

## A General Derivation of the Temperature Factor

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### Abstract

A general derivation of the (anharmonic) temperature factor is given. The crystal is treated as a giant molecule of periodic structure. The temperature factor is the Fourier transform of the three-dimensional marginal distribution that is obtained from the joint distribution of the positions of all atoms in the crystal. It is shown that coupling of the motions of different atoms, as expressed in the joint distribution, is projected into the marginal distributions of the individual atoms, and, hence, into the temperature factors. Explicit coupling terms in the expression for the Bragg intensity are not needed; structure factors are always sufficient. Positional parameters are shown to have no other immediate meaning than the designation of the origin of the vibrational coordinates in the unit cell.

### Introduction

Rigorous derivations of the temperature factor (abbreviated t.f.) have been given only in the harmonic approximation of lattice dynamics (James, 1948; von Laue, 1948; Cochran & Cowley, 1967; Willis & Pryor, 1975). Anharmonic lattice dynamics are much more complicated, and several approximations are usually introduced (Krivoglaz & Tekhonova, 1961; Maradudin & Flinn, 1963; Kashiwase, 1965; Wolfe & Goodman, 1969). In these calculations, an attempt is made to derive expressions for the Debye-Waller factor (t.f.), but not for the respective anharmonic probability density function (p.d.f.). Since all the lattice-dynamical calculations give the t.f. in exponential form, the respective p.d.f.'s as inverse Fourier transforms of the t.f.'s are not known analytically. However, from a theorem given by Marcinkiewicz (1938) and extended by Gromes (1984, private communication), it is known that these p.d.f.'s always have negative regions (Scheringer, 1985). This is physically unsatisfactory.

Another question is whether or not anharmonicity of thermal motions poses the need to introduce coupling terms which join the t.f.'s of two different atoms in the expression for the Bragg intensity. Such coup-

ling terms were found by Kashiwase [1965, equation (2.24)] in his lattice-dynamical derivation. Such coupling terms were also used by Pryor & Sanger [1970, Appendix 3, equations (A3.7)-(A3.9)] in the refinement of urea, but the respective parameters were all found to be smaller than their e.s.d.'s. Explicit coupling terms imply that the Bragg intensities can no longer be represented by structure factors, *i.e.*  $I(\text{Bragg}) = FF^*$  would be insufficient. The question arises whether or not  $I(\text{Bragg}) = FF^*$  is sufficient in every case and, if it is, how the effects of interatomic coupling are represented in the t.f.'s and structure factors.

A further matter of practical interest is the fact that the positional parameters obtained in a refinement do not always designate the mean positions. This situation occurs when the t.f. used has first-order terms in the reciprocal-lattice vector  $\mathbf{Q}$  (Scheringer, 1986). A general derivation of the (anharmonic) t.f. should formally contain this result.

In this paper, the t.f. will be established as the Fourier transform of the p.d.f., including anharmonic motions, but the form of the p.d.f. will not be specified. It will be shown that the effects of coupled motions of different atoms are formally included in the p.d.f. and the t.f. The fact that the positional parameters can have many different meanings will be a by-product of the derivation given here.

### Derivation of the temperature factor

The derivation given here is an expansion of the following statements:

(i) Bragg scattering is coherent elastic scattering by crystals.

(ii) For large ensembles (crystals), elastic scattering is scattering by the thermodynamic average density.

(iii) In a crystal, the thermodynamic average density is periodic.

(iv) The scattering units are particles of spherical symmetry that do not change their shape during thermal motion.

