), (2.11) are related to definite representations \(\Gamma\) and \(\Gamma'\) of respectively the site and the molecule symmetry groups so that \(e^{i k r L_j}\) depends on time only through the factor \(A_{lmm'}^{a\beta}(\Omega_L(t))\).

2.2 COHERENT ROTATIONAL TERM. — The coherent rotational structure factor appearing in (2.4a)

\[
F_{\text{rot},c}^c(\bar{k}, t) = \sum_j b_j^c e^{-i k r L_j}\]

(2.14)

can be written according to (2.13)

\[
F_{\text{rot},c}^c(\bar{k}, t) = 4 \pi \sum_{k, l} (- i)^l j_l(kr_j) M_{l}^{\text{c}}(\hat{r}_j) A_{l}^{c\beta}(\Omega_L(t)).
\]

(2.15)

The summation over the different atoms \(j\) of the molecule which appear in formula (2.15) ensure that the coherent rotational structure factor, \(F_{\text{rot},c}^c\), reflects the molecular symmetry. Indeed, the different atoms within a molecule can be arranged into shells of equivalent atoms. Equivalent atoms have the same scattering length \(b_j\), the same radius \(r_j\) and correspond to one another in the molecular symmetry group. Thus, the summation over the different atoms of a given shell is equivalent to a projection on the identity representation of the molecular symmetry group and is zero unless \(\beta\) belongs to this representation.

Thus, the rotational term, \(F_{\text{rot}}(\bar{k}, t, L, L')\), in the coherent scattering law can be written as a sum of correlation functions, involving only symmetry adapted functions which transform according to the unity representation of \(\mathcal{M}\).

\[
F_{\text{rot}}(\bar{k}, t, L, L') = \sum_{\text{shells}} S_{l_1}^{\text{c}}(\bar{k}) S_{l_2}^{\text{c}}(\bar{k}) G_{l_1}^{\text{c}}(k) G_{l_2}^{\text{c}}(k) \left< A_{l_1}^{\text{c}1}(\Omega_L(0)) A_{l_2}^{\text{c}2}(\Omega_L(t)) \right>
\]

(2.16)

with

\[
G_{l_1}^{\text{c}}(k) = \sum_j b_j^c 4 \pi (-i)^l j_l(kr_j) M_{l_1}^{\text{c}}(\hat{r}_j).
\]

(2.17)
2.3 INCOHERENT ROTATIONAL TERM. — In view of (2.13), the incoherent rotational term \( I^{\text{inc}}_{\text{rot}}(k, t) \) can be written, in terms of symmetry adapted functions,

\[
I^{\text{inc}}_{\text{rot}}(k, t) = \sum_{l_1, l_2} \sum_{\alpha, \beta} S_{l_1}^{\alpha}(k) S_{l_2}^{\beta}(k) H_{l_1 l_2}^{\alpha \beta}(k) \langle \Delta_{l_1}^{\alpha \ast}(\Omega_{1}(0)) \Delta_{l_2}^{\beta}(\Omega_{1}(t)) \rangle
\]  

(2.18)

with

\[
H_{l_1 l_2}^{\alpha \beta}(k) = \sum_{j} b_{j}^{\text{inc}} | b_{j}^{\text{inc}} | 2 \pi^{2}(-i)^{l_1 + l_2} j_{l_1}(k r_{j}) j_{l_2}(k r_{j}) M_{l_1}^{\alpha}(r_{j}) M_{l_2}^{\beta}(r_{j}).
\]  

(2.19)

This last factor, involving a summation over the \( j \) atoms of a molecule, reflects also the full molecular symmetry. The summation concerns, here, the contribution of the different nuclei to the scattered intensity and the selection rules result from the projection of the product \( M_{l_1}^{\alpha}(r_{j}) M_{l_2}^{\beta}(r_{j}) \) on the unity representation of the molecular group. This projection will give a non-zero value when the indexes \( l_{1}' = (l_{1}' \mu_{1}' n_{1}') \) and \( l_{2}' = (l_{2}' \mu_{2}' n_{2}') \) verify the selection rule

\[
\Gamma_{1}' = \Gamma_{2}' \quad \text{and} \quad n_{1}' = n_{2}'.
\]  

(2.20)

The difference between coherent and incoherent neutron scattering is thus concentrated in the \( G \) terms of (2.16) and the \( H \) terms of (2.18). They lead to quite different selection rules, those for incoherent scattering (2.20) being less restricted than those for coherent scattering.

3. Elastic scattering. — By definition, we shall call elastic scattering that part of the neutron spectrum which arises from the limit at infinite time of the coherent and incoherent intermediate scattering laws \( I_{c}(k, t) \) and \( I_{\text{inc}}(k, t) \).

\[
I^{\text{coh}}_{\text{el}}(k) = \delta(\omega_{0}) I_{c}(k, t = \infty)
\]  

(3.1)

\[
I^{\text{inc}}_{\text{el}}(k) = \delta(\omega_{0}) I_{\text{inc}}(k, t = \infty).
\]  

(3.2)

The ergocity hypothesis implies that molecular displacements cannot be correlated over an infinite range of time. Thus, in particular the thermal averaging over rotational coordinates \( \Omega_{1}(0) \) and \( \Omega_{L}(\infty) \) reduces to independent averaging which only involves the probability density function \( P_{0}(\Omega) \) introduced in 1:

\[
\forall L', L'' \quad \langle \Delta_{l_{1}}^{\alpha \ast}(\Omega_{1}(0)) \Delta_{l_{2}}^{\beta}(\Omega_{L}(\infty)) \rangle = \langle \Delta_{l_{1}}^{\alpha \ast}(\Omega_{L}) \rangle \langle \Delta_{l_{2}}^{\beta}(\Omega_{L}) \rangle =
\]

\[
= \left( \int P_{0}(\Omega_{L}) \Delta_{l_{1}}^{\alpha \ast}(\Omega_{L}) d\Omega_{L} \right) \left( \int P_{0}(\Omega_{L}) \Delta_{l_{2}}^{\beta}(\Omega_{L}) d\Omega_{L} \right).
\]  

(3.3)

Recalling the canonical development of \( P_{0}(\Omega) \),

\[
P_{0}(\Omega) = \sum_{l_{1}, l_{2}} A_{l_{1}}^{\ast \alpha} A_{l_{2}}^{\beta}(\Omega)
\]  

