

## A General Expression for the Anharmonic Temperature Factor in the Isolated-Atom-Potential Approach

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### Abstract

An explicit expression is given for the anharmonic temperature factor that is gained from an isolated-atom potential in the classical regime. Since the Boltzmann function is not generally suited to form a probability density function (p.d.f.) and its Fourier transform is generally unknown, a meaningful p.d.f. can be obtained by expanding the anharmonic terms into a series. The Fourier transform of this series, *i.e.* the temperature factor, is derived up to any number of desired terms. These series are valid for any covariance matrix and for every crystal metric; site-symmetry restrictions can be imposed. Higher powers of the potential parameters can be introduced. The series given for the temperature factor does not require the cumbersome solution of Fourier integrals. For cubic site symmetry, the low-order terms in  $h$  containing the  $n$ th power of the cubic  $\beta$  and  $\gamma$  parameters are derived explicitly. The terms with  $\beta^n$  ( $n = 1, \dots, 16$ ) and  $\gamma^n$  ( $n = 1, \dots, 6$ ) are evaluated numerically in one example. From a certain power onwards, divergence is observed in all terms. It is shown that divergence is in general to be expected for both the expansions of the temperature factor and the p.d.f. The mere expansion by a power higher neither necessarily leads to a better approximation of the Boltzmann function nor necessarily constitutes a better p.d.f. It is concluded that expansions containing different powers of the potential parameters are equally justified unless the examination in a particular problem with the available set of experimental data has shown that a certain expansion is the best.

### 1. Introduction

In several papers on anharmonic motions of atoms, a temperature factor is used that is derived from an effective one-particle potential, abbreviated as OPP (Dawson, Hurley & Maslen, 1967), or, what is in essence the same, from an isolated-atom potential, abbreviated as IAP (Willis, 1969). For applications see Mair, Barnea, Cooper & Rouse (1974), Willis & Pryor (1975), Mair & Barnea (1975), Matsubara (1975*a, b*), Harada, Suzuki & Hoshino (1976), Merisalo & Larsen (1977, 1979), Whiteley, Moss &

Barnea (1978), Moss, McMullan & Koetzle (1980), Field (1982), Kontio & Stevens (1982), Zucker & Schulz (1982) and other authors. Usually, in the probability density function - abbreviated p.d.f. - the anharmonic terms of the potential are expanded into a (truncated) series, and the conditions of site symmetry are imposed. The temperature factor is the Fourier transform of this series, and its evaluation usually requires a cumbersome solution of Fourier integrals. For cubic site symmetry, the IAP temperature factor was first given by Willis (1969) (up to fourth-order terms), for site symmetry  $3m$  in the hexagonal system by Mair & Barnea (1975) (up to third-order terms), see also Whiteley, Moss & Barnea (1978), for tetragonal site symmetry by Nishiwaki, Sakata & Harada (1979) (up to fourth-order terms) and for site symmetry  $\bar{6}m2$  by Merisalo & Larsen (1977) (up to fourth-order terms). For cubic site symmetry, Mair & Wilkins (1976) have derived the temperature factor (up to sixth-order terms) from consideration of quantum statistics. Willis's (1969) treatment has recently been extended for any site symmetry (up to fourth order terms) by Tanaka & Marumo (1983).

Recently, Mair (1980*a*) has derived a more general formula for the OPP temperature factor through a perturbation expansion about the harmonic Hamiltonian, and has illustrated the power of her formula for the specific case of cubic site symmetry. In particular, Mair determined contributions that are quadratic in the cubic  $\beta$  parameter and have been overlooked by other authors. However, Mair's (1980*a*) temperature factor (8), (9) and (14) is in exponential form and is not the exact Fourier transform of the Boltzmann distribution;\* see the Appendix. Still, it

\* Some of the predominantly mathematical material of this paper has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39686 (12pp.). This material refers to the following topics: derivation of equation (4) for the temperature factor, derivation of equation (18) for  $Z_m$ , proof that series expansions of the Boltzmann function are always divergent, proof that Mair's (1980*a*) temperature factor is not the Fourier transform of the Boltzmann function, numerical data (Table 1) referring to the higher powers of the potential parameters of Al in the structure of  $VA1_{10-42}$ . Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

is justified to ask how meaningful higher powers of the potential parameters are in series expansions. Since Mair, Barnea, Cooper & Rouse (1974) and Mair (1980a) have introduced the  $\beta^2$  terms in the temperature factor for cubic site symmetry, it is commonly stated that this extended form of the temperature factor is more accurate than the one derived by Willis (1969) (which contains only a term linear in  $\beta$ ), because the  $\beta^2$  terms may be of the same order of magnitude as the corresponding terms linear in  $\gamma$ . We shall examine the validity of this statement in this paper.

