

Lattice-Dynamical Applications to Crystallographic Problems: Consideration of the Brillouin Zone Sampling

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In lattice-dynamical calculations, especially of crystallographic temperature factors and thermodynamic functions, a considerable saving of computing time can be obtained by a suitable choice and sampling of the first Brillouin zone. To this purpose, an uneven sampling is proposed and examples of its advantages are given. For a convenient use of this sampling, 'unconventional' Brillouin zones are adopted: in most cases, simplifications due to crystal symmetry can be made.

Introduction

In applications of lattice dynamics to crystallographic problems, especially in connection with evaluation of **B** tensors and thermodynamic functions, an important problem concerns appropriate sampling of the Brillouin zone. We have proposed an uneven sampling (Gramaccioli, Simonetta & Suffritti, 1973; Filippini, Gramaccioli, Simonetta & Suffritti, 1975) which allows a considerable saving of computing time. A detailed description of our procedure is presented here.

Temperature factors and the Brillouin zone

According to a procedure which assumes a Bose-Einstein statistical distribution (Pawley, 1967; Willis & Prior, 1975), the **B** tensors for each atom *k* can be evaluated as:

$$B_{ij(k)} = \sum \xi_{i(k)} \xi_{j(k)} \varepsilon(\omega) / Nm_k \omega^2 \quad (1)$$

where the ξ 's are the components relative to atom *k* of the normalized latent vectors of the dynamical matrix, ω is the angular frequency of the normal mode, m_k is the mass of the atom and $\varepsilon(\omega)$ is the average energy of the mode:

$$\varepsilon(\omega) = hv \left[\frac{1}{2} + [\exp(hv/kT) - 1]^{-1} \right]. \quad (2)$$

The summation (1) is extended to *N* points in a Brillouin zone. For 'rigid' molecules, the tensors **T**, **L**(= ω) and **S** (Cruickshank, 1956; Schomaker & Trueblood, 1968) can be derived in a similar way:

$$T_{ij(p)} = \sum \eta_{i(p)} \eta_{j(p)} \varepsilon(\omega) / Nm_p \omega^2 \quad (3)$$

$$L_{ij(p)} = \sum \zeta_{i(p)} \zeta_{j(p)} \varepsilon(\omega) / N \sqrt{I_{i(p)} I_{j(p)}} \omega^2 \quad (4)$$

$$S_{ij(p)} = \sum \eta_{i(p)} \zeta_{j(p)} \varepsilon(\omega) / Nm_p \sqrt{I_{i(p)} I_{j(p)}} \omega^2 \quad (5)$$

where the η 's are the real and imaginary coefficients of the latent vectors relative to translation of molecule *p* and the ζ 's are relative to rotation of the same molecule. Here m_p is the mass of molecule *p* and $I_{i(p)}$ or $I_{j(p)}$ are the corresponding principal moments of inertia.

Some inconvenience may be met in the use of the above expressions. The contribution tends to infinity for a value of ω approaching zero, as happens in all crystals for acoustic branches (the greatest inconvenience concerns translational motion).

On the other hand, the values of **B** tensors (and **T**) are finite in practice because the number of modes for $\mathbf{q} \rightarrow 0$ tends rapidly to zero; however, the method of carrying out the summation (1), which can also be expressed as an integral, has to be chosen with some caution.

In some works of this kind, the problem is solved by taking into account a considerable number of points ('thick sampling') in the Brillouin zone. This makes the summations in (1) and (3-5) close to an integral and also allows for the possibility of neglecting troublesome points (such as $\mathbf{q}=0$), because of their very limited number with respect to the total. However, a procedure of this kind, in order to be acceptable, necessarily implies a huge amount of calculation, which limits application of lattice-dynamical procedures to crystallographic problems.

'Uneven sampling'

If a function is relatively 'smooth', the approximation of its integral by a summation becomes quite acceptable, even with a 'gross' sampling, whereas, close to steep maxima and minima the sampling must be as thick as possible: such a situation can be explained if one considers a Taylor expansion of the function to be integrated and the influence of higher derivatives.