(3.4)

(with the selection rules \( \lambda \mu' \in \Gamma_{0}^{+}, \Gamma_{0}^{+} \) or \( \lambda \mu' \in \Gamma_{0}^{-}, \Gamma_{0}^{-} \)) and in view of the orthogonality of the canonical basis function, we obtain

\[
\forall L', L'' \quad \langle \Delta_{l_{1}}^{\alpha \ast}(\Omega_{L}(0)) \Delta_{l_{2}}^{\beta}(\Omega_{L}(\infty)) \rangle = \frac{1}{(2 l_{1} + 1) (2 l_{2} + 1)} A_{l_{1}}^{\ast \lambda_{1}} A_{l_{2}}^{\ast \lambda_{2}} A_{l_{1}}^{\lambda_{1}} A_{l_{2}}^{\lambda_{2}}.
\]  

(3.5)

The inferences from this are drawn below in both cases of coherent and incoherent scattering.

3.1 ELASTIC COHERENT SCATTERING. — In view of (2.4), (2.6), (2.16) and (3.1), (3.5) the elastic coherent scattering law appears to be

\[
I^{\text{coh}}_{\text{el}} = \sum_{l} \delta(k - \bar{k}) e^{-2\pi^{2}k} \sum_{l_{1}, l_{2}} \frac{1}{(2 l_{1} + 1) (2 l_{2} + 1)} S_{l_{1}}^{\ast}(k) S_{l_{2}}^{\ast}(k) \times G_{l_{1}}^{\ast}(k) G_{l_{2}}^{\ast}(k) A_{l_{1}}^{\lambda_{1}} A_{l_{2}}^{\lambda_{2}}.
\]  

(3.6)

The first summation in (3.6) involves the reciprocal lattice vectors, and the second summation is written with a prime to recall that there exist selection rules arising from symmetry.
These selection rules arise
a) from the $G_{ij}$ factors which reflect the molecular symmetry:
$$\lambda_1 \in \Gamma_0^+ \quad \text{and} \quad \lambda_2 \in \Gamma_0^+;$$

b) from the coefficients $A_{ij}^{k*}$ of $P_0(\Omega)$ (see eq. (3.4)) which reflects both the molecular and the site symmetry:
$$\lambda_1 \lambda'_1 \in \Gamma_0^+ \Gamma_0^+ \quad \text{or} \quad \Gamma_0^- \Gamma_0^-$$
and
$$\lambda_2 \lambda'_2 \in \Gamma_0^+ \Gamma_0^+ \quad \text{or} \quad \Gamma_0^- \Gamma_0^-.$$

Accordingly, the non vanishing terms in (3.6) are such that
$$\lambda_1 \lambda'_1 \in \Gamma_0^+ \Gamma_0^+ \quad \text{and} \quad \lambda_2 \lambda'_2 \in \Gamma_0^+ \Gamma_0^+$$
and the coherent elastic scattering depends only on those coefficients of $P_0(\Omega)$ which are in the unity representation of the site and the molecular groups.

Thus, from a theoretical point of view, all the coefficients of the first kind in $P_0(\Omega)$, but only those ones, can be derived from an elastic coherent scattering experiment. In practice, as $G_{ij}(k)$ contains a Bessel function, only those coefficients which involve a small value of $l$ can be accurately measured.

Formula (3.6) shows that a scattering experiment performed on a single crystal yields the magnitude and relative sign of those coefficients. The complete determination of the relevant $A_{ij}^{k*}$ arises from the normalization condition $A_0 = 1$. For a tetrahedral molecule in a cubic site, the first non trivial coefficients are $A_4^{00}, A_6^{00}, A_8^{00}$. Using the above technique, W. Press measured $A_4^{00}$ and $A_6^{00}$ for the plastic phases I and II of CD$_4$ (Ref. [1]), M. More obtained up to $A_8^{00}$ in plastic CBr$_4$ (Ref. [6]) and J. P. Amoureux obtained those coefficients up to $l = 10$ in the adamantane case.

3.2 Elastic incoherent scattering. — From (2.5) and (2.18), (3.2) and (3.5), the elastic incoherent scattering law can be written as
$$I_{\text{elic}}^{\lambda}(k) = \sum_{l_1 l_2} S_{l_1 l_2}^{*}(k) S_{l_1 l_2}^{*}(k) H_{l_1 l_2}(k) A_{l_1 l_2}^{\lambda k 1} A_{l_1 l_2}^{\lambda k 2}.$$ 

The selection rule for $H_{l_1 l_2}^{\lambda k 1 2}$, implied by the molecular symmetry, states only that $\lambda_1$ and $\lambda_2$ belongs to the same representation of the molecular group
$$(\Gamma_1 = \Gamma_2, n_1 = n_2).$$

Together with the symmetry properties of $P_0(\Omega)$, this leads to the following selection rules for the above elastic incoherent scattering law (2.8)
$$\lambda_1 \lambda'_1 \in \Gamma_0^+ \Gamma_0^+ \quad \text{and} \quad \lambda_2 \lambda'_2 \in \Gamma_0^+ \Gamma_0^+$$
or
$$\lambda_1 \lambda'_1 \in \Gamma_0^- \Gamma_0^- \quad \text{and} \quad \lambda_2 \lambda'_2 \in \Gamma_0^- \Gamma_0^-.$$

Thus, the coefficients of the second kind in the development of $P_0(\Omega)$ (those belonging to $\Gamma_0^- \Gamma_0^-$) are actually present in the elastic incoherent scattering law as well as those of the first kind. The probability density $P_0(\Omega)$ can, in principle, be totally determined through the elastic part of incoherent neutron scattering (with the same remark as above with regards to the accuracy of the measure with increasing values of $l$). In fact, the actual determination of the elastic incoherent structure factor $EISF$ raises experimental difficulties. For incoherent scattering, no selection rule over momentum transfer can help to distinguish between the purely elastic peak and the low energy inelastic scattering. In fact, as
$$I_{\text{elic}}^{\lambda}(k) = I(k, 0) - \lim_{\omega \to 0} I(k, \omega),$$
where $I(k, 0)$ and $I(k, \omega)$ are the measured intensities at $\omega = 0$ and in the vicinity of $\omega = 0$, the spectrometer resolution must be accurate enough for this limit to be precisely measured. In particular, this resolution must allow for a separation between the elastic peak and the inelastic one related to the largest relaxation time of the molecular dynamics, a time which is crystal dependent.

