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On the Interpretation of Anisotropic Temperature Factors. III. Anharmonic Motions

By C. Scheringer

Fachbereich Geowissenschaften der Universität Marburg, D-3550 Marburg/Lahn, Federal Republic of Germany

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It is shown by means of distribution functions that, with anharmonic motions of the atoms, different probability density functions for the nuclear positions, and also temperature factors, are obtained depending on whether or not interatomic thermal coupling is taken into account. The interatomic thermal coupling is introduced by means of a unit-cell potential, and, thus, the isolated-atom potential approach [Willis (1969). *Acta Cryst.* A**25**, 277–300] is extended for cubic site symmetry. Conditions of the anharmonic potential parameters which result from the fact that the probability density function must be integrable and non-negative everywhere are discussed. The formal expression for the temperature factor obtained is compared to those derived by lattice-dynamical calculations. It is concluded that the imaginary contributions, which were not found in the lattice-dynamical calculations, form a substantial part of the temperature factor for anharmonic motions. The lattice-dynamical calculations suggest that the cumulant expansion is the appropriate form of the temperature factor for anharmonic motions.

1. Introduction

The calculation of temperature factors for the anharmonic motions of atoms on the basis of lattice dynamics is difficult and cumbersome (Maradudin & Flinn, 1963; Wolfe & Goodman, 1969). The way out of performing these which is normally used in structure analysis is to assume an Einstein model of the lattice vibrations in which the coupling of the motions of different atoms is neglected. This model can be represented by an isolated-atom potential (Willis & Pryor, 1975). The isolated-atom approach can readily be handled mathematically '... and is, therefore, the only one likely to be of general interest to a crystallographer' (Willis & Pryor, 1975, p. 146). The purpose of this paper is:

(1) to show that a lattice-dynamical calculation is not the only way to take into account the coupling of the motions of the atoms, but that an approach which refers only to the unit cell will also suffice;

(2) to extend Willis's (1969) derivation of the anharmonic temperature factor so that the coupling of the motions of different atoms is taken into account;

(3) to point out conditions of the anharmonic potential parameters which result from the condition that the probability density function for the nuclear positions must be integrable and everywhere non-negative;

(4) to compare the expressions obtained with a unit-cell approach with those of lattice-dynamical calculations, and to examine both with respect to completeness.

2. A unit-cell approach to the temperature factor

In order to take into account the coupling of the motions of different atoms in the crystal we refer to the following situation, which was shown to hold by Marshall & Lovesey (1971) for neutron diffraction. The structure factor for any form of the density distribution in a crystal is the Fourier transform of the average density in the unit cell. An application to X-ray diffraction was given by Scheringer (1977). Hence, a consideration which is restricted to the unit cell should, in principle, be sufficient for the calculation of structure factors to any desired degree of accuracy. This immediately shows that a lattice-dynamical treatment is not the only alternative to an isolated-atom approach.

In order to realize our concept, we start with the average (dynamic) density in the unit cell. For X-ray diffraction, a temperature factor can only be defined in the convolution approximation; for neutron diffraction, the convolution principle holds rigorously. Hence, with Scheringer's (1977) equation (2.2) we can write for the average dynamic density in the unit cell

$$\varrho(\mathbf{x})_{\mathrm{dyn}} = \sum_{r=1}^{m} \int_{-\infty}^{+\infty} \varrho_r(\mathbf{x}-\mathbf{x}_r-\mathbf{u}_r) f(\mathbf{u}) \mathrm{d}\mathbf{u} \,. \qquad (1)$$

Here, m is the number of atoms (nuclei) in the cell, $\mathbf{x}_r$ the equilibrium position of the rth atom, $\mathbf{u}$ a $3m \times 1$ matrix which contains the m displacement vectors $\mathbf{u}_r$ of the atoms, and $f(\mathbf{u})$ the joint thermal distribution function for the m displacement vectors $\mathbf{u}_r$. In X-ray diffraction, $\varrho_r(\mathbf{x}-\mathbf{x}_r)$ is the density distribution of the rth atom about its mean position $\mathbf{x}_r$, and, in neutron diffraction, $\varrho_r(\mathbf{x}-\mathbf{x}_r)$ is a δ-function at $\mathbf{x}_r$ which corresponds to the constant scattering amplitude for neutrons at the rth nucleus. If the motions of the m atoms are statistically independent, $f(\mathbf{u})$ is equal to the product of the m independent distribution functions $f(\mathbf{u}_r)$. Generally, this does not hold, and we have to assume coupled motions of the atoms. Then, the integration in (1) has to be carried out over $f(\mathbf{u})$. Since (1) represents a sum of terms depending only upon r, except for $f(\mathbf{u})$, we can perform the integration for each term over the remaining $m-1$ displacement vectors and obtain

