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# Negative Volumes and Central Moments of Anharmonic Probability Density Functions

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## Abstract

The suitability of different functions used for anharmonic temperature factors in describing anharmonicity in structures is studied from the point of view of whether the respective probability density functions (p.d.f.'s) (isolated-atom-potential expansions, Gram-Charlier series, p.d.f. of the cumulant expansion of the temperature factor) are non-negative for the final values of the parameters. Certain central moments of the p.d.f. should also not become negative. Analytical formulae have been derived for the central moments of several (different) p.d.f.'s. 20 p.d.f.'s of atoms in published structures have been examined, their negative volumes determined by numerical integration and their central moments calculated. For Al(4) in the structure of $VAl_{10\cdot42}$ at 293 K (strong anharmonicity) the negative volume was $-0\cdot238$ and several moments were negative. Here the temperature factor and p.d.f. used are not acceptable. For the remaining structures (weak anharmonicity) the negative volumes found were $<|-0\cdot03|$ and the respective central moments were positive. Temperature factors and p.d.f.'s proved to be acceptable except for the cumulant expansion. In some cases its p.d.f. is not accessible, and, if it is, its negative volumes were found to be relatively large. A p.d.f. is proposed which is non-negative for all values of the parameters and whose Fourier transform can be derived in analytical form. An explicit formula is given for the cubic site symmetries.

## 1. Introduction

The commonly used functions for anharmonic probability density functions (abbreviated p.d.f.'s), *i.e.* the isolated-atom-potential expansions of the Boltzmann function (Willis, 1969; Willis & Pryor, 1975; Tanaka & Marumo, 1983; Scheringer, 1985*a*), the Fourier-invariant expansions of the Boltzmannn function (Merisalo & Larsen, 1977; Kurki-Suonio, Merisalo & Peltonen, 1979; Rossmanith, 1984) and the Gram-Charlier series (*International Tables for X-ray Crystallography*, 1974, p. 316; Zucker & Schulz, 1982; Kuhs, 1983) do not exclude that they may become negative for certain values of the parameters. By definition, a p.d.f. should be non-negative everywhere. If the negative volume is large, the function used with the set of given parameters cannot be accepted on physical grounds and should be eliminated. For the cumulant expansion (Johnson, 1969, 1970) of the temperature factor (abbreviated t.f.), the p.d.f. is not known but we have shown earlier (Marcinkiewicz, 1938; Scheringer, 1985*b*) that it always has some negative volume, although of unknown size. For the isolated-atom-potential p.d.f. (abbreviated IAP p.d.f.), Mackenzie & Mair (1985) arrive at a similar conclusion: the IAP p.d.f. (moment expansion) '... always [*i.e.* for any set of parameters] goes negative for some value of [the argument] $x$... and so is not a proper p.d.f.'. It will be shown that this statement is not valid to this degree of generality. Apart from this, Mackenzie & Mair (1985) have shown by means of one-dimensional model calculations that the negative volumes of the p.d.f.'s are small in the case of weak anharmonicity.

In this paper several structures are selected from the literature where anharmonic refinements were reported, and the negative volumes of the p.d.f.'s are determined by means of numerical integration. In this way we could examine the usability of a p.d.f. for the given values of the parameters in a structure. Another approach to obtain insight into the quality of a p.d.f. is given by the evaluation of its central moments. Certain moments should be non-negative if the p.d.f. is non-negative everywhere. Calculation of the moments of the p.d.f. renders the numerical integration of the negative volumes superfluous to some extent. We have derived analytical expressions for the central moments of several (different) p.d.f.'s. In this way the control of the quality of a p.d.f. is simplified. The examination of the cumulant expansion of the t.f. (Johnson, 1969, 1970) poses some special problems which we shall discuss. Finally, we shall show that it is possible to construct p.d.f.'s which are non-negative everywhere for every set of parameters.

## 2. Calculation of the negative volumes and central moments of a p.d.f.

### *Negative volumes*

For a p.d.f. $f(\mathbf{u})$, the normalization condition $\int f(\mathbf{u})\,d\mathbf{u}=1$, $\mathbf{u}$ = vibrational coordinates of the

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respective atom, must be fulfilled, so that also

$$\text{negative volume} + \text{positive volume} = 1, \tag{1}$$

where the negative volume has to be counted with a negative sign. With the given values of the parameters of the atom, we have integrated the p.d.f. in the three space dimensions and have summed the negative and positive contributions of the p.d.f. separately. The normalization (1) was fulfilled with deviations of $<10^{-6}$ (IBM double precision, 9261 grid points), except for the cumulant expansion (see below). Moreover, the correct performance of the integration and the correct input of the p.d.f. were controlled, on the one hand, by the numerical integration and, on the other hand, by the analytical calculation of the moments of **u** (see below).