Nevertheless, the $EISF$ has been measured by Lechner and Heideman in the case of plastic adamantane (Ref. [3]). The measured $EISF$ was interpreted in terms of dynamical jump rotational models. This analysis allows only to make a distinction between those models which, in fact, underly different forms of the static disorder characterized by $P_0(\Omega)$.

4. Inelastic rotational scattering. — Inelastic neutron scattering involves both the rotational and translational dynamics of the molecules. As mentioned in the introduction, we shall, here, stick to the basic assumption that the rotational motions (librations and orientations) are independent from the centre of mass displacements. In this approximation, the incoherent intensity simply results from the convolution between the translational and the rotational contributions (2.5), the latter term being now studied in more details.

First, we shall consider the s.o.d.f. $P(\Omega_1, \Omega_2, t)$, already defined as being the joint probability for a molecule to have orientation $\Omega_1$ at time $t_1$ and orientation $\Omega_2$ at a later time $t_2 = t_1 + t$. A canonical development of this function on the basis of symmetry adapted function provides a set of coefficients which describe the individual rotational dynamics. The rotational contribution to the incoherent scattering law can then be analysed in terms of these coefficients.

The situation is much more complicated in the case of inelastic coherent scattering, because the latter involves correlations between neighbouring molecule motions. Correlations between the rotational motions of neighbouring molecules can exist, on top of the
always existing ones between translational motions; none of them have anything to do with the main hypothesis of translation-rotation decoupling used throughout this paper. The collective rotational modes and the lattice phonons interfere to produce the \( \vec{k} \) dependence of the detection process and the usual selection rules over phonon wavevectors are no longer valid (see e.g. (2.4)). We shall here restrict ourselves to the simple case where the rotational dynamics of each molecule is assumed to be independent from that of its neighbours.

4.1 THE SELF-ORIENTATIONAL DISTRIBUTION FUNCTION. — 4.1.1 Canonical development for \( P(\Omega_1, \Omega_2, t) \).

In quite a general way, the expansion of \( P(\Omega_1, \Omega_2, t) \), on the symmetry adapted basis, reads

\[
P(\Omega_1, \Omega_2, t) = \sum_{l_1, l_2} B_{l_1 l_2}^{l_1 l_2}(t) A_{l_1}^{l_1}(\Omega_1) A_{l_2}^{l_2}(\Omega_2)
\]

(4.1)

where

\[
\lambda_1 = \Gamma_1, \mu_1, n_1
\]

\[
\lambda'_1 = \Gamma'_1, \mu'_1, n'_1, \text{ etc.}
\]

with the already mentioned meaning for these symbols.

We shall now show that only some of the coefficients \( B(t) \) are different from zero. Before doing that, let us point out that some coefficients are fixed by the equilibrium properties of the crystal. Indeed, some conditions arise from the very definition of \( P(\Omega_1, \Omega_2, t) \).

First, this function is, of course, real and positive. Second, it is related to the static orientational probability through

a) normalization relations

\[
\forall t, \Omega_2 \quad \int P(\Omega_1, \Omega_2, t) \, d\Omega_1 = P_0(\Omega_2) \quad (4.2a)
\]

\[
\forall t, \Omega_1 \quad \int P(\Omega_1, \Omega_2, t) \, d\Omega_2 = P_0(\Omega_1) \quad (4.2b)
\]

b) and limit conditions

\[
P(\Omega_1, \Omega_2, 0) = P_0(\Omega_1) \delta(\Omega_1 - \Omega_2) \quad (4.3a)
\]

\[
P(\Omega_1, \Omega_2, \infty) = P_0(\Omega_2) P_0(\Omega_2) \quad (4.3b)
\]

The mathematical translation of those conditions in terms of relations among the \( B(t) \) coefficients is given in Appendix A. For instance, the last condition (4.3b) which is an ergodicity condition, was already used in part 3 under the form

\[
B_{l_1 l_2}^{l_1 l_2}(\infty) = A_{l_1}^{l_1} A_{l_2}^{l_2}. \quad (4.3b')
\]

Furthermore, some conditions arise from the molecular and site symmetry. Those symmetry conditions determine the selection rules for the combinations \( (\Gamma_1, \Gamma'_1, \Gamma_2^*, \Gamma'_2^*) \) of the representations of \( S_i \) and \( S_o \) which are actually present in the development of

\[
P(\Omega_1, \Omega_2, t).
\]

In fact, the symmetry properties of \( P(\Omega_1, \Omega_2, t) \) are quite analogous to those of the static probability \( P_0(\Omega) \) which were given in detail in I for each case of molecular and site symmetry. Indeed, it is clear that any rotation of the reduced subgroup \( (S_i S_o) \), will leave the dynamical probability invariant, provided that it acts on both the initial orientation \( \Omega_1 \) and the orientation \( \Omega_2 \) at time \( t_1 + t_2 \).

Thus, the canonical development of \( P(\Omega_1, \Omega_2, t) \) involves only those linear combinations of products \( A_{l_1}^{l_1}(\Omega_1) A_{l_2}^{l_2}(\Omega_2) \) which belong to the unity representation of the reduced subgroup \( (S_i S_o) \). Non trivial coefficients \( B_{l_1 l_2}^{l_1 l_2}(t) \) arise only when the product of representations \( \Gamma_1 \Gamma'_1 \Gamma_2^* \Gamma'_2^* \) contains the unity representation of \( (S_i S_o) \). Relying on I, we can derive the number of symmetry independent self-correlation coefficients as follows:

— Whatever may be the site and symmetry groups the unity representation of \( S_i S_o \) induces the unity representation of the subgroup \( (S_i S_o) \). The unity representation of \( S_i S_o \) is included once in the product \( \Gamma_1 \Gamma'_1 \Gamma_2^* \Gamma'_2^* \) if and only if \( \Gamma_1 = \Gamma_2 \) and \( \Gamma'_1 = \Gamma'_2 \). This solution gives a first series of self-correlation coefficients (which will be called \( B^+ \)) for which the selection rules are

\[
\Gamma_2 = \Gamma_1 \quad B^+_{l_1 l_2}^{l_1 l_2}(t) = B^+ \left[ \begin{array}{c} \Gamma_1 \\
\mu_1 \\
\mu'_1 \\
\mu_2 \\
\mu'_2 \\
n_1 \\
_n_2 \\
1_n_1 \\
1_n_2 \\
\end{array} \right] (t) \delta n_1 n_2 \delta n'_1 n'_2. \quad (4.5)
\]