$$\varrho(\mathbf{x})_{\text{dyn}}=\sum_{r=1}^{m}\int_{-\infty}^{+\infty}\varrho_r(\mathbf{x}-\mathbf{x}_r-\mathbf{u}_r)g(\mathbf{u}_r)\mathrm{d}\mathbf{u}_r\,. \qquad (2)$$

By definition, $g(\mathbf{u}_r)$ is the marginal distribution of the distribution function $f(\mathbf{u})$ with respect to the vector $\mathbf{u}_r$. In general, $g(\mathbf{u}_r)\neq f(\mathbf{u}_r)$. The Fourier transformation of (2) can now be performed term by term, and yields the (dynamic) structure factor in the well-known form; the temperature factor will be identified as the Fourier transform of the marginal distribution $g(\mathbf{u}_r)$.

If we consider the temperature factor to be the Fourier transform of a probability density function (p.d.f.), we may formulate the result of this section as follows: The p.d.f. from which the temperature factor is calculated cannot fully be obtained by an isolated-atom approach, but only by a unit-cell approach; and, for the rth atom, the p.d.f. is given by the marginal density function $g(\mathbf{u}_r)$, which is obtained from the joint density function $f(\mathbf{u})$.

In the harmonic approximation of nuclear motions, we have the simple result $g(\mathbf{u}_r)=f(\mathbf{u}_r)$ (Scheringer, 1977). This is a special case of the general theorem that any marginal distribution of a multi-dimensional Gaussian distribution is again a Gaussian distribution with the correspondingly reduced covariance matrix. For anharmonic motions, however, the p.d.f. is not Gaussian and, hence, the type of distribution function usually changes when the marginal distribution is formed. A simple illustration with a Boltzmann distribution, in which a fourth-order anharmonic term x^2y^2 is added to the harmonic term of the p.d.f., is as follows: The bivariate p.d.f.

$$f(x,y)=C\exp\left[-\tfrac{1}{2}(x^2+y^2+x^2y^2)\right] \qquad (3)$$

has the marginal p.d.f.

$$g(y)=C_m(1+y^2)^{-1/2}\exp\left(-\tfrac{1}{2}y^2\right), \qquad (4)$$

where C and C_m are normalizing constants. This example is credited to Professor V. Mammitzsch, Mathematisches Institut der Universität Marburg.

3. Anharmonic temperature factors for cubic site symmetry

The anharmonic temperature factor for cubic site symmetry was derived by Willis (1969) by an isolated-atom potential approach. Here, we assume the basic idea of this derivation, but extend it by using a unit-cell potential. We form the unit-cell potential as the sum of Willis's isolated-atom potentials plus the coupling terms. Largely using Willis's notation, we write for the isolated-atom potential of the rth atom

$$V(\mathbf{u}_r)=V_0+\tfrac{1}{2}\alpha_r u_r^2+\beta_r u_{r1}u_{r2}u_{r3} + (\gamma_r-\tfrac{3}{5}\delta_r)u_r^4+\delta_r(u_{r1}^4+u_{r2}^4+u_{r3}^4)\,, \qquad (5)$$

where $u_r^2=u_{r1}^2+u_{r2}^2+u_{r3}^2$. We abbreviate the anharmonic β, γ, and δ terms in (5) as $A(\mathbf{u}_r)$. As far as introducing the coupling terms is concerned, we have to observe that neither the marginal p.d.f. nor the temperature factor obtained violates the conditions of cubic site symmetry. The number of coupling terms is thereby restricted. Without going into detail, we state that, for cubic site symmetry, only one fourth-order coupling term γ_{rs} is allowed, and we obtain for the unit-cell potential

$$V(\mathbf{u})=\sum_r V(\mathbf{u}_r)+\sum_{r\neq s}\gamma_{rs}(u_{r1}^2u_{s1}^2+u_{r2}^2u_{s2}^2+u_{r3}^2u_{s3}^2)\,. \qquad (6)$$

