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# Dynamics of molecules in crystals from multi-temperature anisotropic displacement parameters. I. Theory

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A new model for analysing the temperature evolution of anisotropic displacement parameters (ADP's) is presented. It allows for a separation of temperature-dependent from temperature-independent contributions to ADP's and provides a fairly detailed description of the temperature-dependent large-amplitude molecular motions in crystals in terms of correlated atomic displacements and associated effective vibrational frequencies. It can detect disorder in the crystal structure, systematic error in the diffraction data and the effects of non-spherical electron-density distributions on ADP's in X-ray data. The analysis requires diffraction data measured at multiple temperatures.

## 1. Introduction

There are two intrinsic and complementary aspects to atomic motion: energy and displacement. Correspondingly, there are two main techniques to investigate motion: spectroscopy and diffraction. In this work, the focus is on atomic displacements in crystals. Their mean square expectation values are determined routinely in crystal structure analysis and illustrated in structure drawings with the well known anisotropic equiprobability ellipsoids (see Fig. 4 for an example). Mean square displacements or anisotropic displacement parameters (ADP's) reflect the time- and space-averaged distribution of an atom around its mean position in the crystal lattice but say nothing about the relative phases of atomic displacements. In crystallographic practice, ADP's are usually found to be composite quantities with contributions from motion (libration, translation, internal vibrations), from disorder (static or dynamic) and from systematic error (in the data or in the refinement model). This raises the questions of what information about motion can be extracted from ADP's and how the various contributions can be separated. At first sight, answering these questions may appear as an almost hopeless task!

Among the many models developed to describe the motion of atoms in crystals, lattice dynamics is the most complete and rigorous but also the most complicated one (Born & von Kármán, 1912; Born & Huang, 1954). It is based on the theory of displacement waves travelling in a finite unbounded crystal. The computation of ADP's from displacement waves is straightforward; the reverse problem is ill determined; in practice, the computational complexities rapidly increase with the number of atoms in the unit cell (Pawley, 1986).

A simpler much more local model is available for crystals built from molecules that may be considered as rigid bodies (Cruickshank, 1956*a*,*b*; Schomaker & Trueblood, 1968). This model has been widely used to extract mean square amplitudes of translational and librational oscillations from experimentally determined ADP's at a single temperature. An extension of this approach is the segmented-rigid-body model in which specific intramolecular motions are also taken into account (Johnson, 1970*a*; Dunitz & White, 1973; Trueblood, 1978; Trueblood & Dunitz, 1983; Schomaker & Trueblood, 1998; He & Craven, 1985, 1993; Bürgi, 1989). The information available from ADP's is insufficient to fully characterize these models (Schomaker & Trueblood, 1968); in addition, the degree of indeterminacy increases rapidly with the complexity of the model, *i.e.* with the number of intramolecular motions considered (Bürgi, 1989).

An alternative method to analyse ADP's is presented here. It combines a physical model of the temperature evolution of ADP's, which is very similar to that used in lattice dynamics, with a description of molecular motion in the mean crystal field. It allows one to partition ADP's measured as a function of temperature into temperature-dependent and temperature-independent contributions. It is simpler than the lattice dynamic treatment but more powerful than the (segmented-)rigid-body model because it does not suffer from the indeterminacies associated with the latter. Here the general aspects of the method are described. Its application to ADP's obtained from neutron and X-ray diffraction experiments will be illustrated in subsequent papers (Capelli *et al.*, 2000; Bürgi *et al.*, 2000).

## 2. Lattice dynamic considerations

A detailed description of lattice dynamical theory is found in Born & Huang (1954) and Maradudin *et al.* (1971); here we adopt the formulation and notation used by Willis & Pryor (1975), which may be more familiar to crystallographers; it is very similar to that used by Brüesch (1982). In order to establish a basis for discussion, it is useful to recall some basic results of the theory. According to Born & von Kármán (1912), Newton's equations of motion for the atoms in a crystal lead to characteristic equations that relate the frequencies $\omega_j^2(\mathbf{q})$ of travelling waves with corresponding vectors of correlated mass-weighted atomic displacements $\mathbf{e}(j\mathbf{q})$:

$$\omega_j^2(\mathbf{q})\mathbf{e}(j\mathbf{q}) = \mathbf{D}(\mathbf{q})\mathbf{e}(j\mathbf{q}). \qquad (1)$$

For a unit cell with $n$ atoms, the frequencies $\omega_j(\mathbf{q})$ and the detailed shape of the normalized displacement vectors $\mathbf{e}(j\mathbf{q})$, each with $3n$ components, depend on the direction and length of the momentum propagation vector $\mathbf{q}$ of the travelling wave. In a crystal with $N$ unit cells, there are $N\mathbf{q}$ vectors distributed regularly in momentum space, *i.e.* throughout the Brillouin zone. The mass-adjusted dynamic matrix $\mathbf{D}(\mathbf{q})$ depends in a complicated way on the potential functions associated with the interaction of all atoms in the crystal and on the atomic masses (Pawley, 1986).

In the context of crystal spectroscopy, it is the solution of the eigenvalue equation (1) as a function of $\mathbf{q}$ that matters. It gives rise to $3n$ *dispersion relations* $\omega_j(\mathbf{q})$ of which 3 are called *acoustic* branches and the remaining $3n - 3$ are called *optic* branches. Dispersion relations describe the behaviour of individual phonons along a specific $\mathbf{q}$ direction. For a three-dimensional crystal, the number of unit cells and thus the number of frequencies can be large; this makes numerical calculations tedious and time consuming.

It is often sufficient to consider only the *frequency distribution function* or *density of states* $g(\omega)$ of the phonons. In Fig. 1, the dispersion relations and the density of states for a monodimensional crystal built of homonuclear diatomic molecules are shown. In this simple case, there are only two phonon branches: one acoustic, representing mostly translational displacements of the diatomic molecule, and one optic, representing mostly molecular deformation. Note the singularities in the density-of-states function, especially the closely spaced ones of the optical branch. If there were no dispersion, the branches could be represented with horizontal lines and the corresponding density of states with $\delta$ functions (Fig. 2), *i.e.* all phonons in a branch would be degenerate and the problem could equally well be described in terms of molecules moving independently of each other. The condition of no dispersion is the basis of the *Einstein model*, the first quantum model for calculating the specific heat of a solid (Einstein, 1907). Einstein's original assumption was that each atom in a crystal moves independently with frequency $\omega_E$ (= Einstein frequency).

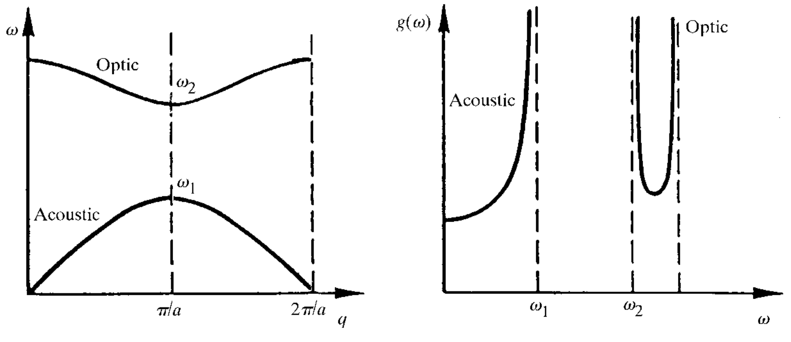

**Figure 1**
Dispersion curves and density of states for the acoustic and optic phonons of a monodimensional crystal built from homonuclear diatomic molecules.

