CORBEAU, J. (1964). *J. Phys. Radium*, **25**, 295.

FRAZER, B. C., DANNER, H. R. & PEPINSKI, R. (1957). *Phys. Rev.* **105**, 856.

GUINIER, A. (1963). *X-ray Diffraction in Crystals, Imperfect Crystals and Amorphous Bodies.* San Francisco: Freeman.

HARADA, J. & HONJO, G. (1967). *J. Phys. Soc. Japan*, **22**, 45.

HARADA, J., WATANABE, M., KODERA, S. & HONJO, G. (1965). *J. Phys. Soc. Japan*, **20**, 630.

HONJO, G., KODERA, S. & KITAMURA, N. (1964). *J. Phys. Soc. Japan*, **19**, 351.

HÜLLER, A. (1969). *Solid State Comm.* 7, 589.

JAYNES, E. T. (1953). *Ferroelectricity.* Princeton Univ. Press.

KATZ, L. & MEGAW, H. D. (1967). *Acta Cryst.* **22**, 639.

KAY, H. F. & VOUSDEN, P. (1949). *Phil. Mag. Ser.* 7, **40**, 1019.

LAMBERT, M. & COMÈS, R. (1969). *Solid. State Comm.* **7**, 305.

MASON, W. P. & MATHIAS, B. T. (1948). *Phys. Rev.* **74**, 1622.

TRIEBWASSER, S. (1956). *Phys. Rev.* **101**, 993.

YOUNG, R. A. (1965). Rapport interne non publié.

ZACHARIASEN, W. H. (1965). *Acta Cryst.* **18**, 710.

The Temperature Factor of an Atom in a Rigid Vibrating Molecule. I. Isotropic Thermal Motion

BY B. T. M. WILLIS

Atomic Energy Research Establishment, Harwell, Berkshire, England

AND G. S. PAWLEY

Department of Natural Philosophy, Edinburgh University, Scotland

The temperature factor of an atom in a molecular crystal has been derived in terms of the rigid-body parameters $\langle u^2 \rangle$ and $\langle \omega^2 \rangle$, where $\langle u^2 \rangle$ is the mean-square amplitude of translational displacement of the molecule in any direction and $\langle \omega^2 \rangle$ is the mean-square amplitude of angular (librational) displacement about any axis through the centre of inertia of the molecule. The analysis, which is appropriate to a cubic crystal containing rigid molecules undergoing isotropic thermal motion, is correct to the second power of $\langle \omega^2 \rangle$; the second-order treatment is necessary for interpreting accurate Bragg intensity data such as those discussed in a subsequent paper. Substitution of the temperature factor into the structure-factor equation yields an expression containing terms which can be identified with the first, second and third cumulants of the 'cumulant expansion' model of thermal motion.

1. Introduction

The conventional Debye–Waller treatment of the influence of thermal motion on diffracted intensities (see, e.g., James, 1962) is restricted in several ways. One restriction relates to the use of the harmonic approximation in describing the displacements of the atoms from their equilibrium positions. The extension of the Debye–Waller treatment to include anharmonic effects has been considered by Dawson, Hurley & Maslen (1967) and by Willis (1969); experimental evidence in support of this modified treatment has been reported by Rouse, Willis & Pryor (1968) and by Cooper, Rouse & Willis (1968).

A second restriction is that the vibrations of the atoms consist of rectilinear (translational) displacements from their equilibrium positions. For an atom undergoing librational motion it is usually assumed that the temperature factor can be expressed in a form appropriate to translational motion with an equivalent mean-square amplitude of displacement. This assumption requires that the atomic thermal-motion probability density function (p.d.f.) is centrosymmetric: this cannot be correct, as is evidenced by the need to apply a 'libration correction' (Cruickshank, 1956b, 1961) to the atomic coordinates *after* the coordinates have been refined by the centrosymmetric analysis.

In this paper we show how the Debye–Waller treatment can be extended in a simple way to take into account skewness of the p.d.f. arising from torsional oscillations of a rigid molecule in a cubic crystal. We use the harmonic approximation to derive the atomic temperature factor in terms of $\langle u^2 \rangle$ and $\langle \omega^2 \rangle$, although there is no difficulty (see Appendix) in introducing anharmonic terms into the analysis. (The parameter $\langle u^2 \rangle$ is the mean-square amplitude of translational displacement of the molecule in any direction and $\langle \omega^2 \rangle$ is the mean-square amplitude of angular (librational) displacement about any axis through the centre of inertia of the molecule.) The analysis is correct to the second power of $\langle \omega^2 \rangle$ whereas earlier treatments of this problem (Cruickshank, 1956a; Kay & Behrendt, 1963; Pawley, 1964, 1966; Maslen, 1968) are correct to the first power only, *i.e.* for very small amplitudes of libration.