The treatment of the cumulant expansion of the t.f. needs some special comments because the p.d.f. is not known analytically and in many cases is not accessible to the investigator. The p.d.f. is defined only if the inverse Fourier transform of the t.f. $T(\mathbf{Q})$ exists, *i.e.* if $\int |T(\mathbf{Q})|\, \mathrm{d}\mathbf{Q}$ is finite ($\mathbf{Q} = 2\pi\mathbf{h}$ = vector in reciprocal space). With the majority of structures, however, the t.f. diverges for $\mathbf{Q} \to \infty$. Then, formally, a p.d.f. of the cumulant expansion would not exist, but in the crystal some p.d.f. is present. In this situation a p.d.f. of the cumulant expansion is fitted to the p.d.f. present in the crystal by virtue of the fact that, in the interpretation of experimental data, the t.f. is only used in a limited range, $Q < Q_{\max}$. In the range $Q > Q_{\max}$ a continuation of the t.f. other than the cumulant expansion can be used (Scheringer, 1985*b*). The optimum continuation of the t.f., *i.e.* that continuation which fits best the motions of the atom in the crystal, is unknown and thus the corresponding optimum p.d.f. is not accessible to the investigator. In this situation, the investigator may choose a sufficiently convergent continuation of the t.f. in the range $Q > Q_{\max}$ and thus establish a p.d.f. which he might be able to evaluate numerically in favourable cases. Here we have chosen almost the simplest procedure possible. We have calculated the t.f. up to its minimum in reciprocal space according to the cumulant expansion, and beyond the minimum we have put the t.f. equal to zero (certainly, this is not the optimum continuation). The values of the p.d.f. were then calculated for 9261 grid points by numerical Fourier inversion of the t.f. This inversion was calculated in the range $|T(\mathbf{Q})| \geq \text{minimum}\,\{|T(\mathbf{Q})|\}$ with more than 10 000 grid points, and so a numerical precision of at least five decimal places was achieved.

### *Central moments*

The numerical evaluation of the moments of **u** follows from their definition *via* the integral

$$\langle u_i u_j \ldots u_k \rangle_n = \int u_i u_j \ldots u_k f(\mathbf{u})\, \mathrm{d}\mathbf{u}\big|_n . \tag{2}$$

$i, j, k = 1, 2, 3$ denote the directions of space, $n$ is the order of the moment [*i.e.* there are $n$ factors $u_i, \ldots$ in (2)]. The moments can also be obtained from the Fourier transform of the p.d.f. $f(\mathbf{u})$, *i.e.* from the t.f. $T(\mathbf{Q})$ according to

$$\langle u_i u_j \ldots u_k \rangle_n = \left. \frac{\partial^n T(\mathbf{Q})}{i^n \partial Q_i \partial Q_j \ldots \partial Q_k} \right|_{\mathbf{Q}=\mathbf{0}} \tag{3}$$

(Kendall & Stuart, 1969). The evaluation of (2) requires numerical integration procedures (in most cases) whereas (3) denotes essentially an analytical formalism. We assume $\langle \mathbf{u} \rangle = \mathbf{0}$ throughout and thus obtain the central moments. We have derived several explicit formulae from (3) and collected them in the Appendix. The evaluation of (3) is straightforward in principle but is cumbersome for $n > 4$ and open to chances for making errors. However, the results obtained from (2) and (3) can be used to control each other mutually. In this way we have controlled all formulae given in the Appendix by numerical integration *via* (2). Formulae for the moments of the cumulant expansion up to $n = 4$ are given in *International Tables for X-ray Crystallography* (1974, p. 317); however, they are only valid if the t.f. does not diverge.

For the Gram–Charlier series, another and simpler way of calculating the central moments can be found than from (3). Equations (6.30) and (6.31) of Kendall & Stuart (1969) (one-dimensional case) show that the quasi-moments ${}^n\mathbf{C}$ of order $n$ can be linearly expressed by the central moments, where the coefficients occurring are those in the Hermite polynomial of order $n$. If one solves these equations for the moments, the coefficients are preserved but all signs become positive. The three-dimensional extension of this procedure leads to the result

$$\begin{aligned} \langle u_i u_j \ldots u_p \rangle_n = {}&{}^nC_{ij\ldots p} + \{{}^{n-2}C_{ij\ldots k}\sigma_{op}\} \\ &+ \{{}^{n-4}C_{ij\ldots k}\sigma_{lm}\sigma_{op}\} \\ &+ \ldots + \text{last term}. \end{aligned} \tag{4}$$