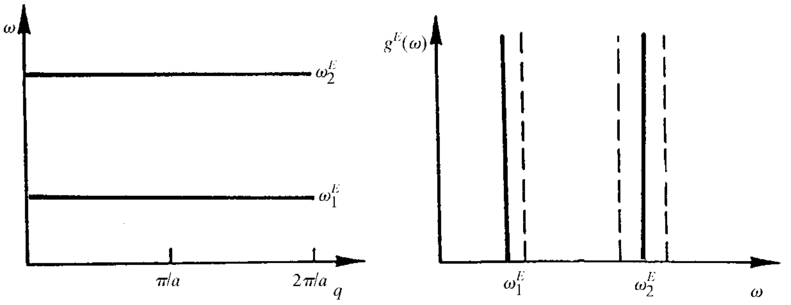

**Figure 2**
Dispersion curves and density of states for the Einstein model of a monodimensional crystal built from homonuclear diatomic molecules.

The idea of independent atomic oscillators does not account for the fact that in molecular crystals atoms belonging to the same molecule are more strongly tied to each other than atoms in different molecules. In a modified Einstein approach, each molecule, instead of each atom, is considered as a collection of independent oscillators moving in a potential given by the average crystal environment [*molecular mean field model* (Bürgi, 1995)]. Of course, the condition of no dispersion is never fulfilled exactly; however, if dispersion is small throughout a substantial volume of the Brillouin zone, an Einstein approach remains a good approximation and allows substitution of the lattice dynamical description with a molecular one. Equation (1) simplifies to

$$\omega_j^2\mathbf{e}(j) = \mathbf{D}\mathbf{e}(j). \qquad (1a)$$

In the notation of molecular spectroscopy, (1*a*) is written as

$$\omega_j^2\mathbf{e}(j) = \mathbf{m}^{-1/2}\mathbf{f}\mathbf{m}^{-1/2}\mathbf{e}(j), \qquad (1b)$$

where $\mathbf{f}$ is a force-constant matrix and $\mathbf{m}^{-1/2}$ performs the mass adjustment. This relation will be discussed in more detail below.

## 3. Mean square displacement matrix

In the context of a diffraction experiment, the emphasis is on atomic displacements. The total instantaneous displacement $\mathbf{u}(k_l, t)$ of atom $k$ in the unit cell $l$ at time $t$ is given by the superposition of the displacements coming from all $3nN$ modes of vibration (phonons):

$$\mathbf{u}(k_l, t) = (Nm_k)^{-1/2} \sum_{j\mathbf{q}} [\overline{E_j}(\mathbf{q})/\omega_j^2(\mathbf{q})]^{1/2} \mathbf{e}(k|j\mathbf{q}) \times \exp\{i[\mathbf{q}\cdot\mathbf{r}(k_l) - \omega_j(\mathbf{q})t]\}, \qquad (2)$$

where $\mathbf{e}(k|j\mathbf{q})$ represents the $k$th component of a normalized complex eigenvector $\mathbf{e}(j\mathbf{q})$ (known also as *polarization vector* of atom $k$ in normal mode $j$ along the wavevector $\mathbf{q}$). The quantity $[\overline{E_j}(\mathbf{q})/\omega_j^2(\mathbf{q})]^{1/2}$ is the absolute amplitude of mode $(j\mathbf{q})$. The average energy $\overline{E_j}(\mathbf{q})$ is given by the quantum-mechanical expectation value:

$$\begin{aligned}\overline{E_j}(\mathbf{q}) &= \hbar\omega_j(\mathbf{q})\left\{\tfrac{1}{2} + \left(\exp[\hbar\omega_j(\mathbf{q})/k_BT] - 1\right)^{-1}\right\} \\ &= [\hbar\omega_j(\mathbf{q})/2]\coth[\hbar\omega_j(\mathbf{q})/2k_BT]. \qquad (3)\end{aligned}$$

The second term in the curly brackets is the expectation value of a quantized lattice vibration $j\mathbf{q}$ for a system in equilibrium at temperature $T$, *i.e.* the number of *phonons* in the state $\mathbf{q}$ ($k_B$ is the Boltzmann constant and $\hbar$ is the Planck constant divided by $2\pi$).

Diffraction intensities depend on the *mean square displacement amplitudes* (MSDA) rather than on the instantaneous displacements (Willis & Pryor, 1975):

$$\mathbf{U}(k) = \langle \mathbf{u}(k_l, t)\mathbf{u}^*(k_l, t)^T \rangle. \qquad (4)$$

For each atom $k$, the MSDA's form a symmetric $3 \times 3$ matrix that can be expressed in terms of (2) and (3):

$$\mathbf{U}(k) = (Nm_k)^{-1} \sum_{j\mathbf{q}} [\overline{E_j}(\mathbf{q})/\omega_j^2(\mathbf{q})] \mathbf{e}(k|j\mathbf{q})[\mathbf{e}^*(k|j\mathbf{q})]^T. \qquad (5)$$

A more general expression, which also includes the *inter*-atomic or correlation mean square amplitudes between different atoms $k$ and $k'$, is

$$\mathbf{U}(k, k') = (Nm_k^{1/2}m_{k'}^{1/2})^{-1} \sum_{j\mathbf{q}} [\overline{E_j}(\mathbf{q})/\omega_j^2(\mathbf{q})] \mathbf{e}(k|j\mathbf{q})[\mathbf{e}^*(k'|j\mathbf{q})]^T. \qquad (6)$$

The atomic and interatomic mean square displacement amplitudes taken together define the molecular mean square amplitude matrix $\boldsymbol{\Sigma}^x$. The atomic displacement parameters $\mathbf{U}(k) = \mathbf{U}(k, k)$ are its diagonal $3 \times 3$ blocks and can be determined from single-crystal diffraction experiments, at least in principle. The interatomic or correlation mean square amplitudes $\mathbf{U}(k, k')$ are its off-diagonal $3 \times 3$ blocks. They are not accessible through single-crystal diffraction experiments, not even in principle. All elements of $\boldsymbol{\Sigma}^x$ may be calculated from potential functions and compared with ADP's from diffraction (Gramaccioli *et al.*, 1982; Gramaccioli & Filippini, 1983).

With the no-dispersion approximation, *i.e.* the modified Einstein model, the sum over all normal modes $j\mathbf{q}$ in the crystal reduces to a sum over the normal modes of a molecule:

$$\mathbf{U}(k, k') = (m_k^{1/2}m_{k'}^{1/2})^{-1} \sum_j (\hbar/2\overline{\omega}_j)\coth(\hbar\overline{\omega}_j/2k_BT) \times \overline{\mathbf{e}}(k|j)[\overline{\mathbf{e}}^*(k'|j)]^T, \qquad (7)$$

where $\overline{\omega}_j$ stands for an effective frequency representative of an average over the Brillouin zone and $\overline{\mathbf{e}}(k|j)$ for the corresponding displacement vector. In the notation of (1*b*), the atomic mean square displacement matrix is

$$\boldsymbol{\Sigma}^x = \mathbf{m}^{-1/2}\,\overline{\mathbf{e}}\,\boldsymbol{\delta}\,\overline{\mathbf{e}}^T\mathbf{m}^{-1/2}, \qquad (8)$$

where $\mathbf{m}$ is a diagonal matrix of atomic masses, $\overline{\mathbf{e}}$ is the matrix of all eigenvectors and $\boldsymbol{\delta}$ is a diagonal matrix whose elements are the mean square amplitudes of the normal modes; they depend on vibrational frequencies and temperature according to $\delta_j = (\hbar/2\overline{\omega}_j)\coth(\hbar\overline{\omega}_j/2k_BT)$ [see equation (3)]. We return to $\boldsymbol{\Sigma}^x$ below, after a short digression on coordinate systems in the next section.