A treatment of higher-order effects in the rigid-body motion of hexamethylenetetramine is given by Dawson (1970) and is discussed later. We then derive an expression for the structure factor containing terms which can be identified with the first, second and third cumulants of the 'cumulant expansion' model (Johnson, 1970) of thermal motion. The first cumulant is shown to contain a factor

$$1 - \langle \omega^2 \rangle + \tfrac{5}{12} \langle \omega^2 \rangle^2$$

which multiplies the fractional coordinates and represents explicitly the libration correction. Thus least-squares refinement based on the new structure-factor expression generates coordinates which do not require any *a posteriori* modification.

In the following paper (paper II: Pawley & Willis, 1970) the analysis is generalized to any crystal containing rigid molecules which undergo anisotropic thermal motion about a site fixed by symmetry. The two quantities $\langle u^2 \rangle$, $\langle \omega^2 \rangle$ of the isotropic treatment are replaced by twelve rigid-body parameters, six representing the symmetric translational tensor $\mathbf{T}$ and six representing the symmetric librational tensor $\mathbf{L}$.

Paper III (Duckworth, Willis & Pawley, 1970) describes the results of an experimental investigation by neutron diffraction of the cubic crystal hexamethylenetetramine (HMT). The experimental p.d.f.'s for the three types of atom in this molecular crystal show deviations from the Gaussian form. We show that the second-order treatment ($\langle \omega^2 \rangle^2$) of rigid-body motion, given in paper I, is better than the first-order treatment ($\langle \omega^2 \rangle$) in explaining the experimental results on HMT.
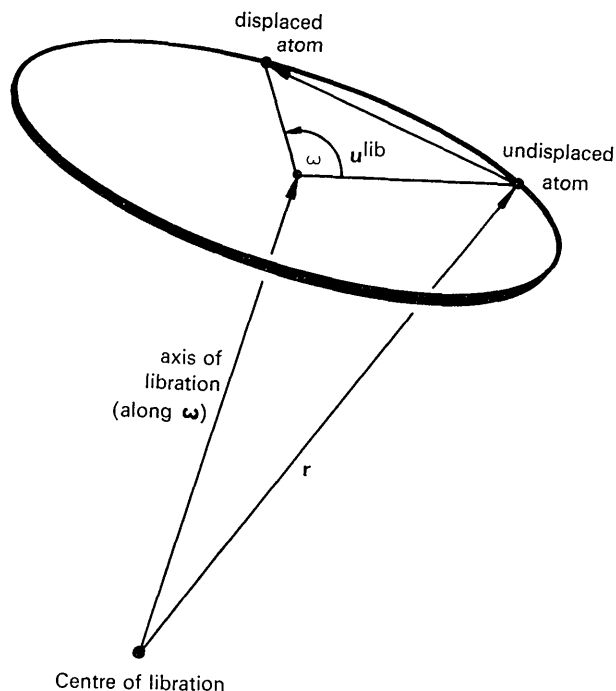

displaced
atom

ω u^{lib} undisplaced
atom

axis of
libration
(along $\boldsymbol{\omega}$)

r

Centre of libration

Fig. 1. Vectors in equation (2·6).

It would be interesting to make a similar detailed test of the predictions in paper II, but unfortunately diffraction data of the required accuracy pertaining to an anisotropic rigid-body system are not yet available.

2. Derivation of the atomic temperature factor

Our aim is to derive the temperature factor $\exp\left[-W_\kappa(\mathbf{Q})\right]$ for the κth atom in the unit cell of a crystal containing rigid molecules undergoing combined translational and librational motion: $\mathbf{Q}$ is the diffraction vector defined by

$$\mathbf{Q} = \mathbf{k} - \mathbf{k}_0 , \qquad (2.1)$$

where $\mathbf{k}$, $\mathbf{k}_0$ are the wave-vectors of the scattered and incident radiation respectively ($\mathrm{k} = \mathrm{k}_0 = 2\pi/\lambda$).

The temperature factor is given by

$$\exp\left[-W_\kappa(\mathbf{Q})\right] = \langle \exp\left(i\mathbf{Q} \cdot \mathbf{u}_\kappa\right) \rangle , \qquad (2.2)$$

where $\mathbf{u}_\kappa$ is the thermal displacement of atom κ and the angular brackets denote an average over a time which is long compared with the periods of the lattice vibrations but short on a macroscopic scale. At a later stage in the analysis we shall replace this time-average, in the usual way, by an ensemble average.

$\mathbf{u}_\kappa$ is the sum of the atomic displacements due to translational and librational motion of the molecule:

$$\mathbf{u} = \mathbf{u}^{\mathrm{trans}} + \mathbf{u}^{\mathrm{lib}} . \qquad (2.3)$$

(The subscript κ is dropped temporarily in order to simplify the notation.) Thus the exponent, $W(\mathbf{Q})$, of the temperature factor is

$$W(\mathbf{Q}) = W^{\mathrm{trans}}(\mathbf{Q}) + W^{\mathrm{lib}}(\mathbf{Q}) \qquad (2.4)$$

where

$$- W^{\mathrm{trans}}(\mathbf{Q}) = \ln \langle \exp\left(i\mathbf{Q} \cdot \mathbf{u}^{\mathrm{trans}}\right) \rangle \qquad (2.4a)$$

and

$$- W^{\mathrm{lib}}(\mathbf{Q}) = \ln \langle \exp\left(i\mathbf{Q} \cdot \mathbf{u}^{\mathrm{lib}}\right) \rangle . \qquad (2.4b)$$

We shall assume that the libration axes are constrained by symmetry to intersect in a fixed point. This is equivalent to assuming that there is no correlation between the translational and librational modes of motion (Schomaker & Trueblood, 1968), as is implied by equation (2.4) [see § 2(c)].