This suggests that close to $\mathbf{q}=0$ a particularly 'thick' sampling of the Brillouin zone is necessary, but not away from the origin, since (at least for physically significant cases) no other point corresponds to zero frequency. This is also evident if one considers the nature of phonon dispersion curves.

Accordingly, we developed the idea of an 'uneven' sampling of the Brillouin zone. In order to account for the disparity in size of the intervals, a weight is assigned proportional to the extension of the interval surround-

ing a 'sampled' point. A simple scheme of this way of sampling, as applied in our calculations (Filippini, Gramaccioli, Simonetta & Suffritti, 1973, 1974*a, b*, 1975), is the following: each reciprocal axis is divided into unequal intervals (Figs. 1, 2), following a certain progression. Such a progression can be used either for establishing directly the sampled points, or for establishing intervals: in the first case, interval borders are taken as equidistant from adjacent points, whereas in the second the sampled points are taken as equidistant from adjacent borders [cases (a) and (b) in Fig. 1]. For lower symmetries, when it is necessary to sample both positive and negative values along one reciprocal axis (Table 2), we take points and intervals symmetric with respect to the origin.

Fig. 2 shows the procedure for a two-dimensional case: the weight corresponding to each interval is proportional to the product of weights corresponding to axes, *i.e.* to the area (or to the volume in the three-dimensional case) of the dashed zones.

An important point is establishing the minimum number of points to be sampled. This can be done by comparing the results obtained from various samplings with different 'thickness'. Another question concerns the nature of the function to be used in establishing the progression for sampling intervals. In other words, if increasing the number of points does not involve appreciable variation in the results (especially temperature factors), the number taken can be as small as possible.

In Fig. 3 the results relating to some components of the T tensor for 1,6:8,13-butane-1,4-diylidene[14]annulene are reported. Each line relates to results obtained for the same component of T , using the same progression formula (A, B, C, D), with a different number n of points per reciprocal axis in the asymmetric part of the Brillouin zone (the same conditions have been assumed for all parameters in these calculations); in other words, extrapolating the lines to $1/n \rightarrow 0$ gives a plausible value for convergence, *i.e.* for the value obtained with a practically infinite number of sampled points in the Brillouin zone. In this figure, formula A corresponds to an 'even' sampling ($\Delta x_i = \text{constant}$); B is proportional to the progression $\Delta x_i = n^{3/2}$; C to $\Delta x_i = [n^2/(3+n^2)]^{1/3}$, and D to $\Delta x_i = n_i$. In all these formulae, $n_i = 1, 2, 3, \dots$ etc.

The convergence limit is the same for all the lines of the same T_{ij} ; the rapidity of convergence, however, is not the same. This can be seen by comparing the distance from the limiting value (dashed) for the same number of sampled points, *i.e.* for equal abscissae. For instance, the results obtained with C with only four points per axis are comparable or even better than results obtained from a 'regular' (evenly spaced) sampling with 32 points per axis, *i.e.* an uneven sampling with only $4^3 = 64$ points in the asymmetric unit is comparable with a 'regular' sampling of $32^3 = 32768$ points; the saving of computing time is accordingly very considerable. A similar situation occurs for

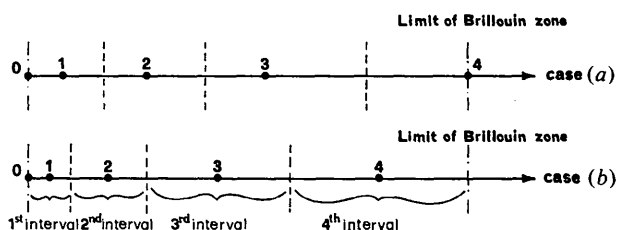


Fig. 1. Definition of points and intervals on the reciprocal axes for sampling the Brillouin zone (see text).

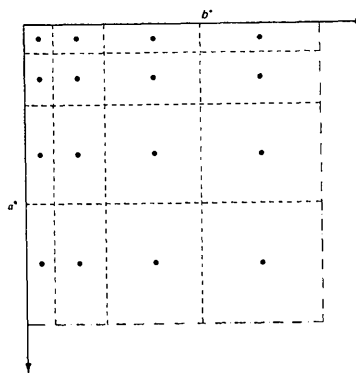


Fig. 2. Two-dimensional sampling, as derived from application of case (b) (Fig. 1) to two reciprocal axes; the results of calculations relative to each point are weighted proportionally to the surrounding area.