The last term in (4) for $n$ even (zero-order term) is

$$\{\sigma_{ij} \ldots \sigma_{op}\}, \tag{5a}$$

and for $n$ odd (third-order term, since ${}^1\mathbf{C} = \mathbf{0}$)

$$\{{}^3C_{ijk}\sigma_{lm} \ldots \sigma_{op}\}, \tag{5b}$$

with $i, j, k, \ldots, o, p = 1, 2, 3$. $\sigma_{ij}$ are the elements of the covariance matrix of the leading Gaussian function in the Gram–Charlier series. The brackets { } denote that all permutations of the space indices $i, j, k, \ldots$ which produce different results have to be included. [This situation is fully parallel to the evaluation of the coefficients in the Hermite polynomials; see *International Tables for X-ray Crystallography* (1974), p. 316.] The number of permutations for site symmetry 1, and for the case $i = j = k = \ldots$ for all site symmetries, is $p_{ns} = n!/[2^s(n-2s)!\,s!]$ where $s$

denotes the number of $\sigma$'s in a bracket { } of (4); see Scheringer (1985*a*). If some of the indices $i, j, k, \ldots$ refer to different directions of space, the number of permutations is reduced for site symmetries higher than 1. Since it is often not trivial to evaluate the remaining permutations, we have given the central moments up to $n=8$ for the cubic site symmetries explicitly in the Appendix. With $\langle \mathbf{u}\rangle = \mathbf{0}$, the origin of $\mathbf{u}$ being at the mean of the p.d.f., we have ${}^1\mathbf{C}=\mathbf{0}$. One usually also puts ${}^2\mathbf{C}=\mathbf{0}$ since there is no chance to determine anharmonic second-order terms separately from $\boldsymbol{\sigma}$. With ${}^1\mathbf{C}=\mathbf{0}$ there are $(n-1)/2$ terms in (4) for $n$ odd, and with ${}^2\mathbf{C}=\mathbf{0}$ there are $n/2$ terms in (4) for $n$ even.

For p.d.f.'s which are non-negative everywhere, the following statements hold:

(1) All moments which contain only even powers of $u_i, \ldots$ are positive.

(2)

$$\langle u_i^6\rangle^{1/6} \geq \langle u_i^4\rangle^{1/4} \geq \langle u_i^2\rangle^{1/2}. \tag{6}$$

For a Gaussian distribution with $\langle u_i^2\rangle = 1$, (6) assumes the form $15^{1/6} > 3^{1/4} > 1$, *i.e.* $1{\cdot}5704 > 1{\cdot}3161 > 1$. Furthermore, physical arguments require that $\langle u_i^2\rangle$ should grow with increasing temperature. Unfortunately, there are no conditions for the moments of odd order.

## 3. Results obtained for some structures from the literature

Most of the anharmonic investigations were performed for atoms with high site symmetry [see, for example, Tanaka & Marumo (1983), Table 1]. Our own selection is correspondingly restricted. The structures, the atoms in the structure whose p.d.f. was examined and the calculated negative volumes are given in Table 1. Except for Al in $VAl_{10\cdot42}$ and Pb in $CsPbCl_3$, the negative volumes found are small ($<|-0{\cdot}028|$). Correspondingly, the central moments (up to $n=6$ or $n=8$ respectively) with even powers of $u_i, \ldots$ are all positive, and (6) is fulfilled. With these structures, the anharmonic standard functions used prove to be sufficient. The physical reason is probably that in these structures the anharmonicity is weak. In the following we shall discuss some of the results obtained in more detail.

Al, NaCl and KCl represent a case where the IAP p.d.f. is non-negative everywhere in the full range of '$\gamma$ negative'. Even the exceedingly large absolute value of $\gamma = -38\times10^{-19}$ J Å$^{-4}$ (Willis & Pryor, 1975, p. 164) for Na in NaCl does not produce a negative value of the p.d.f. Thus the IAP expansion appears to be particularly favourable for this sort of anharmonicity.

Table 1. *Negative probability density volumes calculated for* 20 *p.d.f.'s taken from the literature*

The atom concerned is given in parentheses. RT = room temperature. IAP = isolated-atom potential, FOUR INV = Fourier invariant formulation of the isolated-atom potential, CUM = cumulant expansion of the t.f., GRCH = Gram–Charlier series. GRCH* indicates that the Gram–Charlier series was calculated by us with the parameters taken from the cumulant expansion.

