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Evaluation of Atomic Displacement Parameters by Lattice-Dynamical Calculations. Efficiency in Brillouin-Zone Sampling

BY TULLIO PILATI AND RICCARDO BIANCHI

*Centro CNR per lo Studio delle Relazioni tra Struttura e Reattività Chimica,
Via Golgi 19, I-20133 Milano, Italy*

AND CARLO MARIA GRAMACCIOLI

Dipartimento di Scienze della Terra, Università, Via Botticelli 23, I-20133 Milano, Italy

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Abstract

Some progression formulae for uneven and 'asymmetric' sampling of the Brillouin zone are shown to be particularly useful to attain fast convergence in the calculation of atomic displacement parameters and thermodynamic functions by lattice-dynamical procedures.

Introduction

Lattice dynamics provides a useful way for deriving important crystal properties from structural and spectroscopic (or force-field) data. Among these properties, there are thermodynamic functions and also information about thermal behaviour (*e.g.* TDS, atomic displacement parameters or a.d.p.'s).

For instance, the atomic displacement tensor $U(p)$ relative to a certain atom p can be obtained as follows:

$$U(p) = (Nm_p)^{-1} \sum_{\psi, \mathbf{q}} E_{\psi}(\mathbf{q}) [2\pi\nu_{\psi}(\mathbf{q})]^{-2} \times \mathbf{e}(p|\psi\mathbf{q})[\mathbf{e}^*(p|\psi\mathbf{q})]^t \quad (1)$$

Here $\mathbf{e}(p|\psi\mathbf{q})$ is the mass-adjusted polarization vector of the atom p , $E_{\psi}(\mathbf{q})$ is the average energy of the mode, N is the total number of unit cells in the crystal and m_p is the mass of the atom (see, for instance, Willis & Pryor, 1975).

Similarly, thermodynamic functions such as the molar heat c_v and entropy S can be derived from the same data:

$$c_v = 3R \sum_{\nu} g_{\nu} (h\nu/kT)^2 \exp(h\nu/kT) \times [\exp(h\nu/kT) - 1]^{-2} \Delta\nu \quad (2)$$

$$S = E_{\text{vib}}/T - 3R \sum_{\nu} g_{\nu} \ln [1 - \exp(h\nu/kT)] \Delta\nu, \quad (3)$$

where E_{vib} is the vibrational energy of the crystal and g_{ν} is a density-of-states function, normalized so that $\sum_{\nu} g_{\nu} \Delta\nu = 1$. The summations are extended to all the vibrational modes (ψ) of frequency ν_{ψ} for a certain point of the Brillouin zone corresponding to a certain value of the wave vector \mathbf{q} and (in principle) to all the values of \mathbf{q} in the Brillouin zone.

The necessity of sampling the Brillouin zone at a sufficient number of points is one of the major practical difficulties. For some thermodynamic functions, considerable efforts have already been made to define an efficient way to obtain an accurate description of the density of states of a material from a limited sampling (see, for instance, Baldereschi, 1972; Chadi & Cohen, 1973; Price, Parker & Leslie, 1987). The situation becomes considerably more critical if a.d.p.'s or their molecular counterparts [such as T, L and S in Schomaker-Trueblood's (1968) notation]

are estimated. This happens because the contributions go to infinity at the origin [see (1)]; a similar problem occurs also for entropy, but the contributions go to infinity so slowly that for a small volume around $\mathbf{q} = \mathbf{0}$ they are negligible with respect to the rest of the Brillouin zone.

For instance, Reid & Smith (1970) in one of the best theoretical estimations of the \mathbf{B} 's for some alkali halides have considered sampling up to over 8000 symmetry-independent points in the Brillouin zone. A strategy of uneven sampling whose thickness is a maximum in proximity of the origin of the Brillouin zone ($\mathbf{q} = \mathbf{0}$) was proposed by some of us (Filippini, Gramaccioli, Simonetta & Suffritti, 1976) (FGSS). From the various possibilities, each of them corresponding to a different progression, the choice of the most appropriate sampling was made by examining convergence as a function of the number n of grid intervals Δx_k along the reciprocal crystal axes. For each interval, two criteria for defining the sampling point at the interior of it were used and discussed.

