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# The X-ray Scattering from a Hindered Rotator*

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An expression is derived for the X-ray scattering from a crystal containing groups of atoms in hindered rotation about fixed axes. A Maxwell–Boltzmann distribution of the orientation angles of the groups is assumed, with a sinusoidally varying hindering potential.

Although a corresponding expression is not derived for the hindered rotator without a fixed axis, it is shown that structure-factor data in the particular case of perfluorocyclohexane lead to the conclusion that the molecule is not a free rotator in the crystal, but either may be a hindered rotator or may show orientational disorder.

Heretofore, the problem of the intensity of X-ray scattering from a crystal containing rotating groups has been solved only in the case in which the groups rotate without hindrance or other influence on each other. Expressions for the X-ray scattering under such conditions have been given by Coster (1919), Kolkmejer (1920), Bijvoet & Ketelaar (1932), Finbak (1938), and Zachariasen (1945, pp. 223 ff.). Although the case of the hindered rotator is of great interest in crystallography, the calculation of the intensity of X-ray scattering from a crystal containing groups in hindered rotation has not been made heretofore.

In the first part of this paper, an expression for the amplitude of X-ray scattering for a particular case of the hindered rotator will be derived. The group of atoms will be considered to rotate about a fixed axis with a hindering potential varying sinusoidally with the angle of rotation. The rotator will be considered as a classical rotator with a Maxwell–Boltzmann distribution in the probability function of the rotation angle.

Since, according to Zachariasen (1945, p. 213), the amplitude of Laue–Bragg scattering from a crystal containing rotating groups may be calculated as the complex sum of the average amplitudes of scattering from each of the atoms, disregarding the way in which the atoms are linked into groups, the problem reduces to the calculation of the X-ray scattering from a single atom in hindered rotation.

No expression was derived for the X-ray scattering from the hindered rotator without a fixed axis, because of the great variety of potential functions which might be assumed. However, in the second part of this paper, the special case of rotation of molecules of perfluorocyclohexane in the crystalline state will be treated. It will be shown that the observed structure factors do not agree with the structure factors calculated for free rotation of the molecules, the discrepancy being in the direction to be expected if the rotation of the molecules is hindered or if the molecules show orientational disorder without rotation.

## Part I. Theoretical section

### *Notation*

$\mathbf{r}$ = the instantaneous position vector of the atom in question. This vector may be resolved into two components:

$\mathbf{k}$, the position vector of the center of rotation of the atom; and

$\mathbf{v}$, the vector from the center of rotation to the instantaneous position of the atom.

$g$ = the instantaneous complex scattering power of the atom (this is the quantity which Zachariasen denotes by $g_k^L$).

$\bar{g}$ = the average complex scattering power of the atom (this is the quantity which Zachariasen denotes by $g_k$).

$f$ = the atomic scattering factor of the given atom.

$\mathbf{h}$ = the reciprocal-lattice vector of the reflection considered.

$\theta$ = the rotation angle of the atom considered, measured from the projection of $\mathbf{h}$ on the plane of rotation of the atom.

$V_0$ = the height above the minimum of the potential barrier to rotation.

$V$ = the value of the potential for the given rotation angle $\theta$.

$\psi$ = the angle between the axis of rotation and the vector $\mathbf{h}$.

$\gamma$ = the rotation angle corresponding to a potential minimum.

$n$ = the number of potential minima.

### *Calculation of complex scattering power*

The instantaneous complex scattering power $g$ is given by

$$g=f\exp[2\pi i\mathbf{h}.\mathbf{r}]=f\exp[2\pi i\mathbf{h}.\mathbf{k}]\exp[2\pi i\mathbf{h}.\mathbf{v}].$$

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For any given probability function $P(\theta)$, the average value of the complex scattering power is given by

$$\bar{g}=f\exp[2\pi i\mathbf{h}.\mathbf{k}]\int_0^{2\pi}P(\theta)\exp[2\pi i\mathbf{h}.\mathrm{v}]\,d\theta.$$

Now, the probability distribution is to be a Maxwell–Boltzmann distribution with a potential function

$$V=-\tfrac{1}{2}V_0\cos n(\theta-\gamma).$$

Hence, the probability distribution is given by

$$P(\theta)=\frac{\exp[V_0\cos n(\theta-\gamma)/2kT]}{\int_0^{2\pi}\exp[V_0\cos n(\theta-\gamma)/2kT]\,d\theta}.$$