This paper will give a general expression for the anharmonic temperature factor with the following aims: (1) to constitute and maintain the exact Fourier transform relation between p.d.f. and temperature factor; (2) to formulate the temperature factor for any covariance matrix and for every crystal metric (so that it can easily be programmed); (3) to give a series for the p.d.f. and the temperature factor for any desired order of terms; (4) to establish the possibility of introducing higher powers of the potential parameters; (5) to make the solution of Fourier integrals superfluous.

## 2. The p.d.f. and the temperature factor

In the IAP approach, the origin for the displacements  $\mathbf{u}$  of an atom is conceptually given by the minimum of the potential for this atom. For the p.d.f. actually used [see below, equation (3)], it can only be derived that the origin for  $\mathbf{u}$  is located at the maximum of the p.d.f. (which does not necessarily coincide with the minimum of a potential). In order to make our notation more efficient for what follows, we do not use the commonly used symbols  $\alpha, \beta, \gamma, \delta$  for the potential parameters, but rather denote these by tensor components  $A_{ij}, A_{ijk}$  and  $A_{ijkl}$ . These are covariant to the base vectors of the crystal and also contain the factor  $(k_B T)^{-1}$ .  $k_B$  is Boltzmann's constant and  $T$  the absolute temperature. Then the IAP is given by

$$V(\mathbf{u}) = k_B T \left[ \sum_{ij} \left( \frac{1}{2} p_{ij} + A_{ij} \right) u^i u^j + \sum_{ijk} A_{ijk} u^i u^j u^k + \sum_{ijkl} A_{ijkl} u^i u^j u^k u^l + \dots \right], \quad (1)$$

where  $p_{ij}$  denote the harmonic components and  $A_{ij}$  the anharmonic second-order components [as they may arise from a unit-cell-potential approach (Scheringer, 1977) or from consideration of quantum statistics (Mair & Wilkins, 1976)]. The atomic displacements  $u^i$ ,  $i = 1, 2, 3$  for the three directions of space, are counted in lattice units (as are the potential parameters). In the classical regime, the p.d.f. is obtained from the potential according to the

Boltzmann distribution, *i.e.*

$$f(\mathbf{u}) = C \exp[-V(\mathbf{u})/(k_B T)], \quad (2)$$

where  $C$  is the normalization constant. In order to avoid divergence for large values of  $\mathbf{u}$ , we expand the anharmonic terms in (2) into a series in the linear approximation  $\exp x = 1 + x$ , *i.e.*

$$f(\mathbf{u}) = \frac{g(\mathbf{u})}{P} \left[ 1 - \sum_{ij} A_{ij} u^i u^j - \sum_{ijk} A_{ijk} u^i u^j u^k - \sum_{ijkl} A_{ijkl} u^i u^j u^k u^l - \dots \right]. \quad (3)$$

$P$  is chosen so that  $f(\mathbf{u})$  is normalized (to one).  $g(\mathbf{u})$  denotes the Gaussian p.d.f. that results from the harmonic parameters  $p_{ij}$  of (1), *i.e.*  $\mathbf{p}^{-1}$  is the covariance matrix of  $g(\mathbf{u})$ . Let

$$\int_{-\infty}^{+\infty} g(\mathbf{u}) d\mathbf{u} = P_0.$$

We denote the Miller indices by  $h_i$  or  $\mathbf{h}$ , respectively, and  $\sqrt{-1} = i$ . The temperature factor is the Fourier transform of  $f(\mathbf{u})$  and, with (3), has the form of a series, *i.e.*

$$T(\mathbf{h}) = g(\mathbf{h}) \frac{P_0}{P} \left\{ 1 - \left[ i^2 \sum_{ij} A_{ij} G^{ij}(\mathbf{h}) + i^3 \sum_{ijk} A_{ijk} G^{ijk}(\mathbf{h}) + i^4 \sum_{ijkl} A_{ijkl} G^{ijkl}(\mathbf{h}) + \dots \right] \right\}, \quad (4)$$

with correspondingly higher terms in (3) and (4).  $g(\mathbf{h})$  is the harmonic temperature factor. We now explain what the functions  $G$  and  $P$  in (4) mean and how they can be calculated.  $G^{ij}, G^{ijk}, G^{ijkl}, \dots$  are Hermite polynomial tensors that are contravariant to the crystal base vectors, and are analogously defined as the covariant Hermite polynomial tensors in *International Tables for X-ray Crystallography* (1974, pp. 316–317). To specify the  $G$  polynomials in detail we denote  $\boldsymbol{\sigma} = \mathbf{p}^{-1}$  and define the vector  $\mathbf{t}$  according to