According to the conventional Debye–Waller theory, equation (2.4a) reduces to the expression

$$W^{\mathrm{trans}}(\mathbf{Q}) = \tfrac{1}{2}\langle (\mathbf{Q} \cdot \mathbf{u}^{\mathrm{trans}})^2 \rangle = \tfrac{1}{2}Q^2 \langle u^2 \rangle \qquad (2.5)$$

where the mean-square translational displacement $\langle u^2 \rangle$ is the same in all directions. In the remaining part of § 2 we evaluate the corresponding expression for the librational contribution to $W(\mathbf{Q})$ in terms of the isotropic parameter $\langle \omega^2 \rangle$. We shall start from equation (2.4b) and ignore all terms in the analysis of higher order than $\langle \omega^2 \rangle^2$.

2.1 *Expression for* $\mathbf{u}^{\mathrm{lib}}$

The first step is the evaluation of the librational contribution, $\mathbf{u}^{\mathrm{lib}}$, to the total atomic displacement. Ac-

cording to Euler's theorem (Goldstein, 1950), a general displacement u^{lib} of any atom in a rigid molecule constrained to move about a fixed point ('centre of libration') can be expressed as a finite rotation about some axis through the fixed point. If $\omega = |\omega|$ represents the magnitude of this rotation, where ω is along the axis of rotation and r is the vector from the centre of libration to the equilibrium position of the atom, then

$$u^{lib} = \omega \wedge r \left(\frac{\sin \omega}{\omega}\right) + [(r \cdot \omega)\omega - \omega^2 r]\left(\frac{1 - \cos \omega}{\omega^2}\right). \quad (2.6)$$

[For a proof of (2.6), which holds exactly for any finite rotation, see Schomaker & Trueblood (1968).] If $\omega \ll 1$, equation (2.6) reduces to

$$u^{lib} = \omega \wedge r, \quad (2.6a)$$

which is the expression used by Cruickshank (1956a) and Pawley (1964, 1966). The quantities in (2.6) are illustrated in Fig. 1.

In matrix notation (2.6) becomes

$$u^{lib} = \frac{\sin \omega}{\omega} \begin{pmatrix} 0 & -\omega_3 & \omega_2 \\ \omega_3 & 0 & -\omega_1 \\ -\omega_2 & \omega_1 & 0 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix}$$

$$+ \left(\frac{1 - \cos \omega}{\omega^2}\right) \begin{pmatrix} -\omega_2^2 - \omega_3^2 & \omega_1\omega_2 & \omega_1\omega_3 \\ \omega_1\omega_2 & -\omega_1^2 - \omega_3^2 & \omega_2\omega_3 \\ \omega_1\omega_3 & \omega_2\omega_3 & -\omega_1^2 - \omega_2^2 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix}$$

$$(2.7)$$

where ω_1, ω_2, ω_3 are the Cartesian components of ω and r_1, r_2, r_3 the Cartesian components of r. For the case of isotropic motion, we can, without any loss of generality, align the z axis along r, so that

$$\begin{aligned} &r_1 = r_2 = 0 \\ \text{and} \quad &r_3 = |r| = r, \end{aligned} \quad \left.\vphantom{\begin{aligned}&\\&\end{aligned}}\right\} \quad (2.8)$$

where $|r|$ is the distance of the undisplaced atom from the centre of libration. We also have the relations:

$$\left.\begin{aligned} &\omega^2 = \omega_1^2 + \omega_2^2 + \omega_3^2, \\ &\frac{\sin \omega}{\omega} = 1 - \frac{1}{3!}\omega^2 + \frac{1}{5!}\omega^4 \ldots \\ \text{and} \quad &\frac{1 - \cos \omega}{\omega^2} = \frac{1}{2!} - \frac{1}{4!}\omega^2 + \frac{1}{6!}\omega^4 \ldots \end{aligned}\right\} \quad (2.9)$$