## 4. Coordinates

ADP's are usually expressed in terms of positional displacements in the directions of the unit-cell axes (Trueblood *et al.*, 1996). A description in terms of molecular displacement coordinates like translation, rotation, bond stretching, angle bending, torsion *etc.* would be much closer to the chemist's way of thinking about interatomic and intermolecular interactions. The necessary transformations between positional and molecular displacement coordinates are well known. The transformation of atomic displacement coordinates $\mathbf{u}$ into molecular displacement coordinates $\mathbf{S}$ is

$$\mathbf{S} = \mathbf{B}\mathbf{u} \qquad (9)$$

and has been discussed in detail by Wilson *et al.* (1955) and by Cyvin (1968). For the reverse transformation

$$\mathbf{u} = \mathbf{A}\mathbf{S}, \qquad (10)$$

see Higgs (1955) and Cyvin (1968). It follows that $\mathbf{A}\cdot\mathbf{B} = \mathbf{I}$, where $\mathbf{I}$ is an identity matrix.

The matrices $\mathbf{A}$ and $\mathbf{B}$ also relate the corresponding mean square displacement matrices (He & Craven, 1985):

$$\boldsymbol{\Sigma}^S = \mathbf{B}\boldsymbol{\Sigma}^x\mathbf{B}^T \qquad (11)$$

$$\boldsymbol{\Sigma}^x = \mathbf{A}\boldsymbol{\Sigma}^S\mathbf{A}^T, \qquad (12)$$

where $\boldsymbol{\Sigma}^x$ is the mean square displacement matrix in atomic displacement coordinates and $\boldsymbol{\Sigma}^S$ is the matrix of mean square displacements along molecular coordinates. In principle, $\mathbf{A}$ and $\mathbf{B}$ are square matrices because the number of independent degrees of freedom for a molecule is independent of the coordinate system. In practice, some degrees of freedom can be much more important than others. For example, in the case of rigid-body motion, only the 'external' modes of vibration, *i.e.* the three translations of the centre of mass and the three librational oscillations of the molecule about its centre of mass, are important. Thus, the number of degrees of freedom is only six and the $\boldsymbol{\Sigma}^S$ matrix has only six rows and columns, whereas $\boldsymbol{\Sigma}^x$ has dimensions $3n \times 3n$. In this case, $\mathbf{A}$ and $\mathbf{B}$ are rectangular matrices. This has the consequence that $\mathbf{A}$ cannot be calculated from $\mathbf{A}\cdot\mathbf{B} = \mathbf{I}$. However, the methods to calculate $\mathbf{A}$ and $\mathbf{B}$ given in the references above are still valid.

## 5. The model

Cyvin (1968) expresses the dependence of the molecular mean square amplitude matrix $\boldsymbol{\Sigma}^S$ on molecular displacement coordinates $\mathbf{S}$ as follows:

$$\boldsymbol{\Sigma}^S = \langle \mathbf{S}\mathbf{S}^T \rangle = \mathbf{L}\boldsymbol{\delta}\mathbf{L}^T, \tag{13}$$

where $\mathbf{L}$ is the transformation matrix from normal to molecular displacements. Unlike $\mathbf{e}$ [equation (8)], $\mathbf{L}$ is not mass weighted; this implies $\mathbf{L}\mathbf{L}^T = \mathbf{G}$, where $\mathbf{G}$ is Wilson's matrix of reduced masses (Wilson *et al.*, 1955). The transformed equation (13) is

$$\boldsymbol{\Sigma}^S \mathbf{G}^{-1} \mathbf{L} = \mathbf{L}\boldsymbol{\delta}. \tag{14}$$

This relationship is remarkable because it is closely related to Wilson's relationship between force constants $\mathbf{F}$ and vibrational frequencies (Wilson *et al.*, 1955):

$$\mathbf{G}\mathbf{F}\mathbf{L} = \mathbf{L}\boldsymbol{\lambda}. \tag{15}$$

Equations (14) and (15) are both eigenvalue problems. Their eigenvectors $\mathbf{L}$ are the same and their eigenvalues, $\boldsymbol{\lambda}$ and $\boldsymbol{\delta}$, respectively, are both functions of the frequencies. In the classical limit, normal mode analysis from mean square amplitudes [equation (14)] is the inverse of normal mode analysis from vibrational frequencies [equation (15)] because for a classical oscillator $\lambda_j = \overline{\omega}_j^2$ and $\delta_j = k_B T/\overline{\omega}_j^2$. The inverse relation between $\mathbf{G}\mathbf{F}$ and $\boldsymbol{\Sigma}^S \mathbf{G}^{-1}$ implies that $\boldsymbol{\Sigma}^S = k_B T \mathbf{F}^{-1}$. In the mean field approximation used here, $\mathbf{F}$ is an effective force-constant matrix related to the average of the $\mathbf{q}$-dependent dynamical matrices [for the analogous formulation of the relation between $\boldsymbol{\Sigma}^x$ and the dynamical matrix $\mathbf{D}(\mathbf{q})$, see Scheringer (1972)].

More symmetrical and more practical forms of (14) and (15) are obtained as follows: $\mathbf{G}$ and $\mathbf{G}^{-1}$ are decomposed into the lower triangular matrices $\mathbf{g}$ and $\mathbf{g}^{-1}$ (Aldous & Mills, 1962):

$$\mathbf{G} = \mathbf{g}\mathbf{g}^T, \quad \mathbf{G}^{-1} = (\mathbf{g}^{-1})^T \mathbf{g}^{-1}. \tag{16}$$

The matrix $\mathbf{L}$ is redefined in terms of $\mathbf{g}$ and the orthonormal eigenvector matrix $\mathbf{V}$ (Förtsch, 1997):

$$\mathbf{g}\mathbf{V} = \mathbf{L}. \tag{17}$$

[$\mathbf{g}\mathbf{V}$ is analogous to $\mathbf{m}^{-1/2}\mathbf{e}$ in equation (8).] This gives

$$\boldsymbol{\Sigma}^S = \mathbf{g}\mathbf{V}\boldsymbol{\delta}\mathbf{V}^T\mathbf{g}^T \tag{18}$$

$$\mathbf{F} = \mathbf{g}^{-1}\mathbf{V}\boldsymbol{\lambda}\mathbf{V}^T(\mathbf{g}^{-1})^T. \tag{19}$$

The atomic mean square displacements in $\boldsymbol{\Sigma}^x$ thus depend on the molecular and normal mode mean square displacements through a series of straight-forward transformations:

$$\boldsymbol{\Sigma}^x = \mathbf{A}\boldsymbol{\Sigma}^S\mathbf{A}^T = \mathbf{A}\mathbf{g}\mathbf{V}\boldsymbol{\delta}\mathbf{V}^T\mathbf{g}^T\mathbf{A}^T. \tag{20}$$

In the rest of this paper, it is shown how a maximum of information on the motion of molecules in their mean crystal field, *i.e.* on $\mathbf{V}$, $\boldsymbol{\delta}$ and $\overline{\omega}_j$, can be extracted from the limited information available on $\boldsymbol{\Sigma}^x$, *i.e.* from the ADP's.

## 6. The indeterminacy problem

Wilson's and Cyvin's formulations of the normal-mode problem are not only formally similar but they also suffer from a similar practical problem. In the spectroscopic approach, force constants are extracted from observed vibrational frequencies. The number of observable frequencies is proportional to the number of atoms, insufficient to determine the independent elements of the force-constant matrix $\mathbf{F}$ whose number is proportional to the square of the number of atoms.

