Thermal Motion in Crystallography

Carlo Maria Gramaccioli

Dip.to Scienze d.Terra, Università, Via Botticelli 23, I-20133 Milano, Italy

Abstract

Thermal motion in crystallography is an important problem. Here two main aspects are especially evident for crystallographers: one is taking account of it for improving the fit of the model to experimental data obtained by X-ray or neutron diffraction; another aspect concerns interpretation of thermal motion, especially (for purely crystallographic work) in connection with correction of bond lengths.

[1]Thermal motion has long been considered in crystallographic structure determining operations; in routine structure-factor calculations, a temperature factor T_k as the Fourier transform of the probability distribution of the atom K in space mostly due to this effect was introduced already at the beginning of the development of X-ray crystallography . Here we have the usual expression:

$$f_k(\mathrm{hkl}) = f_{0k}(\mathrm{hkl}) T_k \exp\left[2\pi i(hx + ky + lz)\right], \tag{1}$$

where $f_k(\mathrm{hkl})$ is the contribution of the atom K to the structure factor $f(\mathrm{hkl})$, F_{0k} is the form factor and T_k is the so-called temperature factor. In the first applications, the distribution was assumed to be Gaussian and the same in all directions (isotropic); in this case T_k can be written as:

$$T_k(\mathrm{hkl}) = \exp\left(\frac{-B_k \sin^2\theta}{\lambda^2}\right), \tag{2}$$

where B_k is the isotropic atomic displacement parameter (or, something, more improperly, the isotropic “temperature factor” of the atom K). B_k can be shown to be related to the mean-square displacement of K, $\langle u_k^2\rangle$, as follows:

$$B_k = 8\pi^2\langle u_k^2\rangle \tag{3}$$

On improving the techniques of data collection, the approximation of isotropic atomic displacement proved at once to be inadequate. This inadequacy is often already evident in the final difference Fourier synthesis, where if isotropic displacement parameters are used, then strong positive and negative zones can be clearly seen around the various atoms, showing a preferential direction in the

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distribution. This phenomenon clearly indicates that if an appropriate model for thermal vibration is adopted, the overall agreement between the observed and calculated structure factors can be significantly improved. On referring to the *classic* R index, on the whole such index cannot be smaller than about 8–10% if only isotropic displacement parameters are used.

For this reason, already in the mid-fifties (Cruickshank, 1956abc) the displacement—whose distribution was still assumed to be Gaussian—was considered to be *anisotropic*, that is, different in the various directions, and anisotropic temperature factors were consequently introduced, as Fourier transforms of a tri-variate normal distribution:

$$T_k(\mathrm{hkl}) = \exp\big(2\pi^2 \mathbf{H}^2 \mathbf{U}_k \mathbf{H}\big), \tag{4}$$

where $\mathbf{H}$ is the reciprocal lattice vector referred to Cartesian axes, and $\mathbf{U}_k = \langle \mathbf{u}_k {\mathbf{u}_k}^T \rangle$ is the second-moment matrix of the probability distribution function, referred to the same Cartesian set. Instead of using a Cartesian reference, in most common crystallographic routine, the $\mathbf{U}$'s are sometimes multiplied by $2\pi^2$ and referred (as $\mathbf{B}$'s, or β's) to the crystal axes, so that instead of $\mathbf{H}$ a vector $\mathbf{h}$ is used, whose components are the Miller indices. We have, accordingly:

$$T_k(\mathrm{hkl}) = \exp\big(-\mathbf{h}^T \beta_k \mathbf{h}\big). \tag{5}$$

Since $\mathbf{H} = \mathbf{C}^T\mathbf{h}$, where $\mathbf{C}$ is the transformation matrix from a crystallographic reciprocal unit-cell reference to a Cartesian set of axes, it must be:

$$\beta_k = 2\pi^2 \mathbf{C}\mathbf{U}_k\mathbf{C}^T. \tag{6}$$

It will also be:

$$\mathbf{U}_k = \frac{1}{2}\pi^2 \mathbf{C}^{-1}\beta_k(\mathbf{C}^{-1})^T \tag{7}$$

or:

$$\mathbf{U}_k = \frac{1}{2}\pi^2 \mathbf{O}\beta_k\mathbf{O}^T, \tag{8}$$

where $\mathbf{O}(=\mathbf{C}^{-1})$ is the transformation matrix from a unit-cell basis to a Cartesian reference system.