Substituting (2.8) and (2.9) into equation (2.7):

$$u^{lib} = (1 - \tfrac{1}{6}\omega^2 \ldots)\begin{pmatrix} 0 & -\omega_3 & \omega_2 \\ \omega_3 & 0 & -\omega_1 \\ -\omega_2 & \omega_1 & 0 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ r \end{pmatrix}$$

$$+ (\tfrac{1}{2} - \tfrac{1}{24}\omega^2 \ldots)\begin{pmatrix} -\omega_2^2 - \omega_3^2 & \omega_1\omega_2 & \omega_1\omega_3 \\ \omega_1\omega_2 & -\omega_1^2 - \omega_3^2 & \omega_2\omega_3 \\ \omega_1\omega_3 & \omega_2\omega_3 & -\omega_1^2 - \omega_2^2 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ r \end{pmatrix}$$

or

$$u^{lib} = r(\omega_2 + \tfrac{1}{2}\omega_1\omega_3, \ -\omega_1 + \tfrac{1}{2}\omega_2\omega_3, \ -\tfrac{1}{2}\omega_1^2 - \tfrac{1}{2}\omega_2^2)$$

$$- \frac{r}{6}\,\omega^2(\omega_2 + \tfrac{1}{4}\omega_1\omega_3, \ -\omega_1 + \tfrac{1}{4}\omega_2\omega_3, \ -\tfrac{1}{4}\omega_1^2 - \tfrac{1}{4}\omega_2^2)$$

$$(2.10)$$

where terms of higher order than ω^4 are neglected.

2.2 Expression for $\langle \exp(iQ \cdot u^{lib})\rangle$

For a cubic crystal the diffraction vector Q, equation (2.1), is given by

$$Q = \frac{2\pi}{a_0}(h_1, h_2, h_3) \quad (2.11)$$

where a_0 is the lattice parameter and h_1, h_2, h_3 are the indices of the reflecting plane. These indices will be referred to the same Cartesian system as the components of r, so that h_3 is along r. Taking the scalar product of (2.10) and (2.11):

$$Q \cdot u^{lib} = \frac{2\pi r}{a_0}(h_1\omega_2 + \tfrac{1}{2}h_1\omega_1\omega_3 - h_2\omega_1 + \tfrac{1}{2}h_2\omega_2\omega_3$$

$$- \tfrac{1}{2}h_3\omega_1^2 - \tfrac{1}{2}h_3\omega_2^2) - \frac{\pi r}{3a_0}\,\omega^2(h_1\omega_2 + \tfrac{1}{4}h_1\omega_1\omega_3$$

$$- h_2\omega_1 + \tfrac{1}{4}h_2\omega_2\omega_3 - \tfrac{1}{4}h_3\omega_1^2 - \tfrac{1}{4}h_3\omega_2^2). \quad (2.12)$$

Putting $\beta = \dfrac{2\pi r}{a_0}$, equation (2.12) becomes

$$\begin{aligned} Q \cdot u^{lib} = &\beta(h_1\omega_2 - h_2\omega_1) \\ &+ \tfrac{1}{2}\beta(h_1\omega_1\omega_3 + h_2\omega_2\omega_3 - h_3\omega_1^2 - h_3\omega_2^2) \\ &+ \tfrac{1}{6}\beta(-h_1\omega_1^2\omega_2 - h_1\omega_2^3 - h_1\omega_2\omega_3^2 \\ &\quad + h_2\omega_1^3 + h_2\omega_1\omega_2^2 + h_2\omega_1\omega_3^2) \\ &+ \tfrac{1}{24}\beta(-h_1\omega_1^3\omega_3 - h_1\omega_1\omega_2^2\omega_3 - h_1\omega_1\omega_3^3 \\ &\quad - h_2\omega_1^2\omega_2\omega_3 - h_2\omega_2^3\omega_3 - h_2\omega_2\omega_3^3 \\ &\quad + h_3\omega_1^4 + 2h_3\omega_1^2\omega_2^2 + h_3\omega_1^2\omega_3^2 \\ &\quad + h_3\omega_2^4 + h_3\omega_2^2\omega_3^2) \\ = &\beta(A + \tfrac{1}{2}B + \tfrac{1}{6}C + \tfrac{1}{24}D), \quad (2.13) \end{aligned}$$

where the quantities A, B, C, D represent the contents of the brackets enclosing successively the first, second, third and fourth order terms in ω. Equation (2.13) gives the complete set of terms in the expansion of $Q \cdot u^{lib}$ which are necessary in evaluating the temperature factor correct to $\langle \omega^2 \rangle^2$.

$\langle \exp(iQ \cdot u^{lib})\rangle$ is now obtained by multiplying $\exp(iQ \cdot u^{lib})$ by the Boltzmann probability factor and averaging over all possible displacements. Thus

$$\langle \exp(iQ \cdot u^{lib})\rangle = \frac{\displaystyle\int \exp(iQ \cdot u^{lib}) \exp(-V(\omega)/k_B T)d\omega}{\displaystyle\int \exp(-V(\omega)/k_B T)d\omega} \quad (2.14)$$

where $V(\omega)$ is the average potential 'seen' by a single molecule as it executes librational motion, k_B is Boltzmann's constant and T is the absolute temperature.