In the mean-square-amplitude approach, vibrational frequencies and collective atomic displacement vectors must be extracted from the experimentally observable ADP's, the $3 \times 3$ diagonal blocks of $\boldsymbol{\Sigma}^x$. This means that for an $n$-atomic molecule $6n$ observations are available, not enough to determine the $3n(3n-1)$ independent components of the displacement vectors $\mathbf{V}$ and the corresponding $3n$ frequencies. This indeterminacy is sometimes referred to as the second phase problem in crystal structure determination: only ADP's $\mathbf{U}(k,k)$ that measure the extent of atomic displacements are determinable from crystal structure analysis; correlation ADP's $\mathbf{U}(k,k')$ that fix their relative phases are indeterminable.

In both cases, the indeterminacy problem can be overcome or at least alleviated in several ways: (*a*) by increasing the

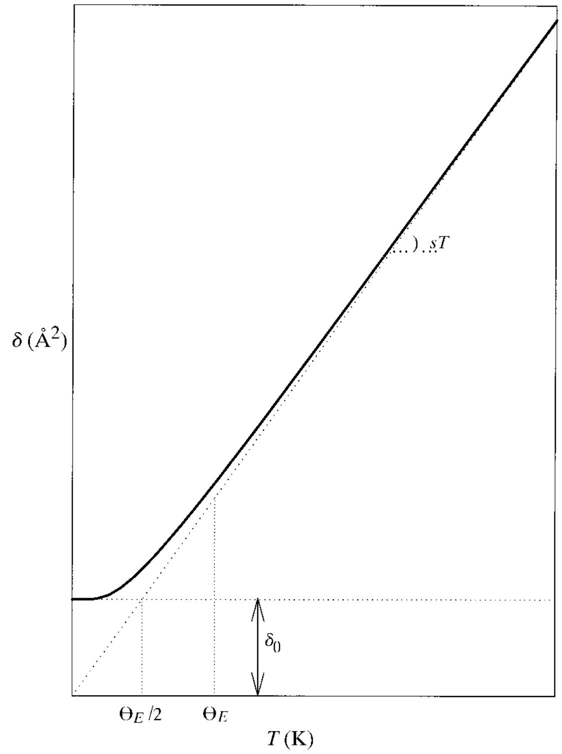

**Figure 3**
Mean square displacement of a single harmonic oscillator as a function of temperature. The zero-point amplitude $\delta_0$ and the linear dependence at high temperature are shown by dotted lines. Note that the intersection of the quantum and classical regimes occur at half the Einstein temperature ($\Theta_E/2$), and that above the Einstein temperature the mean square amplitude closely follows the classical linear description.

amount of independent information; (*b*) by restricting the model of motion to its most essential parts, *i.e.* by reducing the number of model parameters; (*c*) by making full use of symmetry. These possibilities will be addressed in the following three sections.

## 7. The temperature dependence of MSDA's

In vibrational spectroscopy, additional information is obtained from isotopically substituted molecules, for which the changes in the potential-energy function and thus in **F** are negligibly small. The isotopic shifts of the frequencies of vibration allow one to determine off-diagonal elements of the force-constant matrix (Herzberg, 1950).

In mean-square-amplitude studies, there is a simpler way to obtain additional information, namely by measuring the temperature dependence of ADP's, which is determined entirely by the temperature dependence of $\boldsymbol{\delta}$ [see (20)]. Fig. 3 shows the temperature dependence of an element $\delta_j$ of $\boldsymbol{\delta}$:

$$\delta_j = (\hbar/2\overline{\omega}_j)\coth(\hbar\overline{\omega}_j/2k_BT). \qquad (21)$$

At low temperature, $\delta_j$ simplifies to the temperature-independent quantity:

$$\delta_j = \hbar/2\overline{\omega}_j = \delta_0. \qquad (22)$$

The limiting behaviour at high temperature coincides with that of a classical harmonic oscillator:

$$\delta_j = k_BT/\overline{\omega}_j^2. \qquad (23)$$

The classical mean square amplitude extrapolates to zero at $T = 0$ K, whereas the quantum-mechanical one assumes a finite value as $T$ approaches 0 K. This difference in limiting behaviour allows the retrieval of the off-diagonal elements of the $\boldsymbol{\Sigma}^x$ matrix from the temperature dependence of its diagonal $3 \times 3$ blocks. This is easily illustrated with the help of the simple example mentioned earlier: a homonuclear diatomic molecule in a centrosymmetric crystal environment. The motions along the axis of the diatomic include molecular translation and bond-length deformation. The motions perpendicular to the axis are translation and libration. In both cases, the mean square amplitudes can arise from one or the other or from some combination of these motions (Fig. 4).

Assuming that the total mean square amplitude of atoms $k$ and $k'$ in a given direction has contributions from the two independent motions $A$ and $B$, with frequency $\omega_A$ and $\omega_B$, respectively, one can write:

$$\begin{aligned}\langle u^2(k,T)\rangle &= \langle u^2(k',T)\rangle \\ &= \langle u^2(k,T)\rangle_A + \langle u^2(k,T)\rangle_B \\ &= \hbar/(2\mu_A\overline{\omega}_A)\coth(\hbar\overline{\omega}_A/2k_BT) \\ &\quad + \hbar/(2\mu_B\overline{\omega}_B)\coth(\hbar\overline{\omega}_B/2k_BT), \end{aligned} \qquad (24)$$

where $\mu_A$ and $\mu_B$ are the reduced masses of motion $A$ and $B$, respectively. (For the translational motion of the diatomic molecule $\mu = 2m_k$, while for the bond stretching $\mu = m_k/2$, and for the librational motion $\mu = r^2m_k/2$, with $r$ the internuclear separation.)

In the high- and low-temperature regimes, the expressions for the total mean square amplitude become

$$\langle u^2(k,0)\rangle = \hbar(\mu_A^{-1}\overline{\omega}_A^{-1} + \mu_B^{-1}\overline{\omega}_B^{-1})/2 \qquad (25)$$

$$\langle u^2(k,T\to\infty)\rangle = k_BT(\mu_A^{-1}\overline{\omega}_A^{-2} + \mu_B^{-1}\overline{\omega}_B^{-2}). \qquad (26)$$

From measurements at a single temperature, it is impossible to distinguish between the two contributions $\langle u^2(k,T)\rangle_A$ and $\langle u^2(k,T)\rangle_B$. However, if $\langle u^2(k,T)\rangle$ can be measured in both the zero-point and classical regimes, $\overline{\omega}_A$ and $\overline{\omega}_B$ and thus $\langle u^2(k,T)\rangle_A$ and $\langle u^2(k,T)\rangle_B$ can be determined because (25) and (26) are linearly independent in $\overline{\omega}_A$ and $\overline{\omega}_B$. As a consequence, it becomes possible to calculate the interatomic or correlation mean square amplitudes. For the homonuclear diatomic, the result is simply

$$\begin{aligned}\langle u(k,T)u(k',T)\rangle &= \langle u(k,T)u(k',T)\rangle_A + \langle u(k,T)u(k',T)\rangle_B \\ &= \langle u^2(k,T)\rangle_A - \langle u^2(k,T)\rangle_B. \end{aligned} \qquad (27)$$

Thus, the off-diagonal elements of $\boldsymbol{\Sigma}^x$, which are not available from Bragg diffraction experiments, have been determined indirectly from the temperature dependence of the diagonal elements. This solves the phase problem.