We may express the quantity $2\pi i\mathbf{h}.\mathrm{v}$ in terms of $\theta$ and certain quantities determined by the conditions of diffraction:

$$2\pi i\mathbf{h}.\mathrm{v}=2\pi i\,|\,\mathbf{h}\,||\,\mathrm{v}\,|\sin\psi\cos\theta.$$

Now let us represent the quantity $V_0/2kT$ by the symbol $b$, and the quantity $2\pi\,|\,\mathbf{h}\,||\,\mathrm{v}\,|\,\sin\psi$ by the symbol $a$. We may now give an expression for the integral in the equation defining $\bar{g}$ in terms of $a$, $b$, $n$ and $\gamma$. Using the symbol $M_n^\gamma(a,b)$ for this integral, we find

$$M_n^\gamma(a,b)=\int_0^{2\pi}P(\theta)\exp[2\pi i\mathbf{h}.\mathrm{v}]\,d\theta$$
$$=\frac{\int_0^{2\pi}\exp[b\cos n(\theta-\gamma)+ia\cos\theta]\,d\theta}{\int_0^{2\pi}\exp[b\cos n(\theta-\gamma)]\,d\theta}.$$

The integral in the numerator of this expression is related to the integral expressions of the Bessel function. A search for an integral expression of this form was unsuccessful. However, it was possible to expand the integrand in an infinite series, and thus evaluate the integral as an infinite series.

From an expansion given by Watson (1944, p. 22),

$$\exp[iz\sin\theta]=J_0(z)+2\sum_{m=1}^{\infty}J_{2m}(z)\cos 2m\theta$$
$$+2i\sum_{m=0}^{\infty}J_{2m+1}(z)\sin(2m+1)\theta,$$

we may derive, letting $z=-ix$, and remembering that $J_n(-iz)=(-i)^n I_n(z)$, and $\cos\theta=\sin(\tfrac{1}{2}\pi-\theta)$,

$$\exp[x\cos\theta]=I_0(x)+2\sum_{m=1}^{\infty}I_m(x)\cos m\theta$$
$$=\sum_{m=0}^{\infty}\epsilon_m I_m(x)\cos m\theta,$$

where $\epsilon_m=1$ when $m=0$, and $\epsilon_m=2$ when $m\neq 0$.

Then the integral in the numerator of the $M$ function becomes

$$\int_0^{2\pi}\left[\sum_{m=0}^{\infty}\epsilon_m I_m(ia)\cos m\theta\right]$$
$$\times\left[\sum_{p=0}^{\infty}\epsilon_p I_p(b)\cos pn(\theta-\gamma)\right]d\theta$$
$$=\sum_{m=0}^{\infty}\sum_{p=0}^{\infty}\epsilon_m\epsilon_p I_m(ia)\,I_p(b)\int_0^{2\pi}\cos m\theta(\cos pn\theta\cos pn\gamma$$
$$+\sin pn\theta\sin pn\gamma)\,d\theta.$$

Making use of the orthogonality of sines and cosines, we may simplify this integral to

$$\sum_{p=0}^{\infty}\epsilon_{pn}\epsilon_p I_{pn}(ia)\,I_p(b)\int_0^{2\pi}\cos^2 pn\theta\cos pn\gamma\,d\theta$$
$$=2\pi\sum_{p=0}^{\infty}\epsilon_p i^{pn}J_{pn}(a)\,I_p(b)\cos pn\gamma.$$

According to this formula, the integral in the denominator of the $M$ function is equal to $2\pi I_0(b)$. Hence we may give as an expression of the $M$ function

$$M_n^\gamma(a,b)=\sum_{p=0}^{\infty}\epsilon_p i^{pn}J_{pn}(a)\,I_p(b)\cos pn\gamma/I_0(b).$$

Then the expressions for $\bar{g}$ and for the structure factor $F$ in terms of the $M$ function are

$$\bar{g}=f\exp[2\pi i\mathbf{h}.\mathbf{k}]\,M_n^\gamma(a,b),$$
$$F=\sum_j\bar{g}_j=\sum_j f_j\exp[2\pi i\mathbf{h}.\mathbf{k}_j]\,M_{nj}^{\gamma_j}(a_j,b_j),$$

where the summation is over the atoms in the unit cell.

