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Rotational Displacements in Crystals

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The problem of random rotational displacement is solved and the theory of Brownian motion of molecules in crystals is developed. The probability distribution of orientations of a molecule is found as a decomposition into matrix elements of irreducible representations of point groups.

KEY WORDS: Rotational Brownian motion; rotational displacements.

1. The problem of rotational displacements of a Brownian particle in a liquid was solved, in general form, in Ref. 1. Characteristic details of the theory of rotational motion are revealed more distinctly in a two-dimensional model, with rotational displacements occuring around one axis.(2) The solution of the problem of rotational movement(1,2) has found wide application in the study of magnetic relaxation, light scattering, and slow neutron scattering in liquids.

The problem of rotational displacements of molecules in crystals has its own peculiarities because of which the general solution,(1) in this case is inconvenient for practical calculations. When considering light scattering(2) and nuclear magnetic relaxation(3) in molecular crystals it is possible to use only the solution for the two-dimensional problem; actually, in real crystals reorientations around several axes are possible with, generally speaking, different activation energies corresponding to axes of different orders. The latter circumstance leads to reorientational probabilities which are different for different axes.

In the present work the solution of the problem of random rotational displacement in crystals is given. Physical conditions for the theory are as follows. The molecule under consideration is considered to have equilibrium

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orientations determined by the symmetry of the environment. The jumps of molecules from one equilibrium orientation to another are caused by random rotational movements due to thermal motion. The probability of transition p from one orientation to another is assumed known.

The set of symmetry operations corresponding to jumps evidently forms some point group. The problem lies in determining the distribution of orientation probabilities of the molecule at a time t, the initial distribution having been given.

2. Let $W(g, t)$ be the probability of orientation we wish to determine at a time t, with $g \in G$ (G is a point group). The determination of $W(g, t)$ is performed in two steps. First, the probability distribution of the orientation of the molecule after N jumps, $P(g, N)$, is calculated. Then, postulating some analytic expression (Poisson distribution) for the probability of N jumps occurring in time, t, $W(g, t)$ is determined.

Assume that the probability p of transition depends only upon initial orientation k and final orientation g, i.e., $p = p(k, g)$. If $P(k, N-1)$ is the distribution of probabilities of orientations after $N-1$ jumps, then we have

$$P(g, N) = \sum_{k \in G} p(k, g)\, P(k, N-1) \tag{1}$$

This equation serves as a basis for the determination of $P(g, N)$.

Assume now that the probability $p(k, g)$ depends only upon the rotation g_1 that causes orientation k to transfer into g. i.e., $p(k, g) = p(g_1)$. Let $\tau(g_1)$ be an operator transforming $P(k, N-1)$ into $P(g, N-1)$:

$$P(g, N-1) = \tau(g_1)\, P(k, N-1) \tag{2}$$

Using Eq. (2), Eq. (1) may be represented as follows:

$$P(g, N) = \sum_{g_1 \in G} p(g_1)\, \tau^{-1}(g_1)\, P(g, N-1) \tag{3}$$

Since $P(g, N)$ and $P(g, N-1)$ are functions on the group G, they can be presented as a decomposition of the irreducible representations of the group G over matrix elements$^{(4)}$:

$$P(g, N) = \sum_{lmn} C^{l}_{mn}(N)\, \tau^{(l)}_{mn}(g) \tag{4}$$

where l is the dimension of the irreducible representation. The decomposition for $P(g, N-1)$ is similar. Substituting these decompositions into (3), we find

$$\sum_{lmn} C^{l}_{mn}(N)\, \tau^{(l)}_{mn}(g) = \sum_{lmn} \sum_{g_1 \in G} p(g_1)\, \tau^{-1}(g_1)\, C^{l}_{mn}(N-1)\, \tau^{(l)}_{mn}(g) \tag{5}$$

The transformation law for matrix elements $\tau^l_{mn}(g)$ of an irreducible representations is

$$\tau(g_1^{-1})\,\tau^{(l)}_{mn}(g) = \sum_s \tau^{(l)}_{ms}(g_1^{-1})\,\tau^{(l)}_{sn}(g) \tag{6}$$

Taking into account the completeness of the function $\tau^{(l)}_{mn}(g)$, and using Eq. (6), we have equations for determining the coefficients C^l_{mn} in (5):

$$C^l_{mn}(N) = \sum_s \sum_{g_1 \in G} p(g_1)\,\tau^{(l)}_{sm}(g_1^{-1})\,C^l_{sn}(N-1) \tag{7}$$

