

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

I thank Professor Dr W. Gromes, Mathematisches Institut der Universität Marburg, for a discussion on the problem of divergence and Dr S. L. Mair, Clayton, Australia, for her correspondence on the higher powers of the potential parameters, which was adverse but stimulating.

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operators, is expanded into a series, can be so evaluated but no longer represent the exact Fourier transform of the Boltzmann function.

References

- DAWSON, B., HURLEY, A. C. & MASLEN, V. W. (1967). *Proc. R. Soc. London Ser. A*, **298**, 289-306.
- FIELD, D. W. (1982). *Acta Cryst.* **A38**, 10-12.
- HARADA, J., SUZUKI, H. & HOSHINO, S. (1976). *J. Phys. Soc. Jpn*, **41**, 1707-1715.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press (Present distributor: D. Reidel, Dordrecht).
- KENDALL, M. G. & STUART, A. (1969). *The Advanced Theory of Statistics*, Vol. I, ch. 6. London: Griffin.
- KONTIO, A. & STEVENS, E. D. (1982). *Acta Cryst.* **A38**, 623-629.
- KUHS, W. F. (1983). *Acta Cryst.* **A39**, 148-158.
- KURKI-SUONIO, K., MERISALO, M. & PELTONEN, H. (1979). *Phys. Scr.* **19**, 57-63.
- MAGNUS, W., OBERHETTINGER, F. & SONI, R. P. (1966). *Formulas and Theorems for the Special Functions of Mathematical Physics*, pp. 249-250. New York: Springer.
- MAIR, S. L. (1980a). *J. Phys. C*, **13**, 1419-1425.
- MAIR, S. L. (1980b). *J. Phys. C*, **13**, 2857-2868.
- MAIR, S. L. & BARNEA, Z. (1975). *Acta Cryst.* **A31**, 201-207.
- MAIR, S. L., BARNEA, Z., COOPER, M. J. & ROUSE, K. D. (1974). *Acta Cryst.* **A30**, 806-813.
- MAIR, S. L. & WILKINS, S. W. (1976). *J. Phys. C*, **9**, 1145-1158.
- MATSUBARA, T. (1975a). *J. Phys. Soc. Jpn*, **38**, 1076-1079.
- MATSUBARA, T. (1975b). *Prog. Theor. Phys.* **53**, 1210-1211.
- MERISALO, M. & LARSEN, F. K. (1977). *Acta Cryst.* **A33**, 351-354.
- MERISALO, M. & LARSEN, F. K. (1979). *Acta Cryst.* **A35**, 325-327.
- MOSS, B., McMULLAN, R. K. & KOETZLE, T. F. (1980). *J. Chem. Phys.* **73**, 495-508.
- NISHIWAKI, T., SAKATA, M. & HARADA, J. (1976). *J. Phys. Soc. Jpn*, **41**, 355-356.
- SCHERINGER, C. (1977). *Acta Cryst.* **A33**, 879-884.
- TANAKA, T. & MARUMO, F. (1982). *Acta Cryst.* **B38**, 1422-1427.
- TANAKA, T. & MARUMO, F. (1983). *Acta Cryst.* **A39**, 631-641.
- TITCHMARSH, E. C. (1948). *Introduction to the Theory of Fourier Integrals*. Oxford: Clarendon Press.
- WHITELEY, B., MOSS, G. & BARNEA, Z. (1978). *Acta Cryst.* **A34**, 130-136.
- WILLIS, B. T. M. (1969). *Acta Cryst.* **A25**, 277-300.
- WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*. Cambridge Univ. Press.
- ZUCKER, U. H. & SCHULZ, H. (1982). *Acta Cryst.* **A38**, 563-568, 568-576.

Acta Cryst. (1985). **A41**, 79-81.

A Deficiency of the Cumulant Expansion of the Anharmonic Temperature Factor

BY C. SCHERINGER

Institut für Mineralogie der Universität Marburg, Lahnberge, D-3550 Marburg/Lahn, Federal Republic of Germany

(Received 21 October 1983; accepted 14 August 1984)

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

may be an inadequate tool for describing anharmonic motions. Five examples from the literature are quoted where the cumulant expansion gave worse results than other anharmonic expansions.