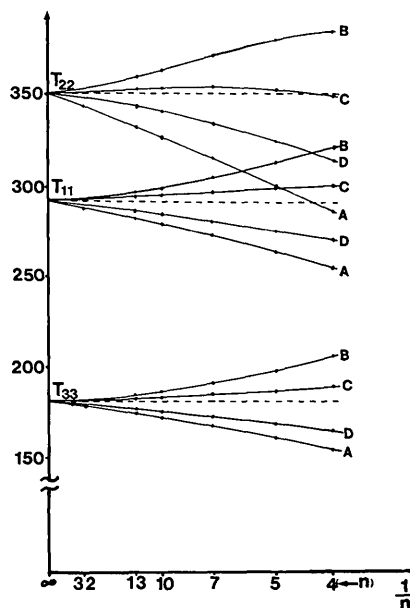


Fig. 3. Some calculated values of components of the T tensor for 1,6:8,13-butane-1,4-diylidene[14]annulene, obtained for Brillouin zone sampling of different thickness. Each line connects results relative to the same progression formula: A corresponds to an 'even' sampling ($\Delta x_i = \text{constant}$), B is proportional to the progression $\Delta x_i = n^{3/2}$, C to $\Delta x_i = [n^2/(3+n^2)]^{1/3}$, and D to $\Delta x_i = n_i$. These formulae are applied as for case (a) in Fig. 1 (A, B, C) or for case (b) (formula D). The values (\AA^2) have been multiplied by 10^4 .

other compounds, such as anthracene or perdeutero-naphthalene, and gives us confidence in the generality of our results. For instance, Fig. 4 shows the eigenvalues of the T tensor in anthracene: these values, obtained with C for only four points per axis, are already very near to the limiting value, whereas the regular sampling should be carried out with a much greater number of points in order to obtain results of comparable significance.

Evaluation of thermodynamic functions

A similar situation occurs in evaluating thermodynamic functions. For instance, the value of the logarithm of the vibrational partition function Z is given by:

$$\ln Z = \sum g(\nu_j) \ln [1 - \exp(-h\nu_j/kT)] \Delta\nu_j \quad (6)$$

where $g(\nu_j)$ is the density of states for frequency ν_j . Inspection of (6) shows that for $\mathbf{q} \rightarrow 0$ the logarithm corresponding to acoustic branches tends to infinity; accordingly, one may expect to encounter problems.

In a previous article (Filippini *et al.*, 1975) this prob-

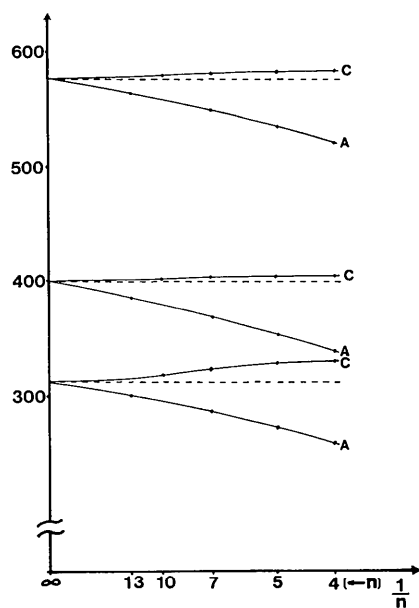


Fig. 4. Eigenvalues of calculated T tensors for anthracene ($\times 10^4 \text{ \AA}^2$). In this figure, the lettering $A-C$ has the same meaning as in Fig. 3. Here, since the sampling is made for both positive and negative regions of the a^* axis (see Table 2), along this axis we actually have $2n$ points.

lem has already been considered (see for instance Table 2 of the mentioned work, where values of the T tensor and thermodynamic functions for naphthalene derived with a different sampling of the Brillouin zone are shown). In spite of the large variation in T , the results for specific heat, entropy and free energy do not seem to vary significantly, even with widely different ways of sampling: that the situation had to be better, as for T 's (or B 's), is also clear if the nature of (1) or (3) is compared with (6).