For isotropic harmonic motion we can write the potential in the form

$$V(\omega) = V(\omega) = V_0 + \tfrac{1}{2}\alpha\omega^2 ; \qquad (2.15)$$

V_0 is the potential at the equilibrium position ($u^{lib} = 0$) and α is a constant which is readily shown to be

$$\alpha = k_B T / \langle \omega^2 \rangle .$$

Putting (2.13) and (2.15) into equation (2.14) gives

$$\langle \exp{(iQ \cdot u^{lib})} \rangle = \frac{\iiint_{-\infty}^{\infty} \exp{[i\beta(A + \tfrac{1}{2}B + \tfrac{1}{6}C + \tfrac{1}{24}D)]} \exp{[-(\omega_1^2 + \omega_2^2 + \omega_3^2)/(2\langle \omega^2 \rangle)]} d\omega_1 d\omega_2 d\omega_3}{\iiint_{-\infty}^{\infty} \exp{[-(\omega_1^2 + \omega_2^2 + \omega_3^2)/(2\langle \omega^2 \rangle)]} d\omega_1 d\omega_2 d\omega_3} . \qquad (2.16)$$

2.3 Evaluation of integrals in equation (2.16)

The integral in the deonominator of (2.16) is

$$(2\pi\langle \omega^2 \rangle)^{3/2} .$$

The remaining integration in the numerator of (2.16) is not straightforward; it is instructive to evaluate it in stages which represent successively better approximations to the final answer.

(a) $B = C = D = 0$

The numerator of (2.16) simplifies to

$$\iiint_{-\infty}^{\infty} \exp{[i\beta(h_1\omega_2 - h_2\omega_1)]}$$
$$\times \exp{[-(\omega_1^2 + \omega_2^2 + \omega_3^2)/(2\langle \omega^2 \rangle)]} d\omega_1 d\omega_2 d\omega_3. \qquad (2.17)$$

Using the standard formula

$$\int_{-\infty}^{\infty} \exp{(-ax^2)} \exp{(2ibx)} \, dx$$

$$= \sqrt{\frac{\pi}{a}} \exp{(-b^2/a)}, \qquad (2.17a)$$

(2.17) becomes

$$(2\pi\langle \omega^2 \rangle)^{3/2} \exp{[-\tfrac{1}{2}\beta^2 \langle \omega^2 \rangle (h_1^2 + h_2^2)]} .$$
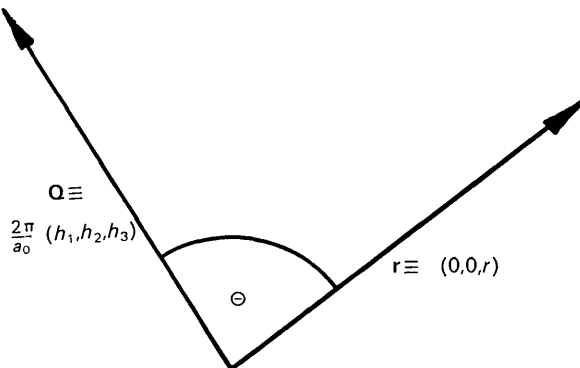

Fig.2. Definition of the angle Θ.

Thus the librational contribution to $W(Q)$ is

$$W^{lib}(Q) = \tfrac{1}{2}\beta^2 \langle \omega^2 \rangle (h_1^2 + h_2^2) . \qquad (2.18)$$

Using the relation

$$Q^2 \sin^2 \Theta = \frac{4\pi^2}{a_0^2} (h_1^2 + h_2^2)$$

where Θ is the angle between Q and r (see Fig. 2), (2.18) becomes

$$W^{lib}(Q) = \tfrac{1}{2}Q^2 r^2 \sin^2 \Theta \langle \omega^2 \rangle . \qquad (2.19)$$

The exponent $W(Q)$ of the total temperature factor is obtained by adding the translational contribution, equation (2.5):

$$W(Q) = \tfrac{1}{2}Q^2(\langle u^2 \rangle + r^2 \sin^2 \Theta \langle \omega^2 \rangle) . \qquad (2.20)$$

Equation (2.20) is the isotropic form of the temperature factor exponent first introduced by Cruickshank (1956a). It assumes an expression for u^{lib} given by equation (2.6a), i.e. it ignores the component of librational displacement parallel to r, and so it is necessary to introduce an a posteriori 'libration correction' to the atomic coordinates (Cruickshank, 1956b). This libration correction appears explicitly when equation (2.16) is evaluated to a better approximation.