$$t^i = 2\pi \sum_{m=1}^3 \sigma^{im} h_m \quad (5)$$

and obtain

$$G^{ij} = t^i t^j - \sigma^{ij}, \quad (6)$$

$$G^{ijk} = t^i t^j t^k - t^i \sigma^{jk} - t^j \sigma^{ik} - t^k \sigma^{ij}$$

*etc.*, cf. the corresponding expressions in *International Tables for X-ray Crystallography* (1974, p. 316). The derivation of (4), in conjunction with (5) and (6), has been deposited.\* Comparison of the IAP series (3) and the temperature factor (4) with the Gram-Charlier series and its Fourier transform (*International Tables for X-ray Crystallography*, 1974, pp. 316–317)

\* See deposition footnote.

shows that the two approaches essentially differ in that the power series and the Hermite polynomial series are exchanged in direct and reciprocal space. Since  $P$  in (4) normalizes  $f(\mathbf{u})$  (to one), we can obtain  $P$  from the Fourier transform of  $f(\mathbf{u})$  at the position  $\mathbf{h}=\mathbf{0}$ . Thus we obtain the condition  $T(\mathbf{h}=\mathbf{0})=1$  or

$$P = P_0[1 - (i^2 O_2 + i^4 O_4 + \dots)]. \quad (7)$$

$O_2, O_4, \dots$  are the constant terms in (4), which do not depend on  $\mathbf{h}$  and arise when the summations in (4) are carried out. Potential terms with odd powers of  $u^i$  do not contribute to  $P$ .

In actual practice one may prefer not to use (4) directly, but rather insert (5) and (6) into (4) and evaluate the sums as far as possible. Furthermore, (4) can be simplified with the use of (7). We write out the constant terms in (4), divide by  $P$  and order the terms according to powers of  $h_i$ . Then the series (4) assumes the form

$$T(\mathbf{h}) = g(\mathbf{h}) \left\{ 1 - \frac{P_0}{P} \left[ 2\pi i \sum_i W^i h_i + (2\pi i)^2 \sum_{ij} W^{ij} h_i h_j + (2\pi i)^3 \sum_{ijk} W^{ijk} h_i h_j h_k + (2\pi i)^4 \sum_{ijkl} W^{ijkl} h_i h_j h_k h_l + \dots \right] \right\}. \quad (8)$$

The contravariant components of the  $\mathbf{W}$  tensors are functions of the anharmonic potential parameters  $A_{ij}, A_{ijk}, A_{ijkl}, \dots$  and of the variance-covariance matrix  $\sigma$ , according to (4), (5) and (6).

Merisalo & Larsen (1977, equation 5) and Kurki-Suonio, Merisalo & Peltonen (1979, equations 27 and 28) used a Fourier-invariant Fourier transform relation with Hermite polynomials, which seems to contradict our equations (3) and (4) as well as equations (2) and (9) of *International Tables for X-ray Crystallography* (1974, ch. 5.2.3). We found, however, that both transform relations are correct. There are two different definitions of Hermite polynomials, which are usually not distinguished as such, but which lead to different coefficients in the polynomials. Both definitions are given by Magnus, Oberhettinger & Soni (1966, pp. 249–250). The one-dimensional Fourier-invariant relation is given by Titchmarsh (1948, p. 76, equation 3.5.1 and p. 81, theorem 57) and the one-dimensional non-invariant relation by Kendall & Stuart (1969, p. 157).

### 3. Comparison with results from the literature

*The results of Willis (1969) and Mair & Barnea (1975)*

For cubic site symmetry, we obtain Willis's (1969) equation (4.11), and for site symmetry  $3m$  Mair &