On the other hand, one might expect the computed value of Z to be affected by the channel width used in building up the density of states. For instance, the first interval ($\nu \simeq 0$) contains several frequencies, whose contributions to Z are calculated later on, referring to the average value of the channel; these contributions may however be almost all grouped near $\nu=0$, and the actual contribution to Z may be different.

In order to test the validity of our procedure, a calculation of free energy was carried out for solid α -nitrogen; the results are given in Table 1.

We see that the agreement between the various results corresponding to more or less thick sampling is quite good, as for naphthalene. Moreover, the comparison between values of free energy calculated with a channel width of 2 cm^{-1} , which is our usual procedure, and 'directly' (*i.e.* accumulating contributions relative to partition functions due to each single frequency) supports the validity of our calculations.

Symmetry of the Brillouin zone

Some difficulties regarding 'uneven' sampling concern the correct application of symmetry. A review of the problem of symmetry for the Brillouin zone is given by Schnepf & Jacobi (1972); here, however, we are not greatly interested in determining specially symmetrical points and a much simpler treatment is sufficient.

Complete exploration of the Brillouin zone is unnecessary, because the results proper to $\mathbf{q}'' = \mathbf{qM}_k$, where \mathbf{M}_k is a rotation matrix of the crystal symmetry group, can be derived from results proper to \mathbf{q} . In fact, for a certain value of the wave vector \mathbf{q} , the contribution to the temperature factors or thermodynamic functions of a molecule related to the 'original' molecule E by a rotation \mathbf{M}_k is the same as the contribution relative to E for $\mathbf{q}'' = \mathbf{qM}_k$ (all these contributions are relative to the principal axes of each molecule): a simple demonstration is given in Appendix I.

Table 1. Values of some thermodynamic functions for $\alpha\text{-N}_2$ at 20 K and 0 atm, as obtained from different Brillouin zone sampling, or density of states accumulation procedure

Number of points per reciprocal axis*	Gibbs free energy (cal mol^{-1})		Entropy ($\text{cal mol}^{-1} \text{K}^{-1}$)	Specific heat c_p ($\text{cal mol}^{-1} \text{K}^{-1}$)
	'direct'	2.0 cm^{-1} channel		
4	89.490	89.496	2.619	4.92
7	89.486	89.474	2.610	4.92
10	89.485	89.482	2.614	4.92

* A sequence following C , as represented in Fig. 3, has been used.

Consequently, it is sufficient to refer to the 'asymmetric unit' of the Brillouin zone, adding up for each value of \mathbf{q} all contributions corresponding to symmetrically related molecules in the unit cell, as shown by Pawley (1967).

However, whereas for primitive unit cells it is possible to handle matters so that the choice of the 'asymmetric' part of the Brillouin zone is easy, for uneven sampling in non-primitive cells the problem may become more complex.

In order to obviate this difficulty, taking account of the relative arbitrariness of defining a Brillouin zone, our procedure refers to 'unconventional' zones, chosen so that their surfaces are parallel to principal planes (Figs. 5, 6); no effort has been made to provide for some properties, such as keeping limiting surfaces as close as possible to the origin, because this is unnecessary for our purpose. Our choice also brings about a considerable simplification in deriving the asymmetric unit directly from space-group operations (Table 2).

For some cases, our Brillouin zones are not the most satisfactory. For instance, for Laue group $m\bar{3}m$ the sampling proceeds as for a tetragonal crystal if the lattice is non-primitive; for Laue group $m\bar{3}$, the sampling proceeds as for an orthorhombic crystal.

However, in spite of this inconvenience, which involves a waste of computing time by a factor of two or four, this is the only procedure as far as we know which permits 'uneven' sampling, and the advantages of this kind of sampling more than compensate the disadvantages.

