

Bernal (1964) and Scott, Charlesworth & Mak (1964) have considered the mechanical packing of hard spheres, and showed how a plane surface can initiate order in vibrating balls. Opal forms in cavities which are frequently parallel sided seams, so that a similar process could operate. Occasional specimens have been found where the fault plane is parallel to the sides of the cavities, but a systematic examination of many specimens showed that the effect is not general, and the fault planes mostly take up random orientations.

The optical micrograph, Fig. 12(a), shows a series of grey domains separated by parallel black or white lines. In this sample $\lambda_{\max} = 5500 \text{ \AA}$ (green), *i.e.* $r = 1100 \text{ \AA}$, and the spacing of the layers is 1800 \AA . At the magnification of the micrograph, the layers would appear 0.2 mm apart. The line widths therefore correspond to a few layers, and their separation is between 5 and 20 interlayer distances. Because this image is made from diffracted beams only, the intensities of the bands represent the relative intensities of diffraction from these areas, and therefore the extent of ordering within them. In this orientation [sample set as in Fig. 10(a)] the diffracted intensities from domains whose structures were h.c.p., random, or f.c.c. would be expected to decrease in that order. The fringes crossing the bands [Fig. 12(b)] are probably Fourier images (Cowley & Moodie, 1957), produced by the diffracted beam passing back through the periodic structure.

In 1845 Sir David Brewster examined opal in an optical microscope and recorded that 'the colours are generally arranged in parallel bands', and deduced 'that the colorific planes or patches consists of minute pores or vacuities arranged in parallel lines... to occupy a space in three dimensions' (Brewster, 1845). It

seems unlikely that he could have resolved the pore structure of opal, and it is more likely that he saw the fringe pattern [Fig. 12(b)] and interpreted it correctly.

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An Expression for the Temperature Factor of a Librating Atom

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The temperature factor for an atom undergoing librational motion is usually expressed in the form of the Debye-Waller factor appropriate to a translational oscillation with an equivalent root-mean-square amplitude. As a result of this the atomic positions may depart significantly from their true positions, and in an X-ray structure analysis the effect on the final difference density hinders the study of bonding electron distributions. A new form of the temperature factor for thermal librations which obviates these difficulties is proposed.

The Debye-Waller factor (Debye, 1913, 1914) was introduced to account for the effect of translational oscillations, *i.e.* vibrations, on the scattering of X-rays. The original expressions have been generalized to include the effects of anisotropy on this type of thermal motion (Cruickshank, 1956a), and these have generally

been used as an approximation to describe mixtures of anisotropic translational and librational motions.

The effect of this assumption on the atomic positions from a structure analysis have been investigated by Cruickshank (1956b, 1961) and by Busing & Levy (1964). Cruickshank proposed corrections which are

readily applied when the thermal motion of the system may be described by a rigid body model, but Busing & Levy showed that in more general cases the corrections take on a wide range of values depending on the nature of the oscillatory motion that is assumed. The central problem in calculating these corrections is the determination of the angle of oscillation, which for a given linear amplitude is specified by the distance of the librating atom from the oscillation centre. The shortcomings of this treatment of librational motion also hamper the study of the effects of the bonding electron distribution in the difference synthesis if these are obscured by residual features resulting from inadequate thermal corrections. (See, *e.g.* Tulinsky & Worthington, 1959.)

The scattering from a hindered rotator has been considered in detail by Atoji, Watanabé & Lipscomb (1953) and more recently by Brown & Chidambaram

(1967). The exact expressions are rather cumbersome, however, and simpler temperature factors appropriate to librational motions of small amplitude may be derived as follows: Assuming that each element of scattering density in the atom executes the same motion as the nucleus the temperature factor T_H of an atom is given by

$$T_H = \exp \{2\pi i \mathbf{H} \cdot \mathbf{r}\} \quad (1)$$

where \mathbf{H} is a vector in reciprocal space, \mathbf{r} is a vector from the rest position of the nucleus to a point along the trajectory, and the mean is taken over all positions weighted according to their relative probability. Consider Fig. 1(a) and (b), from which it is obvious that

$$T_H = \exp \{4\pi i R \sin(\delta/2) H \sin[\alpha - (\delta/2)] \cos \beta\}. \quad (2)$$

For a harmonic libration the probability distribution over each of the points in the trajectory may be described by the smearing function $(2\pi\Delta^2)^{-1/2} \exp\{-\delta^2/2\Delta^2\}$ (Bloch, 1932), where Δ is the r.m.s. angular amplitude of oscillation. For small corrections $\sin \delta$ and $\sin^2(\delta/2)$ may be replaced by δ and $\delta^2/4$ to a good approximation, so that

$$T_H = (2\pi\Delta^2)^{-1/2} \int \exp \left\{ - \left(\frac{1}{2\Delta^2} + \pi i R H_R \right) \delta^2 + 2\pi i R H_{\parallel} \delta \right\} d\delta. \quad (3)$$