The information on the two types of motion can be obtained even if ADP's have been measured in a temperature range that is too small for one of the normal modes (say mode $B$) to be significantly excited:

$$\langle u^2(k,0)\rangle = \hbar(\mu_A^{-1}\overline{\omega}_A^{-1})/2 + \hbar(\mu_B^{-1}\overline{\omega}_B^{-1})/2 \qquad (28)$$

$$\langle u^2(k,T\to\infty)\rangle = k_BT(\mu_A^{-1}\overline{\omega}_A^{-2}) + \hbar(\mu_B^{-1}\overline{\omega}_B^{-1})/2. \qquad (29)$$

Mode $B$ gives a constant contribution to the mean square amplitude which is independent of temperature. Its contribution can be calculated from the high-temperature behaviour alone by linear extrapolation of $\langle u^2(k,T)\rangle$ to 0 K.

What has been shown for the homonuclear diatomic is true in general. For a treatment of more complex molecules, the more complicated equation (20) is necessary but the basic idea for solving the phase problem of atomic motions remains the same: for any molecule, irrespective of the number of atoms, ADP's determined in the high- and low-temperature limits provide information on the correlation of atomic motion.

## 8. Low-frequency and high-frequency approximations

The indeterminacy problem can be further mitigated by reducing the model of motion to the minimum necessary to account for the main features in the experimental data. In this section, we discuss the simplifications that follow if low and high frequencies are treated separately.

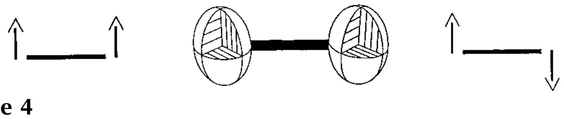

**Figure 4**
Equiprobability ellipsoids of a homonuclear diatomic. The ADP components perpendicular to the molecular axis may be due to rigid-body translation (motion *A*, left) or rigid-body libration (motion *B*, right) or some combination of both.

The eigenvalues $\delta_j$ or $\lambda_j$ are split into two groups: one containing the low-frequency motions (subscript $L$) and the other containing the high-frequency motions (subscript $H$). Similarly, the internal coordinates $\mathbf{S}$ can be partitioned into soft ($s$), intermediate ($i$) and hard ($h$) coordinates associated with small, intermediate and large force constants, respectively. From this, a corresponding subdivision of the eigenvector matrix $\mathbf{V}$ follows [equation (30)]. In principle, the eigenvectors of all normal modes may contain contributions from all molecular coordinates. However, hard coordinates are usually involved in high-frequency modes ($\mathbf{V}_{hH}$) while soft coordinates contribute primarily to low-frequency motions ($\mathbf{V}_{sL}$). A clear line between hard and soft coordinates cannot usually be drawn; there are always a few intermediate coordinates that mix into both high- and low-frequency normal modes ($\mathbf{V}_{iL}$ and $\mathbf{V}_{iH}$). It is unlikely that hard deformation coordinates contribute substantially to the eigenvector of a low-frequency normal mode and *vice versa*. It is therefore a good approximation to set the corresponding elements of $\mathbf{V}$ to zero.

$$\boldsymbol{\delta} = \left[\begin{array}{c|c} \boldsymbol{\delta}_L & 0 \\ \hline 0 & \boldsymbol{\delta}_H \end{array}\right], \quad \mathbf{V} = \left[\begin{array}{c|c} \mathbf{V}_{sL} & 0 \\ \hline \mathbf{V}_{iL} & \mathbf{V}_{iH} \\ \hline 0 & \mathbf{V}_{hH} \end{array}\right]. \tag{30}$$

The subdivisions of $\boldsymbol{\delta}$ and $\mathbf{V}$ require corresponding subdivisions of $\mathbf{g}$ and $\mathbf{A}$:

$$\mathbf{g} = \left[\begin{array}{c|c|c} \mathbf{g}_{ss} & 0 & 0 \\ \hline \mathbf{g}_{si} & \mathbf{g}_{ii} & 0 \\ \hline \mathbf{g}_{sh} & \mathbf{g}_{ih} & \mathbf{g}_{hh} \end{array}\right], \quad \mathbf{A} = \left[\begin{array}{c|c|c} \mathbf{A}_s & \mathbf{A}_i & \mathbf{A}_h \end{array}\right]. \tag{31}$$

With this approximation, the $\boldsymbol{\Sigma}^S$ matrix [equation (18)] separates into

$$\begin{aligned} \boldsymbol{\Sigma}^S = \mathbf{g}\left\{\left[\begin{array}{cc|c} \mathbf{V}_{sL}\boldsymbol{\delta}_L\mathbf{V}_{sL}^T & \mathbf{V}_{sL}\boldsymbol{\delta}_L\mathbf{V}_{iL}^T & 0 \\ \mathbf{V}_{iL}\boldsymbol{\delta}_L\mathbf{V}_{sL}^T & \mathbf{V}_{iL}\boldsymbol{\delta}_L\mathbf{V}_{iL}^T & 0 \\ \hline 0 & 0 & 0 \end{array}\right]\right. \\ \left. + \left[\begin{array}{c|cc} 0 & 0 & 0 \\ \hline 0 & \mathbf{V}_{iH}\boldsymbol{\delta}_H\mathbf{V}_{iH}^T & \mathbf{V}_{iH}\boldsymbol{\delta}_H\mathbf{V}_{hH}^T \\ 0 & \mathbf{V}_{hH}\boldsymbol{\delta}_H\mathbf{V}_{iH}^T & \mathbf{V}_{hH}\boldsymbol{\delta}_H\mathbf{V}_{hH}^T \end{array}\right]\right\}\mathbf{g}^T \\ = \boldsymbol{\Sigma}_L^S + \boldsymbol{\Sigma}_H^S. \end{aligned} \tag{32}$$

The elements of $\boldsymbol{\Sigma}_L^S$ derive from the strongly temperature dependent elements of $\boldsymbol{\delta}_L$ associated with the low-frequency motions. The elements of $\boldsymbol{\Sigma}_H^S$ can be viewed as a constant contribution to $\boldsymbol{\Sigma}^S$ (and thus to $\boldsymbol{\Sigma}^x$) because of the negligible temperature dependence of the high-frequency contribution from $\boldsymbol{\delta}_H$.

The partitioning of $\boldsymbol{\Sigma}^S$ into two terms, one temperature dependent and another temperature independent, shows that not all $3n$ normal modes need to be considered explicitly in the calculation. The low-frequency normal modes, which usually are far less in number than the high-frequency ones, are sufficient (the $\boldsymbol{\delta}_L$ block is much smaller than the $\boldsymbol{\delta}_H$ block). Furthermore, not all $3n$ molecular deformation coordinates will contribute significantly to the low-frequency modes and therefore the $\mathbf{V}$ matrix can be drastically reduced to the two blocks labelled $\mathbf{V}_{sL}$ and $\mathbf{V}_{iL}$ in (32). $\mathbf{V}$ then becomes a rectangular matrix of size $p \times q$, where $q$ is the number of low-frequency normal modes and $p$ is the number of coordinates needed to represent these normal modes; in general, $q < p < 3n$. Note the difference between the low-frequency approximation presented here and the high-frequency approximation usually given in text books on normal-mode analysis (see for example Wilson *et al.*, 1955). In the latter, it is usually assumed that the number of high-frequency normal modes equals the number of hard coordinates ($q = p$). Thus, the spectroscopic problem simplifies to:

$$\mathbf{F}_H = \mathbf{g}_{hh}^{-1}\mathbf{V}_{hH}\boldsymbol{\lambda}_H\mathbf{V}_{hH}^T(\mathbf{g}_{hh}^{-1})^T. \tag{33}$$

The analogous low-frequency approximation of $\boldsymbol{\Sigma}^S$ would be

$$\boldsymbol{\Sigma}_L^S = \mathbf{g}_{ss}\mathbf{V}_{sL}\boldsymbol{\delta}_L(T)\mathbf{V}_{sL}^T\mathbf{g}_{ss}^T \tag{34}$$

but was found to be too restrictive in practice, because both $\mathbf{V}_{iL}$ and $\boldsymbol{\Sigma}_H^S$ can sometimes contribute significantly to the ADP's as will be illustrated in the accompanying paper (Capelli *et al.*, 2000).