Barnea's (1975) equation (14) (the sign of Mair & Barnea's  $\beta_1$  term should be reversed) if we first write down the series (4) and then reorder it to the form (8). [The results of these authors are given in a form which corresponds to (8).] Since in (4) and (8) all indices have to be summed from 1 to 3, one has to observe that the multiplicities  $m$  of the  $\mathbf{A}$  tensors are correctly taken into account if they are expressed by the potential parameters  $\beta, \gamma$  and  $\delta$  as used by these authors. According to the definition of  $\beta, \gamma$  and  $\delta$  by Willis (1969) we have:  $A_{123} = \beta/(6k_B T)$  since  $m=6$ ;  $A_{1111} = A_{2222} = A_{3333} = (\gamma + \frac{2}{5}\delta)/(k_B T)$ ;  $A_{1122} = A_{1133} = A_{2233} = \frac{2}{6}(\gamma - \frac{3}{5}\delta)/(k_B T)$  since  $m(A_{1122})=6$  and  $(u^1 u^2)^2$  appears twice. With site symmetry  $3m$  in the hexagonal system the following restrictions are valid for the potential parameters (*International Tables for X-ray Crystallography*, 1974, Table 5.5C, row C37\*):  $A_{122} = -A_{112}$ ,  $A_{223} = A_{113}$ ,  $A_{123} = -\frac{1}{2}A_{113}$ .  $m(A_{112}) = m(A_{113}) = 3$ . According to the definition by Mair & Barnea (1975) of  $\beta_1 \beta_2$  and  $\beta_3$  we have:  $A_{112} = \beta_1/(3k_B T)$ ,  $A_{113} = \beta_2/(3k_B T)$ ,  $A_{333} = \beta_3/(k_B T)$ . Since Willis (1969) and Mair & Barnea (1975) count the atomic displacements in  $\text{\AA}$  but we in lattice units, one has to transform the potential parameters correspondingly further. In our results for the temperature factor this implies that the Miller indices have to be divided by the corresponding lattice constants.

### Results obtained from quantum statistics

Mair & Wilkins (1976, equations 19–21) have derived a p.d.f. for cubic site symmetry on the basis of quantum statistics and have determined the temperature factor as the Fourier transform of this p.d.f. In addition, Mair (1980*b*, Table 1) has listed contributions to the temperature factor for an OPP model. Mair & Wilkins (1976) have formulated the normalization condition in a manner different from ours in (3). Their p.d.f. contains an anharmonic second-order term, which classically is not obtained in an OPP model but in a unit-cell-potential approach (Scheringer, 1977). The number of expansion coefficients in Mair & Wilkins's p.d.f. (19) and temperature factor (20) and (21) is the same as in our expressions (3) and (4) (for the square of the third-order term see § 4), but the meaning of the coefficients is different, particularly with respect to dependence on temperature. The same conclusion can be drawn by inspecting Mair's (1980*b*) Table 1. Thus, in general, the examination of quantum statistics does not produce new terms beyond those given in (3) and (4). The reason is that a tensor formulation up to a given power of  $\mathbf{u}$  is mathematically complete and cannot be extended by more profound physical arguments. Such arguments at most give rise to a change in the meaning of the expansion coefficients.

#### 4. Higher powers of the potential parameters

In (3) we have terminated the expansion after the terms linear in the anharmonic potential parameters, and we now show how one can use (3) and (4) to take into account higher powers of the potential parameters. In (3), one has to express the higher powers of the potential parameters by linear parameters of correspondingly higher order. This then constrains these linear parameters without affecting, however, the formal application of the Fourier transform relation (3) and (4). Thus, one can use (3) and (4) but has to expand to correspondingly higher terms. Since all terms (3) and (4) have a minus sign and since in the expansion to even powers a plus sign arises, one has to observe this change of sign when using (3) and (4). In order to demonstrate the effect of the higher powers of the potential parameters, we shall restrict ourselves in what follows to the case of cubic site symmetry.

To illustrate in detail the method of our calculation, we first calculate the  $\beta^2$  terms that were already found by other authors.  $\beta^2$  terms are of sixth order in  $\mathbf{u}$  and, by the definition of the  $\mathbf{A}$  tensors in (1), we obtain the restriction  $90 A_{112233} = -\frac{1}{2}(6A_{123})^2$ , because  $m(A_{112233}) = 90$  and  $m(A_{123}) = 6$ . Hence, we also obtain  $\frac{1}{2}\beta^2/(k_B T)^2 = -90 A_{112233}$ . With (3) and (4), the  $\beta^2$  terms in the temperature factor are then given by

$$i^6 g(\mathbf{h}) \frac{P_0}{P} \frac{\beta^2}{2(k_B T)^2} G^{112233}(\mathbf{h}). \quad (9)$$

Writing out the  $G$  polynomial in (9), observing  $\sigma^{ii} = k_B T/\alpha$  and  $\sigma^{ij} = 0$ , gives exactly the same terms (except for the factor  $P_0/P$ ), which one obtains by expanding Mair's (1980a) equation (14) correctly to quadratic terms in her  $\lambda$  parameter. The p.d.f. to Mair's  $\lambda^2$  expansion is given in the deposited material.\*