In common practice, however, it has been observed that it is better to refer to an axial system of unit lengths; then, since referring to a Cartesian set implies the definition of an orthogonalization matrix, which is not uniquely established, the indices are referred instead to an axial frame coinciding in direction with the *reciprocal* crystal axes, but with unit lengths of 1, and the direct reference system for the $\mathbf{U}$'s becomes the reciprocal of this reciprocal axial frame. Therefore, whereas for crystals with orthogonal axes the reference is Cartesian, for crystals with non-orthogonal axes, the reference is *not Cartesian*; in any case, this choice implies that the transformation matrix $\mathbf{C}$ is always diagonal, with $C_{ii} = {a_i}^*$, that is, the corresponding reciprocal unit-cell parameter.

All these transformations are typical of second-rank tensors, and the anisotropic *atomic displacement parameters* or *ADP*'s ($\mathbf{U}$'s, $\mathbf{B}$'s, or β's) so defined are second-rank symmetric tensors. The surfaces corresponding to the set of equations:

$$\mathbf{x}^T \mathbf{U}_k{}^{-1} \mathbf{x} = \text{constant} \tag{9}$$

or similar are ellipsoids (or should be such !) and they are generally used to represent these tensors. In case the matrix **U** is not positive-definite, as sometimes it may result from a refinement of a crystal structure, the surface is not an ellipsoid, but there is something *wrong*, either concerning the data used, or the procedure used in refining (unappropriate weights, etc.), or also the interpretation (nature of the atom, which is heavier than it was supposed). A critical examination of these surfaces, as they can be easily drawn for instance by ORTEP (Johnson, 1965, 1980) often provides one of the easiest checks of the *quality* of a crystal.

Besides the conventions specified above, there area number of additional ways for defining anisotropic displacement parameters (for instance, where the off-diagonal terms are multiplied by 2, etc.), and unfortunately no unique formulation has been universally accepted so far, although the last definition of **U**'s here given seems to be the most widely accepted at present, and has been officially recommended by the IUCr Commission on crystallographic Nomenclature in a recent article (Trueblood *et al., 1996*. For this reason, in all crystallographic works, the temperature factor expression [such as, for instance, (4) or (5)] should be always indicated clearly. Accordingly, the corresponding expression for the most widely accepted **U**'s is the following:

$$T_k(\text{hkl}) = T_k(\mathbf{h}) = \exp\big[-2\pi^2\big(U_{11}h^2{a^*}^2 + \cdots + 2U_{23}klb^*c^*\big)\big]. \tag{10}$$

The use of anisotropic temperature factors of this kinds has greatly improved the agreement between observed and calculated structure factors (the so-called R index can routinely reach values around 3% or even less if accurate measurements and corrections for effects such as absorption, etc. have been carried out); however, the *number* of parameters to be determined in crystal structure refinment becomes considerable. In fact, whereas for isotropic temperature factors we have an additional parameter for each atom, with respect to the atomic coordinates, for anisotropic temperature factors we have *six* additional parameters, corresponding to the components of the symmetric second-rank tensors $\mathbf{U}_k$ or β_k. Therefore, anisotropic temperature factors involve a number of parameters which is twice the number of atomic coordinates.

In more recent times, also possible deviation from the normal distribution has been accounted form leading to additional terms in the Edgeworth expansion (Johnson, 1969, 1970 a,b), and corresponding to the introduction of further tensors of rank higher than two. Using this formulation, for the temperature factors we have expressions of the kind:

$$T_k(\mathbf{h}) = T'_k(\mathbf{h}) \exp\big(-2\pi i \beta_k h_i h_j h_m + \cdots\big), \tag{11}$$

where $T'_k(h)$ is a temperature factor expression corresponding to a second-rank tensor [such as, for instance, (4), (5), or (10)]; for the following terms (as usually for tensor notation) the so-called *dummy-suffix notation* is adopted, which implies summation over all the possible values (here 1,2,3, corresponding to the crystallographic indices $h, k, \mathrm{or} l$) when the suffix occurs twice in the same term.

It is easy to see that if such an expression is adopted, then the number of thermal motion parameters to be determined becomes indeed formidable. For instance, the third-rank tensors will involve 10 additional parameters per atom (with a total of 19), the fourth-rank tensors imply a total of 34, etc.

For this reason, the use of higher-rank tensors (3 or more) should be restricted only to the cases where an extensive number of highly accurate data are available, and—on the other hand—there is positive evidence for an unusually large amplitude of motion, generally connected with anharmonic behaviour, or when it is necessary to obtain very accurate results, as for instance in electron-density studies.