After combination of (20) and (32), the mean square displacement matrix becomes

$$\begin{aligned} \boldsymbol{\Sigma}^x(T) &= \mathbf{A}\boldsymbol{\Sigma}^S(T)\mathbf{A}^T \\ &= \begin{bmatrix} \mathbf{A}_s & \mathbf{A}_i \end{bmatrix}\begin{bmatrix} \mathbf{g}_{ss} & 0 \\ \mathbf{g}_{si} & \mathbf{g}_{ii} \end{bmatrix}\begin{bmatrix} \mathbf{V}_{sL} \\ \mathbf{V}_{iL} \end{bmatrix}\boldsymbol{\delta}_L(T)\begin{bmatrix} \mathbf{V}_{sL}^T & \mathbf{V}_{iL}^T \end{bmatrix} \\ &\quad \times \begin{bmatrix} \mathbf{g}_{ss}^T & \mathbf{g}_{si}^T \\ 0 & \mathbf{g}_{ii}^T \end{bmatrix}\begin{bmatrix} \mathbf{A}_s^T \\ \mathbf{A}_i^T \end{bmatrix} + \begin{bmatrix} \mathbf{A}_i & \mathbf{A}_h \end{bmatrix}\boldsymbol{\Sigma}_H^S\begin{bmatrix} \mathbf{A}_i^T \\ \mathbf{A}_h^T \end{bmatrix}. \end{aligned} \tag{35}$$

The second term, which depends on the high-frequency normal modes, does not show a significant variation with temperature and may be considered as a small correction $\boldsymbol{\varepsilon}^x$; only its $3 \times 3$ diagonal blocks can be obtained from and are relevant for $\boldsymbol{\Sigma}^x(T)$. The $3 \times 3$ block $\boldsymbol{\varepsilon}^x(k)$ for atom $k$ is usually expressed in a local molecule-based coordinate system and transformed to the working coordinate system of $\boldsymbol{\Sigma}^x$ according to $\boldsymbol{\varepsilon}^x = \mathbf{T}\boldsymbol{\varepsilon}\mathbf{T}^T$. This allows the same matrix $\boldsymbol{\varepsilon}$ to be used for chemically and crystallographically equivalent atoms and to keep the number of independent components of $\boldsymbol{\varepsilon}^x$ minimal.

The final form of the mean square amplitude matrix, the one used for numerical calculations, is thus

$$\boldsymbol{\Sigma}^x = \mathbf{A}\mathbf{g}\mathbf{V}\boldsymbol{\delta}\mathbf{V}^T\mathbf{g}^T\mathbf{A}^T + \boldsymbol{\varepsilon}^x. \tag{36}$$

In the interest of a compact notation, the indices $s$, $i$ and $L$ are dropped from here on. Note that (36) and all following expressions are not as general as (20), although they look very similar.

## 9. Symmetry

A third aspect of the indeterminacy problem is *symmetry*. It reduces the number of parameters to be determined from the experimental observation by requiring specific elements of $\mathbf{V}$ and $\boldsymbol{\delta}$ to be equal or zero (Cotton, 1990).

Displacement coordinates $\mathbf{S}$ and normal coordinates can be classified according to the irreducible representation of the point group of the molecule. This implies that each normal mode is built from only a limited number of displacement coordinates, namely those with a common irreducible representation. As a consequence, the off-diagonal blocks between different irreducible representations are zero in the eigenvector matrix $\mathbf{V}$, in the symmetrized force constant matrix $\mathbf{F}$ and in the mean square displacement matrix $\boldsymbol{\Sigma}^S$ (Bishop, 1973).

Eigenvalues of symmetric systems can show degeneracy. Any linear combination of eigenvectors associated with degenerate eigenvalues is a valid eigenvector of the problem (Atkins, 1983). The direct consequence is that the eigenvectors associated with degenerate degrees of freedom are not uniquely determined. To prevent singularities in the numerical least-squares calculations described in the next section, appropriate constraints must be applied to the eigenvector matrix. Accidental degeneracy, which is difficult to predict, must be handled on a case-to-case basis.

## 10. Parameter determination from observed ADP's

The unknowns in (36) are the elements of the eigenvector matrix $\mathbf{V}$, the normal frequencies $\overline{\omega}_j$ and the diagonal $3 \times 3$ blocks of $\boldsymbol{\varepsilon}^x$. They are determined *via* a non-linear least-squares procedure. First, (36) is expanded in a Taylor series to first order in the parameters

$$\boldsymbol{\delta} = \boldsymbol{\delta}(\overline{\omega}^0) + \boldsymbol{\delta}'(\overline{\omega}^0 0)\Delta\boldsymbol{\omega} \tag{37}$$

$$\mathbf{V} = \mathbf{V}^0 + \Delta\mathbf{V} \tag{38}$$

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}^0 + \Delta\boldsymbol{\varepsilon}, \tag{39}$$

where $\boldsymbol{\omega}^0$, $\mathbf{V}^0$ and $\boldsymbol{\varepsilon}^0$ are the parameter values for a suitable starting model. The orthonormality condition on the eigenvectors is expanded in a similar way:

$$\mathbf{0} = (\mathbf{V}^0)^T\Delta\mathbf{V} + (\Delta\mathbf{V})^T\mathbf{V}^0, \tag{40}$$

where $\mathbf{0}$ is the zero matrix.

Equation (36) then becomes

$$\begin{aligned}\boldsymbol{\Sigma}^x &= \boldsymbol{\Sigma}^{x,0} + \Delta\boldsymbol{\Sigma}^x \\ &= \mathbf{A}\mathbf{g}\mathbf{V}^0\boldsymbol{\delta}(\overline{\omega}^0)(\mathbf{V}^0)^T\mathbf{g}^T\mathbf{A}^T + \mathbf{T}\epsilon^0\mathbf{T} \\ &\quad + \mathbf{A}\mathbf{g}[\Delta\mathbf{V}\boldsymbol{\delta}(\overline{\omega}^0)(\mathbf{V}^0)^T + \mathbf{V}^0\boldsymbol{\delta}(\overline{\omega}^0)(\Delta\mathbf{V})^T \\ &\quad + \mathbf{V}^0\boldsymbol{\delta}'(\overline{\omega}^0)\Delta\boldsymbol{\omega}(\mathbf{V}^0)^T]\mathbf{g}^T\mathbf{A}^T + \mathbf{T}\Delta\boldsymbol{\varepsilon}\mathbf{T}.\end{aligned} \tag{41}$$

The first two terms in the detailed expression on the right represent the mean square displacement matrix $\boldsymbol{\Sigma}^{x,0}$ of the starting model and the second two terms express the deviation $\Delta\boldsymbol{\Sigma}^x$ between the starting model and the observations in $\boldsymbol{\Sigma}^x_{\rm obs}$. An iterative least-squares program has been written (Förtsch, 1997) to minimize the weighted sum of the deviations $\sum_{ij} w_{ij}[(\boldsymbol{\Sigma}^x_{\rm obs})_{ij} - (\boldsymbol{\Sigma}^x)_{ij}]^2$ by optimizing the parameter shifts $\Delta\boldsymbol{\omega}$, $\Delta\mathbf{V}$ and $\Delta\boldsymbol{\varepsilon}$. The program, which is still under development, is available from the authors on request.