When the molecule is in a special position, the results

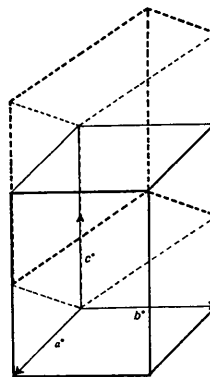


Fig. 5. Unconventional primitive reciprocal unit cell (continuous lines) used for deriving the Brillouin zone for body-centred lattices. The reciprocal axes define the non-primitive reciprocal cell, the dashed lines show the corresponding 'standard' primitive reciprocal cell. The Brillouin zone corresponds to this unit cell by shifting the origin to the centre of the zone and multiplying the sides by 2π .

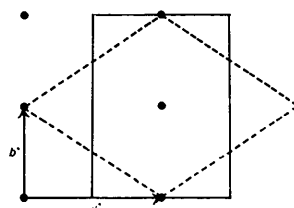


Fig. 6. Unconventional primitive unit-cell (continuous lines) used for deriving the Brillouin zone for C-centred lattices; dashed and continuous lines have the same meaning as in Fig. 5.

Table 2. Brillouin-zone sampling limits for different symmetry groups

If the lattice is non-primitive, limits are referred to a non-primitive reciprocal cell.

Laue group	Primitive lattices	Non-primitive lattices
$\bar{1}$	$a^* \pm$ $b^* \pm$ $c^* \pm$	
$2/m$	$a^* \pm$ $b^* +$ $c^* +$	
mmm	$a^* +$ $b^* +$ $c^* +$	<i>A</i> $a^* +$ $b^* +$ $2c^* \pm$
		<i>C</i> $2a^* \pm$ $b^* +$ $c^* +$
		<i>C</i> $2a^* +$ $b^* +$ $c^* +$
		or $a^* +$ $2b^* +$ $c^* +$
		<i>I</i> as <i>C</i>
		<i>F</i> $a^* +$ $2b^* +$ $2c^* +$, or similar
		If <i>R</i> -centred refer to rhombohedral axes and
		$a^* \pm$ $b^* \pm$ $c^* \pm$
		($a^* \geq b^*$, $c^* \geq b^*$ etc. as for $m\bar{3}$)
$\bar{3}$ (hexagonal axes)	$a^* +$ $b^* -$ $c^* +$	If <i>R</i> -centred refer to rhombohedral axes and
$\bar{3}m$ (hexagonal axes) space groups as $P\bar{3}1m$	$a^* +$ $b^* +$ $c^* +$	$a^* \pm$ $b^* \pm$ $c^* \pm$
$\bar{3}m$ (hexagonal axes) space groups as $P\bar{3}1m$	$a^* +$ $b^* -$ $c^* +$	($a^* \geq b^*$, $c^* \geq b^*$, $a^* \leq c^*$ etc. as for $m\bar{3}m$).
$4/m$ and $6/m$	$a^* +$ $b^* +$ $c^* +$	
$4/mmm$ and $6/mmm$	$a^* +$ $b^* +$ $c^* +$	
$m\bar{3}$	$a^* \geq b^*$ (if $a^* = b^*$ weight = $\frac{1}{2}$)	If <i>I</i> -centred as for <i>P</i> with $2c^*$ instead of c^*
	$a^* +$ $b^* +$ $c^* +$	If non-primitive as for mmm
	$a^* \geq b^*$, $c^* \geq b^*$	
	(if $a^* = b^*$ or $b^* = c^*$ weight = $\frac{1}{2}$,	
	if $a^* = b^* = c^*$ weight = $\frac{1}{3}$)	
$m\bar{3}m$	$a^* +$ $b^* +$ $c^* +$	If non-primitive as for $4/mmm$
	$a^* \geq b^*$, $c^* \geq b^*$, $a^* \leq c^*$	
	(if $a^* = b^*$ or $a^* = c^*$ weight = $\frac{1}{2}$,	
	if $a^* = b^* = c^*$ weight = $\frac{1}{3}$)	

as shown in Table 4 of Schomaker & Trueblood (1968) can be derived: a short and simple way to demonstrate this is given in Appendix II.