The  $\beta^2$  terms given by Mair, Barnea, Cooper & Rouse (1974) and by Kontio & Stevens (1982) are all reproduced by (9). However, (9) also produces a  $h_1^2 h_2^2 h_3^2$  term which is not given by these authors. Thus, we conclude that equation (6) of Kontio & Stevens (1982) is *not* the Fourier transform of their equations (3) and (5). The p.d.f. to equation (6) of Kontio & Stevens can be established, if the inverse Fourier transform to the missing  $h_1^2 h_2^2 h_3^2$  term is subtracted from the p.d.f. (which is expanded to  $\beta^2$ ). With a non-diagonal covariance matrix and in a general metric, such a procedure is no longer possible. This example shows that omission of the higher terms in  $\mathbf{h}$  (which are obtained from the  $G$  polynomials) cannot be recommended, for then the Fourier transform relation, expressed in (3) and (4), is invalidated and the p.d.f. can no longer be calculated.

\* See deposition footnote.

In the following we give general expressions for the zero- to fourth-order terms in  $\mathbf{h}$  with higher powers of  $\beta$  and  $\gamma$  and calculate some numerical values. Terms with even powers of  $\beta$  are obtained from the  $G$  polynomials of order  $3n$  with three different indices, each of which occurs  $n$  times.  $n$  is even. Evaluation of these polynomials yields for the zero-order terms in  $\mathbf{h}$

$$\frac{1}{n!} \left( \frac{\beta}{k_B T} \right)^n \left( \frac{k_B T}{\alpha} \right)^{3n/2} Z_n^3, \quad s = \frac{n}{2}, \quad n \text{ even}, \quad (10)$$

for the second-order terms in  $\mathbf{h}$

$$\begin{aligned} & -\frac{1}{n!} \left( \frac{\beta}{k_B T} \right)^n \left( \frac{k_B T}{\alpha} \right)^{(3n+2)/2} \left( \frac{2\pi}{a_0} \right)^2 Z_{n,1} Z_{n,2}^2 \\ & \times (h_1^2 + h_2^2 + h_3^2), \quad s_1 = n/2 - 1, \\ & \quad \quad \quad s_2 = n/2, \quad n \text{ even}, \quad (11) \end{aligned}$$

and for the fourth-order terms in  $\mathbf{h}$

$$\begin{aligned} & \frac{1}{n!} \left( \frac{\beta}{k_B T} \right)^n \left( \frac{k_B T}{\alpha} \right)^{(3n+4)/2} \left( \frac{2\pi}{a_0} \right)^4 Z_{n,1}^2 Z_{n,3} \\ & \times (h_1^2 h_2^2 + h_1^2 h_3^2 + h_2^2 h_3^2), \\ & s_1 = n/2 - 1, \quad s_3 = n/2, \quad n \text{ even}, \quad (12) \end{aligned}$$

and

$$\begin{aligned} & \frac{1}{n!} \left( \frac{\beta}{k_B T} \right)^n \left( \frac{k_B T}{\alpha} \right)^{(3n+4)/2} \left( \frac{2\pi}{a_0} \right)^4 Z_{n,1} Z_{n,2}^2 \\ & \times (h_1^4 + h_2^4 + h_3^4), \\ & s_1 = n/2 - 2, \quad s_2 = n/2, \quad n \geq 4, \quad n \text{ even}. \quad (13) \end{aligned}$$

The values of  $Z_n$  are calculated from (18) below with the given values of  $s$ .  $s_1$  refers to  $Z_{n,1}$ ,  $s_2$  to  $Z_{n,2}$  and  $s_3$  to  $Z_{n,3}$ . The common factor  $g(\mathbf{h})P_0/P$  is not given in (10) to (13) but the minus sign in (4) has been taken into account. For the odd powers of  $\beta$  we only give the terms with  $h_1 h_2 h_3$ . They are obtained from  $G$  polynomials of order  $3n$  according to

$$\begin{aligned} & \frac{i}{n!} \left( \frac{\beta}{k_B T} \right)^n \left( \frac{k_B T}{\alpha} \right)^{(3n+3)/2} \left( \frac{2\pi}{a_0} \right)^3 Z_n^3 h_1 h_2 h_3, \quad (14) \\ & s = (n-1)/2, \quad n \text{ odd}. \end{aligned}$$

Each of the expressions (10) to (14) has the same sign for all values of  $n$ .