The limits of integration may be extended to infinity in either direction without introducing further error, so that

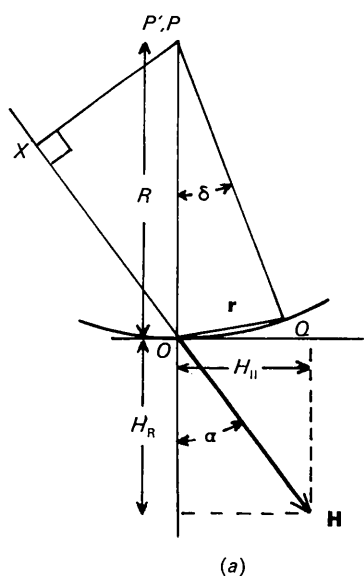
$$T_H = (1 + 2\pi i R H_R \Delta^2)^{-1/2} \exp \left\{ -2(\pi R H_{\parallel} \Delta)^2 \times (1 + 2\pi i R H_R \Delta^2)^{-1} \right\}. \quad (4)$$

Setting

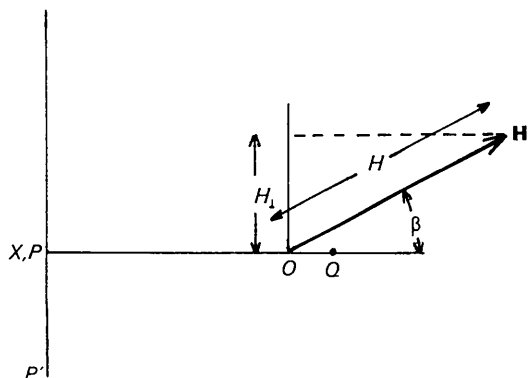
$$\begin{aligned} A &= \pi R H_{\parallel} H_R \Delta^2, & B &= 1 + 4A^2 H^{-2} \\ \gamma &= \tan^{-1}(2\pi R H_R \Delta^2); & & -\pi/2 < \gamma < \pi/2 \\ \eta &= 4\pi R A^2 H_R^{-1} B^{-1} - \gamma/2 \\ T_H &= B^{-1/4} \exp \left\{ -2\pi^2 R^2 H_{\parallel}^2 \Delta^2 B^{-1} + i\eta \right\}. \end{aligned} \quad (5)$$

The accuracy of the expression is limited by the one-term expansions for $\sin \delta$ and $\sin^2(\delta/2)$ in equation (3), but this approximation should be satisfactory for all but the most extreme cases. Greater precision could be obtained by including further terms in the expansion.

Assuming that the rest position of a librating atom is known the amplitude and the axis of rotation must be defined in order to specify the libration completely. This requires five parameters, which may be chosen in several different ways. One suitable set is illustrated in Fig. 2. r_R , r_{\parallel} and r_{\perp} give the coordinates of the point P on the rotation axis nearest the librating atom at O . The angle φ specifies the orientation of the rotation axis in the plane perpendicular to OP with respect to an arbitrarily chosen axis PN . Δ is the r.m.s. angular amplitude for the libration. It is convenient to choose the coordinate system in which P is defined such that r_R , r_{\parallel} and r_{\perp} are parallel to PO , the direction of motion



(a)



(b)

Fig. 1. (a) Librational motion projected down the rotation axis PP' . α is the angle between OP and \mathbf{H} projected on the plane OPQ . OX is the continuation of the projection of \mathbf{H} . (b) Projection on a plane perpendicular to XP .

at the rest position and the rotation axis respectively. It is likewise convenient to choose the initial value of φ as zero. The derivatives of T_H with respect to each of the parameters are given in Table 1.

Table 1. Derivatives of T_H with respect to $r_R, r_{||}, r_{\perp}, \Delta$ and φ

$$\begin{aligned} \frac{\partial T_H}{\partial r_R} &= T_H \pi B^{-3} [4\pi R H_{||}^2 \Delta^2 \exp\{-i\gamma\} + H_R \Delta^2 \exp\{i(\pi/2 - \gamma)\} \\ &\quad - 4A^2 H_R^{-1} B^{-3} \exp\{i(\pi/2 - 2\gamma)\}]. \\ \frac{\partial T_H}{\partial r_{||}} &= -T_H \pi B^{-3} [4A \exp\{-i\gamma\} + H_{||} \Delta^2 \exp\{i(\pi/2 - \gamma)\} \\ &\quad - 4A^2 H_{||} H_R^{-2} B^{-3} \exp\{i(\pi/2 - 2\gamma)\}]. \\ \frac{\partial T_H}{\partial r_{\perp}} &= T_H \pi H_{\perp} B^{-3} [\Delta^2 \exp\{i(\pi/2 - \gamma)\} \\ &\quad - 4A^2 H_R^{-2} B^{-3} \exp\{i(\pi/2 - 2\gamma)\}]. \\ \frac{\partial T_H}{\partial \Delta} &= -2T_H \pi R \Delta B^{-3} [2\pi R H_{||}^2 \exp\{-i\gamma\} + H_R \exp\{i(\pi/2 - \gamma)\} \\ &\quad - 4A^2 H_R^{-1} \Delta^{-2} B^{-3} \exp\{i(\pi/2 - 2\gamma)\}]. \\ \frac{\partial T_H}{\partial \varphi} &= 4T_H \pi^2 R^2 H_{||} H_{\perp} \Delta^2 B^{-3} \exp\{-i\gamma\}. \end{aligned}$$