(i) may be considered as a definition of Bragg scattering. This definition places us in agreement with all lattice-dynamical approaches in which Bragg

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scattering is classified as elastic (zero-order phonon scattering), and thermal diffuse scattering (TDS) is classified as inelastic (higher-order phonon scattering). The validity of (ii) for large ensembles has been shown to hold very generally by Van Hove [1954, equations (19) and (23)], and by Marshall & Lovesey [1971, pp. 23-24 and equations (3.5) and (3.30)] for neutrons, and by Stewart & Feil [1980, equations (1), (11), (14)-(16)] and Scheringer [1980, equation (7)] for X-rays. For the case of static disorder, von Laue [1948, equation (20.8)] has shown that Bragg intensities can be understood as scattering by the average density of the crystal. (iii) is self-evident. If the thermodynamic average is not periodic, the solid is not a crystal. (iv) represents the so-called convolution approximation. Spherical symmetry is not necessary if, instead, it is required that the particles perform translational motions only (and not rotations as occur with librations of molecules); see Scheringer (1978). The crystal is treated as a giant molecule in which the external motions are eliminated.

The derivation will be performed in the following steps. Firstly, using the validity of (ii), we calculate the scattering amplitude and Bragg intensity from the thermodynamic average. Secondly, the convolution approximation is introduced, and finally the condition of periodicity is imposed.

Since we wish to include neutron scattering and scattering from Mössbauer radiation in our consideration, and the scattering events are not short compared with the time periods of the lattice vibrations, we calculate the thermal average as the average of the canonical ensemble representing the crystal. As is always assumed in statistical mechanics, this average is equal to the average over the (long) time of observation. The ensemble average is given by

$$\rho(\mathbf{x})_{\text{av}} = \sum_m P_m \rho_m(\mathbf{x}), \quad (1a)$$

where  $m$  denotes a state of vibrational energy of the ensemble,  $P_m$  is the probability of its occurrence (a Boltzmann factor) with  $\sum_m P_m = 1$ , and  $\rho_m(\mathbf{x})$  is the density distribution for the state  $m$ . Since we are not primarily interested in energies but rather in configurations of the lattice, we introduce coordinates  $\mathbf{p}_m$  for the  $3nN$  nuclear coordinates ( $N$  cells,  $n$  atoms per cell). Emphasizing the configurational aspect of our problem we can rewrite (1a) as

$$\rho(\mathbf{x})_{\text{av}} = \sum_m P_m \rho_m(\mathbf{x}, \mathbf{p}_m). \quad (1b)$$

For X-ray scattering, where the scattering events are much shorter than the time periods of lattice vibrations (by a factor of about  $10^{-6}$ ), we can also interpret (1b) as a time average:  $P_m$  is the (relative) frequency of a scattering event having taken place at the density distribution  $\rho_m$  with the nuclear configuration  $\mathbf{p}_m$ . Summation over all distributions  $\rho_m$  gives the average

density  $\rho(\mathbf{x})_{\text{av}}$ . According to our statements (i) and (ii) the Bragg scattering amplitude is the Fourier transform of (1), *i.e.*

$$G(\mathbf{Q})_{\text{av}} = \int \rho(\mathbf{x})_{\text{av}} \exp(i\mathbf{Q} \cdot \mathbf{x}) d\mathbf{x}, \quad (2)$$

and the Bragg intensity is given by

$$I(\mathbf{Q})_{\text{Bragg}} = |G(\mathbf{Q})_{\text{av}}|^2. \quad (3)$$

Now we introduce the convolution approximation (iv). First we evaluate the position of an atom  $lk$  ( $l = 1, \dots, N$ ,  $k = 1, \dots, n$ ) in the crystal for the configuration  $\mathbf{p}_m$  as

$$\mathbf{p}_{m,lk} = \mathbf{r}_l + \mathbf{r}_k + \mathbf{u}_{m,lk}. \quad (4)$$

$\mathbf{u}_{m,lk}$  is the position of the atom  $lk$ , relative to a fixed reference position  $\mathbf{r}_l + \mathbf{r}_k$ , in the state (configuration)  $m$ . Let  $\rho_{lk}$  be the (spherically symmetric) distribution of the atom  $lk$  about its nucleus; then the average density is given in the convolution approximation by

$$\rho(\mathbf{x})_{\text{av}} = \sum_m P_m \sum_{lk} \rho_{lk}(\mathbf{x} - \mathbf{p}_{m,lk}). \quad (5)$$