The terms with the higher powers of  $\gamma$  are derived from  $G$  polynomials of order  $4n$ . We restrict ourselves to  $G$  polynomials with equal indices. For the zero-order terms in  $\mathbf{h}$  we obtain

$$\frac{(-1)^n}{n!} \left( \frac{\gamma}{k_B T} \right)^n \left( \frac{k_B T}{\alpha} \right)^{2n} 3Z_{4n}, \quad s = 2n, \quad (15)$$

for the second-order terms in  $\mathbf{h}$

$$\begin{aligned} & -\frac{(-1)^n}{n!} \left(\frac{\gamma}{k_B T}\right)^n \left(\frac{k_B T}{\alpha}\right)^{2n+1} \left(\frac{2\pi}{a_0}\right)^2 \\ & \times Z_{4n}(h_1^2 + h_2^2 + h_3^2), \quad s = 2n - 1, \end{aligned} \quad (16)$$

and for the fourth-order terms in  $\mathbf{h}$

$$\begin{aligned} & \frac{(-1)^n}{n!} \left(\frac{\gamma}{k_B T}\right)^n \left(\frac{k_B T}{\alpha}\right)^{2n+2} \left(\frac{2\pi}{a_0}\right)^4 \\ & \times Z_{4n}(h_1^4 + h_2^4 + h_3^4), \quad s = 2n - 2. \end{aligned} \quad (17)$$

$Z_n$  is obtained as follows.\*

$$Z_n = \frac{n!}{2^s (n-2s)! s!}, \quad (18)$$

where  $s$  denotes the number of  $\sigma^{ij}$  factors in a given term of a  $G$  polynomial. We do not calculate the terms that arise from  $G$  polynomials with mixed indices because their coefficients  $Z$  are more difficult to determine. Since  $\sigma$  is diagonal these coefficients are smaller than  $Z_{4n}$ . Hence, the expansions (15) to (17) represent the main contributions. As for (10) to (17), the terms with orders higher than four in  $\mathbf{h}$  can also be given.

We have calculated numerical values for (10) to (17) with the potential parameters of Kontio & Stevens (1982) and with  $T = 293\text{K}$ ; (10) to (13) up to  $n = 16$ , (14) up to  $n = 13$ , and (15) to (17) up to  $n = 6$ .\* The most important result is the following: from a certain power  $n$  onwards, divergence is observed for all terms. Thus, none of the expressions (10) to (17) converges to zero for increasing  $n$ . Formally, the divergence arises from the fact that, for larger values of  $n$ , the greatly increasing coefficients  $Z$  begin to dominate.\* Since  $Z_{4n}$  represents the full number of terms and, with  $\sigma$  diagonal,  $Z_n^3 < Z_{3n}$ ,  $Z_{n,1} Z_{n,2}^2 < Z_{3n}$ ,  $Z_{n,1}^2 Z_{n,3} < Z_{3n}$ , divergence is most pronounced with the  $\gamma^n$  terms. In the expression (17), it already begins with  $n = 2$ .\*

For low site symmetry and for a non-diagonal covariance matrix, the temperature factor is still unambiguously described by the  $G$  polynomials when higher powers of the potential parameters are included in the p.d.f. (3). But as can be seen from (18), the number of terms,  $Z_n$ , grows rapidly as  $n$  increases. Thus, for  $n > 6$  and for low site symmetry, the terms of the  $G$  polynomials cannot usually be written out explicitly. The necessary permutations of the indices should then be generated in the computer and the terms summed up numerically.

### 5. Analysis of divergence

The divergence observed in our example did not happen by chance. It is ultimately caused by the fact

that, with the potential expansion (1), the Boltzmann function (2) can be divergent, *i.e.*  $f(\mathbf{u}) \rightarrow \infty$  for  $u \rightarrow \infty$ . For cubic site symmetry, divergence occurs if only a  $\beta$  parameter is used (Matsubara, 1975*a, b*) or if  $\gamma$  is negative. A one-dimensional Boltzmann distribution converges only (*i.e.*  $f(\mathbf{u}) \rightarrow 0$  for  $u \rightarrow \infty$ ) if the highest power of  $u$  is even and if the coefficient of the highest power is negative. For a three-dimensional Boltzmann distribution this result holds correspondingly. The signs of the several terms of the highest power in  $\mathbf{u}$  (which must be even) have to be inspected. Divergence is likely to occur more frequently than convergence because the condition for convergence is more rigorous (the sphere in  $\mathbf{u}$  must be 'tight' everywhere). When divergence occurs, the Boltzmann distribution (2) does not establish a p.d.f. and the Fourier transform of (2), in the integral definition, does not exist and, thus, a temperature factor cannot be derived.