In other cases, caution is recommended, because otherwise the use of an extensive number of thermal parameters might prove to be substantially an expedient to increase the number of refinable variables, with a consequent lowering of the R index without involving however too much physical significance; this point of view is still widely considered, even for usual anisotropic parameters, in spite of extensive evidence for their physical meaning, at least for those determined by crystal structure refinement of good quality.

Already in the late fifties, the importance of knowing thermal parameters with some degrees of accuracy was pointed out, in connection with the problem of correcting this correction is necessary when the bond lengths obtained from crystal-structure refinement are to be compared with theoretical estimates, even at very low temperature (see below). For instance, errors around 0.01 $\overset{\circ}{A}$ or 0.003 $\overset{\circ}{A}$ are usually encountered for room-temperature study of molecular crystals or minerals (included synthetic inorganic compounds), respectively, and these errors (especially in the first case) substantially exceed the standard deviation in the bond lengths.

Unfortunately, the general correction for thermal motion of a bond lenght implies knowing besides the $\mathbf{U}$'s, also the correlation tensors $\mathbf{U}_{ik}$'s=$\langle \mathbf{u}_i \mathbf{u}_k^T \rangle$, which cannot be obtained from Bragg diffraction measurements. We have, in fact (Johnson 1970ab, 1980; Scheringer, 1972):

$$d = d' + \frac{\left[\mathrm{tr}(\mathbf{Z}) - \underset{.}{;}^{T} \mathbf{Z} \frac{\overset{,}{.}}{d'^{2}} \right]}{2d'}, \tag{12}$$

where d and d' are the corrected and the uncorrected distance, respectively, $\mathbf{d}'$ is the vector corresponding to the distance d' and $\mathbf{Z}$ is a matrix defined as:

$$\mathbf{Z} = \mathbf{U}_i + U_k - U_{ik} - U_{ki}. \tag{13}$$

The need of the correlation tensors U_{ik} and U_{ki} can be envisaged as a requirement of knowing the relative phase in crystal motion: there is, in fact, a phase problem not only concerning the structure factors, but also in thermal motion. In fact, it is easy to see that the average distance between the atoms does not depend on the distribution only, but also on the phase of their motion.

For a molecule behaving as a rigid body, a model allowing this correction to be made using crystal structure parameters only was proposed by Cruickshank (1956ab) and a more complete one by Schomaker and Trueblood (1968). These models express the thermal motion of the whole molecule in terms of three tensors, **T**, **L**, and **S**, which correspond to translation, rotation and translational-rotational coupling, respectively. We have:

$$\mathbf{U}_k = \mathbf{T} + \mathbf{A}_k \mathbf{L} \mathbf{A}_k^T + A_k \mathbf{S} + \mathbf{S}_k^T \mathbf{A}_k^T, \tag{14}$$

where

$$\mathbf{A}_k = \begin{bmatrix} 0 & r_{3k} & r_{2k} \\ -r_{3k} & 0 & r_{1k} \\ -r_{2k} & -r_{1k} & 0 \end{bmatrix} \tag{15}$$

and r_{1k}, r_{2k}, and r_{3k} are the components of the vector distance $\mathbf{r}_k$ from the mean position of the atom k from an arbitrary reference point (usually, the center of mass of the molecule), **T** is a translational displacement vector of the whole molecule, **L** is a tensor representing the rotation of the molecule as a whole, and **S** is another tensor accounting for the translational-rotational coupling.

The values of the components of these tensors (apart from an indeterminacy concerning the trace of **S**) can be obtained froma least squares fit to the individual atomic parameters; the tensor **L** is used together with the molecular geometry for correcting the bond lengths.

whenever indeterminacies are given(as for instance when all the atoms lie on a conic section, etc) the use of regression on principal components has been recommended(Johnson, 1970ab). however, some caution should be used in applying such a criterion, since if the undeterminacy concerns some elements of the rotational tensor **L**, then the corrections of bond lengths become physically meaningless (for examples of such an inconvenience, see Filippini et al., 1974a).

Extension of these models to partly rigid molecules has been carried out by several authors [dunitz and white (1973), Johnson (1970a), Trueblood (1978), Schomaker & Trueblood (1984), trueblood & Dunitz (1983), Hummel, Rasell & Burgi (1990), and he & Craven(1993)]; however, the interpretation of intramolecular motion,especially if the molecule is complex,might result in partly undefined tensors, and the above-suggested caution becomes even more necessary.Another delicate point is the number of the tensors necessary for a "segmented-rigid" molecule even of moderate complexity, due to the coupling between the various rotations of the different parts and also with the molecular translation:an example of the complexity of the problem has been given by Filippini & Gramaccioli (1986).