— If the molecular and site symmetry groups contain improper rotations, there is another representation of \( S_i S_o(\Gamma_1^* \Gamma'_1^* \Gamma_2^* \Gamma'_2^* \) which induces the unity representation of \( (S_i S_o) \). The product \( \Gamma_1 \Gamma'_1 \Gamma_2^* \Gamma'_2^* \) contains \( \Gamma_2^* \Gamma_1^* \) once if and only if \( \Gamma_2 = \Gamma_1 \) and \( \Gamma'_2 = \Gamma'_1 \). This solution generates a second series of self-correlation coefficients (which will be called \( B^- \)) for which the selection rules are

\[
\Gamma_2 = \Gamma_1 \quad B^-_{l_1 l_2}^{l_1 l_2}(t) = B^- \left[ \begin{array}{c} \Gamma_1 \\
\mu_1 \\
\mu'_1 \\
\mu_2 \\
\mu'_2 \\
n_1 \\
_n_2 \\
1_n_1 \\
1_n_2 \\
\end{array} \right] (t) \delta n_1 n_2 \delta n'_1 n'_2. \quad (4.6)
\]

4.1.2 Remark and examples. — 4.1.2.1 The coefficients \( B^+ \) (or coefficients of the first kind) arise
Table 1. — Number of independent s.o.d.f. coefficients (for the first value of \( l_1 \) and \( l_2 \)) in the case of site groups \( O_h, D_{4h} \), and molecular group \( T_d \) or \( C_3 \).

<table>
<thead>
<tr>
<th>( l_1, l_2 )</th>
<th>( S.h )</th>
<th>( O_h )</th>
<th>( O_h, C_3v )</th>
<th>( D_{4h}, C_3v )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( l_1 = 1 ) ( l_2 = 1 )</td>
<td>( B^+(F_{1u}, F_2) )</td>
<td>( B^+(F_{1u}, A_1) )</td>
<td>( B^+(A_2u, A_1) )</td>
<td>( B^+(A_2u, E) )</td>
</tr>
<tr>
<td>( l_1 = 1 ) ( l_2 = 2 )</td>
<td>( B^+(F_{1u}, F_2) )</td>
<td>( 2B^+(F_{1u}, A_1) )</td>
<td>( 2B^+(A_2u, A_1) )</td>
<td>( 2B^+(A_2u, E) )</td>
</tr>
<tr>
<td>( l_1 = 1 ) ( l_2 = 3 )</td>
<td>( B^+(F_{1u}, F_2) )</td>
<td>( 2B^+(F_{1u}, A_1) )</td>
<td>( 4B^+(E_u, A_1) )</td>
<td>( 4B^+(E_u, E) )</td>
</tr>
<tr>
<td>( l_1 = 2 ) ( l_2 = 2 )</td>
<td>( B^+(E_u, E) ) ( B^+(F_{2u}, F_2) )</td>
<td>( B^+(E_u, A_1) ) ( 4B^+(E_u, E) )</td>
<td>( B^+(A_2u, A_1) ) ( 4B^+(A_1u, E) )</td>
<td>( B^+(B_1u, A_1) ) ( 4B^+(B_1u, E) )</td>
</tr>
</tbody>
</table>

from the product of one representation \( \Gamma \) of \( S.h \) by the conjugate representation \( \Gamma^* \) \( \Gamma' \). The coefficients of the second kind arise from the product of \( \Gamma \) \( \Gamma' \) with another associated representation \( \Gamma_0^{-*} \Gamma_0^{-*} \Gamma_1^{-*} \Gamma_1^{-*} \).

4.1.2.2 For a given value of the indices \( l_1 \) and \( l_2 \), a representation \( \Gamma' \) of \( S.h \) generates \( v_1 v_1' v_2 v_2' \) independent \( B^+ \) coefficients if the manifold \( \left\{ Y_{\mu_m}^\alpha \right\} \) included \( v_1 \sim \Gamma \) subspaces \( v_1' \sim \Gamma' \) subspaces \( v_2 \sim \Gamma \) subspaces \( v_2' \sim \Gamma' \) subspaces. The number of \( B^+ \) coefficients can be evaluated in a similar way. It is noteworthy that when one of the molecular and site symmetry groups is a centred group, the self-correlation coefficients are all of the first kind if \( h \) and \( l_2 \) have the same parity and all of the second kind on the other case.

4.1.2.3 We shall illustrate the preceding procedure and remarks by studying a few examples for which the molecular and site symmetry groups correspond to the plastic phases of \( \alpha \) neopentane \((S = O_h, .h = T_d)\), \( \beta \) high-temperature tertiobutylchlorine \((S = O_h, .h = T_d)\), and \( \gamma \) low temperature tertiobutylchlorine \((S = D_{4h}, .h = C_3v)\) all cases which have been considered in I.

Note that (see Appendix) the self-correlation coefficients for \( l_1 = 0 \) and \( l_2 = 0 \) are constant in time and given by

\[
B_{01}^{1,1} = A_{l_1}^{1,1} \quad (4.7a)
\]
\[
B_{00}^{1,1} = A_{l_1}^{1,1} \quad (4.7b)
\]

Table II of I gives, for the first values of \( l \), the decomposition of \( \left\{ Y_{\mu_m}^\alpha \right\} \) into irreducible subspaces for the group \( O_h, T_d, C_3v \), and \( D_{4h} \). From this, we can list in table I the first independent self-correlation coefficients.

4.1.2.4 Another case is that of molecular liquids. The site group is the full rotational group, the irreducible subspaces of which are the \( \left\{ Y_{\mu_m}^\alpha \right\} \) subspaces themselves. Thus independent self-correlation coefficients arise only when \( l_1 = l_2 \) and they are all of the first kind. The selection rule can be written

\[
B_{l_1}^{l_1} \delta_{l_2}^{l_2} (t) = \mathcal{B} \begin{bmatrix} l_1' \\ \mu_1' \\ \mu_2' \\ l_2' \\ \delta l_1' l_2' \delta m_1 m_2 \delta n_1 n_2 \end{bmatrix} \quad \text{with} \quad l_1' = l_2', \quad l_2' = l_2' \quad (4.8)
\]
a result which may be compared to the work of V. F. Sears (Ref. [14]).