A finite series expansion (3), containing higher powers of the potential parameters, always has a finite integral and, hence, its Fourier transform always exists. (The expansion may have negative regions and thus may not entirely fulfil the requirements for a p.d.f.) However, the Boltzmann function can never be approximated sufficiently closely by a series expansion with any powers of the potential parameters. This is true for a divergent and a convergent Boltzmann function.\* The reason is that the absolute values of the coefficients in the series are the same for both a divergent and a convergent Boltzmann function. Since the series is also designed to approximate the divergent Boltzmann function, the sequence of its coefficients is diverging and, hence, the series is also diverging for a convergent Boltzmann function. One-dimensional calculations that we have performed show the following. For *small* values of  $u$ , the series approximates the Boltzmann function better the higher the powers that are included. For *large* values of  $u$ , the series diverges more strongly the higher the powers that are included. The best possible approximation (to a convergent Boltzmann function) is usually obtained with a series with powers  $\leq 4$ , or with a series with damping factors at the higher powers. Thus, it appears that, for large values of  $u$ , a variety of solutions is offered by the expansions (3) depending on what powers of the potential parameters are actually included. We note that, for large values of  $u$ , Matsubara (1975*a, b*) has set  $f(\mathbf{u}) = 0$  beyond a certain maximum value of  $u$ .

### 6. Discussion

Since Mair, Barnea, Cooper & Rouse (1974) introduced the  $\beta^2$  terms into the temperature factor for

\* See deposition footnote. We are indebted to Drs J.K. Mackenzie and S.L. Mair for having drawn our attention to the fact that the IAP expansion (3) also does not converge to a convergent Boltzmann function.

\* See deposition footnote.

cubic site symmetry there seems to be common agreement that the temperature factor is thereby improved. Thus, Moss, McMullan & Koetzle (1980) and Kontio & Stevens (1982) also used the  $\beta^2$  terms. Some people consider the Willis expansion (4.11), in which the  $\beta^2$  terms are neglected, to be incorrect because  $\gamma$  and  $\beta^2$  terms are of the same order in the van Hove order parameter  $\lambda$ . Obviously, the aim is to approximate the Boltzmann function as closely as possible. We shall now discuss the problem in the light of our present results.

The aim (to approximate the Boltzmann function) rests on the assumption that the Boltzmann function itself represents the best p.d.f. possible. We give different arguments for the two cases, the divergent and the convergent Boltzmann function. Clearly, this assumption cannot be applied to the expansion (3) when the signs of the parameters correspond to a divergent Boltzmann function. In this case many forms of the expansion (3) may represent an acceptable p.d.f. whereas the Boltzmann function itself breaks down. For a convergent Boltzmann function, the validity of the assumption has not been proved because the Fourier transform of the Boltzmann function is generally unknown (see, however, the Appendix) and thus a temperature factor corresponding exactly to the Boltzmann function has never been used. Mackenzie & Mair (private communication) suggest evaluation of the Fourier transform of the Boltzmann function by numerical integration. Until now, the assumption that the convergent Boltzmann function represents the ideal p.d.f., which should be approximated as closely as possible, has been established neither by theoretical arguments nor by experimental evidence and is a matter of belief. We further point out a limitation of the Boltzmann function as a p.d.f. if it could be used in the refinement. Since the Boltzmann function is not allowed to diverge, some of the parameters are not allowed to change their sign during the refinement.

Historically, the Boltzmann distribution has only proved to be a physically useful idea that enables one to establish an acceptable form of the p.d.f., like the expansion (3). From the mathematical point of view, the Boltzmann distribution is distinguished by making use of the particularly convenient form of the potential expansion (1), for which one has to pay with severe deficiencies; see the Appendix. To deduce that the Boltzmann distribution also represents a good p.d.f. is at least premature. In our opinion, one should be flexible in choosing a p.d.f. and examine its usefulness by means of experimental data. Apart from several forms of the IAP series (3), the Gram-Charlier series has proved to be useful (Zucker & Schulz, 1982; Kuhs, 1983). Willis & Pryor (1975) report on several structures with cubic site symmetry where the Willis (1969, equation 4.11) expansion, which is linear in  $\beta$ , has been used successfully. More recently, Tanaka

& Marumo (1982, 1983), working on  $\text{KCuF}_3$  and  $\alpha\text{-Al}_2\text{O}_3$ , showed that the Willis expansion proved to be satisfactory. With Al(4) in the structure of  $\text{VAl}_{1.042}$  (Kontio & Stevens, 1982), the contribution from  $\beta^2$  ( $-0.090$ ) to the  $\mathbf{h}^2$  term cannot be neglected compared to that from  $\gamma$  ( $0.311$ )\* and thus may be important in the interpretation of the potential parameters. However, in the refinement Kontio & Stevens (1982) used the cumulant expansion (and not the IAP temperature factor). Hence, this example also does not prove the need to use the  $\beta^2$  term in the refinement.