By examining various cases of molecular crystals, the best progression along each reciprocal axis was found to correspond to the formula

$$\Delta x_k = N[k^2/(3+k^2)]^{1/3}, \quad (4)$$

where N is a normalization constant so that $\sum \Delta x_k = 1/2$ (or π) in reciprocal axial units, according to our definition of \mathbf{q} . The location of the sampling point within each interval was chosen so that the border line between two subsequent intervals was located at equal distance between the corresponding sampling points. Similar results could be obtained by using simpler progression formulae of the kind

$$\Delta x_k = Nk^r \quad (5)$$

where the optimum sequence corresponded to a value of r around 1.25.

Another way of solving the same problem has been proposed by Kroon & Vos (1978, 1979) (KV). These authors use a more elaborate division of the reciprocal space into pyramids of three kinds around the origin; they show their own procedure to be satisfactory and definitely better with respect even to the best progression series proposed by FGSS; for this reason the criterion of uneven sampling was rejected by them as impractical.

Whereas some of the results shown by KV are in their turn open to discussion (for instance, they show a very good convergence for the values of L , but the critical contribution of the acoustic branches in the proximity of the origin imply the tensor \mathbf{T} almost exclusively), on reading FGSS's paper again after some years we have noticed the presence of some statements which are not clear and this might have led to substantial misunderstanding. For instance, in defining the position of sampling points within each

zone [see Fig. 1 in FGSS, case (a)], the authors omitted to define the position q_1 of the first point.*

In a new series of calculations concerning (this time) minerals and inorganic substances in general (Pilati, Bianchi & Gramaccioli, 1990), we wanted to extend these tests on sampling the Brillouin zone using various progression formulae and different criteria for choosing the sampling point within each interval. For this reason, a more detailed explanation of this procedure and extension of such techniques to further examples appeared to us as necessary and interesting.

Results and discussion

Our 'new' progression formulae establish an interval Δx_k in a certain direction of the reciprocal space (usually along a reciprocal axis) as in (5). Since the choice of the zone is always made so that the Γ point is in the centre (see FGSS, 1976), in many cases the asymmetric unit coincides with the region of all positive coordinates, or (for lower symmetry) a similar construction for the negative regions can be added if necessary. Using this criterion, the boundaries of each interval x_{k-1} and x_k (referred to reciprocal-space units) are given by

$$x_k = x_{k-1} + Nk^r \quad (x_0 = 0). \quad (6)$$

The position (the corresponding coordinate q_k in the reciprocal-space reference) of the sampling point within each interval is given by the expression

$$q_k = x_{k-1} + t\Delta x_k \quad (7)$$

where $0 < t < 1$.

Several kinds of sequences differing for the values of r and t have been tested for two substances, NaCl and forsterite α - Mg_2SiO_4 ; for each sequence the number of intervals was allowed to vary from 1 to a maximum value in order to test the speed of convergence.

The lattice-dynamical calculations for NaCl have been made by assuming Kellermann's (1940) rigid-ion model; no emphasis is made here to claim these results to be a particularly good estimation of the a.d.p.'s and other properties with respect to a series of recent applications of sophisticated models (see, for instance, Reid & Smith, 1970). Here the calculations are performed on a simple model to show these convergence properties. For forsterite Mg_2SiO_4 , our calculations using Iishi's (1978) RI3 rigid-ion model have been used as a basis for this test (Pilati, Bianchi & Gramaccioli, 1990).

* In FGSS's calculations, the positions q_k of the subsequent sampling points are given in their case (a) by the following expressions:

$$q_1 = \Delta x_1 - 0.75\Delta x_2 + 0.25\Delta x_3;$$

$$q_2 = \Delta x_1 + 0.75\Delta x_2 - 0.25\Delta x_3;$$

$$q_k = q_{k-2} + 2\Delta x_{k-1} \quad (k \geq 3).$$

Table 1. *Estimated values of entropy ($J mol^{-1} K^{-1}$) at 298 K for various kinds of sampling*

The parameter n corresponds to the number of intervals along the asymmetric unit of each reciprocal axis; r corresponds to the exponent in (5) and t determines the position of the sampling point within each interval, according to (7).

