

4.1. THERMAL DIFFUSE SCATTERING OF X-RAYS AND NEUTRONS

Raman (1941), but these objections were safely disposed of by Ledermann (1944).

4.1.2.1. Equations of motion

As a result of thermal fluctuations, the atoms vibrate about their equilibrium positions, so that the actual position of the κ th atom in the l th primitive cell is given by

$$\mathbf{R}(\kappa l) = \mathbf{r}(\kappa l) + \mathbf{u}(\kappa l)$$

with \mathbf{r} representing the equilibrium position and \mathbf{u} the thermal displacement. (In lattice-dynamical theory it is advantageous to deal with the primitive cell, as it possesses the fewest degrees of freedom.) The kinetic energy of the vibrating crystal is

$$(1/2) \sum_{\kappa l \alpha} m(\kappa) \dot{u}_{\alpha}^2(\kappa l),$$

where $m(\kappa)$ is the mass of atom κ and the index α ($\alpha = 1, 2, 3$) refers to the Cartesian components of the displacement. (The dot denotes the time derivative.)

If the adiabatic approximation is invoked, the potential energy V of the crystal can be expressed as a function of the instantaneous atomic positions. Expanding V in powers of $\mathbf{u}(\kappa l)$, using the three-dimensional form of Taylor's series, we have

$$V = V^{(0)} + V^{(1)} + V^{(2)} + V^{(3)} + \dots,$$

where $V^{(0)}$ is the static (equilibrium) potential and $V^{(1)}$, $V^{(2)}$ are given by

$$V^{(1)} = \sum_{\kappa l \alpha} \left. \frac{\partial V}{\partial u_{\alpha}(\kappa l)} \right|_0 u_{\alpha}(\kappa l)$$

$$V^{(2)} = \frac{1}{2} \sum_{\kappa l \alpha} \sum_{\kappa' l' \alpha'} \left. \frac{\partial^2 V}{\partial u_{\alpha}(\kappa l) \partial u_{\alpha'}(\kappa' l')} \right|_0 u_{\alpha}(\kappa l) u_{\alpha'}(\kappa' l').$$

The subscript zero indicates that the derivatives are to be evaluated at the equilibrium configuration. In the harmonic approximation, $V^{(3)}$ and all higher terms in the expansion are neglected.

At equilibrium the forces on an atom must vanish, so that

$$V^{(1)} = 0.$$

Ignoring the static potential $V^{(0)}$, the quadratic term $V^{(2)}$ only remains and the Hamiltonian for the crystal (the sum of the kinetic and potential energies) is then

$$H = \frac{1}{2} \sum_{\kappa l \alpha} m(\kappa) \dot{u}_{\alpha}^2(\kappa l)$$

$$+ \frac{1}{2} \sum_{\kappa l \alpha} \sum_{\kappa' l' \alpha'} \Phi_{\alpha \alpha'} \begin{pmatrix} \kappa & \kappa' \\ l & l' \end{pmatrix} u_{\alpha}(\kappa l) u_{\alpha'}(\kappa' l'),$$

(4.1.2.1)

where $\Phi_{\alpha \alpha'}$ is an element of the 3×3 'atomic force-constant matrix' and is defined (for distinct atoms κl , $\kappa' l'$) by

$$\Phi_{\alpha \alpha'} \begin{pmatrix} \kappa & \kappa' \\ l & l' \end{pmatrix} = \left. \frac{\partial^2 V}{\partial u_{\alpha}(\kappa l) \partial u_{\alpha'}(\kappa' l')} \right|_0.$$

It is the negative of the force in the α direction imposed on the atom (κl) when atom ($\kappa' l'$) is displaced unit distance along α' with all the remaining atoms fixed at their equilibrium sites. $\Phi_{\alpha \alpha'}$ is defined differently for the self-term with $\kappa = \kappa'$ and $l = l'$:

$$\Phi_{\alpha \alpha'} \begin{pmatrix} \kappa & \kappa \\ l & l \end{pmatrix} = - \sum_{\substack{\kappa l \\ \kappa l' \neq \kappa l}} \sum_{\substack{\kappa' l' \\ \kappa' l' \neq \kappa l}} \Phi_{\alpha \alpha'} \begin{pmatrix} \kappa & \kappa' \\ l & l' \end{pmatrix}.$$

Thus the self-matrix describes the force on (κl) when the atom itself is displaced with all the remaining atoms kept stationary.

There are restrictions on the number of distinct force constants $\Phi_{\alpha \alpha'}$: these are imposed by symmetry and by the requirement that the potential energy is invariant under infinitesimal translations and rotations of the rigid crystal. Such constraints are discussed in the book by Venkataraman *et al.* (1975).