The joint p.d.f. is now obtained from the Boltzmann distribution of the potential, *i.e.*

$$f(\mathbf{u})=C\exp\left[-V(\mathbf{u})/kT\right], \qquad (7)$$

where C is a normalizing constant. In order to evaluate (7), it is usually assumed that the anharmonic contributions are small relative to the harmonic term, and thus they can be expanded into a series up to linear terms (Willis, 1969). Hence, in this approximation,

$$f(\mathbf{u})=C'\prod_r G(\mathbf{u}_r)\Big[1-(kT)^{-1}\sum_r A(\mathbf{u}_r) -(kT)^{-1}\sum_{r\neq s}\gamma_{rs}(u_{r1}^2u_{s1}^2+u_{r2}^2u_{s2}^2+u_{r3}^2u_{s3}^2)\Big]\,. \qquad (8)$$

$G(\mathbf{u}_r)$ denotes the harmonic term, *i.e.* a Gaussian distribution. In order to obtain the marginal distribution with respect to $\mathbf{u}_r$, we have to integrate over all coordinates $\mathbf{u}_s$, $s\neq r$. Since in (8) all terms can be factored with respect to r and s, we obtain

$$g(\mathbf{u}_r)=N_r^{-1}G(\mathbf{u}_r)\Big[1-(kT)^{-1}A(\mathbf{u}_r) -(kT)^{-1}\sum_s C_{rs}\gamma_{rs}(u_{r1}^2+u_{r2}^2+u_{r3}^2)\Big], \quad s\neq r\,. \qquad (9)$$

N_r^{-1} is the normalizing constant and is determined below. C_{rs} are integration constants. We do not determine them explicitly, but take all unknown constants together as one coupling constant Γ_r, *i.e.* $\Gamma_r=\sum_s C_{rs}\gamma_{rs}$, $s\neq r$. (9) is similar to Willis (1969); only the coupling term with Γ_r is new. For this term we have to determine the Fourier transform. It is the product of three one-dimensional transforms which we obtain explicitly from the tables of Oberhettinger (1957). For the remaining terms in (9), we use Willis's expressions for the Fourier transforms, and obtain for the temperature factor

$$T_r(\mathbf{h})=N_r^{-1}\exp\left[-2\pi^2kT\alpha_r^{-1}(h_1^2+h_2^2+h_3^2)\right] \times\{N_r+(kT\gamma_r\alpha_r^{-1}+\Gamma_r)kT(2\pi)^2\alpha_r^{-2}(h_1^2+h_2^2+h_3^2) + W(\beta_r,\gamma_r,\delta_r)\}\,, \qquad (10a)$$

$$N_r=1-3\Gamma_r\alpha_r^{-1}-15kT\gamma_r\alpha_r^{-2}. \qquad (10b)$$

$W(\beta_r,\gamma_r,\delta_r)$ denotes the anharmonic third- and fourth-order terms in Willis's (1969) equation (4.11). In (10) we have omitted the cubic lattice constant (as given by Willis) and refer $\mathbf{u}_r$ and $\mathbf{h}$ to the crystal basis, as is customary in structure factor calculation. Compared to Willis's equation (4.11), the two terms with the coupling constant Γ_r are new. We find Γ_r in the zero and second-order term, because the Fourier transform is represented by a second-order Hermitian polynomial. Although γ_r and Γ_r appear together in N_r and in the second-order term, they constitute two distinguishable parameters: the linear combinations in N_r and the second-order term are different, and, moreover, γ_r is also determined by the fourth-order term. How accurately all four anharmonic parameters β_r, γ_r, δ_r, and Γ_r can be determined in practice depends on the quality of the data, on the strength of the anharmonic vibrations, and on the degree of internuclear thermal coupling present in the given crystal.

4. Conditions of the potential parameters

In the preceding section, we made use of Willis's (1969) approach without comment, in order to complete the calculation. Here we add some remarks about the procedure, which have their origin in the following (formal) condition: all p.d.f.'s $f(\mathbf{u})$, $f(\mathbf{u}_r)$, $g(\mathbf{u}_r)$ must be non-negative and integrable from $-\infty$ to $+\infty$ (by definition of a p.d.f.). Certain restrictions arise thereby for the potential parameters. They begin with those already on an isolated-atom potential. We can sum up the condition of the p.d.f. that $V(\mathbf{u})$ in (7) must be positive definite. The most important restrictions refer to the β_r and γ_r parameters.