The cumulant expansion of the anharmonic temperature factor,

$$T(\mathbf{h}) = g(\mathbf{h}) \exp \left\{ [(2\pi i)^3/3!] \sum_{ijk} K^{ijk} h_i h_j h_k + [(2\pi i)^4/4!] \sum_{ijkl} K^{ijkl} h_i h_j h_k h_l + \dots \right\} \quad (1)$$

[$\mathbf{h}(h_1, h_2, h_3)$ = Miller indices, K^{ijk} , K^{ijkl} = cumulant tensors, $g(\mathbf{h})$ = harmonic temperature factor], was first proposed by Johnson (1969, 1970) as a formal expansion of the harmonic temperature factor in powers of $2\pi i \mathbf{h}$, see also *International Tables for X-ray Crystallography* (1974). The inverse Fourier transform of (1) (if it exists) is given by the 'theoretical' Edgeworth series, which has differential operators in the exponent operating on the Gaussian function (Kendall & Stuart, 1969, p. 158). This series cannot be evaluated analytically and, thus, it is difficult to examine its behaviour as a function. Approximations to the 'theoretical' series (the 'practical' Edgeworth series) are obtained by expanding the exponential function and letting the differential operators of the first terms operate on the Gaussian function. In this way a series of Hermite polynomials is obtained in direct space. The first terms up to Hermite polynomials of sixth order are given by Johnson (1969, 1970).

The inverse Fourier transform of (1) does not exist when $T(\mathbf{h})$ is diverging and thus the integral over $T(\mathbf{h})$ is infinite. This happens when the highest even power of \mathbf{h} has predominantly positive coefficients (*i.e.* when the sphere in \mathbf{h} is not 'tight' everywhere). It is the purpose of this note to point out that the inverse Fourier transform of (1) (if it exists), *i.e.* the 'theoretical' Edgeworth series has always negative regions and thus does not fulfil the requirements of a probability density function (p.d.f.). For this reason, it may happen that the cumulant expansion (1) becomes an inadequate tool for describing anharmonic motions. In an earlier paper (Scheringer, 1977) we considered the cumulant expansion (1) as the best form of the anharmonic temperature factor in view of four lattice-dynamical calculations, which all yielded the temperature factor in the exponential form. We now think that the lattice-dynamical results cannot be correct in this respect in view of our present findings.

The mathematical basis of our statement is a theorem by Marcinkiewicz (1938). It states that, in the one-dimensional case,

$$f(\mathbf{h}) = \exp(a_0 + a_1 h + a_2 h^2 + \dots + a_r h^r + \dots + a_n h^n), \quad n > 2, \quad (2)$$

can never be the Fourier transform of a p.d.f. The theorem implies two cases. Either $f(\mathbf{h})$ is divergent and cannot be the Fourier transform of any function or $f(\mathbf{h})$ is convergent and then it is the Fourier transform of a function that has negative regions. The theorem has been generalized by Professor W. Gromes, Mathematisches Institut der Universität Marburg. He showed that it is also valid for imaginary terms in (2), *i.e.* for powers $(ih)^r$, $1 \leq r \leq n$, and that it holds in n -dimensional space. A copy of Professor Gromes's calculation may be obtained from him on request.

The impact of the Marcinkiewicz-Gromes theorem may become weakened when we take into account experimental resolution, which is always limited. In the refinement we use a data set with $\mathbf{h} \leq \mathbf{h}_{\max}$ and, hence, we do not use the cumulant expansion in the range $\mathbf{h} > \mathbf{h}_{\max}$. This range is not determined by the data and, thus, is open either to speculation or to the design of a meaningful continuation of the temperature factor. Thus, it would be legitimate to give the temperature factor a course different from that fixed by the cumulant expansion. With such a continuation of $T(\mathbf{h})$, the negative regions in the p.d.f. will not necessarily disappear. The chance that they may disappear will be greater the smaller \mathbf{h}_{\max} and the weaker the anharmonicity. Since, with an actual structure, it is (nearly) impossible to calculate the inverse Fourier transform from the cumulant expansion in the range $\mathbf{h} \leq \mathbf{h}_{\max}$ and from a thought optimized course of $T(\mathbf{h})$ in the range $\mathbf{h} > \mathbf{h}_{\max}$, the corresponding p.d.f. cannot be obtained and a control concerning the negative regions cannot be performed.

There are several examples in the literature where it is reported that the cumulant expansion (in direct space sometimes referred to as 'Edgeworth model') fails to converge in the refinement. In such refinements better results were obtained using the Gram-Charlier series as a p.d.f. or an OPP expansion. With the refinement of Li_3N , Zucker & Schulz (1982) report reliability values $R(\text{Gram-Charlier}) = 0.015$, $R(\text{Edgeworth}) = 0.027$, and Kuhs (1983), with the refinement of CsPbCl_3 , $R_w(\text{Gram-Charlier}) = 0.034$, $R_w(\text{Edgeworth}) = 0.043$. With ice Ih , Kuhs (1983) obtained intolerably high R values using the cumulant expansion, stating ' \dots the bad fit ($R_w \approx 10\%$, $S > 10$) undoubtedly indicates an inadequacy of the Edgeworth model in reciprocal space'. Moss, McMullan & Koetzle (1980) used the cumulant expansion and an OPP model in the refinement of ZnS . At low temperatures, the two models proved to be equally good but 'at the two highest temperatures, where anharmonicity is most pronounced, the cumulant refinements have lower agreement factors than the OPP results'. Eriksson, Hermansson, Lind-