| Substance | P.d.f. or t.f. | Negative volume | Reference |
|---|---|---|---|
| Al, NaCl, KCl, RT | IAP | 0·000 | Willis & Pryor (1975) |
| Si, many T | IAP | 0·000 | |
| $CsPbCl_3$ (Pb), RT | CUM | −0·228 | Hutton, Nelmes, Meyer & Eiriksson (1979) |
| $CsPbCl_3$ (Pb), RT | GRCH* | 0·000 | |
| $BaTiO_3$ (Ti), RT | IAP | −0·004 | Tanaka, Shiozaki & Sawaguchi (1979) |
| Zn, RT | FOUR INV | −0·006 | Merisalo & Larsen (1977) |
| Zn, RT | FOUR INV | 0·000 | Rossmanith (1984) |
| Cd, RT | FOUR INV | 0·000 | |
| ZnS (S), 676 K | IAP | −0·002 | Moss, McMullan & Koetzle (1980) |
| ZnS (S), 676 K | CUM | −0·010 | |
| ZnS (S), 676 K | GRCH* | −0·006 | |
| ZnS (Zn), 676 K | IAP | 0·000 | |
| ZnS (Zn), 676 K | CUM | −0·005 | |
| ZnS (Zn), 676 K | GRCH* | 0·000 | |
| $PbF_2$ (Pb), RT | GRCH | −0·005 | Schulz, Perenthaler & Zucker (1982) |
| $PbF_2$ (F), 625 K | GRCH | −0·008 | |
| $Al_2O_3$ (O), 2170 K | IAP | −0·028 | Tanaka & Marumo (1983) |
| $KCuF_3$ (Cu), RT | IAP | −0·001 | |
| $VAl_{10\cdot42}$ (Al), 100 K | CUM | −0·159 | Kontio & Stevens (1982) |
| $VAl_{10\cdot42}$ (Al), 100 K | GRCH* | −0·080 | |
| $VAl_{10\cdot42}$ (Al), 100 K | IAP | −0·124 | |
| $VAl_{10\cdot42}$ (Al), 293 K | CUM | −0·171 | |
| $VAl_{10\cdot42}$ (Al), 293 K | GRCH* | −0·161 | |
| $VAl_{10\cdot42}$(Al), 293 K | IAP | −0·239 | |

With those structures (ZnS, $CsPbCl_3$ and $VAl_{10\cdot42}$) which were refined with the cumulant expansion, we have to take into account the convergence properties of the t.f. With S in ZnS, the t.f. converges and the negative volumes found are reliable. With Zn in ZnS, Pb in $CsPbCl_3$ and Al in $VAl_{10\cdot42}$ the t.f. diverges but to different extents. With Zn divergence occurs in all three directions of space but the minimum of $|T(\mathbf{Q})|$ is $<0{\cdot}004$ everywhere. Termination of the Fourier inversion beyond the minimum does not impair the results and the negative volume of $-0{\cdot}0048$ appears to be reliable. With Pb in $CsPbCl_3$ (divergence in all three directions of space) the minimum of $|T(\mathbf{Q})|$ is 0·067 in the [100] direction, and termination of the Fourier inversion no longer produces a meaningful p.d.f. Thus the negative volume of −0·228 found is an artifact. With Al in $VAl_{10\cdot42}$ (divergence only in the [111] direction) the minimum of $|T(\mathbf{Q})|$ is 0·074 at 100 K and 0·006 at 293 K. Termination of the Fourier inversion impairs the results at 100 K. However, Kontio & Stevens (1982) have derived IAP parameters from the parameters of the cumulant expansion, and we have also used the IAP parameters to calculate the negative volumes of the IAP p.d.f.'s, −0·124 at 100 K and −0·239 at 293 K. These figures show that the negative volume which one would obtain for a p.d.f. corresponding to an optimum continuation of the cumulant t.f. beyond the experimental limit would also be large.

As a further control of the results obtained with cumulant expansion, we have put the parameters of the cumulant expansion into the Gram-Charlier series and calculated the negative volume from this series (GRCH* results in Table 1). (This procedure appears to be legitimate because the cumulant expansion of the t.f. and the Fourier transform of the Gram-Charlier series represent very similar expansions.) For ZnS the GRCH* calculation essentially confirms the results obtained with the cumulant expansion. For Pb in $CsPbCl_3$ the GRCH* calculation (negative volume 0·000) also shows that the value obtained with the cumulant expansion (−0·228) is an artifact. For Al in $VAl_{10\cdot42}$, the GRCH* calculation (−0·080 at 100 K and −0·161 at 293 K) essentially confirms the results obtained with the IAP p.d.f. and shows that the p.d.f. of the cumulant expansion must have a large negative volume.

Obviously, Al in $VAl_{10\cdot42}$ represents a case of strong anharmonicity where the standard anharmonic functions break down. This is also indicated by the occurrence of several negative moments. The Gram-Charlier series at 100 K has negative moments with the indices 111111 and 11111111, and at 293 K with the indices 1111, 111111, 11111111 and 11111122. The IAP p.d.f. at 100 K has negative moments with the indices 1111, 111111, 111122 and 112233, and at 293 K all five moments of fourth and sixth order are negative. Of course (6) is not fulfilled. The second moments $\langle u_i^2\rangle$, $i=1,2,3$, of the IAP p.d.f. at 293 K are smaller than those at 100 K, in contradiction to physical requirements.

We may point out that plots of one-dimensional sections of a p.d.f. may easily lead one to incorrect conclusions. As an example we show the [100] section of the IAP p.d.f. of Al in $VAl_{10\cdot42}$ (see Fig. 1, full line). The negative volume of this section is about −0·05 and thus its absolute value is distinctly smaller than that of the three-dimensional negative volume of −0·239. The negative volumes usually appear at large values of $u$ and are weighted in three dimensions with a factor of $4\pi u^2$, on average. Therefore, the one-dimensional plots published by Mackenzie & Mair (1985) may suggest an incorrect impression of the negative volumes of three-dimensional p.d.f.'s that actually occur.