(b) $C = D = 0$

The numerator of (2.16) is

$$\iiint_{-\infty}^{\infty} \exp{[i\beta(A + \tfrac{1}{2}B)]}$$
$$\times \exp{[-(\omega_1^2 + \omega_2^2 + \omega_3^2)/(2\langle \omega^2 \rangle)]} d\omega_1 d\omega_2 d\omega_3 , \qquad (2.21)$$

and this can be evaluated exactly using the formula (2.17a). The final expression for $W^{lib}(Q)$ works out as

$$W^{lib}(Q) = -\ln \eta + \tfrac{1}{2}(\ln \eta' + \ln \eta'') + \frac{\pi^2 r^2 h_1^2}{a_0^2 \eta'} + \frac{v^2}{\eta''}, \qquad (2.22)$$

where

$$\eta = (2\langle \omega^2 \rangle)^{-1}$$

$$\eta' = \eta + \frac{\pi i r h_3}{a_0} + \frac{\pi^2 r^2 h_2^2}{4a_0^2 \eta}$$

$$\eta'' = \eta + \frac{\pi i r h_3}{a_0} + \frac{\pi^2 r^2 h_1^2}{4a_0^2 \eta} - \frac{\pi^4 r^4 h_1^2 h_2^2}{16a_0^4 \eta^2 \eta'}$$

$$v = -\frac{\pi r h_2}{a_0} \left(1 + \frac{\pi^2 r^2 h_1^2}{4a_0^2 \eta \eta'}\right) .$$

(2.22) is correct to the first power of $\langle \omega^2 \rangle$ only, as we have assumed that $C = D = 0$. Thus (2.22) can be simplified by ignoring terms in $\langle \omega^2 \rangle^2$ and higher powers of $\langle \omega^2 \rangle$, and this leads to the expression

$$W^{11b}(\mathbf{Q}) = i\mathbf{Q} \cdot \mathbf{r}\langle\omega^2\rangle + \tfrac{1}{2}Q^2 \sin^2\Theta\, r^2\langle\omega^2\rangle. \qquad (2.23)$$

The first term in (2.23) is a phase shift representing the libration correction: the effect of libration is to cause a displacement of the mean position of the atom by an amount $r\langle\omega^2\rangle$ towards the centre of libration.

It is appropriate to discuss here the expressions for $W^{11b}(\mathbf{Q})$ derived by Kay & Behrendt (1963), Maslen (1968) and Dawson (1969). All these authors assume that $\sin\omega = \omega$ and $\cos\omega = 1 - \tfrac{1}{2}\omega^2$, i.e. that $C = D = 0$ in equation (2.16). Maslen's treatment is equivalent to the earlier treatment of Kay & Behrendt, but is restricted to one-dimensional librational motion so that the cross terms between the Cartesian components of ω [see equation (2.10)] do not appear. These cross terms are neglected also by Dawson. It can be shown that all three treatments are correct to $\langle\omega^2\rangle$, leading to equation (2.23) for $W^{11b}(\mathbf{Q})$, but that all give different expressions for $W^{11b}(\mathbf{Q})$ when expanded to $\langle\omega^2\rangle^2$.

(c) General case: A, B, C, D non-zero

To evaluate the exponent

$$-W^{11b}(\mathbf{Q}) = \ln\langle\exp(i\mathbf{Q}\cdot\mathbf{u}^{lib})\rangle \qquad (2.24)$$

for the general case, we substitute (2.16) into (2.24) and expand the logarithm using

$$\ln\langle\exp iy\rangle = i\langle y\rangle - \tfrac{1}{2}\langle y^2\rangle + \tfrac{1}{2}\langle y\rangle^2 - \frac{i}{6}\langle y^3\rangle$$
$$- \frac{i}{3}\langle y\rangle^3 + \frac{i}{2}\langle y\rangle\langle y^2\rangle + \tfrac{1}{24}\langle y^4\rangle - \tfrac{1}{4}\langle y\rangle^4$$
$$- \tfrac{1}{8}\langle y^2\rangle^2 - \tfrac{1}{6}\langle y\rangle\langle y^3\rangle + \tfrac{1}{2}\langle y\rangle^2\langle y^2\rangle. \qquad (2.25)$$

The angular brackets in (2.25) indicate mean values. Putting $y = \mathbf{Q}\cdot\mathbf{u}^{lib} = (A + \tfrac{1}{2}B + \tfrac{1}{6}C + \tfrac{1}{24}D)$ into (2.25), $W^{11b}(\mathbf{Q})$ can be evaluated term by term, employing the relation

$$\langle y^n\rangle = \frac{\iiint_{-\infty}^{\infty}(\beta A + \tfrac{1}{2}\beta B + \tfrac{1}{6}\beta C + \tfrac{1}{24}\beta D)^n \exp\left[-(\omega_1^2 + \omega_2^2 + \omega_3^2)/(2\langle\omega^2\rangle)\right]d\omega_1 d\omega_2 d\omega_3}{\iiint_{-\infty}^{\infty}\exp\left[-(\omega_1^2 + \omega_2^2 + \omega_3^2)/(2\langle\omega^2\rangle)\right]d\omega_1 d\omega_2 d\omega_3}. \qquad (2.26)$$