gren & Thomas (1982) report on the application of the cumulant expansion (1) '... that such refinements have not converged successfully, rather than that they have not been tried. Our refinement of ten γ values for hydrogen and four for oxygen in the water molecule of $K_2C_2O_4 \cdot H_2O$ resulted in large standard deviations and large correlations. The results of the refinement were not considered meaningful'. Finally, Johnson (1980) himself has noticed deficiencies of the cumulant expansion and locates them primarily in the 'interactions among even-order (real) and odd-order (imaginary) cumulant coefficients'. As a way out, Johnson has established the α formalism with which several structures have been successfully refined in recent years including structures containing mobile atoms in ionic conductors such as AgI (Cava, Reidinger & Wuensch, 1977). Compared to the cumulant expansion, the α formalism differs primarily in that the exponential form of the temperature factor is discarded and the anharmonic terms are expanded into a series of quasi-Hermite polynomials. There is an unequivocally determined inverse Fourier transform to the α formalism that can serve as a p.d.f.; see also Zucker & Schulz (1982). These results from the literature may have their cause in the deficiency of the cumulant expansion that has been pointed out in this paper.

The experimental evidence reported here may not be conclusive for ruling out the cumulant expansion as a useful description of anharmonic motions.

However, we recommend controlling the results obtained with the cumulant expansion by means of corresponding results obtained with other anharmonic expansions.

I am indebted to Professor Dr W. Gromes, Mathematisches Institut der Universität Marburg, for having proved that the Marcinkiewicz theorem is generally valid.

References

- CAVA, R. J., REIDINGER, F. & WUENSCH, B. J. (1977). *Solid State Commun.* **24**, 411-416.
- ERIKSSON, A., HERMANSSON, K., LINDGREN, J. & THOMAS, J. O. (1982). *Acta Cryst.* **A38**, 138-142.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press (Present distributor: D. Reidel, Dordrecht).
- JOHNSON, C. K. (1969). *Acta Cryst.* **A25**, 187-194.
- JOHNSON, C. K. (1970). *Thermal Neutron Diffraction*, pp. 132-160. Oxford Univ. Press.
- JOHNSON, C. K. (1980). *Computing in Crystallography*, pp. 14.01-14.19. Bangalore: The Indian Academy of Sciences.
- KENDALL, M. G. & STUART, A. (1969). *The Advanced Theory of Statistics*. Vol. I. London: Griffin.
- KUHS, W. F. (1983). *Acta Cryst.* **A39**, 148-158.
- MARCINKIEWICZ, J. (1938). *Math. Z.* **44**, 612-618.
- MOSS, B., MCMULLAN, R. K. & KOETZLE, T. F. (1980). *J. Chem. Phys.* **73**, 495-508.
- SCHERINGER, C. (1977). *Acta Cryst.* **A33**, 879-884.
- ZUCKER, U. H. & SCHULZ, H. (1982). *Acta Cryst.* **A38**, 563-568, 568-576.

Acta Cryst. (1985). **A41**, 81-85

Anharmonic Temperature Factors: the Limitations of Perturbation-Theory Expressions

BY J. K. MACKENZIE AND S. L. MAIR

CSIRO Division of Chemical Physics, PO Box 160, Clayton 3168, Victoria, Australia

(Received 2 January 1984; accepted 14 August 1984)

Abstract

The error in the temperature factor arising from the use of anharmonic perturbation theory is investigated for a one-dimensional one-particle potential by comparison with an exact evaluation of the Fourier transform of the Boltzmann probability density. Results are presented for a range of values of cubic and quartic coefficients for temperature factors derived from moment or cumulant expansions about the harmonic probability density function. It is found that either expansion provides an adequate approximation to the anharmonic temperature factor for moderately small anharmonicity but that both expansions

become increasingly inadequate as the anharmonicity gets larger.

1. Introduction

For temperatures where classical approximations are adequate, the starting point for the derivation of the anharmonic temperature factor is the Boltzmann one-particle probability density function (p.d.f.), $\exp[-V(\mathbf{u})/k_B T]$, where $V(\mathbf{u})$ is the one-particle potential (OPP), \mathbf{u} is the atomic displacement from a reference position, k_B is the Boltzmann constant and T is the absolute temperature. Expansions about the harmonic (Gaussian) p.d.f. are then made as