Cooper, Rouse & Willis (1968) used only a third-order β_r parameter, and no fourth-order parameters. Equations (2) and (3) of these authors do not form a p.d.f. because the exponential function obtained cannot be integrated from $-\infty$ to $+\infty$. When the β_r term is expanded in a series, the function becomes integrable. With the series expansion for β_r, refinement showed that a single β_r term appears to be sufficient; see the examples of Si (Willis & Pryor, 1975, p. 168) and $CuCl_2$ (Sakata, Hoshino & Harada, 1974). Even so, the p.d.f. is not non-negative everywhere: For β_r and u_i positive, $1-(kT)^{-1}\beta_r u_1 u_2 u_3$ becomes negative for sufficiently large u_i. Since for large u_i the Gaussian is nearly zero, the resulting p.d.f. will be only slightly negative. However, for the p.d.f. to be non-negative everywhere, the presence of a fourth-order term with γ_r negative is required.

A more stringent restriction arises for the γ_r parameter, since it questions the transition from the Boltzmann distribution (7) to the series expansion (8). (7) requires that γ_r be positive ('hardening of the potential'), otherwise $f(\mathbf{u}_r)$ cannot be integrated. (8) requires that γ_r be negative, otherwise $f(\mathbf{u}_r)$ becomes negative. (7) and (8) are mutually exclusive with respect to the sign of γ_r; hence the series expansion (8) does not form physically an approximation to the Boltzmann distribution (7), although it forms mathematically a good approximation for small u_i. With respect to integrability from $-\infty$ to $+\infty$, however, the behaviour for large u_i is important, and here the approximation also breaks down mathematically. In practice, when the series expansion was used, γ_r was found to be negative (Willis & Pryor, 1975), in agreement with the restriction to be placed on γ_r.

There are no obvious restrictions for the δ_r parameter, since it only rearranges the p.d.f. to make it anisotropic. For the coupling parameter Γ_r both signs are allowed, and from (10) we obtain the (weak) condition $|\Gamma_r| \leq \alpha_r/3$.

Since γ_r negative appears to be unacceptable for the Boltzmann distribution (7), we consider (8) and (9) for the p.d.f. to be a useful means of treating anharmonic motions in practice, but we hesitate to interpret the p.d.f. (8) and (9) physically as the Boltzmann distribution of a potential.

5. Relation to the cumulant expansion of the temperature factor

Johnson (1969, 1970) discussed the temperature factor from the statistical point of view and showed that the deviations from a Gaussian distribution, *i.e.* the anharmonic contributions, can be expressed in the expansion with cumulants. In particular, he showed that the anharmonic β_r parameter has to be attributed to the third cumulant and *vice versa* (Pawley, 1969). The cumulant expansion, in reciprocal space, expresses the convergence of the anharmonic deviations with respect to a Gaussian distribution in an optimal form (Kendall & Stuart, 1969). Hence, no physical approach is likely to surpass the cumulant expansion in its formal structure. For this reason, the cumulant expansion of the temperature factor can give indications as to the completeness of expressions derived by other methods. As we shall see, the results of lattice-dynamical studies also appear in the form of the cumulant expansion. The expression (10) for the temperature factor, obtained with a unit-cell potential approach, however, differs formally from the cumulant expansion. In the transition from (10) to the cumulant expansion we have to make an approximation, the relevance of which will be discussed in this section.

We obtain formally the cumulant expansion of the temperature factor from (10) by multiplying out the factor N_r^{-1} and making the approximation $1+x \simeq \exp x$ for the anharmonic terms. Thus, we obtain

$$\begin{aligned} T_r(\mathbf{h}) = {} & \exp\left[-2\pi^2 kT\alpha_r^{-1}(h_1^2+h_2^2+h_3^2)\right] \\ & \times \exp N_r^{-1}\left[(10kT\gamma_r\alpha_r^{-1}+\Gamma_r)kT(2\pi)^2\alpha_r^{-2}\right. \\ & \times (h_1^2+h_2^2+h_3^2) + i(kT)^2(2\pi)^3\alpha_r^{-3}\beta_r h_1 h_2 h_3 \\ & -(kT)^3(2\pi)^4\alpha_r^{-4}(\gamma_r-\tfrac{3}{5}\delta_r)(h_1^2+h_2^2+h_3^2)^2 \\ & \left. -(kT)^3(2\pi)^4\alpha_r^{-4}\delta_r(h_1^4+h_2^4+h_3^4)\right]. \end{aligned} \tag{11}$$