## 4. Deficiencies of the cumulant expansion

Since the cumulant expansion of the t.f. and the Fourier transform of the Gram-Charlier series are quite similar expansions (*International Tables for X-ray Crystallography*, 1974, pp. 316-317), one might assume that the two expansions are equally useful in actual refinements. In the past, this assumption has been enforced by the fact that Johnson (1970) has described the p.d.f. of the cumulant expansion by an expansion in Hermite polynomials, quite similar to the Gram-Charlier series. This expansion, however, is only a first approximation and it only holds if the t.f. does not diverge (Scheringer, 1985*b*). We cannot support a high estimation of the cumulant expansion, and here we give the arguments that should contribute to rule out its use in anharmonic refinements. We further refer to the experiences reported by Zucker & Schulz (1982) and Kuhs (1983), which have led these authors to express a similarly negative judgement on the usefulness of the cumulant expansion.

(1) We have performed many model calculations for convergent and slightly divergent cumulant expansions. In all cases the absolute values of the negative volumes found for the p.d.f. of the cumulant expansion were larger than those of the corresponding GRCH* series (larger by a factor of about 1·2-1·8). See also the results for ZnS in Table 1. In this way we could confirm the theorem given by Marcinkiewicz (1938) (Scheringer, 1985*b*) by detailed numerical results.

(2) If the cumulant expansion diverges more strongly (many practical cases), the p.d.f. that is present in the crystal is not accessible to the investigator, not even in an approximate form (example: Pb in $CsPbCl_3$). Similarly, the formulae for the central moments are no longer valid. Hence, the investigator has no chance to judge the results of the refinement by means of the p.d.f.

(3) The absolute values of the third-order tensors in the cumulant expansion cannot be determined, since they only affect the phases of the structure factors but not the intensities (Hazell & Willis, 1978). (With the Gram-Charlier series, this deficiency does not occur.)

## 5. P.d.f.'s which are non-negative everywhere

Certainly, it would be much better if the functions for anharmonic p.d.f.'s were of such a kind that they could never assume negative values. Then there would be no need to determine negative volumes. The Boltzmann function satisfies this requirement but has two severe deficiencies (see below), and the IAP p.d.f. satisfies this requirement for certain ranges of the parameters (see below). A p.d.f. which is non-negative everywhere for all values of the parameters and whose Fourier transform can be evaluated analytically is proposed for the first time in this section.

Although the Boltzmann function is non-negative everywhere, its application in actual refinements is strongly impaired by the following two deficiencies:

(1) For certain signs of the high-order parameter, the Boltzmann function diverges and no longer represents a p.d.f. Thus, in actual refinements the transition from a convergent to a divergent Boltzmann function would always be possible.

(2) The Fourier transform of the (convergent) Boltzmann function is not known analytically and would have to be determined numerically.

The IAP p.d.f. up to anharmonic fourth-order terms is non-negative if all fourth-order parameters are negative and the third-order parameters are small. For the cubic site symmetries $m3m$, 432 and $m3$ this reduces to the parameter range '$\gamma$ negative' (Al, NaCl, KCl). '$\gamma$ negative' is a favourable case for the IAP p.d.f. whereas the Boltzmann function could not be used since it would diverge.

The IAP approach offers the chance for constructing p.d.f.'s which are non-negative everywhere. The expression

$$\exp(-x) \simeq 1 - x + cx^2 = (1 - x/2)^2 + (4c - 1)x^2/4 \tag{7}$$

is non-negative for all values of $x$ if $c \geq \frac{1}{4}$. When we apply this result to the IAP p.d.f., we have to put $x$ equal to the total of the anharmonic terms. For cubic site symmetry the IAP p.d.f. assumes the form

$$f(\mathbf{u}) = g(\mathbf{u})(1 - x + cx^2)/P, \tag{8}$$

where $g(\mathbf{u})$ is the normalized Gaussian function and $P$ the factor of normalization. With the commonly used IAP p.d.f. up to fourth-order terms we have

$$x = [\beta u_1 u_2 u_3 + \gamma u^4 + \delta(u_1^4 + u_2^4 + u_3^4 - \tfrac{3}{5}u^4)]/(k_B T), \tag{9}$$

where $u^4 = (u_1^2 + u_2^2 + u_3^2)^2$ (see Willis & Pryor, 1975). $k_B$ is Boltzmann's constant and $T$ the absolute temperature. The Fourier transform of the p.d.f. (8) and (9) can be evaluated by means of Hermite polynomials in reciprocal space (Scheringer, 1985*a*). The representation in terms of Hermite polynomials is given in the material for deposit,* the final form of the t.f. in the Appendix. The factor of normalization in (8) is found to be

$$P = \frac{1 - \sigma^2 15\gamma}{k_B T} + \frac{c\{\sigma^3\beta + \sigma^4[945\gamma^2 + (144/5)\delta^2]\}}{(k_B T)^2}, \tag{10}$$

where $\sigma^2$ is the variance of the Gaussian function. The final formula of the t.f. has been controlled by a comparison of the second to seventh moments that were obtained analytically from the t.f. and numerically by integration.