Since the correction for thermal libration essentially depends on rotational tensors,once these tensors are known (such for instance L in the rigid body) the problem can be solved quite easily. For instance, according to Cruickshank (1961) in a rigid body each atom, as it is found at the end of the refinement, should be shifted outwards the center as follows:

$$\Delta \mathbf{r}_k = \frac{1}{2}\big[\,\mathrm{tr}(\mathbf{L})\mathbf{r}_k - \mathbf{L}\mathbf{r}_k\big], \tag{16}$$

where $\Delta\mathbf{r}_k$ is the shift and $\mathbf{r}_k$ is the vector distance from the center of the molecule.

For the structures which can be hardly considered as rigid bodies, as for most inorganic compounds, a well-known method proposed by Busing & Levy (1964) can be used. Starting from crystal structure data only, this methods provides at least the interval where the corrected bond length must lie, and it gives a precise answer in two cases:

1. for a riding motion, that is, when a lighter atom is bound to a heavier one, and participates to its motion, besides having its proper motion, as a rider on a horse;

2. for non-correlated motion. For instance, ion the former case, we have:

$$d_{ik} = d'_{ik} + \frac{\big(\langle W_k^2\rangle - \langle W_i^2\rangle\big)}{2d'_{ik}}. \tag{17}$$

Here d_{ik} is the corrected bond length, d'_{ik} is the uncorrected one, and $\langle W^2\rangle$, the mean-square displacement perpendicular to the bond for the atom i and k, erspectively, is given by : $\langle W^2\rangle = \langle r^2\rangle - \langle z^2\rangle$, where $\langle r^2\rangle$ is the mean-square displacement in general and $\langle z^2\rangle$ is that along the bond. It will be (see also (19)):

$$\langle r^2\rangle = \mathrm{Tr}(\mathbf{U}), \qquad \text{and} \qquad \langle z^2\rangle = \mathbf{d}'^T\mathbf{Z}\frac{\mathbf{d}'}{d'^2}. \tag{18}$$

For non-correlated motion, a formula differing from (17) for having a plus sign instead of a minus sign is used.

The use of these methods for bond-length correction has greatly enhanced the importance of thermal parameters in crystallography; at the same time, the excellent fit of individual ADP's to a rigid-body scheme for molecules which can be expected to behave as rigid bodies (and often the ORTEP drawings themselves!) have provided for the first time substantial evidence for the physical validity of these thermal parameters, as deduced from crystallographic work.

Some years later, Hirshfeld (1976) noticed that for well-refined crystal structures, owing to the difficulty of stretching a chemical bond along its direction (compared with the much easier bending, or with the still easier alteration of non-bonded distances) the mean-square displacement of chemically bonded atoms along the bonds should be essentially the same. Since the mean-square displacement $\langle z_k^2\rangle$ of the atom k in the direction of the bond with the atom i is given by:

$$\langle {z_k}^2\rangle = \mathbf{d}'^T\mathbf{U}\frac{\mathbf{d}'}{d'^2}, \tag{19}$$

where $\mathbf{d}$ is the distance vector between these atoms, it will be:

$$d^2\big(\langle {z_k}^2\rangle - \langle {z_i}^2\rangle\big) = \mathbf{d}^T\big(\mathbf{U}_k - \mathbf{U}_i\big)\mathbf{d}, \tag{20}$$

where the U's here are those of expression (4).

This principle (called the rigid-bond test) has been shown to hold in the greatest majority of cases, and the only exceptions so far known have been found to correspond to a particularly interesting co-existence of different bonding schemes (Ammeter *et al.*,1979; Bürgi, 1984; Chandrasenkhar & Bürgi, 1984; Stebler *et al.*, 1986; Stebler & Bürgi, 1987). Together with the rigid-body fit (and with similar fits to partly rigid molecules) this principle has also strongly supported the physical significance of crystallographic thermal parameters, to the point that distinguished crystallographers (see, for instance, Dunitz, Schomaker & Trueblood, 1998) emphasize the need of publishing also three parameters, which are unfortunately omitted from most publications, in view of scarcity of space.