The uniform convergence of the series for the $M$ function as a function of $a$ may be established by the use of a theorem due to Pincherle, demonstrated by Watson (1944, p. 526). This theorem states that a series

$$\sum_{n=0}^{\infty}a_n J_{\nu+n}(z)$$

converges over the same circle of convergence and has the same singularities as an associated power series

$$\sum_{n=0}^{\infty}a_n(\tfrac{1}{2}z)^{\nu+n}/\Gamma(\nu+n+1).$$

The associated power series for the $M$ function as a function of $a$, $b$ being fixed at any arbitrary value, is

$$\sum_{p=0}^{\infty}\epsilon_p i^{pn}I_p(b)\cos pn\gamma(\tfrac{1}{2}a)^{pn}/I_0(b)\,(pn)!.$$

This series is seen to converge in the same manner as

$$\sum_{p=0}^{\infty}(\tfrac{1}{2}ia)^{pn}/(pn)!,$$

which converges uniformly over any bounded interval of $a$ if $n$ is a positive integer.

To test the convergence of the series as a function of $b$, we should note that $I_p(b)$ is positive, and that $I_p(b)/I_0(b)\leqslant 1$ for all positive $b$, including $+\infty$, if $p$ is a positive integer. For this reason, since the series converges when $b=0$, it must converge uniformly for all positive values of $b$ including infinity.

The special values of the $M$ function when $b=0$ and $b=\infty$ are of interest. When $b=0$, the $M$ function becomes $J_0(a)$, which is the result found for the free rotator by Bijvoet & Ketelaar (1938) and Zachariasen (1945, pp. 223 ff.). The physical meaning of setting $b=\infty$ is that only the positions of minimum potential are available for the rotating group, each position having an equal probability. This case is similar to the model of orientational disorder proposed by Frenkel (1935), just as the case in which $b$ is finite is like the model of the hindered rotator proposed by Pauling (1930). The scattering power of an atom which is distributed with equal probability among $n$ equivalent positions in a circle about the origin is

$$(1/n)\sum_{m=1}^{n} f\exp\left[ia\cos\left(\gamma+2\pi m/n\right)\right].$$

Consequently, the limit of the $M$ function as $b$ approaches infinity should be, from physical reasoning,

$$M_n^\gamma(a,\infty)=(1/n)\sum_{m=1}^{n}\exp\left[ia\cos\left(\gamma+2\pi m/n\right)\right].$$

This result was not proved analytically, in the general case, but its validity was proved for the case of $n=2$.

Values of the $M$ function for particular values of $a, b, n$, and $\gamma$ are given in Table 1.

## Part II. Study of the rotating group in perfluorocyclohexane

Perfluorocyclohexane is an example of a crystal containing rotating groups without a fixed axis, according to the data of Christoffers, Lingafelter & Cady (1947). The present work consists in the application of the theory of diffraction of X-rays from crystals containing rotating groups to find whether the groups rotate freely with spherical symmetry on the average, or show hindered rotation or orientational disorder without rotation.

Verweel & Bijvoet (1938) and Zachariasen (1945, pp. 223 ff.) gave an expression for the structure factor of a crystal containing rotating groups under the assumptions of free rotation with spherical symmetry on the average, without interactions between the groups. The expression is

$$F=\sum_j f_j\exp\left[2\pi i\mathbf{h}.\mathbf{k}_j\right]\frac{\sin 2\pi\,|\mathbf{h}|\,|\mathbf{v}_j|}{2\pi\,|\mathbf{h}|\,|\mathbf{v}_j|},$$

where the summation is over the atoms in the unit cell. Discrepancies of the observed structure factors from values calculated from this expression may be caused by internal heat motion of the rotating group, which will reduce the structure factors, or by hindrance of the rotation (or the existence of orientational disorder without rotation), which may increase the structure factors of some of the reflections considerably.