(The integrals in (2.26) reduce to the standard form $\int_{-\infty}^{\infty} x^n \exp(-ax^2)\,dx$.) The terms quoted in the expansion of $\ln\langle\exp iy\rangle$, equation (2.25), are the only ones which contribute factors in $\langle\omega^2\rangle$ or $\langle\omega^2\rangle^2$ in the final expression for $W^{11b}(\mathbf{Q})$. This expression, correct to $\langle\omega^2\rangle^2$, is

$$W^{11b}(\mathbf{Q}) = i\mathbf{Q}\cdot\mathbf{r}(\langle\omega^2\rangle - \tfrac{5}{12}\langle\omega^2\rangle^2)$$
$$+ \tfrac{1}{2}Q^2 r^2(\sin^2\Theta\,\langle\omega^2\rangle + \cos^2\Theta\,\langle\omega^2\rangle^2$$
$$- \tfrac{17}{12}\sin^2\Theta\,\langle\omega^2\rangle^2)$$
$$- \tfrac{1}{2}iQ^3 r^3 \cos\Theta \sin^2\Theta\,\langle\omega^2\rangle^2. \qquad (2.27)$$

From equations (2.4) and (2.5), the exponent $W(\mathbf{Q})$ of the total temperature factor is obtained by adding the

translational contribution $\tfrac{1}{2}Q^2\langle u^2\rangle$ to the right-hand side of equation (2.27).

We noted earlier that there is no correlation between the translational and librational contributions to $W(\mathbf{Q})$. This is readily verified by writing

$$-W(\mathbf{Q}) = \ln\langle\exp[i\mathbf{Q}\cdot(\mathbf{u}^{trans} + \mathbf{u}^{lib})]\rangle \qquad (2.28)$$

and using equations (2.25) and (2.26) to evaluate the right-hand side of (2.28), where

$$y = \mathbf{Q}\cdot(\mathbf{u}^{trans} + \mathbf{u}^{lib}).$$

In this way we find that the coefficients of cross terms such as $\langle u^2\rangle\langle\omega^2\rangle$ vanish identically.

3. Structure-factor expression

The structure-factor equation is given by

$$F(\mathbf{Q}) = \sum_\kappa f_\kappa \exp(i\mathbf{Q}\cdot\mathbf{r}_\kappa)\exp[-W_\kappa(\mathbf{Q})]; \qquad (3.1)$$

f_κ is the scattering amplitude (at rest) of the κth atom in the unit cell and $\mathbf{r}_\kappa$ its vector distance from the unit-cell origin, which coincides with the centre of inertia of the molecule. For simplicity, we assume that there is only one molecule in the unit cell; it is, of course, straightforward to extend the formalism to include several molecules, using the appropriate space group symmetry of the crystal.

From the results derived in § 2(c) for $W(\mathbf{Q})$, equation (3.1) becomes

$$F(\mathbf{Q}) = \sum_\kappa f_\kappa \exp[i\mathbf{Q}\cdot\mathbf{r}_\kappa(1 - \langle\omega^2\rangle + \tfrac{5}{12}\langle\omega^2\rangle^2)]$$
$$\times \exp[-\tfrac{1}{2}Q^2(\langle u^2\rangle + r_\kappa^2\sin^2\Theta\,\langle\omega^2\rangle$$
$$+ r_\kappa^2\cos^2\Theta\,\langle\omega^2\rangle^2 - \tfrac{17}{12}r_\kappa^2\sin^2\Theta\,\langle\omega^2\rangle^2]$$
$$\times \exp[i\tfrac{1}{2}Q^3 r_\kappa^3\cos\Theta \sin^2\Theta\,\langle\omega^2\rangle^2]. \qquad (3.2)$$

A direct physical interpretation of the various components of (3.2) can be given if we assume $\langle\omega^2\rangle^2 = 0$. (3.2) then reduces to

$$F(\mathbf{Q}) = \sum_\kappa f_\kappa \exp[i\mathbf{Q}\cdot\mathbf{r}_\kappa(1 - \langle\omega^2\rangle)]$$
$$\exp(-\tfrac{1}{2}Q^2\langle u^2\rangle)\exp(-\tfrac{1}{2}Q^2 r_\kappa^2\sin^2\Theta\,\langle\omega^2\rangle), \qquad (3.3)$$

where the first exponential represents the phase term in the structure-factor expression, modified by the libration correction $1 - \langle\omega^2\rangle$. The second exponential is the translational contribution to the temperature factor; it can also be written in the well-known form $\exp(-W^{trans})$, where

$$W^{trans} = 8\pi^2\langle u^2\rangle_Q^{trans}\sin^2\Theta/\lambda^2,$$

$\langle u^2 \rangle_Q^{\text{trans}}$ being the mean-square translational displacement of the vibrating atom in the direction of the vector $\mathbf{Q}$. The third exponential is the librational contribution to the temperature factor; this can also be written in the equivalent form $\exp(-W^{\text{lib}})$, where

$$W^{\text{lib}} = 8\pi^2 \langle u^2 \rangle_Q^{\text{lib}} \sin^2 \Theta / \lambda^2,$$

$\langle u^2 \rangle_Q^{\text{lib}}$ being the mean-square displacement due to libration projected along the direction of $\mathbf{Q}$.