Define the matrix A_l :

$$A_l{}^T \equiv \sum_{g_1 \in G} p(g_1)\,\tau^{(l)}(g_1^{-1}) \tag{8}$$

where the superscript T denotes the transpose. So from (7) we have

$$C^l_{mn}(N) = \sum_s (A_l{}^T)_{sm}\,C^l_{sn}(N-1) \tag{9}$$

Equation (9) can be presented conveniently in matrix form:

$$C^l(N) = A_l{}^T C^l(N-1) \tag{10}$$

From this equation we can easily find

$$C^l(N) = (A_l{}^T)^N C^l(0) \tag{11}$$

The matrix $C^l(0)$ in (11) is determined from the decomposition of the initial distribution $P(g, 0)$ over $\tau^{(l)}_{mn}(g)$. For a fixed initial orientational distribution, $P(g, 0)$ has the following form:

$$P(g, 0) = \delta(g, g_0) \tag{12}$$

where $\delta(g, g_0)$ is the Kronecker symbol. Decomposing (12) over $\tau^{(l)}_{mn}(g)$, we have

$$\delta(g, g_0) = \sum_{lmn} C^l_{mn}(0)\,\tau^{(l)}_{mn}(g) \tag{13}$$

Multiplying (13) by $\overline{\tau^{(r)}_{pq}(g)}$ (the bar denotes complex conjugate) and summing over all elements of the group G, we find

$$C^l_{mn}(0) = (l/\mathcal{N})\,\overline{\tau^{(l)}_{mn}(g_0)} \tag{14}$$

We have used the orthogonality relation for dunctions $\overline{\tau^{(l)}_{mn}(g_{mn})}$:

$$\sum_{g\in G} \tau^{(l)}_{mn}(g)\,\overline{\tau^{(r)}_{pq}(g)} = (\mathcal{N}/l)\,\delta_{mp}\delta_{nq}\delta_{lr} \tag{15}$$

Substituting (14) into (11) and (11) into (4), we obtain

$$P(g, N) = (1/\mathcal{N}) \sum_{lmns} \overline{l\tau^{(l)}_{sn}(g_0)}[(A_l{}^T)^N]_{ms}\,\tau^{(l)}_{mn}(g) \tag{16}$$

The latter equation can be also written as

$$P(g, N) = (1/\mathcal{N}) \sum_{l} l\,\mathrm{Sp}[\tau^{(l)}(g_0^{-1})(A_l{}^T)^N\,\tau^{(l)}(g)] \tag{17}$$

The result is an exact solution to the problem of rotational displacements.

3. In practical calculations it is necessary to have the distribution of orientations $W(g, t)$. To determine $W(g, t)$, the number of jumps N for a time t is assumed to obey Poisson's law

$$w_N(t) = (N!)^{-1}\,(t/\tau)^N\,e^{-t/\tau} \tag{18}$$

where τ is the mean time between two subsequent jumps. Weighting (17) by the distribution (18) and summing from 0 to infinity, we obtain

$$W(g, t) = \sum_{l} (l/\mathcal{N})\,\mathrm{Sp}\{\tau^{(l)}(g_0^{-1})\exp[-(t/\tau)(1 - A_l)]\,\tau^{(l)}(g)\} \tag{19}$$

where g_0 is the initial orientation, where $g_0, g \in G$. Relation (19) is the required result.

It easy to verify that both $P(g, N)$ and $W(g, t)$ obey the normalization conditions

$$\sum_{g\in G} P(g, N) = 1, \qquad \sum_{g\in G} W(g, t) = 1 \tag{20}$$

4. The distribution $W(g, t)$ includes orientations g belonging to group G. When calculating correlation functions, we integrate over all g from the continuous group of rotations R. So it is useful to rewrite $W(g, t)$ as

$$W(g, t) = (1/\mathcal{N}) \sum_{h\in G} \delta(g - h) \sum_{l} l\,\mathrm{Sp}\{\tau^{(l)}(g_0^{-1})\exp[-(t/\tau)(1 - A_l)]\,\tau^{(l)}(h)\} \tag{21}$$

Here $g_0 \in G$, but g belongs to group R. In (21) $\delta(g - h)$ denotes the ordinary delta-function. The distribution in (21) obeys the normalization condition

$$\int_R W(g, t)\, dg = 1 \tag{22}$$

5. In the present work the theory of Brownian rotational motion of molecules in crystals has been developed. The distribution obtained, $W(g, t)$ in (21), can be directly used in calculating correlation functions for random functions defined by molecular orientations. Actual calculations of correlation function will be performed later when considering magnetic relaxation and light scattering in molecular crystals.

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