Forsterite

n	$r=0, t=0.500$	$r=1, t=0.375$	$r=1, t=0.400$	$r=1, t=0.425$	$r=1, t=0.450$
1	90.9	92.3	92.0	91.7	91.4
2	91.3	91.7	91.6	91.5	91.3
4	91.3	91.6	91.5	91.4	91.4
8	91.3	91.5	91.4	91.4	91.4
12	91.3	91.4	91.4	91.4	91.4
16	91.3	91.4	91.4	91.4	91.3

NaCl

n	$r=0, t=0.55$	$r=1, t=0.450$	$r=1, t=0.400$
1	17.6	18.0	17.9
2	17.7	17.7	17.9
4	17.7	17.7	17.8
8	17.7	17.7	17.7
16	17.7	17.7	17.7
40	17.7	17.7	17.7

Table 1 shows convergence to be easily attained for entropy with any kind of sampling. This confirms the results found previously by us and other authors (see, for instance, FGSS, 1976). Instead, convergence

is more critical for atomic displacement parameters: the situation is shown in Figs. 1 and 2 as a plot of the B_{eq} 's for the cases of NaCl and forsterite, respectively, against the number n of grid spacings. In these figures, several sequences are represented, depending on the kind of progression formula (as determined by the parameter r) and on the position of the

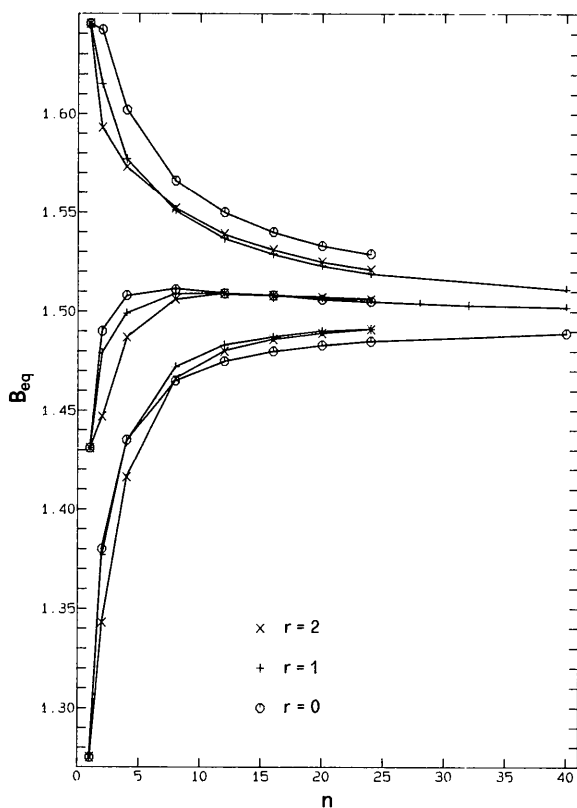


Fig. 1. Change in the estimated B_{eq} values (\AA^2) for the Cl atom in NaCl as a function of the Brillouin-zone sampling. Each curve joins the corresponding points belonging to the same sequence, but differing in the number n of sampling intervals along each reciprocal axis. The highest three curves correspond to $t=0.4$, the curves in the middle to $t=0.45$ and the lowest three to $t=0.5$. In each bundle, the curves differ in the value of r (0 to 2).