Apart from series expansion constants, the cumulants in (11) are the factors at the various combinations of the Miller indices (Johnson, 1969, 1970). For large values of the Miller indices, the approximation made is no longer valid, and the transition from (10) to (11) cannot be performed. With (9), we had to insist that

γ_r be negative; then the fourth-order γ_r term will dominate (11) for large values of $h_1^2+h_2^2+h_3^2$, and $T_r(\mathbf{h})$ will be increased. [In (10) the situation is different: the fourth-order term will always be compensated for by the harmonic exponential term for large values of $h_1^2+h_2^2+h_3^2$.] Hence, the cumulant expansion (11) is meaningful only for sufficiently small values of the Miller indices.

We expect that the difference in (10) and (11) will also become manifest in the respective p.d.f.'s. The p.d.f. to (10) is (9); the p.d.f. to (11) is usually calculated with the Edgeworth series (Johnson, 1970). We calculated the Edgeworth series for (11), and again obtained (9) (except for terms which result from $N_r \neq 1$ and which will be discussed below). Thus, it may appear that the difference between (10) and (11) cannot be seen in the respective p.d.f.'s. This, however, is not true; the Edgeworth series only approximates the p.d.f. for (11). It does so in such a way that it represents the true p.d.f. in an optimal manner with the low-order cumulants that have actually been determined. But it is known that the Edgeworth series with only a few terms yields errors in the representation of the p.d.f. (Kendall & Stuart, 1969). The true inverse Fourier transform to (11) is not (9). The inverse Fourier transform to each term of the cumulant expansion (the Gauss term as a factor being included) is an exponential with a differential operator in its argument (Kendall & Stuart, 1969, equations 6·35–6·40). The exact inverse Fourier transform to (11) cannot be evaluated in practice and hence we cannot state explicitly the differences in the p.d.f.'s for (10) and (11).

We conclude that, in going from (10) to (11), one should examine whether or not the temperature factor is increased for large values of the Miller indices.

As will be discussed in §6, the lattice-dynamical calculations yield the temperature factor in the form of (11), but the factor N_r^{-1} does not appear. In order to examine the effect of N_r, we have calculated the p.d.f. for (11) with the Edgeworth series and $N_r=1$. The resulting p.d.f. is the marginal distribution (9) with $N_r=1$, plus the term $G(\mathbf{u}_r)$ $(15kT\gamma_r\alpha_r^{-2}+3\Gamma_r\alpha_r^{-1})$, plus sixth, fourth, second and zero-order terms in β_r^2. These terms in β_r^2 can be ignored. The constant term, however, is a consequence of putting $N_r=1$. Thus, in the marginal distribution (9) one can either add this term right away and then obtain the cumulant expansion (11) with $N_r=1$, or one has to have $N_r \neq 1$ in (9) and (11). We suggest the first alternative.

Since the number of components of the cumulant tensors is limited (for each particular site symmetry), and is equal to the number of parameters that can be determined, the cumulant expansion allows us to judge critically the number of potential parameters introduced. Here one has to assume that the harmonic parameters are known so that the parameters in the second cumulant describe anharmonic contributions. [In the temperature factor (11), the harmonic and anharmonic second-order parameters cannot be separated formally; however, for the calculation of the p.d.f., the harmonic and anharmonic second-order parameters must both be known.] For the cubic site symmetries 23 and $\bar{4}3m$, there are four components of the cumulants. Thus, beside β_r, γ_r, and δ_r, we have introduced Γ_r legitimately, but a further potential parameter is not appropriate. Without site symmetry there are 34 components of the first four cumulants. Thus, up to fourth-order terms, we expect a maximum of 34 independent potential parameters.