## 11. Discussion

The delocalized lattice dynamical model for describing vibrations in crystals and interpreting ADP's measured as a function of temperature has been reduced to a localized molecular one with the help of a mean field approximation. How good is this approximation? As indicated earlier, the answer depends on the shape of the dispersion surfaces; whenever phonon dispersion is small over a substantial part of the Brillouin zone, entire phonon branches may be replaced by local normal modes. This is more likely to be true for the high-frequency optic branches than for the low-frequency optic or acoustic ones. Dispersion of the latter is unavoidable, especially in the inner part of the Brillouin zone (this is why the Einstein approximation is usually applied only to optical branches).

The error involved in approximating dispersion curves with a single normal-mode frequency can be estimated by comparing the projected lattice dynamical density of states, $g_s(\omega)$, for coordinates $S_j$ and the projected mean field density of states $g_s^E(\overline{\omega})$ [for projections of the density of states in electronic band theory, see Hoffmann (1988)]. If the maxima of the former are concentrated around the discrete frequencies of the latter and if the dispersion in the neighbourhood of such maxima is limited, then the discrete mean field model is a good approximation of the lattice dynamical one (Figs. 1 and 2). Under these conditions, the average $\langle g_s(\omega)/\omega\rangle$ in the neighbourhood of a maximum of $g_s(\omega)$ is closely similar to the average $\langle g_s(\omega)/\omega^2\rangle^{1/2}$ and thus the respective contribution to the mean square amplitude $\langle S_j^2\rangle$ at low temperature $(\sim \hbar/2\overline{\omega})$ can be described by the same effective frequency as the corresponding contribution at high temperature $(\sim k_BT/\overline{\omega}^2)$.[1]

The interpretation of experimentally measured ADP's presented here is a natural extension of previous analyses. As early as 1956, Cruickshank proposed a method to calculate translational and rotational mean square amplitudes of a rigid molecule from ADP's (Cruickshank, 1956*a*,*b*). In 1968, Schomaker & Trueblood generalized Cruickshank's approach and their **TLS** analysis is now the method most frequently applied for studying ADP's (Schomaker & Trueblood, 1968). **TLS** analysis is a special case of relating positional to molecular mean square amplitude displacements; it uses a very limited molecular mean square amplitude matrix, which only includes the six external degrees of freedom, *i.e.* the mean square translation and libration tensors $\mathbf{L}$ and $\mathbf{T}$ and the screw coupling tensor $\mathbf{S}$.

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[1] To estimate the effects of averaging, the two values $\langle 1/\omega\rangle$ and $\langle 1/\omega^2\rangle^{1/2}$ have been calculated and compared for simple, but realistic, spherically symmetric dispersion curves, representative of both optic and acoustic branches. The two mean values typically differ by about 5% in the case of optical branches and up to 10% for acoustic branches, showing that the approximation leads to an error of about the same magnitude as the experimental error in the ADP's measured at low temperatures. Furthermore, for both optic and acoustic branches, $\langle 1/\omega\rangle$ and $\langle 1/\omega^2\rangle^{1/2}$ correspond to the $\omega$ value at $q \sim 0.7 - 0.8(\pi/2a)$, confirming the relevance of the outermost shells of the Brillouin zone in determining the magnitude of ADP's, also in the case of acoustic branches.

$$\boldsymbol{\Sigma}^x = \mathbf{A}\boldsymbol{\Sigma}^S\mathbf{A}^T = \mathbf{A}\begin{bmatrix} \mathbf{L} & \mathbf{S} \\ \mathbf{S}^T & \mathbf{T} \end{bmatrix}\mathbf{A}^T. \tag{42}$$

Rigid-body analysis has a significant shortcoming: the trace of **S** cannot be determined because it depends on correlation amplitudes $\mathbf{U}(k, k')$, which are not determinable by Bragg diffraction.

The rigid-body procedure has been extended in several ways to account for relative motions of rigid molecular segments (Johnson, 1970*a*; Dunitz & White, 1973; Trueblood, 1978; Trueblood & Dunitz, 1983; Schomaker & Trueblood, 1998; He & Craven, 1985, 1993; Bürgi, 1989). When an additional coordinate $\varphi$ is used to describe intramolecular motion, the expression for $\boldsymbol{\Sigma}^x$ becomes

$$\boldsymbol{\Sigma}^x = \mathbf{A}\boldsymbol{\Sigma}^S\mathbf{A}^T = \mathbf{A}\begin{bmatrix} \mathbf{L} & \mathbf{S} & \langle \mathbf{l}\varphi\rangle \\ \mathbf{S}^T & \mathbf{T} & \langle \mathbf{t}\varphi\rangle \\ \langle \mathbf{l}\varphi\rangle^T & \langle \mathbf{t}\varphi\rangle^T & \langle \varphi^2\rangle \end{bmatrix}\mathbf{A}^T, \tag{43}$$

where $\langle \varphi^2\rangle$ is the mean square amplitude of an internal motion, $\langle \mathbf{l}\varphi\rangle$ and $\langle \mathbf{t}\varphi\rangle$ are the coupling terms between internal motion and, respectively, libration and translation. In such models, there are additional indeterminacies; their number increases rapidly with the number of internal motions considered (Bürgi, 1989; Schomaker & Trueblood, 1998).

Our method of ADP analysis introduces three new features: temperature-dependent low-frequency normal modes $\boldsymbol{\delta}(\tau)$, the relation between normal mode and molecular displacements ($\mathbf{gV}$) and temperature-independent high-frequency contributions $\boldsymbol{\varepsilon}^x$ to the ADP's. From this, (43) becomes

$$\begin{aligned} \boldsymbol{\Sigma}^x(\tau) &= \mathbf{A}\begin{bmatrix} \mathbf{L}(\tau) & \mathbf{S}(\tau) & \langle \mathbf{l}\varphi(\tau)\rangle \\ \mathbf{S}^T(\tau) & \mathbf{T}(\tau) & \langle \mathbf{t}\varphi(\tau)\rangle \\ \langle \mathbf{l}\varphi(\tau)\rangle^T & \langle \mathbf{t}\varphi(\tau)\rangle^T & \langle \varphi^2(\tau)\rangle \end{bmatrix}\mathbf{A}^T + \boldsymbol{\varepsilon}^x \\ &= \mathbf{A}\mathbf{g}\mathbf{V}\boldsymbol{\delta}(\tau)\mathbf{V}^T\mathbf{g}^T\mathbf{A}^T + \boldsymbol{\varepsilon}^x \end{aligned} \tag{44}$$

(here the symbol $\tau$ represents the temperature to distinguish it from the translational tensor **T**). The explicit temperature dependence of $\boldsymbol{\delta}(\tau)$ and thus of $\boldsymbol{\Sigma}^x(\tau)$ is the key to overcoming the indeterminacy problems mentioned above because it allows one to express the ADP's in terms of the same displacement vectors $\mathbf{V}_j$ and frequencies $\overline{\omega}_j$ at all temperatures[2] and avoids a determination of the elements of **L**, **S**, **T** *etc.* at each temperature separately.