Returning to the general structure factor expression (3.2), it is useful to compare this with the structure-factor expression derived from Johnson's 'cumulant expansion' model of thermal motion. Johnson (1969) expresses $F(\mathbf{Q})$ in the form

$$F(\mathbf{Q}) = \sum_\kappa f_\kappa \exp(2\pi i x_i^\kappa h_i) \exp(-b_{ij}^\kappa h_i h_j)$$
$$\times \exp(-i c_{ijk}^\kappa h_i h_j h_k) \quad (3.4)$$

where x_i, b_{ij}, c_{ijk} are first, second, third cumulant coefficients and the expansion is truncated after the third cumulant. The suffixes $i, j, k = 1, 2, 3$, and the dummy suffix convention is assumed. The cumulant coefficients are invariant to pair-wise interchange of indices, and so there is a maximum number of three independent coefficients x_i^κ representing the fractional atomic coordinates of the κth atom, six coefficients b_{ij}^κ representing the Gaussian anisotropic temperature factors, and ten coefficients c_{ijk}^κ representing the skewness of the probability density function. Comparison of (3.2) with (3.4) shows that the successive exponential terms in (3.2) can be identified with the first, second and third cumulants of the cumulant-expansion model. The adoption of the rigid-body assumption in deriving (3.2) introduces constraints between the cumulant coefficients in addition to the constraints imposed by the point symmetry of the atoms: this is discussed later (paper III, Duckworth, Willis & Pawley, 1970) with particular reference to the interpretation of experimental data on HMT. We note here that the skewness (third cumulant) term in (3.2) does not involve $\langle \omega^2 \rangle$, and so vanishes in the first-order treatment given in § 2(b). The first cumulant term in (3.2) contains the factor

$$1 - \langle \omega^2 \rangle + \tfrac{5}{12} \langle \omega^2 \rangle^2$$

to be identified as the libration correction.

APPENDIX

The harmonic treatment in § 2 can be extended readily to cover isotropic anharmonic thermal motion (see Willis, 1969) by writing the single-molecule potential as

$$V = V(u) + V(\omega) \quad (A.1)$$

where

$$V(u) = \tfrac{1}{2}\alpha_t u^2 + \gamma_t u^4 + \dots \quad (A.2)$$

$$V(\omega) = \tfrac{1}{2}\alpha_l \omega^2 + \gamma_l \omega^4 + \dots. \quad (A.3)$$

α_t, α_l are constants determining the magnitude of the harmonic component of the translational, librational potential functions; the remaining constants γ_t, $\gamma_l \dots$ determine the magnitude of the isotropic anharmonic components. Anisotropic anharmonic terms can be included in (A.2) and (A.3), in the way described by Willis (1969), and also cross-terms in u and ω.

If the analysis in § 2 is repeated using this modified form of potential function, we find that

$$\exp[-W(\mathbf{Q})]^{\text{anharmonic}} = \exp[-W(\mathbf{Q})]^{\text{harmonic}}$$
$$+ O(\langle u^2 \rangle^3) + O(\langle \omega^2 \rangle^3). \quad (A.4)$$

Thus by limiting the theory to small displacements such that $\langle u^2 \rangle^3$, $\langle \omega^2 \rangle^3$ and higher powers can be neglected, the final structure-factor expression (3.2) remains unchanged for anharmonic motion.

References

COOPER, M. J., ROUSE, K. D. & WILLIS, B. T. M. (1968). Acta Cryst. A24, 484.
CRUICKSHANK, D. W. J. (1956a). Acta Cryst. 9, 754.
CRUICKSHANK, D. W. J. (1956b). Acta Cryst. 9, 757.
CRUICKSHANK, D. W. J. (1961). Acta Cryst. 14, 896.
DAWSON, B. (1970). In Thermal Neutron Diffraction. Ed. B. T. M. WILLIS. Oxford Univ. Press.
DAWSON, B., HURLEY, A. C. & MASLEN, V. W. (1967). Proc. Roy. Soc. A 298, 289.
DUCKWORTH, J. A. K., WILLIS, B. T. M. & PAWLEY, G. S. (1970). Acta Cryst. A26, 263.
GOLDSTEIN, H. (1950). Classical Mechanics. Cambridge, Mass: Addison-Wesley.
JAMES, R. W. (1962). Optical Principles of X-ray Diffraction. London: Bell.
JOHNSON, C. K. (1969). Acta Cryst. A25, 187; more detailed treatment in Thermal Neutron Diffraction. Ed. B. T. M. WILLIS. Oxford Univ. Press.
KAY, M. I. & BEHRENDT, D. R. (1963). Acta Cryst. 16, 157.
MASLEN, E. N. (1968). Acta Cryst. A24, 434.
PAWLEY, G. S. (1964). Acta Cryst. 17, 457.
PAWLEY, G. S. (1966). Acta Cryst. 20, 631.
PAWLEY, G. S. & WILLIS, B. T. M. (1970). Acta Cryst. A26, 260.
ROUSE, K. D., WILLIS, B. T. M. & PRYOR, A. W. (1968). Acta Cryst. B24, 117.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). Acta Cryst. B24, 63.
WILLIS, B. T. M. (1969). Acta Cryst. A25, 277.