In other words, when the molecule is in a crystallographic symmetrical (special) position, our procedure refers to two symmetry groups. The former includes all the symmetry operations of the crystal and is used for finding the asymmetric unit of the Brillouin zone; the latter includes only 'intermolecular' symmetry operations and is used for building up the dynamical matrices.

If intramolecular symmetry is present, at the end of our calculations the tensors \mathbf{T} , \mathbf{L} and \mathbf{S} , as obtained directly from summation along the 'asymmetric' part of the Brillouin zone are transformed according to (13) and added up.

An example showing this procedure is given for adamantane (Table 3): our computer program is fully automated for this purpose, and the results do not require considerations specific to each particular case.

APPENDIX I

'Asymmetric unit' of the Brillouin zone

Let us consider an 'original' molecule E and another molecule E_k , related to E through the k th operation of symmetry:

$$\mathbf{x}' = \mathbf{M}_k \mathbf{x} + \mathbf{t}_k \quad (7)$$

where \mathbf{M}_k is the rotation matrix and \mathbf{t}_k the translation vector relative to this k th operation. The elements of the dynamical matrix \mathbf{M} are essentially of the form

$$\sum \Phi_{ij}(k, k') \exp [iq\Delta\mathbf{r}(k, k')] \quad (8)$$

where $\Phi_{ij}(k, k')$ is a component of a force constant tensor relative to interaction between molecules E_k and $E_{k'}$, and $\Delta\mathbf{r}$ is the vector distance between these molecules; the summation (8) is extended to all molecules related to each other by translation. The reference system for $\Phi_{ij}(k, k')$ consists of principal axes for each molecule E_k and $E_{k'}$.

Table 3. Procedure to evaluate $\mathbf{T}, \mathbf{L}, \mathbf{S}$ tensors for adamantane (low-temperature form; data from Nordman & Schmitkons, 1965)

Space group $P\bar{4}2_1c$; Point group $\bar{4}2m$; Laue group $4/mmm$
Symmetry operations (as 'equivalent positions'):

$$x, y, z; -x, -y, z; y, -x, -z; -y, x, -z; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z; \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z; \frac{1}{2}+y, \frac{1}{2}+x, \frac{1}{2}+z; \frac{1}{2}-y, \frac{1}{2}-x, \frac{1}{2}+z$$

Intermolecular operations (1st subgroup = m):

$$\begin{array}{l} x, y, z; \quad \text{used for building up dynamical} \\ \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z \quad \text{matrices (12} \times \text{12)} \end{array}$$

Intramolecular operations (2nd subgroup = $\bar{4}$):

$$x, y, z; -x, -y, z; -y, x, -z; y, -x, -z$$

Sampling of the Brillouin zone:

$$\begin{array}{l} x^*, y^*, z^* \quad \text{only positive} \\ x^* > y^* \quad \text{(if } x=y \text{ weight}=0.5) \end{array}$$

Evaluation of $\mathbf{T}, \mathbf{L}, \mathbf{S}$ tensors:

$$\begin{aligned} \mathbf{T} = \mathbf{T}_{1t} + \mathbf{T}'_{2t} + \mathbf{T}''_{3t} + \mathbf{T}'''_{4t} &= \mathbf{T}_1 + \mathbf{T}_2 + \mathbf{T}_3 + \mathbf{T}_4 = \mathbf{E}\mathbf{T}_1\mathbf{E} + \begin{bmatrix} -1 & & \\ & -1 & \\ & & +1 \end{bmatrix} \mathbf{T}_1 \begin{bmatrix} -1 & & \\ & -1 & \\ & & +1 \end{bmatrix} \\ &+ \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \mathbf{T}_1 \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} + \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \mathbf{T}_1 \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \\ &= \mathbf{T}_1 + \begin{bmatrix} T_{11} & T_{12} & -T_{13} \\ T_{21} & T_{22} & -T_{23} \\ -T_{31} & -T_{32} & T_{33} \end{bmatrix} + \begin{bmatrix} -T_{22} & -T_{21} & -T_{23} \\ -T_{12} & T_{11} & T_{13} \\ -T_{32} & T_{31} & T_{33} \end{bmatrix} + \begin{bmatrix} T_{22} & -T_{21} & T_{23} \\ -T_{12} & T_{11} & -T_{13} \\ T_{32} & -T_{31} & T_{33} \end{bmatrix} = \begin{bmatrix} T_{11}^* & 0 & 0 \\ 0 & T_{11}^* & 0 \\ 0 & 0 & T_{33}^* \end{bmatrix} \end{aligned}$$

where

$$\begin{array}{l} T_{11}^* = 2(T_{11} + T_{22}) \\ T_{33}^* = 4T_{33} \end{array}$$