Since we have equal atoms in each cell (*i.e.* periodicity),  $\rho_{lk} = \rho_k$ ,  $l = 1, \dots, N$ . The Fourier transform of (5), given (4), is

$$G(\mathbf{Q})_{\text{av}} = \sum_m P_m \sum_{lk} g_k(\mathbf{Q}) \exp[i\mathbf{Q} \cdot (\mathbf{r}_l + \mathbf{r}_k)] \\ \times \exp(i\mathbf{Q} \cdot \mathbf{u}_{m,lk}), \quad (6)$$

where  $g_k(\mathbf{Q})$  is the Fourier transform of  $\rho_{lk} = \rho_k$ , *i.e.* the X-ray or neutron scattering factor for the atom  $k$  in any cell  $l$ . Since the many energy states  $m$  of a crystal are very close to each other, the vibrational amplitudes  $\mathbf{u}_{m,lk}$  of the atoms are correspondingly close and we may replace the summation over  $m$  by an integration over the  $\mathbf{u}_{lk}$ , thus also replacing the probabilities  $P_m$  by a joint p.d.f. There is, however, a formal difficulty. We want only to describe the internal motions of the crystal and hence have to exclude translations and rotations of the whole crystal. Thus there are six redundant coordinates, which can be treated as dependent coordinates. For dependent coordinates, probabilities are still defined but p.d.f.'s are not. This forces us to express the crystal p.d.f. only by the set of  $3nN - 6$  independent coordinates. In the material for deposit\* it is shown that we can express the six dependent coordinates as linear functions of the remaining  $3nN - 6$  independent (internal) coordinates, and that the internal coordinates  $\mathbf{u}_{3nN-6}$  can still be expressed in lattice units, as has been done in (4) and (6). Furthermore, the six dependent coordinates must be chosen from (at least)

\* The evaluation of the six dependent coordinates has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43916 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

three different atoms. The probability  $P_m$  that a given configuration  $\mathbf{u}_m$  of all  $nN$  atoms occurs is equal to the probability calculated from the p.d.f.  $f_m(\mathbf{u}_{3nN-6})$  for the  $3nN-6$  independent coordinates, *i.e.*

$$P_m = f_m(\mathbf{u}_{3nN-6}) d\mathbf{u}_{3nN-6}. \quad (7)$$

We now replace the summation over  $m$  by an integration and obtain

$$G(\mathbf{Q})_{av} = \sum_{lk} g_k(\mathbf{Q}) \exp[i\mathbf{Q} \cdot (\mathbf{r}_l + \mathbf{r}_k)] \\ \times \int \exp(i\mathbf{Q} \cdot \mathbf{u}_{lk}) f(\mathbf{u}_{3nN-6}) d\mathbf{u}_{3nN-6}. \quad (8)$$

Since the integral in (8) occurs separately for each single term of the sum over  $lk$ , the integration over all other coordinates  $\mathbf{u}_{l'k'} \neq \mathbf{u}_{lk}$  can be performed directly in each term  $lk$ , thus leading to

$$\int f(\mathbf{u}_{3nN-6}) d\mathbf{u}'_{3nN-6} = f_{lk}(\mathbf{u}_{lk}), \quad (9)$$