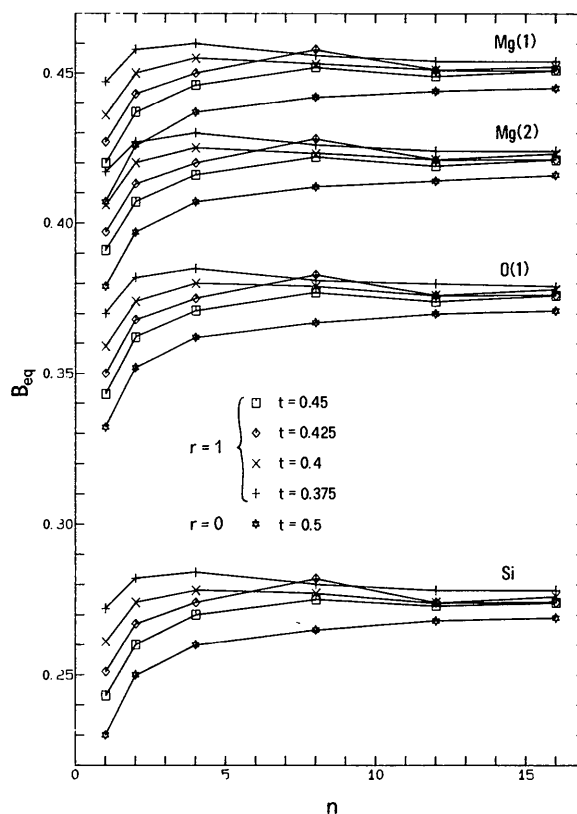


Fig. 2. Change of B_{eq} values (\AA^2) for various atoms in the forsterite structure as a function of the Brillouin-zone sampling. All the curves reported for each atom correspond to $r=1$, with the exception of the lowest one for which $r=0$ (and $t=0.5$).

sampling point within each interval (as determined by the parameter t).

For simplicity, in Fig. 1 only the data relative to the B_{eq} of Cl are reported, since the trend for the corresponding data of the Na atom is exactly the same. In the upper part of the figure, the curves relative to a common value for $t = 0.4$ appear grouped together; in the lower part the curves for which $t = 0.5$ are also grouped together. The curves in the middle correspond to $t = 0.45$. The lowest curve (for $n > 8$) corresponds to $r = 0$ and $t = 0.5$, *i.e.* to an even sampling of the Brillouin zone, with the sampling point 'symmetrically' located, *i.e.* lying at the centre of each reciprocal-lattice interval.

At a first glance the curves in Fig. 1 show the situation of even sampling to be unfavourable with respect to the others; another important point is that the parameter r is relatively much less effective than the parameter t . Therefore, more than the difference in sampling intervals, what counts is the position of the representative point within each interval. Here, a value around 0.45 seems to be the most convenient; our calculations have also been performed in this case with different values of r , but no practical difference between these results occurs for $n \geq 8$ (there is a virtual overlap of the corresponding curves in most of the diagram).

For NaCl, with values of t different from the optimum, the convergence to the final value is very slow. However, even for the most unfavourable situation, the difference between the final value ($n \rightarrow \infty$) and a reasonably limited number of intervals along each axis ($n = 4$) is of the order of 7%, *i.e.* the deviation is substantially smaller than the corresponding accuracy of the best crystallographic experimental data. For $t = 0.45$, *i.e.* with the most favourable situation, the difference between $n = 4$ and the final value is less than 1%. A similar conclusion can be reached by looking at Figs. 3(a) and 4 of Reid & Smith (1970), who plot the percentage contribution of the zero-phonon term to the B_{eq} 's in NaCl.

For forsterite, owing to the greater complexity of the structure, the number of sequences tested here is restricted to $r = 1$, together with the 'even-symmetric' sampling of $r = 0$ and $t = 0.5$, which corresponds in each case to the lowest curve in Fig. 2. In this figure, the trend is shown separately for each different atom, with the exception of the atoms O(2) and O(3), whose values are practically identical to O(1). Although the actual values of the B_{eq} 's are considerably different, the curves relative to the different atoms in Fig. 2 might be virtually superimposed on each other if vertically shifted, and therefore the trend towards convergence is identical. The best results occur for values of t lying between 0.375 and 0.400; therefore, the optimum situation is appreciably *different* from the case of NaCl. However, even for the worst choice of the sampling procedure, here too the difference

between the convergence values and the case of $n = 4$ is well below the accuracy of the best crystallographic experimental data, since it never exceeds 4%, and it is about 1% for the most favourable sampling. Even for $n = 2$ the results are quite reasonable, since for the best sampling they agree with the final value within 2%, and this might suggest the possibility of a considerable saving of computing time.

In conclusion, the *a priori* choice of the best sampling procedure for improving convergence seems to be more difficult than it was before: in fact our experience concerning molecular crystals has shown that the same series could be safely used for a variety of different substances. However, the trend of the function to be integrated (by summation) is linked to the slope of the acoustic branches of the phonon dispersion curves in the proximity of the origin (see above). Since the slope depends on the elastic constants and the density of the substances (see, for instance, Kittel, 1966), and since these properties may vary sensibly for chemically different groups of substances, we may expect that the best performance would be obtained by using the parameters which showed the best behaviour for other chemically similar substances. On the other hand, whenever we are beginning to consider a group of substances which have not been tested before in this respect, some caution is necessary against *a priori* use of the sampling for best convergence. In any case, however, when lattice-dynamical calculations are performed on a certain substance, they are usually repeated for a variety of different conditions (*e.g.* for different values of temperature and other parameters affecting the calculations). In this case, a detailed choice of the best sampling is convenient, since the optimum conditions of convergence can be maintained throughout the work.