Similarly:

$$\mathbf{L} = \begin{bmatrix} L_{11}^* & 0 & 0 \\ 0 & L_{22}^* & 0 \\ 0 & 0 & L_{33}^* \end{bmatrix}$$

$$\mathbf{S} = \mathbf{S}_1 + \begin{bmatrix} S_{11} & S_{12} & -S_{13} \\ S_{21} & S_{22} & -S_{23} \\ -S_{31} & -S_{32} & S_{33} \end{bmatrix} + \begin{bmatrix} -S_{22} & S_{21} & S_{23} \\ S_{12} & -S_{11} & -S_{13} \\ S_{32} & -S_{31} & -S_{33} \end{bmatrix} + \begin{bmatrix} -S_{22} & -S_{21} & -S_{23} \\ S_{12} & -S_{11} & S_{13} \\ -S_{32} & S_{31} & -S_{33} \end{bmatrix} = \begin{bmatrix} S_{11}^* & S_{12}^* & 0 \\ S_{12}^* & -S_{11}^* & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

where

$$\begin{array}{l} S_{11}^* = 2(S_{11} - S_{22}) \\ S_{12}^* = 2(S_{12} + S_{21}) \end{array}$$

The situation is accordingly the same as in Schomaker & Trueblood (1968): see Table 3 of that paper for molecules lying in positions of symmetry $\bar{4}$.

If such a reference system is used, around the molecule E_k , for reasons of symmetry, an array of force constants identical with molecule E is present. However, in building up the dynamical matrix, a certain force constant Φ_{ij} , identical for molecules E and E_k , multiplies a different exponential, since $\Delta\mathbf{r}' = \mathbf{M}_k\Delta\mathbf{r}$, where $\Delta\mathbf{r}'$ is the distance between E_k and its neighbour symmetrically related to $\Delta\mathbf{r}$.

In case $\mathbf{q}' = \mathbf{q}\mathbf{M}_k^{-1}$, the exponentials become equal for molecule E (with wave vector \mathbf{q}) and E_k (with wave vector \mathbf{q}'), and the situation for both molecules, with different wave vectors, becomes indeed identical; all this becomes clear if the 'building up' of the dynamical matrix as specified by Pawley (1972) is kept in mind. In particular, the contribution to \mathbf{B} tensors, as referred to the particular system of each molecule, is the same. Using a short notation, we may write:

$$B_{E_k, \mathbf{q}'} = B_{E, \mathbf{q}} \quad (\mathbf{q}' = \mathbf{q}\mathbf{M}_k^{-1}) \quad (9)$$

where, in the above notation, $B_{E_k, \mathbf{q}'}$ indicates the contribution to the \mathbf{B} tensor of a given atom of molecule E_k , for a certain value \mathbf{q}' of the wave vector.

Since the above relationship is valid for any value of \mathbf{q} , for $\mathbf{q}'' = \mathbf{q}\mathbf{M}_k$ it will be:

$$B_{E_k, \mathbf{q}''} = B_{E, \mathbf{q}'} \quad (\mathbf{q}'' = \mathbf{q}'\mathbf{M}_k^{-1}). \quad (10)$$

Now, since $\mathbf{q}''' = \mathbf{q}''\mathbf{M}_k^{-1} = \mathbf{q}\mathbf{M}_k\mathbf{M}_k^{-1} = \mathbf{q}$, we have:

$$B_{E_k, \mathbf{q}} = B_{E, \mathbf{q}''}, \quad (11)$$

i.e. the contribution to temperature factors of atoms belonging to the E molecule for $\mathbf{q}'' = \mathbf{q}\mathbf{M}_k$ is the same as for molecule E_k with wave vector \mathbf{q} . This limits sampling of the Brillouin zone to an 'asymmetric unit' consisting of points not related to each other by rotation matrices \mathbf{M}_k belonging to the crystal symmetry group. This is in line with the 'usual' symmetry properties of a reciprocal lattice.