As an example of the effect of the parameter $c$ on the shape of the p.d.f., we have calculated the IAP p.d.f.'s for $c = 0$, $c = \frac{1}{4}$, $c = \frac{1}{2}$ and the Boltzmann function for Al in $VAl_{10 \cdot 42}$ at 293 K. The [100] sections of these four p.d.f.'s are shown in Fig. 1. The IAP p.d.f. with $c = \frac{1}{4}$ approximates the Boltzmann function fairly well. Apart from that $c = \frac{1}{4}$ seems to be the best choice for $c$ because the side maxima arising are kept to a minimum.

## 6. Discussion

If we consider the results of this work (Table 1) as characteristic for the universe of structures, we should suppose that the negative volumes will rarely exceed an absolute value of 0·03. In this range the central moments with even powers of $u_i$ up to sixth order are usually positive (exceptions have been found). Thus, the anharmonic standard functions are expected to work well in many cases, probably because the anharmonicity is weak in many structures, even at high temperatures. Still, a control is recommended in a particular investigation. The simplest way is to calculate the central moments up to $n = 6$ analytically. An aid is offered by the formulae given for the moments of the Gram–Charlier series, (4) and (5), and by the formulae given in the Appendix for cubic site symmetries and $\bar{6}m2$. Unfortunately, the test with the moments breaks down if the negative volumes are due to large values of the odd-order tensors; here the numerical integration of the p.d.f. is the only safe device. The cumulant expansion of the t.f. suffers from severe deficiencies and should no longer be used in refinements. If the anharmonicity is strong and the standard functions break down, one can introduce quadratic terms of all anharmonic terms in an IAP p.d.f. and so obtain a p.d.f. which is non-negative everywhere. The corresponding t.f. can be evaluated

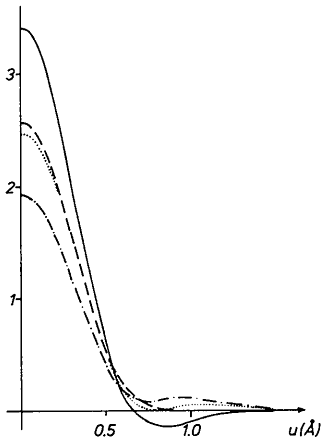

Fig. 1. Plots of four [100] sections of IAP p.d.f.'s for Al in $VAl_{10 \cdot 42}$ at 293 K. The parameters used in all four p.d.f.'s were taken from Kontio & Stevens (1982, Table 3). Linear IAP expansion ($c = 0$): full line. Boltzmann function: dashed. Quadratic IAP expansion ($c = \frac{1}{4}$): dotted (otherwise indistinguishable from the Boltzmann function in this drawing). Quadratic IAP expansion ($c = \frac{1}{2}$): dash-dotted.

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* The Hermite polynomials up to eighth order and the polynomial representation of the t.f. have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44630 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

by means of Hermite polynomials in reciprocal space and thus can be obtained in analytical form. This can be done for every site symmetry. For cubic site symmetry we have derived the t.f. explicitly. Among all values of the parameter $c$, $c=\frac{1}{4}$ approximates the (convergent) Boltzmann function best.

## APPENDIX

### Central moments for cubic site symmetry

We abbreviate the variance of the leading Gaussian function by $\langle u_i^2\rangle=\sigma$ for $i=1,2,3$, and the moments by writing only their indices, *e.g.* $\langle u_i^2\rangle=11$.

*Moments of the IAP p.d.f.* (8), (9) *and* (10)

We abbreviate $C=c(k_BT)^{-2}$.

$$\begin{aligned}11&=\sigma+P^{-1}(-20\gamma\sigma^3/(k_BT)\\&\quad+C\{2\beta^2\sigma^4+[2520\gamma^2+(1920/25)\delta^2]\sigma^5\}),\end{aligned}$$

$$123=P^{-1}\{-\beta\sigma^3/(k_BT)+c\beta[198\gamma-(144/5)\delta]\sigma^5\},$$

$$\begin{aligned}1111&=3\sigma^2+P^{-1}(-(k_BT)^{-1}[144\gamma+(48/5)\delta]\sigma^4\\&\quad+C\{12\beta^2\sigma^5+[24192\gamma^2+(13728/5)\gamma\delta\\&\quad+(21888/25)\delta^2]\sigma^6\}),\end{aligned}$$

$$\begin{aligned}1122&=\sigma^2+P^{-1}(-(k_BT)^{-1}[48\gamma-(24/5)\delta]\sigma^4\\&\quad+C\{8\beta^2\sigma^5+[8064\gamma^2-(6864/5)\gamma\delta\\&\quad+(4416/25)\delta^2]\sigma^6\}),\end{aligned}$$