6. Lattice-dynamical calculations

Several lattice-dynamical calculations of the anharmonic contributions to the temperature factor exist. Maradudin & Flinn's (1963) (lattice waves) and Wolfe & Goodman's (1969) (lattice sums in direct space) calculations were restricted to a monatomic crystal (site symmetry $\bar{1}$). These authors also calculated numerical results for Pb. For polyatomic crystals, two calculations (lattice waves) were carried out by Krivoglaz & Tekhonova (1961) and by Kashiwase (1965). A brief discussion of the effect of anharmonic motions on the temperature factor was given by Cochran & Cowley (1967).

The expressions derived by Maradudin & Flinn (1963) and Wolfe & Goodman (1969) are essentially the same although two different methods of calculation were employed. Maradudin & Flinn, however, did not find an isotropic fourth-order term, which corresponds to the fourth-order γ_r term in (11), but only an anisotropic fourth-order term, *cf.* their equations (5.12), (5.13), (6.11), (6.27). According to Wolfe & Goodman, an isotropic fourth-order term appears to be possible. But this term is not coupled to the second-order term by one and the same parameter, as with the parameter γ_r in (10) and (11), and this term need not be positive, which would give rise to a divergence of the temperature factor. The second-order terms are the predominant anharmonic contributions in both calculations; Maradudin & Flinn even found two different contributions to the second-order term. This suggests that, even for monoatomic crystals, a second-order anharmonic parameter should be introduced into the p.d.f. (For polyatomic crystals, such a parameter is introduced by taking into account the interatomic thermal coupling.)

The two lattice-dynamical calculations for polyatomic crystals confirm, on the whole, the results obtained for monatomic crystals. All four calculations yield the temperature factor in the form of an exponential function. Thus, the cumulant expansion is suggested to be the correct form of the temperature factor [and not a series expansion, such as (10)].

With respect to the effect of interatomic coupling, the two calculations contradict each other: Krivoglaz & Tekhonova (1961) did not find any effect, whereas Kashiwase found an explicit term of the form $\exp(-\Delta M_{rs})$ for two atoms r and s in the expression for the Bragg intensity (Kashiwase, 1965, equation 2.24). In our opinion, neither result is correct. Krivoglaz & Tekhonova (1961) did not calculate the contribution of the zero-phonon transitions for the intensity, but only for the structure amplitude (according to $\langle \exp 2\pi i\mathbf{h}\,.\,\mathbf{u}_{lr}\rangle$), *cf.* their equations (5) and (10). With such a reduced form of the average, one cannot expect to obtain results with respect to interatomic thermal coupling. Kashiwase (1965) sets up the correct average for the intensity, $\langle \exp 2\pi i\mathbf{h}\,.\,(\mathbf{u}_{lr}-\mathbf{u}_{l'r'})\rangle$. However, a coupling term of the form $\exp(-\Delta M_{rs})$ in the expression for the Bragg intensity means that the Bragg intensity can no longer be represented by a structure factor F, with $I_{\rm Bragg}=FF^*$ (Kashiwase, 1965, equation 2.24), since the term $\exp(-\Delta M_{rs})$ cannot be factored into two terms which depend solely on r and s respectively.† Kashiwase's equation (2.24) contradicts Marshall & Lovesey's (1971, ch. 2) proof concerning Bragg scattering. Cochran & Cowley (1967, p. 126) also exclude a coupling term of the type suggested by Kashiwase.

A further remarkable result of both lattice-dynamical calculations for polyatomic crystals is the fact that no imaginary contributions to the temperature factor (odd-order cumulants) were found. There is, however, no doubt that such contributions are physically real. They mean that the p.d.f. of the nuclear motions need not necessarily be centrosymmetric. Structural examples were reported by Sakata, Hoshino & Harada (1974) and by Willis & Pryor (1975). A further example is the curvilinear motions of atoms with large librations of molecules.

In order to state where to look for the imaginary contributions of the temperature factor we write, for the Bragg intensity,

$$I_{\rm Bragg}=FF^*=\sum_r f_r f_r^* T_r T_r^* + \sum_{r\neq s} f_r f_s^* T_r T_s^* \exp\left[2\pi i\mathbf{h}\,.\,(\mathbf{x}_r-\mathbf{x}_s)\right]. \quad (12)$$