APPENDIX II

Special position of a molecule

When a molecule is in a special position, it consists of two or more physically equivalent parts. If parts of the same molecule are related by the rotation matrix \mathbf{M}_k , each force constant will have at least one 'symmetrical' counterpart, which will be used in building up the dynamical matrix. These Φ_{ij} will multiply a different exponential, since $\Delta\mathbf{r}' = \mathbf{M}_k\Delta\mathbf{r}$, as in Appendix I. For $\mathbf{q}' = \mathbf{q}\mathbf{M}_k^{-1}$ the dynamical matrix should become identical with the dynamical matrix relative to \mathbf{q} , provided the reference system of the molecule is changed by taking a symmetrically related system (Fig. 7).

For instance, let us suppose the molecule to have two (crystallographic) symmetrical parts, related to each other by the symmetry operation \mathbf{M}_k . We have:

$$\mathbf{T} = \mathbf{T}_{1i} + \mathbf{T}_{2i}; \quad \mathbf{L} = \mathbf{L}_{1i} + \mathbf{L}_{2i}; \quad \mathbf{S} = \mathbf{S}_{1i} + \mathbf{S}_{2i} \quad (12)$$

where \mathbf{T}_{1i} is the contribution to the molecular tensor \mathbf{T} for a certain value of the wave vector \mathbf{q} ; \mathbf{T}_{2i} is the

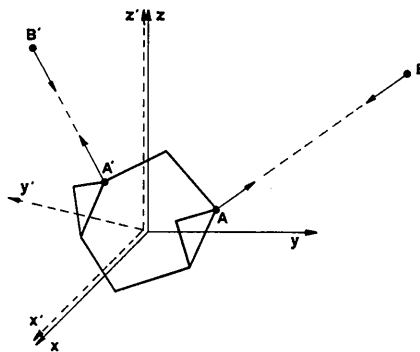


Fig. 7. If the molecule has a plane of symmetry, the interactions (here indicated by arrows) between symmetrically corresponding atoms A or A' and B or B' are the same, provided they are referred to symmetrically related reference systems.

contribution to \mathbf{T} for $\mathbf{q}' = \mathbf{q}\mathbf{M}_k^{-1}$, etc.; the summation (12) is extended to one-half of the Brillouin zone.

For the reasons given above (Appendix I) $\mathbf{T}_{1i}(\mathbf{q}) = \mathbf{T}_{2i}(\mathbf{q}\mathbf{M}_k^{-1})$, etc.; here \mathbf{T}_{1i} and \mathbf{T}_{2i} are related to different reference systems, *i.e.* to the ones pertinent to each half of the molecule. Referring now to the same system as for \mathbf{T}_{1i} , the tensors \mathbf{T}_{2i} , \mathbf{L}_{2i} , \mathbf{S}_{2i} are transformed as follows:

$$\begin{aligned} \mathbf{T}'_{2i} &= \mathbf{M}_k\mathbf{T}_{2i}\mathbf{M}_k^T = \mathbf{M}_k\mathbf{T}_{1i}\mathbf{M}_k^T \\ \mathbf{L}'_{2i} &= \mathbf{M}_k\mathbf{L}_{2i}\mathbf{M}_k^T = \mathbf{M}_k\mathbf{L}_{1i}\mathbf{M}_k^T \\ \mathbf{S}'_{2i} &= \mathbf{M}_k|\mathbf{M}_k|\mathbf{S}_{2i}\mathbf{M}_k^T = \mathbf{M}_k|\mathbf{M}_k|\mathbf{S}_{1i}\mathbf{M}_k^T. \end{aligned} \quad (13)$$

A practical application of this procedure is given in Table 3; in these expressions, the prime symbol indicates reference to the system of \mathbf{T}_{1i} , *i.e.* the one of the first part of the molecule.

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