4.1.3 Orientational self-correlation function. — Any molecular property, \( F(t) \), which depends on time through the molecular orientation \( \mathbf{Q}(t) \) can be expanded on the basis of symmetry adapted function \( \mathcal{F}^{l_2,l_2} (\mathbf{Q}(t)) \). The rotational self-correlation function \( \mathcal{F}^{l_2,l_2} (\mathbf{Q}(t)) \) thus appears as a linear combination of basic correlation functions \( \mathcal{F}^{l_2,l_2} (\mathbf{Q}(t)) \) which are nothing but the self-correlation coefficients \( B(l) \). Indeed,

\[
\langle \mathcal{F}^{l_2,l_2} (\mathbf{Q}(t)) \mathcal{F}^{l_2,l_2} (\mathbf{Q}(t)) \rangle = \int \mathcal{F}^{l_2,l_2} (\mathbf{Q}(t)) \mathcal{F}^{l_2,l_2} (\mathbf{Q}(t)) \mathcal{P} (\mathbf{Q}_1, \mathbf{Q}_2, t) \, d\mathbf{Q}_1 \, d\mathbf{Q}_2 =
\]
\[
B^{l_1,l_2} (t) \times \frac{1}{(2l_1 + 1)(2l_2 + 1)} \quad (4.9)
\]
The formalism developed in here, relying only on symmetry considerations, yields the maximum number of independent rotational self-correlation functions. A model for the rotational dynamics of the molecules is of course required to further predict the time behaviour of those correlation functions. The result obtained, with regards to the number of independent correlation functions, can be compared with previous works on molecular systems where rotational correlation functions have been evaluated in the framework of a particular dynamical model. For instance, P. Rigny (Ref. [7]) and Thibaudier and Volino (Ref. [8]) assumed for the rotational dynamics a jump diffusion model where the molecules are allowed to perform instantaneous rotations which belong to a certain point group. This model assigns to each possible reorientation jump a probability which is independent from the initial orientation of the molecule; this hypothesis reduces further the number of independent self-correlation functions. Volino and Dianoux (Ref. [9]) evaluated rotational correlation functions for the diffusion motion of a uniaxial rotator in a N-fold cosine potential. Their method could be generalized to a three dimensional rotator in a potential with a given symmetry, and lead, again, to a reduction of the independent coefficients entering into correlation functions.

4.2 Incoherent inelastic scattering. — With the basic approximation of complete decoupling between the translational and rotational dynamics of the molecules, the rotational contribution to incoherent scattering is given by (2.18) which in view of (4.9) can be rewritten as

$$I_{\text{rot}}(k, t) = \sum_{\tau}^\prime S_{\tau}^{2i}(k) S_{\tau}^{2j}(k) H_{\tau 1 \tau 2}^{2i 2j}(k) B_{\tau 1 \tau 2}^{2i 2j}(t). \tag{4.10}$$

In (4.10) the selection rules arising from the molecular symmetry of $H_{\tau 1 \tau 2}^{2i 2j}(k)$ must be combined with those of the self-correlation coefficients $B$. Due to (2.20), (4.5) and (4.6) one easily finds that incoherent rotational scattering involves a priori all the self-correlation coefficients of the first kind $B^*$. The second kind coefficients $B^-$ are thus unobservable through incoherent neutron scattering. As in the case of elastic scattering, in a powder experiment, only the diagonal coefficients $B^*$, which satisfy the additional rules $l_1 = l_2$ and $k_1 = k_2$, will be measured.

4.3 Coherent inelastic scattering. — As previously said, we confine ourselves here to the case where the rotational dynamics of neighbouring molecules are not correlated. In that case, there still coherence between the scattering from the different nuclei inside the molecule, but the contribution of different molecules are now incoherent. The selection rule over momentum transfer $k$ is now lost and the product of a translational term (which is identical to the incoherent translational term) with a rotational term

$$I_0(k, t) = N \int_{\text{trans}}(k, t, L, L' = L) \times I_0^\text{rot}(k, t, L' = L). \tag{4.11}$$

The rotational term is given by (2.6) where one sets

$$L = L'$$

and in view of (4.9) one obtains

$$I_{\text{rot}}^\text{rot}(k, t) = \sum_{\tau}^\prime S_{\tau}^{2i}(k) S_{\tau}^{2j}(k) G_{\tau}^{2i}(k) G_{\tau}^{2j}(k) B_{\tau 1 \tau 2}^{2i 2j}(t). \tag{4.12}$$

Owing to the selection rules implied by the molecular symmetry of $G_{\tau}^{2i}$ and $G_{\tau}^{2j}$, the above rotational term involves only the self-correlation coefficients $B$ which arise from the identity representation of the molecular symmetry group.

4.4 Discussion. — Once deconvoluted from the translational phonon spectrum, the quasi-elastic part of neutron scattering essentially reflects the rotational dynamics of the molecules. The above formalism allows to derive which are the basic rotational correlation functions actually measured through neutron scattering experiments performed on single crystals or powder samples. The symmetry of the problem a priori implies non trivial correlation functions, $B^+ \neq B^-$, for the two representations of the product group $S.M$, which induce the unity representation of the subgroup $(S.M)_\tau$. Nevertheless, inelastic neutron scattering involves only the functions $B^+$ which are in the unity representation of $S.M$; the other one $B^-$ being unobservable by this technique.

In this paper, the neutron coherent and incoherent cross sections have been analysed in terms of symmetry adapted functions in the general case of three dimensional molecules. This formalism can also be applied to the simpler case of linear molecules (see Appendix B). This leads in particular to an analysis of incoherent scattering which quite agrees with the work of B. de Raedt and K. H. Michel (Ref. [11]) concerning the rotational scattering arising from CN$^-$ impurities in an octahedral crystalline field.