where  $d\mathbf{u}'_{3nN-6}$  denotes that the integration is performed only over the coordinates  $\mathbf{u}_{l'k'} \neq \mathbf{u}_{lk}$ . In statistics,  $f_{lk}(\mathbf{u}_{lk})$  is called the three-dimensional marginal p.d.f. of the  $(3nN-6)$ -dimensional joint p.d.f. with respect to the three coordinates  $\mathbf{u}_{lk}$ . For the three atoms carrying the six dependent coordinates, we express the dependent coordinates in  $\exp(i\mathbf{Q} \cdot \mathbf{u}_{lk})$  by the independent ones. Integration over  $\mathbf{u}'$  no longer leads to a marginal p.d.f. for these atoms, and the final integration over the remaining independent coordinates (none, one and two) of these atoms leads to some unknown function of  $\mathbf{Q}$  [instead of to the t.f.  $T(\mathbf{Q})$  as obtained in (13)]. We can neglect this situation in the following, since only three atoms of the crystal are involved. This amounts to an inaccuracy of  $3/nN$ , *i.e.* of the order of  $10^{-10}$  or less. Our statement (iii) (periodicity) implies that the position of an atom  $k$  is equally distributed in all cells  $l$ ; hence we have

$$f_{lk}(\mathbf{u}_{lk}) = f_k(\mathbf{u}_k), \quad l = 1, \dots, N. \quad (10)$$

We use (9) and (10), and obtain from (8)

$$G(\mathbf{Q})_{av} = \sum_l \exp(i\mathbf{Q} \cdot \mathbf{r}_l) \sum_k g_k(\mathbf{Q}) \exp(i\mathbf{Q} \cdot \mathbf{r}_k) \\ \times \int f_k(\mathbf{u}_k) \exp(i\mathbf{Q} \cdot \mathbf{u}_k) d\mathbf{u}_k. \quad (11)$$

From (3) we now obtain

$$I(\mathbf{Q})_{\text{Bragg}} = \left| \sum_l \exp(i\mathbf{Q} \cdot \mathbf{r}_l) \right|^2 |F(\mathbf{Q})|^2, \quad (12)$$

where  $F(\mathbf{Q})$  represents the sum over  $k$  in (11), *i.e.* the structure factor. The first factor on the right-hand side of (12) is Laue's interference function, which has the effect that the Bragg intensity can only be observed at the reciprocal-lattice points  $\mathbf{h} = \mathbf{Q}/2\pi$ . The t.f. which occurs in  $F(\mathbf{Q})$ , *i.e.*

$$T_k(\mathbf{Q}) = \int f_k(\mathbf{u}_k) \exp(i\mathbf{Q} \cdot \mathbf{u}_k) d\mathbf{u}_k, \quad (13)$$

is the Fourier transform of the three-dimensional marginal p.d.f.  $f_k(\mathbf{u}_k)$  of the joint p.d.f.  $f(\mathbf{u}_{3nN-6})$  of all atoms in the crystal.

Finally, we show that  $f_k(\mathbf{u}_k)$  is also the marginal p.d.f. of the joint p.d.f. of all atoms in a unit cell. Since, in (9), the sequence of integration does not matter, it can be performed first over all coordinates  $\mathbf{u}_{l'k'}$  referring to all other cells  $l' \neq l$ . This integration yields the corresponding  $3n$ -dimensional marginal p.d.f.'s  $f_l(\mathbf{u}_l)$  of  $f(\mathbf{u}_{3nN-6})$  with respect to the  $n$  atoms of a cell  $l$ . Since the crystal is periodic,  $f_l(\mathbf{u}_l)$  is the same for all cells. Further integration over  $\mathbf{u}_{k'l}$  with  $k' \neq k$  yields the three-dimensional marginal p.d.f.  $f_k(\mathbf{u}_k)$  of  $f_l(\mathbf{u}_l)$  with respect to the atom  $k$ .

## Results

The inverse Fourier transform of the t.f. is the marginal p.d.f., which, as such, must be non-negative everywhere. The coupling of motions by different atoms in a crystal is expressed in the joint p.d.f.  $f(\mathbf{u}_{3nN-6})$ . By projection, interatomic coupling is transferred to the three-dimensional marginal p.d.f.'s  $f_k(\mathbf{u}_k)$ , and thus also to their Fourier transforms, the t.f.'s.  $f(\mathbf{u}_{3nN-6})$  is unknown and cannot be determined from experimental data. In the harmonic approximation, however,  $f(\mathbf{u}_{3nN-6})$  is known to be Gaussian, as are its marginal p.d.f.'s  $f_k(\mathbf{u}_k)$ . This knowledge is utilized in the following paper (Scheringer, 1987), and some general results are derived clarifying how interatomic coupling affects the vibration tensors of the individual atoms.