Table 1. *Values of the M functions*

| $M_2^0(a, b)$ | $b=0$ | 1 | 2 | 3 | 4 | 5 | 6 | $\infty$ |
|---|---|---|---|---|---|---|---|---|
| $a=0$ | 1·0000 | 1·0000 | 1·0000 | 1·0000 | 1·0000 | 1·0000 | 1·0000 | 1·0000 |
| 1 | 0·7652 | 0·6632 | 0·6064 | 0·5814 | 0·5696 | 0·5632 | 0·5590 | 0·5403 |
| 2 | 0·2239 | −0·0838 | −0·2481 | −0·3168 | −0·3475 | −0·3638 | −0·3736 | −0·4162 |
| $M_4^0(a, b)$ | | | | | | | | |
| $a=0$ | 1·0000 | 1·0000 | 1·0000 | 1·0000 | 1·0000 | 1·0000 | 1·0000 | 1·0000 |
| 0·2 | 0·9900 | 0·9900 | 0·9900 | 0·9900 | 0·9900 | 0·9900 | 0·9900 | 0·9900 |
| 0·4 | 0·9604 | 0·9605 | 0·9605 | 0·9605 | 0·9605 | 0·9605 | 0·9605 | 0·9605 |
| 0·6 | ~~0·9120~~ | 0·9123 | 0·9124 | 0·9125 | 0·9125 | 0·9125 | 0·9125 | 0·9127 |
| 0·8 | 0·8463 | 0·8472 | 0·8477 | 0·8479 | 0·8480 | 0·8481 | 0·8481 | 0·8484 |
| 1·0 | 0·7652 | 0·7674 | 0·7687 | 0·7692 | 0·7695 | 0·7697 | 0·7698 | 0·7702 |
| 1·2 | 0·6711 | 0·6756 | 0·6781 | 0·6792 | 0·6797 | 0·6800 | 0·6802 | 0·6812 |
| 1·4 | 0·5669 | 0·5750 | 0·5796 | 0·5816 | 0·5826 | 0·5832 | 0·5835 | 0·5850 |
| 1·6 | 0·4554 | 0·4688 | 0·4763 | 0·4797 | 0·4813 | 0·4822 | 0·4828 | 0·4854 |
| 1·8 | 0·3400 | 0·3607 | 0·3724 | 0·3776 | 0·3801 | 0·3814 | 0·3823 | 0·3864 |
| 2·0 | 0·2239 | 0·2543 | 0·2713 | 0·2790 | 0·2826 | 0·2846 | 0·2859 | 0·2919 |
| 2·2 | 0·1104 | 0·1530 | 0·1770 | 0·1878 | 0·1929 | 0·1958 | 0·1976 | 0·2057 |
| 2·4 | 0·0025 | 0·0599 | 0·0923 | 0·1068 | 0·1137 | 0·1175 | 0·1200 | 0·1313 |
| 2·6 | −0·0968 | −0·0218 | −0·0206 | 0·0395 | 0·0485 | 0·0535 | 0·0568 | 0·0716 |
| 2·8 | −0·1850 | −0·0898 | −0·0360 | −0·0120 | −0·0006 | 0·0059 | 0·0099 | 0·0289 |
| 3·0 | −0·2601 | −0·1421 | −0·0756 | −0·0458 | −0·0316 | −0·0236 | −0·0185 | 0·0050 |
| $M_4^{\frac{1}{4}\pi}(a, b)$ | | | | | | | | |
| $a=0$ | 1·0000 | 1·0000 | 1·0000 | 1·0000 | 1·0000 | 1·0000 | 1·0000 | 1·0000 |
| 0·2 | 0·9900 | 0·9900 | 0·9900 | 0·9900 | 0·9900 | 0·9900 | 0·9900 | 0·9900 |
| 0·4 | 0·9604 | 0·9603 | 0·9603 | 0·9603 | 0·9603 | 0·9603 | 0·9603 | 0·9603 |
| 0·6 | 0·9120 | 0·9117 | 0·9116 | 0·9115 | 0·9115 | 0·9115 | 0·9115 | 0·9113 |
| 0·8 | 0·8463 | 0·8454 | 0·8449 | 0·8447 | 0·8446 | 0·8445 | 0·8445 | 0·8442 |
| 1·0 | 0·7652 | 0·7630 | 0·7617 | 0·7612 | 0·7609 | 0·7607 | 0·7606 | 0·7602 |
| 1·2 | 0·6711 | 0·6666 | 0·6641 | 0·6630 | 0·6625 | 0·6622 | 0·6620 | 0·6611 |
| 1·4 | 0·5669 | 0·5588 | 0·5542 | 0·5522 | 0·5512 | 0·5506 | 0·5503 | 0·5487 |
| 1·6 | 0·4554 | 0·4420 | 0·4345 | 0·4311 | 0·4295 | 0·4286 | 0·4280 | 0·4254 |
| 1·8 | 0·3400 | 0·3193 | 0·3076 | 0·3024 | 0·2999 | 0·2986 | 0·2977 | 0·2936 |
| 2·0 | 0·2239 | 0·1935 | 0·1765 | 0·1688 | 0·1652 | 0·1632 | 0·1619 | 0·1560 |
| 2·2 | 0·1104 | 0·0678 | 0·0439 | 0·0332 | 0·0281 | 0·0253 | 0·0235 | 0·0152 |
| 2·4 | 0·0025 | −0·0549 | −0·0872 | −0·1016 | −0·1084 | −0·1123 | −0·1147 | −0·1260 |
| 2·6 | −0·0968 | −0·1718 | −0·2139 | −0·2327 | −0·2416 | −0·2466 | −0·2498 | −0·2645 |
| 2·8 | −0·1850 | −0·2802 | −0·3336 | −0·3574 | −0·3688 | −0·3751 | −0·3791 | −0·3978 |
| 3·0 | −0·2601 | −0·3778 | −0·4440 | −0·4735 | −0·4875 | −0·4953 | −0·5003 | −0·5231 |