In general the thermal motion of an atom will result from several vibrational and librational motions. Provided these are not correlated the total temperature factor is the product of those for each separate motion. Once satisfactory trial parameters for the atomic motions have been obtained it is possible in principle to refine them by a least-squares method. For a molecular structure, however, such a procedure introduces more parameters than are necessary. If constancy of bond lengths is assumed many of the parameters are restricted, and those for different atoms may be related. The best procedure involves refining the minimum number of parameters required to specify completely each independent motion, which may involve several atoms. It is necessary, therefore, to calculate the derivatives for all the atoms undergoing a libration with respect to the frame of reference defined by any one of them, say atom 1. Consider an atom with cylindrical coordinates R_2, θ_2, Z_2 in the frame of reference with atom 1 at $R_1, 0, 0$. The derivatives with respect to the parameters defining the frame are given in Table 2. A term such as $\partial F_c / \partial r_R$, which appears in the least-squares equations, then has the form

$$\sum f_n \frac{\partial T_H}{\partial r_R} \exp\{2\pi i(H \cdot r_n)\}$$

where f_n is the atomic scattering factor of an atom with rest position r_n , and the summation is over all the atoms affected by the libration.

The procedure can be extended to systems with more than one degree of librational freedom. Consider for example, the system with two degrees of freedom shown in Fig. 3, in which an atom at O librates about a fixed point P . The rotation axes are confined to the plane perpendicular to OP . The motion is specified by three parameters, Δ_{\max} and Δ_{\min} being the maximum

Table 2. Derivatives of T_H for an atom at R_2, θ_2, Z_2 , in the frame of references specified by the parameters $r_R, r_{||}, r_{\perp}, \Delta$ and φ for an atom at $R_1, 0, 0$.

$r_R', r_{||}', r_{\perp}', \Delta'$ and φ' are the libration parameters for the second atom in its own frame of reference.

$$\begin{aligned} \frac{\partial T_H}{\partial r_R} &= \frac{\partial T_H}{\partial r_R'} \cos \theta_2 - \frac{\partial T_H}{\partial r_{||}'} \sin \theta_2. \\ \frac{\partial T_H}{\partial r_{||}} &= \frac{\partial T_H}{\partial r_R'} \sin \theta_2 + \frac{\partial T_H}{\partial r_{||}'} \cos \theta_2. \\ \frac{\partial T_H}{\partial r_{\perp}} &= \frac{Z_2 \partial T_H}{R_1 \partial r_R'} \cos \theta_2 - \frac{Z_2 \partial T_H}{R_1 \partial r_{||}'} \sin \theta_2 \\ &\quad + \frac{R_2 \partial T_H}{R_1 \partial r_{\perp}'} \cos \theta_2 - \frac{1}{R_1} \frac{\partial T_H}{\partial \varphi'} \sin \theta_2. \\ \frac{\partial T_H}{\partial \Delta} &= \frac{\partial T_H}{\partial \Delta'}. \\ \frac{\partial T_H}{\partial \varphi} &= R_2 \frac{\partial T_H}{\partial r_{\perp}'} \sin \theta_2 + \frac{\partial T_H}{\partial \varphi'} \cos \theta_2. \end{aligned}$$

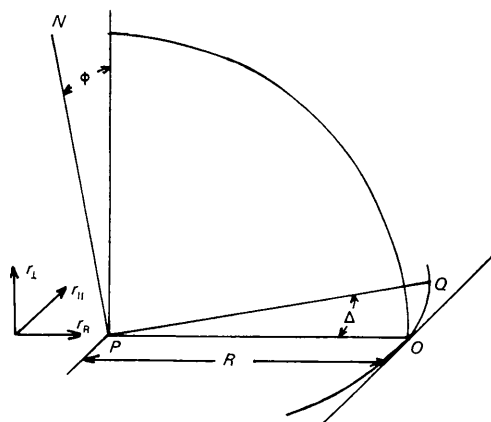


Fig. 2. Parameters $r_R, r_{||}, r_{\perp}, \varphi$ and Δ used to define the oscillation. Δ is the root mean square angular amplitude of oscillation.