We conclude that the Willis (1969, equation 4.11) expansion should not be rated 'incorrect' relative to other expansions that contain higher powers of the potential parameters, for the following three reasons.

(1) If the signs of the potential parameters in the expansion are such that the corresponding Boltzmann function diverges, the Boltzmann function does not form a p.d.f. and there is no reason for trying to approximate it.

(2) The convergent Boltzmann function has not been shown to be the best possible p.d.f., either by theoretical arguments or by experimental evidence.

(3) Since the series (3) diverges in any case and can never approximate the (convergent) Boltzmann function sufficiently closely, it is difficult to assess the usefulness of the higher powers of the potential parameters. In general, the mere expansion by a power higher does not necessarily constitute the better proposal for a p.d.f.

Since there is no formal expression for the anharmonic temperature factor for which one can claim unique correctness, we suggest flexibility in the choice of the p.d.f. At present, the usefulness of a given p.d.f. (provided it is non-negative everywhere) can be assessed only if the p.d.f. has been examined in a particular problem with the available set of experimental data.

If one wishes to calculate the course of the potential when the refinement is completed, this can always be done according to the procedure suggested by Zucker & Schulz (1982). These authors rewrite the Boltzmann approach according to

$$V(\mathbf{u}) = -k_B T [\ln f(\mathbf{u}) - \ln f(\mathbf{u} = \mathbf{0})]. \quad (19)$$

With (19), it is assumed that the p.d.f.  $f(\mathbf{u})$  is non-negative, *i.e.* that a certain minimum quality of the p.d.f. has been obtained. The potential can even in those cases be calculated from (19) where the Boltzmann function (2) is divergent (*e.g.*  $\gamma$  negative with cubic site symmetry) but the temperature factor (4) has been used in the refinement. Equation (4) then leads to a p.d.f. (3) that can be used in (19). Thus, with a free choice of the p.d.f. one loses the possibility of interpreting the parameters directly as potential parameters but, with (19), one has gained

\* See deposition footnote.

the physically meaningful possibility of calculating the course of the potential.

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### APPENDIX

We indicate the problems of Fourier transformation of the Boltzmann function (2) when it is used with the potential expansion (1). The Boltzmann function is divergent [ $f(u) \rightarrow \infty$  for  $u \rightarrow \infty$ ] and its Fourier transform does not exist if (i) the highest power of  $u$  is odd and (ii) if the highest power of  $u$  is even and has predominantly positive coefficients. If the Boltzmann function is convergent its Fourier transform is generally unknown but can be derived for the special case of site symmetry  $\bar{1}$  from a known Fourier transform relation. Kendall & Stuart (1969, p. 158) give the Fourier transform of the one-dimensional Edgeworth series, which is real for even powers. Setting up the corresponding inverse Fourier transform relation and rewriting it into a Fourier transform relation, we show that the Fourier transform of the Boltzmann function with even powers  $u$  (site symmetry  $\bar{1}$ ) is given by an Edgeworth series in reciprocal space, with differential operators occurring in the exponent. Thus, for example,

$$\int_{-\infty}^{+\infty} \exp\left(-\frac{1}{2}x^2 - ax^4\right) \exp(itx) dx \\ = (2\pi)^{1/2} \exp(-aD^4) \exp\left(-\frac{1}{2}t^2\right), \quad (A1)$$

$a > 0$ .  $D$  is a differential operator operating on  $\exp(-\frac{1}{2}t^2)$ . Expressions like (A1) cannot be exactly evaluated analytically. Approximations in which the exponential function, containing the differential

operators, is expanded into a series, can be so evaluated but no longer represent the exact Fourier transform of the Boltzmann function.

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## A Deficiency of the Cumulant Expansion of the Anharmonic Temperature Factor

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### Abstract

It is shown that the cumulant expansion of the anharmonic temperature factor is a function whose inverse Fourier transform either does not exist or has negative

regions. Since the probability density function for an atom should always be non-negative, the inverse Fourier transform of the cumulant expansion may be a poor approximation to the true probability density function. Correspondingly, the cumulant expansion