The relative contribution of the correction term $\boldsymbol{\varepsilon}^x$ to $\boldsymbol{\Sigma}^x(\tau)$ is usually small at high temperatures but may become important at very low temperatures. The term $\boldsymbol{\varepsilon}^x$ can also absorb temperature-independent contributions to $\boldsymbol{\Sigma}^x$ other than those due to high-frequency motions, *e.g.* disorder (static or dynamic) and systematic error (both in the diffraction data and in the model used to interpret these data). Sometimes, independent information is useful in interpreting the principal origin of the values of $\boldsymbol{\varepsilon}^x$. Mean square amplitudes due to internal motions can be evaluated from IR and Raman data, with the help of (18) and (19), and these values can be directly compared to $\boldsymbol{\varepsilon}^x$ derived from diffraction data. Empirically, we find that the refined values of $\boldsymbol{\varepsilon}$ are often in good agreement with the ones calculated from spectroscopic data (Capelli *et al.*, 2000), provided effects of disorder, anharmonicity or large systematic errors can be excluded or properly accounted for. In the case of disorder, the components of the $\boldsymbol{\varepsilon}$ tensors tend to be significantly bigger than the spectroscopic values (Capelli, 1999), while in the case of anharmonicity they are often smaller or even negative (Bürgi *et al.*, 2000).

The theory outlined above is based on the harmonic approximation of vibrational motions. At low temperature, this approximation may be satisfactory but with increasing temperature thermal expansion tends to reduce the crystal field. In an extension of the model presented here, anharmoncity has been taken into account summarily by a simple Grüneisen-type correction of the frequency of each normal mode:

$$\overline{\omega}_j = \overline{\omega}_j^0(1 - \gamma_j^G \chi T), \tag{45}$$

where $\gamma_j^G$ is known as the Grüneisen constant of frequency $\overline{\omega}_j$, $\chi$ is the thermal expansion coefficient and $T$ is the temperature. A more detailed discussion of this modification is given elsewhere (Bürgi *et al.*, 2000).

There are some difficulties in applying the model presented here to interpreting the temperature evolution of ADP's. The first is the choice of a suitable starting model of motion for the least-squares optimization [$\overline{\omega}^0$, $\mathbf{V}^0$, $\boldsymbol{\varepsilon}^0$, equation (41)]. As mentioned in §8, *Low-frequency and high-frequency approximations*, only a few low-frequency normal modes can usually be derived from the observed ADP's. Their number needs to be fixed and the internal coordinates, which are likely to contribute to these modes, must be selected. Often the rigid-body model with six normal modes composed of translational and librational displacement coordinates represents a good starting point. Such a minimal model, which should also include one $\boldsymbol{\varepsilon}$ tensor per element, can give useful information regarding the presence of disorder or of anharmonicity and can serve as a basis for elaborating a more complete model including internal degrees of freedom (*e.g.* torsion around single bonds, out-of-plane bending *etc.*). If the latter mix significantly with librations and translations, they contribute significantly to the ADP's. They may even dominate one or more low-frequency normal modes. The choice of coordinates depends somewhat on the intuition of the user and is not always unique. Note, however, that there are tests on the results: they must be physically meaningful, *i.e.* $\boldsymbol{\Sigma}^S$ and $\boldsymbol{\varepsilon}^x$ must be positive definite. In addition, the goodness of fit of any model has to conform to the usual statistical criteria.

The range of experimentally accessible temperatures can be a second factor limiting the analysis of ADP's. The phase problem can be solved reliably only when data sets in both the zero-point and classical regimes are available and, of course, when $n_{\rm obs} > n_{\rm par}$. If no ADP's from the quantum regime are

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[2] So far, only one exception to this conclusion has been found. Because the general expressions relating $\mathbf{U}(k)$ to the diagonal elements of **S** depend on differences $S_{ii} - S_{jj}$, the individual elements $S_{ii}$, $S_{jj}$ cannot be determined from ADP's at a single temperature but can be derived from the temperature evolution of the ADP's and thus of the differences $S_{ii} - S_{jj}$. However, for molecules with the cubic molecular symmetries $23(T)$ and $432(O)$, all diagonal elements of **S** are equal (see Table 4 in Schomaker & Trueblood, 1968), *i.e.* the difference $S_{ii} - S_{jj}$ is zero at all temperatures. It is therefore not possible to determine $S_{ii}$ and a unique eigenvector matrix **V**.

available, it may not be possible to identify the low-frequency modes uniquely; however, extrapolation to 0 K of the temperature-dependent contributions may still allow the determination of the temperature-independent $\boldsymbol{\varepsilon}$'s. It is difficult to quantify the optimal number of measurements and the respective measurement temperatures because these depend on the system under study (symmetry, number of independent observations) and on the model of motion (coordinates, frequencies of vibrations, total number of parameters); of course, the more the better. Ideally, experiments should be designed to optimize the analysis of specific models of motion (Hamilton, 1964).

The third problem is systematic error in the ADP's which may be due to limited resolution of the diffraction experiment, inappropriate structure-factor refinements, lack of corrections for absorption and extinction *etc*. In our experience, such errors tend to be absorbed into the translational degrees of freedom and in the $\boldsymbol{\varepsilon}$ tensors, giving rise to model-dependent frequencies with relatively large standard uncertainties in the first case and to negative or unreasonably large positive $\boldsymbol{\varepsilon}$ values in the latter. Systematic errors can also be introduced through the model of motion, *e.g.* by an inappropriate choice of displacement coordinates or of the number of normal modes or by inadequate corrections for anharmonicity.

ADP's from X-ray diffraction tend to be more difficult to interpret than those from neutron diffraction data unless they are the result of high-quality charge-density studies. This is because ADP's tend to absorb features of valence-electron density if spherical atomic form factors are used in standard structure refinements (Brock *et al.*, 1991; Pichon-Pesme *et al.*, 1995). This leads to unusual $\boldsymbol{\varepsilon}$ tensors, reflecting a combination of intramolecular motion and artefacts from a promolecule refinement.

Finally, one more word on the correlation of atomic motions. As mentioned earlier, single-crystal X-ray or neutron diffraction analysis provides mean square displacements from mean positions (ADP's) but not the correlation of atomic motion. Are there techniques that can measure correlation information directly? EXAFS spectroscopy (or gas-phase electron diffraction) measures distances between atoms and their mean square fluctuations. Distance fluctuations depend on the displacements of two atoms from their mean positions as well as on the correlation of these displacements (Johnson, 1970*b*). EXAFS measurements, preferably over a range of temperature, thus provide information that is complementary to ADP's from single-crystal diffraction and is easily introduced into the analysis of ADP's described here.

## 12. Conclusions

In this contribution, we have presented a method to analyse ADP's that goes a step beyond the conventional rigid-body or segmented-rigid-body approaches applicable at a single temperature (Schomaker & Trueblood, 1968; Johnson, 1970*a*; Dunitz & White, 1973; Trueblood, 1978; Trueblood & Dunitz, 1983; Schomaker & Trueblood, 1998; He & Craven, 1985, 1993). The method assumes a physically plausible model of the temperature evolution of ADP's in a mean crystal field and leads to a description of motion in terms of effective frequencies and correlated atomic displacements. It allows one to test the quality of the results of diffraction experiments, especially the consistency of ADP's measured at different temperatures and with different methods; it can reveal the presence of disorder, anharmonicity and systematic error in the diffraction data. In the best case, the model of motion obtained with this method adds the dimension of molecular dynamics to the usual results of single-crystal structure analyses.

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