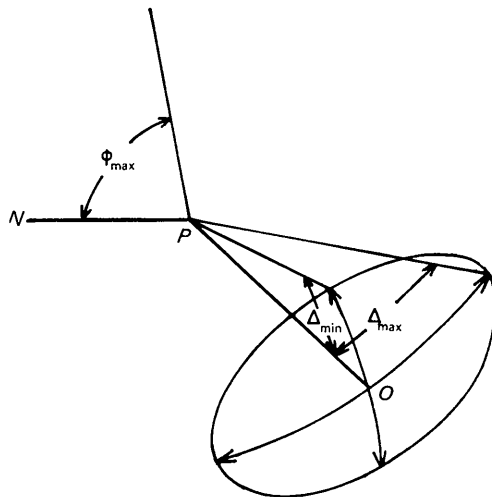


Fig. 3. A system with two degrees of librational freedom. Δ_{\max} and Δ_{\min} are the maximum and minimum r.m.s. angular amplitudes.

and minimum amplitudes as a function of φ , and φ_{\max} being the azimuthal angle for the principal axis with the larger amplitude. The temperature factor is the product of two terms $T_{\max\text{H}}$ and $T_{\min\text{H}}$, and its derivatives with respect to Δ_{\max} , Δ_{\min} , and φ are

$$T_{\min\text{H}} \frac{\partial T_{\min\text{H}}}{\partial \Delta_{\max}}, \quad T_{\max\text{H}} \frac{\partial T_{\min\text{H}}}{\partial \Delta_{\min}}$$

and

$$T_{\min\text{H}} \frac{\partial T_{\max\text{H}}}{\partial \varphi_{\max}} + T_{\max\text{H}} \frac{\partial T_{\min\text{H}}}{\partial \varphi_{\max}}$$

respectively. The partial derivatives have the same form as the corresponding terms in Table 1.

The most important case of three degrees of freedom is rigid body libration. If correlated motions are excluded nine parameters are required. It is convenient to choose three of these as coordinates r_1 , r_2 and r_3 specifying the point of intersection of the principal axes in a right handed system parallel to these axes. Three r.m.s. amplitudes Δ_1 , Δ_2 and Δ_3 and three azimuthal angles φ_1 , φ_2 , and φ_3 , defined in a similar manner to the analogous quantities in two dimensions, are also required. The temperature factor is the product of three terms $T_{1\text{H}}$, $T_{2\text{H}}$, and $T_{3\text{H}}$, and its derivatives with respect to r_1 , Δ_1 and φ_1 are

$$T_{1\text{H}} \left(T_{2\text{H}} \frac{\partial T_{3\text{H}}}{\partial r_1} + T_{3\text{H}} \frac{\partial T_{2\text{H}}}{\partial r_1} \right), \quad T_{2\text{H}} T_{3\text{H}} \frac{\partial T_{1\text{H}}}{\partial \Delta_1}$$

and

$$T_{1\text{H}} \left(T_{2\text{H}} \frac{\partial T_{3\text{H}}}{\partial \varphi_1} + T_{3\text{H}} \frac{\partial T_{2\text{H}}}{\partial \varphi_1} \right)$$

respectively. The remaining derivatives are obtained by symmetry. The partial derivatives are identical in form with the corresponding terms in Table 1.

The procedure can also be extended to include the effect of correlated motions. It has been shown recently

by Schomaker & Trueblood (1966, 1968) that a general treatment of rigid body motion should allow for correlation between vibrations and librations. The effect of the component of the correlated vibration in the same plane as a libration may be approximated closely by a lateral displacement of the rotation axis, while that of the perpendicular, or screw component, may be described by a rotation of the true rotation axis about the radius vector. The amount of the rotation is inversely proportional to the length of the radius vector. The lateral displacement and the constant of proportionality can be included in the least-squares refinement as parameters for the in plane and screw components respectively.

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Structural Imperfections in Hexagonal Gold–Cadmium Alloys

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The structural imperfections in hexagonal gold–cadmium alloys containing 18, 19 and 20 wt.% Cd have been investigated by X-ray diffraction methods. An analysis of X-ray diffraction line breadths of fault-broadened as well as unbroadened reflexions has been carried out. The stacking fault probability is greatest in 18 wt.% Cd alloy and decreases as the cadmium content increases. Evidence for the clustering of faults has been found.

X-ray diffraction provides a good method of studying structural defects in metals and alloys. The broadening of lines in the X-ray powder spectrum of deformed

hexagonal metals and alloys is anomalous (Edwards & Lipson, 1942). The anomalies are such that only those reflexions for which $h-k=3t \pm 1$, t being an integer,