$$\begin{aligned}11123&=P^{-1}\{-3\beta\sigma^4/(k_BT)\\&\quad+C[858\beta\gamma-(624/5)\beta\delta]\sigma^6\},\end{aligned}$$

$$\begin{aligned}111111&=15\sigma^3+P^{-1}\{-(k_BT)^{-1}(1260\gamma+144\delta)\sigma^5\\&\quad+C[90\beta^2\sigma^6+(275400\gamma^2+56160\gamma\delta\\&\quad+11520\delta^2)\sigma^7]\},\end{aligned}$$

$$\begin{aligned}111122&=3\sigma^3+P^{-1}\{-(k_BT)^{-1}[252\gamma-(96/5)\delta]\sigma^5\\&\quad+C[42\beta^2\sigma^6+(55080\gamma^2-7488\gamma\delta\\&\quad+1152\delta^2)\sigma^7]\},\end{aligned}$$

$$\begin{aligned}112233&=\sigma^3+P^{-1}\{-(k_BT)^{-1}[84\gamma-(72/5)]\sigma^5\\&\quad+C[26\beta^2\sigma^6+(18360\gamma^2-5616\gamma\delta\\&\quad+576\delta^2)\sigma^7]\},\end{aligned}$$

$$\begin{aligned}1111123&=P^{-1}\{-15\beta\sigma^5/(k_BT)\\&\quad+C(5850\beta\gamma-720\beta\delta)\sigma^7\},\end{aligned}$$

$$\begin{aligned}1222333&=P^{-1}[-9\beta\sigma^5/(k_BT)\\&\quad+C(3510\beta\gamma-576\beta\delta)\sigma^7].\end{aligned}$$

*Moments of the Gram–Charlier series*

The p.d.f. is given by equation (2) of *International Tables for X-ray Crystallography* (1974, p. 316), and should be correspondingly extended to higher terms.

$$11=\sigma,\qquad 123=C_{123},\qquad 1111=C_{1111}+3\sigma^2,$$

$$1122=C_{1122}+\sigma^2,\qquad 11123=3C_{123}\sigma,$$

$$111111=C_{111111}+15C_{1111}\sigma+15\sigma^3,$$

$$111122=C_{111122}+(C_{1111}+6C_{1122})\sigma+3\sigma^3,$$

$$112233=C_{112233}+3C_{1122}\sigma+\sigma^3,$$

$$1111123=C_{1111123}+10C_{11123}\sigma+15C_{123}\sigma^2,$$

$$1222333=C_{1222333}+6C_{11123}\sigma+9C_{123}\sigma^2,$$

$$\begin{aligned}11111111&=C_{11111111}+28C_{111111}\sigma+210C_{1111}\sigma^2\\&\quad+105\sigma^4,\end{aligned}$$

$$\begin{aligned}11111122&=C_{11111122}+(C_{111111}+15C_{111122})\sigma\\&\quad+(15C_{1111}+45C_{1122})\sigma^2+15\sigma^4,\end{aligned}$$

$$\begin{aligned}11112222&=C_{11112222}+12C_{111122}\sigma\\&\quad+(6C_{1111}+36C_{1122})\sigma^2+9\sigma^4,\end{aligned}$$

$$\begin{aligned}11112233&=C_{11112233}+(2C_{111122}+6C_{112233})\sigma\\&\quad+(C_{1111}+15C_{1122})\sigma^2+3\sigma^4.\end{aligned}$$

### Moments of the Fourier-invariant p.d.f. for site symmetry $\bar{6}m2$

The p.d.f. is given by Merisalo & Larsen (1977), equations (2), (4), and (7), as used for Zn and Cd. We first express the quantities $A$, $B$, $C$, $D$ and $E$ in terms of the thermal parameters $\alpha_{20}$, $\beta_{00}$, $\alpha_{40}$, $\beta_{20}$, $\gamma_{00}$ used by Merisalo & Larsen (1977).

$$A^2=(2\beta_{00}-\alpha_{20})/(k_BT)=\sigma_1^{-1},$$

$$B^2=2(\beta_{00}+\alpha_{20})/(k_BT)=\sigma_3^{-1},$$

$$C=(3\alpha_{40}-4\beta_{20}+8\gamma_{00})/(8A^4k_BT),$$

$$D=(\alpha_{40}+\beta_{20}+\gamma_{00})/(B^4k_BT),$$

$$E=(6\alpha_{40}-\beta_{20}-4\gamma_{00})/(2A^2B^2k_BT).$$

The central moments are then given by

$$11=\sigma_1-2(8C-E)/(A^2N),$$

$$33=\sigma_3-2(6D-2E)/(B^2N),$$

$$1111=3\sigma_1^2+(-120C+12E)/(A^4N),$$

$$1122=\sigma_1^2+(-40C+4E)/(A^4N),$$

$$3333=3\sigma_3^2+(-96D+24E)/(B^4N),$$

$$1133=\sigma_1\sigma_3+(-16C-12D+10E)/(A^2B^2N),$$

where the normalization factor $N$ is given by Merisalo & Larsen (1977), equation (7).