All this study relies only on symmetry considerations and assumes nothing about the actual rotational dynamics of the molecules. In any actual experiment, a dynamical model must be introduced and its prediction compared to the time behaviour of the measured $B^+$ correlation functions. These models can include, in particular, librations around fixed orientations as well as finite time large angle reorientations. In other words, the self-correlation coefficients $B$...
5. Conclusion. — The formalism of symmetry adapted functions which has been developed here allows for a precise analysis of the various informations arising from neutron scattering experiments on powder or single crystals of ODIC phases. In particular, it shows that the number of independent informations which can be obtained, even in quasi-elastic incoherent scattering, depend on the symmetry of the molecule and of the site, a point which might have not been fully recognized up to now. The same method can, of course, be applied to analyse data arising from other experimental techniques, and in the third paper of this series we shall apply it to Raman and infrared spectroscopy of plastic phases. The virtue of this method is to allow for a straightforward comparison between informations provided by different techniques, a point which may turn out to be very useful in ODIC phases.

Appendix A. — ADDITIONAL RULES FOR THE s.o.d.f. COEFFICIENTS. — The normalization and limit conditions (4.2 and 4.3) fulfilled by the s.o.d.f. P(Q1, Q2, t), implies some restrictive conditions on the time behaviour of self-correlation coefficients. These conditions are derived below.

1. Let us first introduce G(Q1, Q2, t) the conditional probability of finding a molecule with orientation Q2 at time t if it had orientation Q1 at time zero.

This function is, of course, related to P(Q1, Q2, t) through the relation

\[ P(Q_1, Q_2, t) = P_0(Q_1) G(Q_1, Q_2, t) \] (A.1)

and satisfies the normalization and limit conditions

\[ P_0(Q_1) G(Q_1, Q_2, t) \, dQ_1 = P_0(Q_2) \] (A.2a)

\[ \int G(Q_1, Q_2, t) \, dQ_2 = 1 \] (A.2b)

\[ G(Q_1, Q_2, 0) = \delta(Q_1 - Q_2) \] (A.3a)

\[ G(Q_1, Q_2, \infty) = P_0(Q_2) \] (A.3b)

The conditional probability \( G(Q_1, Q_2, t) \) can be developed over the canonical basis :

\[ G(Q_1, Q_2, t) = \sum C_{l_1 l_2}^{j_1 j_2 j_3} A_{l_1 l_2}^{j_1 j_2 j_3}(Q_1) A_{j_2 j_3}(Q_2), \]

\( G(Q_1, Q_2, t) \) obviously has the same symmetry properties as \( P(Q_1, Q_2, t) \) and the \( C \) coefficients follows the selection rules given in 4 for the \( B \) coefficients.

The relation (A.1) can be expressed in terms of relations among the coefficients \( A, B(t), C(t) \) of the canonical developments of \( P_0(Q) \), \( P(Q_1, Q_2, t) \) and \( G(Q_1, Q_2, t) \) :

\[ B_{L_1 l_2}^{A_1 A_2 j_1 j_2 j_3}(t) = \sum_{l_{12} l_{12} l_{12}} \begin{pmatrix} A_1 & A_2 & j_1 & j_2 & j_3 \\ L_1 & l_{12} & l_{12} & l_{12} \end{pmatrix} \begin{pmatrix} \lambda^{j_2 j_3} \\ \lambda^{l_{12} l_{12} l_{12}} \\ \lambda^{l_{12} l_{12} l_{12}} \end{pmatrix} A_{l_{12} l_{12} l_{12}}^{j_1 j_2 j_3}(t) \] (A.4)

where

\[ \begin{pmatrix} A_1 & A_2 & j_1 & j_2 & j_3 \\ L_1 & l_{12} & l_{12} & l_{12} \end{pmatrix} \]

is derived from usual Clebsch-Gordon coefficients \( (LM \mid l_{12} m_l m_m) \), and from the \( \alpha \) and \( \beta \) coefficients which define the symmetrized spherical harmonics related to the site and molecular symmetry group :

\[ \begin{pmatrix} A_1 & A_2 & j_1 & j_2 & j_3 \\ L_1 & l_{12} & l_{12} & l_{12} \end{pmatrix} = \sum_{M_1, M_2, M_3, M_4} (\alpha_{l_{12} l_{12} l_{12}}^{l_{12} l_{12} l_{12}}) \times (\beta_{l_{12} l_{12} l_{12}}^{l_{12} l_{12} l_{12}}) \times (L_1 \mid M_1 \mid l_{12} m_l m_m) \times (L_1 \mid M_2 \mid l_{12} m_l m_m) \times (A.5) \]

2. We can now express the normalization and limit conditions in terms of the \( B(t), C(t) \) and \( A(t) \) coefficients — relation (4.2a) and (A.2a)

\[ \forall t \quad B_{j_{12}}^{A_1 A_2 j_1 j_2 j_3}(t) = A_{l_{12} l_{12} l_{12}}^{j_1 j_2 j_3} \quad \text{and} \quad \sum_{l_{12} l_{12} l_{12}} \begin{pmatrix} \lambda^{j_1 j_2 j_3} \\ \lambda^{l_{12} l_{12} l_{12}} \\ \lambda^{l_{12} l_{12} l_{12}} \end{pmatrix} A_{l_{12} l_{12} l_{12}}^{j_1 j_2 j_3}(t) = A_{j_{12} j_{12}}^{j_1 j_2 j_3} \] (A.6)
— relation (4.2b) and (A.2b)

\[ B_{i1}^{(1)}(t) = A_{i1}^{(1)}(t) \quad C_{i2}^{(1)}(t) = \delta(l_1, 0); \quad (A.7) \]

— relation (4.3a) and (A.3a)

\[ B_{i1}^{\xi_1 \xi_2}(0) = \sum_{l_1 \xi_1} \left( \begin{array}{c} \xi_1 \\ l_1 \end{array} \right) \left( \begin{array}{c} \xi_2 \\ l_2 \end{array} \right) A_{i1}^{\xi_1 \xi_2}(0) = \delta(l_1, 0) \delta(l_2, 0) \delta(\xi_1, \xi_2); \quad (A.8) \]

— relation (4.3b) and (A.3b)

\[ B_{i1}^{\xi_1 \xi_2}(x) = \sum_{l_1, l_2} A_{i1}^{\xi_1 \xi_2}(x) C_{i2}^{(1)}(0) = \delta(l_1, 0) A_{i2}^{\xi_1 \xi_2}(x); \quad (A.9) \]

3. Conclusion. — The consequences of the normalization and limit conditions (4.2 and 4.3) fulfilled by the s.o.d.f. \( P(\Omega_1, \Omega_2, t) \) are easily drawn in terms of the \( B \) coefficients:

— At initial time \((t = 0)\) every \( B \) coefficients which satisfy the symmetry selection rules can \( a \ p r i o r i \) be non zero. Nevertheless, their values are not independent, and are, in fact, completely fixed by the value of the \( A \) coefficients (cf. (A.8)).