In the same years, substantial efforts for deriving ADP's theoretically on a routine basis even for moderately complex crystal structures have been made. For this purpose, lattice-dynamical calculations following the Born-von Karman model were considered; the vibrational frequencies of the crystal are also obtained during this process, providing a good link to spectroscopic data; through the vibrational partition function, temperature-dependent values of thermodynamic functions can be also evaluated.

For such calculations, dynamical matrices $\mathbf{D}(\mathbf{q})$ for each value of the so-called wave vector $\mathbf{q}$ should be built and diagonalized; the elements of such matrices correspond to *the second derivatives of the potential energy* with respect to the shifts of the different atoms in the primitive unit-cell along the reference axes; such derivatives are multiplied by $\exp 2\pi i(\mathbf{q}^T\mathbf{r})$, where $\mathbf{r}$ is the vector distance between the atoms involved in each interaction. The eigenvalues of $\mathbf{D}(\mathbf{q})$ correspond to the frequencies $\nu_i(\mathbf{q})$ of the various normal modes of vibration in the crystal.

According to theory of harmonic motion (see for instance Willis & Proyr, 1075), from the average energy $E_i(\mathbf{q})$ of the ith vibrational mode:

$$E_i(\mathbf{q}) = h\nu_i(\mathbf{q}) \left(\frac{1}{2} \left\{ \exp\left[\frac{h\nu(\mathbf{q})}{kT} \right] - 1 \right\}^{-1} \right) \tag{21}$$

the contribution of the mode to the tensor $\mathbf{U}_k$ will be the following:

$$\mathbf{U}_k = (Nm_k)^{-1} \sum_{i,q} E_i(\mathbf{q})[2\pi\nu_i(\mathbf{q})]^{-2} \mathbf{e}(k \mid i\mathbf{q}) \mathbf{e}^*(k \mid i\mathbf{q})^T, \tag{22}$$

where $\mathbf{e}(k \mid i\mathbf{q})$ is the mass-adjusted polarization vector of the atom in the unit cell, which is a part of the corresponding eigenvector of the dynamical matrix $\mathbf{D}(\mathbf{q})$. Omitting a number of interesting considerations, here some interest should be pointed out on the nature of $\mathbf{D}(\mathbf{q})$, and its relationship with similar matrices occurring in crystal-structure modelling. For a more detailed account of the situation, see for instance Gramaccioli & Pilati (1992).

For lattice-dynamical calculations on molecular crystals, the rigid-body model was first selected as a good approximation for limiting the size of dynamical matrices (Pawley, 1967; Gramaccioli *et al.*, 1973, 1974ab, 1975ab, 1976ab, 1977, 1980, 1981ab, 1984; Criado *et al.*, 1984, 1988; Dianez *et al.*, 1986; Criado, 1989, 1990). In a second stage, also semi-rigid molecules were considered, taking into account additional degrees of freedom, corresponding to the lowest vibration frequencies of the isolated molecule. (Bonadeo & Burgos, 1982; Gramaccioli *et al.*, 1982; Gramaccioli & Filippini, 1983, 1985ab; Filippini & Gramaccioli, 1984ab, 1986); for minerals and inorganic compounds in general, a complete lattice-dynamical derivation considering all the degrees of freedom has been performed (Pilati *et al.*, 1990abc, 1993ab, 1994, 1995, 1996ab, 1997).

All these calculations showed essential agreement with the experimental crystallographic data, thereby confirming their validity (see also Brock, Dunitz & Hirshfeld, 1991); for molecular crystals there is also in general a good agreement between the tensors **T**, **L**, and **S** derived from a Schomaker-Trueblood fit and the corresponding lattice-dynamical results; on such grounds, there is a definite possibility for future routine application of these lattice-dynamical calculations to the problem of correcting bond lengths in any case.

A further interesting application of theoretical (lattice-dynamical) calculations of ADP's has been the quantitative evaluation of the mean-square displacement at temperature close to the absolute zero (0 K); here, owing to well-known quantum effects, the mean-square displacement is not zero, contrarily to a widespread belief. For instance, for benzene, the zero-point mean-square displacement of the carbon atoms is about one quarter of the corresponding one at 123 K and about 90% of the value at 15 K (Filippini & Gramaccioli, 1989; Jeffrey *et al.*, 1987; David & Ibberson, 1989; Jeffrey, 1992). For minerals and other similar inorganic structures, the zero-point displacement may exceed one half (up to 70%) the corresponding value at room temperature (Pilati *et al.*, 1990abc, 1993ab, 1994, 1995, 196ab, 1997). Therefore, at the right of such results, the idea of referring to still atoms and molecules needs critical revision and reformulation.

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