### The temperature factor of the IAP p.d.f. (8), (9) and (10)

We abbreviate $\sigma 2\pi h_i=t_i$ where $h_i$ are the Miller indices. The leading Gaussian function in reciprocal space is $g(\mathbf{t})=\exp[-(2\sigma)^{-1}(t_1^2+t_2^2+t_3^2)]$. Then the temperature factor is given by

$$T(\mathbf{t})=g(\mathbf{t})[1+P^{-1}A],$$

where

$$\begin{aligned}A={}&i\beta(k_BT)^{-1}t_1t_2t_3-(\gamma+\tfrac{2}{5}\delta)(k_BT)^{-1}(t_1^4+t_2^4+t_3^4)\\&-2(\gamma-\tfrac{3}{5}\delta)(k_BT)^{-1}(t_1^2t_2^2+t_1^2+t_3^2+t_2^2t_3^2)\\&+10\gamma(k_BT)^{-1}(t_1^2+t_2^2+t_3^2)\sigma+[C/(k_BT)^2]\\&\times\Big\{-\beta^2[t_1^2t_2^2t_3^2-(t_1^2t_2^2+t_1^2t_3^2+t_2^2t_3^2)\sigma\\&+(t_1^2+t_2^2+t_3^2)\sigma^2]-i\{2\beta(\gamma+\tfrac{2}{5}\delta)(t_1^5t_2t_3+t_1t_2^5t_3\\&+t_1t_2t_3^5)+4\beta(\gamma-\tfrac{3}{5}\delta)(t_1t_2^3t_3^3+t_1^3t_2t_3^3+t_1^3t_2^3t_3)\\&-\beta[44\gamma-\tfrac{32}{5}\delta](t_1^3t_2t_3+t_1t_2^3t_3+t_1t_2t_3^3)\sigma\\&+\beta[198\gamma-\tfrac{144}{5}\delta]t_1t_2t_3\sigma^2\}\\&+[\gamma^2+\tfrac{4}{5}\gamma\delta+\tfrac{4}{25}\delta^2](t_1^8+t_2^8+t_3^8)\\&+[4\gamma^2-\tfrac{4}{5}\gamma\delta-\tfrac{24}{25}\delta^2]\\&\times[t_1^6(t_2^2+t_3^2)+t_2^6(t_1^2+t_3^2)+t_3^6(t_1^2+t_2^2)]\\&+[6\gamma^2-\tfrac{16}{5}\gamma\delta+\tfrac{44}{25}\delta^2](t_1^4t_2^4+t_1^4t_3^4+t_2^4t_3^4)\\&+[12\gamma^2-\tfrac{52}{5}\gamma\delta+\tfrac{48}{25}\delta^2](t_1^4t_2^2t_3^2+t_1^2t_2^4t_3^2+t_1^2t_2^2t_3^4)\\&-[36\gamma^2+\tfrac{104}{5}\gamma\delta+\tfrac{64}{25}\delta^2](t_1^6+t_2^6+t_3^6)\sigma\\&-[108\gamma^2-\tfrac{208}{5}\gamma\delta-\tfrac{48}{25}\delta^2]\\&\times[t_1^4(t_2^2+t_3^2)+t_2^4(t_1^2+t_3^2)+t_3^4(t_1^2+t_2^2)]\sigma\\&-[216\gamma^2-\tfrac{936}{5}\gamma\delta+\tfrac{864}{25}\delta^2]t_1^2t_2^2t_3^2\sigma\\&+[378\gamma^2+\tfrac{572}{5}\gamma\delta+\tfrac{432}{25}\delta^2](t_1^4+t_2^4+t_3^4)\sigma^2\\&+[756\gamma^2-\tfrac{1716}{5}\gamma\delta+\tfrac{144}{5}\delta^2](t_1^2t_2^2+t_1^2t_3^2+t_2^2t_3^2)\sigma^2\\&-[1260\gamma^2+\tfrac{960}{25}\delta^2](t_1^2+t_2^2+t_3^2)\sigma^3\Big\}.\end{aligned}$$

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# On the Application of Phase Relationships to Complex Structures. XXV. *TRITAN* – or Recycled Failure

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## Abstract

Even when direct methods fail to give a clear solution, *E* maps from some of the phase sets obtained contain correctly oriented fragments. It is shown that such information from several phase sets can be amalgamated by an automatic procedure to give estimates of the values of three-phase invariants. These estimates are incorporated into a modified tangent formula which is used in a new run of a multisolution direct-methods procedure. Tests of the total process, called *TRITAN*, reveal that it is very effective in determining structures which otherwise would not be found routinely.

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