— At infinite time, only these \( B \) coefficients which arise from products of the two allowed representations \( \Gamma_0^+ \Gamma_0^-, \Gamma_0^- \Gamma_0^- \) have a non zero limit (A.9).

— At intermediate time, it turns out that only very few constraints on these \( B \) coefficients. One is that the \( l_1 = 0 \) and \( l_2 = 0 \) coefficients is constant; the other, which is in fact difficult to impose, is that \( P(\Omega_1, \Omega_2, t) \geq 0, \forall \Omega_1, \Omega_2 \text{ and } t. \)

Appendix B. — The case of linear molecules. — In order to compare our result concerning incoherent rotational neutron scattering with those of B. de Raedt and K. H. Michel (Ref. [11]), we show in here how the general formalism can be applied to the special case of a linear molecule.

1. Let us consider a linear molecule. We can choose the molecular axis \( \{ x, y, z \} \) in such a way that the \( z \) axis coincides with the \( \text{C}_\infty \) molecular axis. The orientation of the molecular axis in the crystal system is described through the three Euler angles \( \Omega = (\psi, \theta, \phi) \); only \( \theta \) and \( \psi \) are relevant to describe the orientation of the \( \text{C}_\infty \) molecular axis, the spherical coordinates of which, \((\Theta, \Phi)\), are:

\[ \begin{align*}
\Theta &= \theta \\
\Phi &= \psi - \pi/2.
\end{align*} \quad (B.1) \]

The symmetry group of a linear molecule is either \( \text{D}_{\infty h} \) if the molecule has an inversion centre or \( \text{C}_{\infty v} \) otherwise. The irreducible representations of these groups are given, for example, in reference [13].

It is easily seen that for each value of \( l \), the space \( \{ Y_l^m, m = -l, \ldots, +l \} \) splits into irreducible subspaces of \( \text{C}_{\infty v} \) as follows:

\[ \begin{align*}
\text{for } m = 0 & \quad Y_0^0 \text{ transform according to the identity representation } \Gamma_0^+ \text{ of } \text{C}_{\infty v}; \\
\text{for } m \neq 0 & \quad \{ Y_l^m, Y_l^{-m} \} \text{ transform according to a two dimensional representation of } \text{C}_{\infty v}, \Gamma_m; \text{ depending only on the value of } m.
\end{align*} \]

The irreducible subspaces with respect to \( \text{D}_{\infty h} \) are:

\[ \begin{align*}
\{ Y_l^0 \} & \text{ which transform according to the identity representation, } \Gamma_0^+, \text{ of } \text{D}_{\infty h} \text{ for even } l \text{ and according to } \Gamma_0^- \text{ for odd } l; \\
\text{and } \{ Y_l^m, Y_l^{-m} \} & \text{ with } m \neq 0, \text{ which transform according to a two dimensional representation, } \Gamma_{m_e} \text{ or } \Gamma_{m_o}, \text{ of } \text{D}_{\infty h}, \text{ according to the parity of } l.
\end{align*} \]

Thus, according to the definition of paper I, the symmetry adapted functions for a \( \text{C}_{\infty v} \) or a \( \text{D}_{\infty h} \) molecule in a site of symmetry \( S \) are:

\[ A_l^m(\Omega) = \sum_{m'} \alpha_{lm} D_{lm'}^m(\Omega). \quad (B.2) \]

However, as long as we consider linear molecule as rigid unit (in particular with no bending modes), the molecular orientation is fully described by the two Euler angles \( \theta \) and \( \psi \), and we can restrict the set of symmetry adapted functions to those which are independent of the third Euler angle \( \phi \). These relevant functions are
obtained for \( m' = 0 \) and they are just proportional to the surface harmonics \( S^i_j \) related to the site symmetry group:

\[
D^m\omega(\psi, \theta, \varphi) = \sqrt{\frac{4\pi}{2l+1}} Y^m\omega(\Theta, \Phi) \quad (B.3a)
\]
\[
A^m\omega(\psi, \theta, \varphi) = \sqrt{\frac{4\pi}{2l+1}} S^i_j(\Theta, \Phi) . \quad (B.3b)
\]

2. We shall now restrict in here to the case of a dumbbell (\( \mathcal{D}_{\alpha\beta} \)) molecule in a site of symmetry group \( S \) containing improper rotations. The other cases could be treated in the same way.

— The pdf \( P_0(\Omega) \). — According to I, the development of \( P_0(\Omega) \) involve only functions of the representation \( \Gamma^r_0 \Gamma^s_0 \) or \( \Gamma^r_0 \Gamma^s_{-} \) of \( \mathcal{D}_{\alpha\beta} \), therefore \( P_0(\Omega) \) writes

\[
P_0(\Omega) = \sum_{\lambda_0 \in \Gamma^r_0} A^{\lambda_0_0}_l A^{\lambda_0_0_0}_0(\Omega) + \sum_{\lambda_0 \in \Gamma^r_0} A^{\lambda_0_0}_l A^{\lambda_0_{-}0}_0(\Omega) \quad (B.4a)
\]

which in view of (B.3) gives

\[
P_0(\Theta, \Phi) = \sum_{\lambda_0 \in \Gamma^r_0} a^{\lambda_0_0}_l S^j_i(\Theta, \Phi) + \sum_{\lambda_0 \in \Gamma^r_0} a^{\lambda_0_{-}0}_l S^j_i(\Theta, \Phi) . \quad (B.4b)
\]

— The s.o.d.f. \( P(\Omega_1, \Omega_2, t) \). — According to (B.2) the development of \( P(\Omega_1, \Omega_2, t) \) writes

\[
P(\Omega_1, \Omega_2, t) = \sum_{l_1 l_2} B^\pm_{l_1 l_2} A^i_{l_1} A^i_{l_2}(\Omega_1) A^i_{l_1} A^i_{l_2}(\Omega_2) . \quad (B.5a)
\]