Explicit coupling terms in the expression for the Bragg intensity, as found by Kashiwase [1965, equation (2.24)] and as used by Pryor & Sanger (1970, Appendix 3), are not appropriate since they do not contribute to the thermal average. In accordance with (3) and (12), the Bragg intensities can always be represented by structure factors. This conclusion also seemed to be reached by Cochran & Cowley (1967, p. 126) (for elastic scattering).

In anharmonic lattice-dynamical calculations of the t.f., it is sufficient to calculate the thermal average  $\langle \exp(i\mathbf{Q} \cdot \mathbf{u}_{lk}) \rangle$  [as was done by Krivoglaz & Tekhonova (1961) and Wolfe & Goodman (1969)]. This is shown by (6) and (8). Calculation of the average  $\langle \exp[i\mathbf{Q} \cdot (\mathbf{u}_{lk} - \mathbf{u}_{l'k'})] \rangle$ , as was done by Maradudin & Flinn [1963, equation (1.3)] and Kashiwase [1965, equation (2.1)] and stated by Willis & Pryor [1975, equations (5.4) and (5.6)], implies an unnecessary complication and may have led to the error in Kashiwase's [1965, equation (2.24)] result.

The vector  $\mathbf{r}_k$  describing the position of an atom in a unit cell can be arbitrarily defined in many different ways (being the same for each cell  $l$ ). This is obvious in our calculation, from (4) onwards. At any rate,  $\mathbf{r}_k$  serves as the origin of the vibrational

coordinates  $\mathbf{u}_{jk}$ , i.e.  $\mathbf{u}_{jk} = \mathbf{0}$  at  $\mathbf{r}_k$ . The consequences of this situation concerning the meaning of the positional parameters are discussed elsewhere (Scheringer, 1986).

In establishing anharmonic p.d.f.'s, parameters of an 'effective potential' or 'isolated-atom potential' are often used (Willis & Pryor, 1975, ch. 5; Zucker & Schulz, 1982). Our basic result that any atomic p.d.f. has to be conceived as a marginal p.d.f. of the crystal p.d.f. gives rise to the following interpretation: the parameters of the effective potential describe the motions of an atom as if it would vibrate under this potential, *no matter where the remaining atoms of the crystal are actually located* (but within the limits set by the crystal p.d.f.). Note the difference of this interpretation from the common interpretation with the Einstein model (Willis & Pryor, 1975, p. 12) where the atoms are assumed to vibrate independently.

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## On the Interpretation of Anisotropic Temperature Factors. IV. The Effect of Interatomic Coupling on the Vibration Tensors

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### Abstract

In the harmonic approximation of thermal vibrations, the probability density function (p.d.f.) of a crystal is discussed and the p.d.f. of a single atom is derived. It is shown that Bragg intensities and temperature factors are affected by statistical dependences among the vibrational coordinates but not the covariances (correlations) of the atoms in the crystal. The relation between statistical dependences and interatomic force constants is established, and effective potential parameters are derived as functions of the interatomic force constants. It is shown that a decrease in the

diagonal elements or an increase in the off-diagonal elements of statistical dependence increases the mean-square amplitudes  $\langle u^2 \rangle$  of the atoms. An increase in statistical dependence between different coordinates of space always increases the  $\langle u^2 \rangle$ . Some experimental results ( $\langle u^2 \rangle$ ) in different types of structures are interpreted with simple models of statistical dependence.

### 1. Introduction

The effect of coupling the motions of different atoms in crystals on Bragg intensities and atomic vibration tensors is difficult to analyse. Vibration tensors determined by means of diffraction experiments support

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