Let the form factors f_r, f_s be real. The temperature factor is given in the cumulant expansion as

$$T_r(\mathbf{h})=\exp\left[R_r(\mathbf{h})+iI_r(\mathbf{h})\right], \quad (13)$$

where $R_r(\mathbf{h})$ and $I_r(\mathbf{h})$ denote the real and imaginary parts respectively. From (12) and (13) we obtain

$$I_{\rm Bragg}=\sum_r f_r^2\exp(2R_r) + \sum_{r\neq s} f_r f_s \exp(R_r+R_s)\cos\left[I_r-I_s+2\pi\mathbf{h}\,.\,(\mathbf{x}_r-\mathbf{x}_s)\right]. \quad (14)$$

With (14), the imaginary part of the temperature factor only appears in the mixed terms, $r\neq s$, and here it should be found with a lattice-dynamical calculation. (14) means, furthermore, that for the calculation of the recoil free fraction of a Mössbauer active atom, only the real part of the temperature factor is needed.

The numerical results obtained for Pb by the different authors show remarkable differences. This holds in particular for the anisotropic fourth-order terms. One reason for this is that Maradudin & Flinn (1963) made certain approximations in the theoretical evaluation of this term. Furthermore, certain models, which are to some extent arbitrary, for the interatomic forces always have to be assumed. In view of these difficulties, it appears that a reliable determination of anharmonic parameters by means of lattice-dynamical calculations is at present impossible. Hence, the experimental determination of these parameters recommends itself, although this involves collecting diffraction data of the highest quality.

7. Conclusion

In this paper, we have tried to compare the various approaches to the calculation of the anharmonic contributions to the temperature factor. After the analysis in §§4–6, we arrive at the following conclusions:

(1) The cumulant expansion of the temperature factor represents the best convergence of the anharmonic deviations with respect to the harmonic basic term. The formal expression of the cumulant expansion is confirmed by the lattice-dynamical calculations, in that these are complete.

(2) We consider the lattice-dynamical results hitherto obtained for polyatomic crystals to be incomplete; the imaginary contributions to the temperature factor, *i.e.* the odd-order cumulants, are missing. They should be found in the mixed terms, $r\neq s$, of the expression for the Bragg intensity.

(3) The p.d.f. which corresponds to the expression for the temperature factor found by lattice-dynamical calculations is the inverse Fourier transform of the cumulant expansion. This inverse Fourier transform is an exponential function with differential operators in its argument, and, hence, cannot be represented with simple physical terms such as potential parameters. Thus we consider all attempts to establish the exact p.d.f. for anharmonic motions with simple physical terms to be meaningless.

(4) A potential approach to the calculation of temperature factors appears to be insufficient in its physical interpretation. Since the Boltzmann distribution, with γ_r negative, does not represent a p.d.f., we cannot accept it as the physical basis for the evaluation of the temperature factor. Furthermore, the Boltzmann distribution of a potential is not confirmed as a p.d.f. by the lattice-dynamical calculations. Hence we consider the Boltzmann distribution of a potential to be only a simple means of obtaining a useful form of the temperature factor.

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† Our calculation in §2 and 3 yields a formally different expression; although the interatomic coupling has been taken into account, the Bragg intensity can be calculated from a structure factor, and in each term the temperature factors $T_r(\mathbf{h})$ and $T_s(\mathbf{h})$ appear in the form of a product.

(5) For practical application of the potential approach we give the following recommendations:

(*a*) Never use only third-order β_r parameters.

(*b*) Introduce a zero-order term

$$G(\mathbf{u}_r)[15kT\gamma_r\alpha_r^{-2}+3\Gamma_r\alpha^{-1}]$$

into the p.d.f. (9) for cubic site symmetry, and put $N_r=1$.

(*c*) Use independent anharmonic second-order parameters (Γ_r as coupling parameter for polyatomic crystals). (*b*) and (*c*) are suggested mainly by the lattice-dynamical results.

In two earlier papers (Scheringer, 1972, 1973), we investigated the effect of interatomic thermal coupling by lattice-dynamical calculations. Our considerations were restricted to the harmonic approximation, and had the result that the form of the temperature factor remains the same whether there is interatomic thermal coupling or not. The present discussion, in which we consider the distribution function of the nuclear positions, is much simpler and confirms this result. In the anharmonic case, however, we obtain formally different expressions for the temperature factor depending on whether we take into account interatomic thermal coupling or not. This more general result corresponds to the supposition that the author has held for a long time, but it was concealed in the special case of the harmonic approximation by the distinctive properties of the Gaussian distribution.

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