As usual, we set

\[
I_1 = \Gamma_1, \mu_1, n_1 \\
I_2 = \Gamma_2, \mu_2, n_2 .
\]

The application of the selection rules derived in part 4 to the groups \( \mathcal{S} \) and \( \mathcal{D}_{\alpha\beta} \) gives:

\[
\begin{cases}
I_2 = \Gamma_1 \\
\left( -1 \right)^{l_1 + l_2} = 1 \\
\left( -1 \right)^{l_1 + l_2} = 1 \\
\end{cases}
\]

\[
B^\pm_{l_1 l_2} = B^\pm_{\Gamma_1} \left( \begin{array}{c} \Gamma_1 m' \\ \mu_1 \mu_2 \end{array} \right) (t) \delta n_1 n_2
\]

or

\[
\begin{cases}
I_2 = \Gamma_0 \Gamma_1 \\
\left( -1 \right)^{l_1 + l_2} = -1 \\
\end{cases}
\]

\[
B^\pm_{l_1 l_2} = B^\pm_{\Gamma_1} \left( \begin{array}{c} \Gamma_1 m' \\ \mu_1 \mu_2 \end{array} \right) (t) \delta n_1 n_2 . \quad (B.5b)
\]

These selection rules ensure that \( P(\Omega_1, \Omega_2, t) \) does not depend on both Euler angles \( \varphi_1 \) and \( \varphi_2 \) but only on the difference \( \varphi = \varphi_1 - \varphi_2 \) which is in agreement with the \( \mathcal{D}_{\alpha\beta} \) molecular symmetry. However for a rigid linear molecular, the \( \varphi \) dependence has no sense and in view of (B.3) the development of the s.o.d.f. can be restricted to

\[
P(\Omega_1, \Omega_2, t) = \sum_{l_1 l_2} b^\pm_{l_1 l_2}(t) S^i_{l_1}(\Theta_1, \Phi_1) S^i_{l_2}(\Theta_2, \Phi_2) \quad (B.6a)
\]

where

\[
b^\pm_{l_1 l_2}(t) = b^\pm_{\Gamma_1} \left( \begin{array}{c} \Gamma_1 \\ \mu_1 \mu_2 \end{array} \right) (t) \delta n_1 n_2
\]

with

\[
\Gamma_2 = \Gamma_1, (-1)^{l_1 + l_2} = 1 \
\Gamma_2 = \Gamma_0 \Gamma_1, (-1)^{l_1 + l_2} = -1
\]

for \( b^+ \) coefficients

\[
\Gamma_2 = \Gamma_0 \Gamma_1, (-1)^{l_1 + l_2} = 1 \
\Gamma_2 = \Gamma_0 \Gamma_1, (-1)^{l_1 + l_2} = -1
\]

for \( b^- \) coefficients.

Once more, we underly here that the independent coefficients \( b^\pm_{l_1 l_2}(t) \) of the s.o.d.f. \( P(\Omega_1, \Omega_2, t) \) are just proportional to the different correlation functions of the molecular axis orientation

\[
b^\pm_{l_1 l_2}(t) = \left< S^i_{l_1}(\Theta_1(0), \Phi_1(0)) S^i_{l_2}(\Theta_2(t), \Phi_2(t)) \right> \quad (B.7a)
\]
which, in agreement with reference [11], can be written in a shortway:

\[ b_{12}^{+} = \langle S_1^{+0}(0) S_2^{0}(t) \rangle. \]  

(B.7b)

—the elastic and quasi-elastic neutron cross section. — For every atom \( j \) of a linear molecule we have

\[ Y_{nm}(r_j) = \pm \delta m' 0 \sqrt{\frac{2l + 1}{4\pi}}. \]  

(B.8)

Thus, the factors \( G(k) \) and \( H(k) \), characteristic of the molecular symmetry, and introduced in (2.17) and (2.19) are:

- for \( l \) odd \( G_{n}^{m}(k) = 0 \) \hspace{1cm} (B.9a)
- for \( l \) even \( G_{n}^{m}(k) = \sqrt{\frac{4\pi(2l + 1)}{2}} g_{\delta}^{m-\delta} 0 \) \hspace{1cm} (B.9b)

with

\[ g_{\delta}^{m-\delta} = i \left( \sum_{\delta' \delta''} h_{\delta'}^{m-\delta''} \right) \]  

(B.9c)

for \((-1)^{l_1 + l_2} = -1 \) \hspace{1cm} (B.10a)

for \((-1)^{l_1 + l_2} = 1 \)

Then, from (2.16) and (2.18), the rotational part of neutron coherent and incoherent scattering law writes:

\[ I_{c}^{m}(k, t, L, L') = 16 \pi^{2} \sum_{\text{even } l_1, l_2} \sum_{\text{even } \delta, \delta'} g_{\delta}^{m-\delta} g_{\delta'}^{m-\delta'} S_{1}^{l_1 \delta}(k) S_{2}^{l_2 \delta'}(k) \langle S_{1}^{l_1 \delta}(0)* S_{2}^{l_2 \delta'}(t) \rangle \]  

(B.11a)

and

\[ I_{i}^{m}(k, t) = 16 \pi^{2} \sum_{\text{even } l_1, l_2} \sum_{\text{even } \delta, \delta'} h_{\delta}^{m-\delta} g_{\delta}^{m-\delta} S_{1}^{l_1 \delta}(k) S_{2}^{l_2 \delta}(k) \langle S_{1}^{l_1 \delta}(0)* S_{2}^{l_2 \delta}(t) \rangle \]  

(B.11b)

with \((-1)^{l_1 + l_2} = 1 \).

Let us consider the incoherent scattering. The symmetry of \( P(\Omega_1, \Omega_2, t) \) leads to the selection rule \( \Gamma_1 = \Gamma_2 \) in the formula (B.11b) and we recover here the results of K. H. Michel and B. de Raedt (cf. to formula (3.6) of reference [11]). Furthermore, the elastic part of the scattering is submitted to the selection rule arising from \( P_0(\Omega_1) \) and \( P_0(\Omega_2) \) which leads to \( \Gamma_1 = \Gamma_2 = \Gamma_0 \) or \( \Gamma_1 = \Gamma_2 = \Gamma_0^* \).

References


References