In the cases shown above, however, the problem of the choice of a convenient Brillouin-zone sampling does not seem to be very important for most applications concerning comparison with experimental data since the errors deriving from an inadequate sampling are usually inferior to the corresponding experimental uncertainties. This complex problem can become delicate only for some very particular cases, such as, for instance, when accurate evaluation of the a.d.p.'s is considered: a possible future need for such data might occur when a particularly accurate evaluation of electron density in crystals is considered.

All calculations were performed using our program FREMIN running on a Gould NP1 computer.

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Lattice Dynamics and Thermal Parameters in Azahydrocarbons

BY A. CRIADO

Departamento de Física de la Materia Condensada, Instituto de Ciencia de Materiales, Universidad de Sevilla, Apto 1065, 41080 Sevilla, Spain

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Abstract

Lattice frequencies and crystallographic thermal parameters are calculated for some azahydrocarbons with the external Born-von Karman formalism using an atom-atom potential model which accounts explicitly for electrostatic interactions modelled as atomic point charges. Results are satisfactory, encouraging the application of this procedure to a wider range of molecular crystals. Comparison of calculated thermal parameters with experimental data obtained with different techniques increases the need for reliable experimental thermal parameters in order to make meaningful deductions.

Introduction

Lattice dynamics of molecular crystals based on semi-empirical models for atomic forces has been a field of growing interest stemming from the basic work (Cochran & Pawley, 1964) where the complete lattice dynamics of a molecular crystal was studied for the first time, followed by a series of papers (Pawley, 1967, 1972) which established the practical formulation for these calculations. The development of optical spectroscopy probing the far-infrared lattice region and the advent of neutron spectroscopy have also increased the activity in this field.

Lattice dynamics also finds a very important application as an aid to crystallographic studies (see Willis & Pryor 1975). For instance, an adequate lattice-dynamical model can help to correct experimental Bragg intensities for thermal-diffuse-scattering (TDS) contributions. Another interesting application is the calculation of crystallographic thermal parameters using potential-energy models for comparison with the experimental values obtained in a least-squares

structure refinement process. This procedure can reveal possible bias in the experimental thermal parameters as a consequence of systematic errors; some information on the different contributions of crystal forces to thermal motion can also be obtained.

These calculations have been successful especially in connection with hydrocarbons. Here atom-atom potential models in the form $V(r) = -A/r^6 + B \exp(-Cr)$ seem to work particularly well for both rigid and non-rigid molecules (Filippini, Gramaccioli, Simonetta & Suffritti, 1973, 1974). In the latter case, the contribution of internal modes tends to increase the thermal parameters; a further increase is observed if coupling between internal and external modes is taken into account (Gramaccioli, Filippini & Simonetta, 1982; Gramaccioli & Filippini, 1983). Other studies which successfully calculate thermal parameters from lattice dynamics for hydrocarbons are: *o*-terphenyl (Gramaccioli & Filippini, 1985), tetraphenylmethane (Filippini & Gramaccioli, 1986), biphenyl (Bonadeo & Burgos, 1982) and benzene (Filippini & Gramaccioli, 1989). There are also some applications to heteroatomic crystals (Filippini, Gramaccioli, Simonetta & Suffritti, 1976; Filippini, Gramaccioli & Simonetta, 1981).

The remarkable success of calculations of thermal motion for hydrocarbons resides in the fact that the crystal force field can be modelled adequately using 6-exp potential functions. Nevertheless, if we try to extend the method to other kinds of molecular crystals where atoms very different in electronegativity are bound together, electrostatic forces arising from molecular static-multipole moments appear which must be accounted for. If these forces are small they can be absorbed into effective 6-exp models (although these turn out to be non-transferable to other molecules) but if the electrostatic interactions are