The structure factors were calculated according to the expression given above without the introduction of a temperature factor, and with the assumption of either the chair or the boat form of the $C_6F_{12}$ molecule with the distances $r_{CC} = 1{\cdot}50$ A. and $r_{CF} = 1{\cdot}35$ A. The structure was assumed to be the face-centered cubic packing of rotating molecules with $a_0 = 10{\cdot}00$ kX. reported by Christoffers *et al.* (1947). The values of the structure factor found experimentally by these authors are compared with the calculated values in Table 2. All sets of values are reduced to a scale with $F_{111} = 10{\cdot}0$.

Table 2. *Comparison of calculated and observed structure factors*

| *hkl* | $F_{calc.}$ (chair) | $F_{calc.}$ (boat) | $F_{obs.}$ |
|---|---|---|---|
| 111 | +10·0 | +10·0 | 10·0 |
| 200 | + 5·2 | + 5·3 | 5·5 |
| 220 | − 2·9 | − 2·7 | 4·5 |
| 222 | − 2·9 | − 2·9 | 7·7 |
| 311 | − 3·3 | − 3·2 | 5·5 |
| 331 | − 0·4 | − 0·2 | 1·4 |
| 333 | + 0·5 | + 0·5 | 3·2 |
| 400 | − 1·4 | − 1·2 | 3·9 |
| 420 | − 0·1 | 0·0 | 2·0 |
| 422 | + 0·4 | + 0·5 | 0·0 |
| 440 | + 0·2 | + 0·1 | 1·7 |

The decline of the observed structure factors is seen to be much slower than the decline of the calculated structure factors. There was apparently no appreciable difficulty due to absorption, since the size of the sample was about 30 % smaller than the optimum size. It is reasonable to conclude that we are dealing with highly hindered rotation of the molecules or with orientational disorder. This conclusion is corroborated by the point raised by Christoffers *et al.* (1947) that the fluorine atoms of adjacent molecules would approach each other with a minimum distance much smaller than twice the van der Waals radius of fluorine, if the molecules rotated freely. Values of the minimum distance of approach of fluorine atoms calculated by the present authors are 1·78 A. for the boat form and 1·68 A. for the chair form of the $C_6F_{12}$ molecule, although the value of the van der Waals radius of fluorine is 1·35 A., according to Pauling (1945, p. 176).

Further study of the hindered rotator without a fixed axis could be carried out by calculation of the scattering powers of assumed models of the hindered rotator, or by preparation of electron-density maps of the crystal. An attempt was made to find the orientations of maximum probability for the molecules of $C_6F_{12}$ by a three-dimensional Fourier summation. However, the signs of some of the terms could not be fixed because of difficulties with non-convergence, and no conclusions could be drawn.

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# Short Communications

*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about* 500 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

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## A rapid approximate method for correcting low-angle scattering measurements for the influence of the finite height of the X-ray beam.

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Application of the method of Fournet & Guinier (1947) for correcting low-angle scattering measurements for the influence of the finite height of the X-ray beam is limited to materials for which the intensity of low-angle scattering decreases to virtually zero at a small angle. An alternative method of correction described by Shull & Roess (1947) requires that the observed intensity curve be represented by the sum of a number of Gaussian curves, and this is not always possible. The approximate method described below can be applied very rapidly to a low-angle scattering curve of any form.

Any point $A$ on the equator $A_1A_2$ (Fig. 1) receives