Applying Hamilton's equations of motion to equation (4.1.2.1) now gives

$$m(\kappa) \ddot{u}_{\alpha}(\kappa l) = - \sum_{\kappa' l' \alpha'} \Phi_{\alpha \alpha'} \begin{pmatrix} \kappa & \kappa' \\ l & l' \end{pmatrix} u_{\alpha'}(\kappa' l').$$

(4.1.2.2)

These represent $3nN$ coupled differential equations, where n is the number of atoms per primitive cell ($\kappa = 1, \dots, n$) and N is the number of cells per crystal ($l = 1, \dots, N$).

By applying the periodic boundary conditions, the solutions of equation (4.1.2.2) can be expressed as running, or travelling, plane waves extending throughout the entire crystal. The number of independent waves (or normal modes) is $3nN$. Effectively, we have transferred to a new coordinate system: instead of specifying the motion of the individual atoms, we describe the thermal motion in terms of normal modes, each of which contributes to the displacement of each atom. The general solution for the α component of the displacement of (κl) is then given by the superposition of the displacements from all modes:

$$u_{\alpha}(\kappa l) = [m(\kappa)]^{-1/2} \sum_{j \mathbf{q}} |A_j(\mathbf{q})| e_{\alpha}(\kappa | j \mathbf{q})$$

$$\times \exp\{i[\mathbf{q} \cdot \mathbf{r}(\kappa l) - \omega_j(\mathbf{q})t]\}.$$

(4.1.2.3)

Here \mathbf{q} is the wavevector of a mode (specifying both its wavelength and direction of propagation in the crystal) and $\omega(\mathbf{q})$ its frequency. There are N distinct wavevectors, occupying a uniformly distributed mesh of N points in the Brillouin zone (reciprocal cell); each wavevector is shared by $3n$ modes which possess, in general, different frequencies and polarization properties. Thus an individual mode is conveniently labelled ($j \mathbf{q}$), where j is an index ($j = 1, \dots, 3n$) indicating the *branch*. The scalar quantity $|A_j(\mathbf{q})|$ in equation (4.1.2.3) is the amplitude of excitation of ($j \mathbf{q}$) and $e_{\alpha}(\kappa | j \mathbf{q})$ is the element of the eigenvector $\mathbf{e}(j \mathbf{q})$ referring to the displacement in the α direction of the atom κ . The eigenvector itself, with dimensions $n \times 1$, determines the pattern of atomic displacements in the mode ($j \mathbf{q}$) and its magnitude is fixed by the orthonormality and closure conditions

$$\sum_{\alpha \kappa} e_{\alpha}^*(\kappa | j \mathbf{q}) e_{\alpha}(\kappa | j' \mathbf{q}) = \delta_{jj'}$$

and

$$\sum_j e_{\alpha}(\kappa | j \mathbf{q}) e_{\alpha'}^*(\kappa' | j \mathbf{q}) = \delta_{\alpha \alpha'} \delta_{\kappa \kappa'}$$

with $*$ indicating complex conjugate and δ the Kronecker delta.

The pre-exponential, or amplitude, terms in (4.1.2.3) are independent of the cell number. This follows from Bloch's (1928) theorem which states that, for corresponding atoms in different cells, the motions are identical as regards their amplitude and direction and differ only in phase. The theorem introduces an enormous simplification as it allows us to restrict attention to the $3n$ equations of motion of the n atoms in just one cell, rather than the $3nN$ equations of motion for all the atoms in the crystal.

Substitution of (4.1.2.3) into (4.1.2.2) gives the equations of motion in the form

$$\omega_j^2(\mathbf{q}) e_{\alpha}(\kappa | j \mathbf{q}) = \sum_{\alpha' \kappa'} D_{\alpha \alpha'}(\kappa \kappa' | \mathbf{q}) e_{\alpha'}(\kappa' | j \mathbf{q}),$$

(4.1.2.4)

in which $D_{\alpha \alpha'}$ is an element of the dynamical matrix $\mathbf{D}(\mathbf{q})$. $D_{\alpha \alpha'}$ is

defined by

$$D_{\alpha\alpha'}(\kappa\kappa'|\mathbf{q}) = [m(\kappa)m(\kappa')]^{-1/2} \exp\{i\mathbf{q}[r(\kappa') - r(\kappa)]\} \\ \times \sum \Phi_{\alpha\alpha'} \begin{pmatrix} \kappa & \kappa' \\ 0 & L \end{pmatrix} \exp[i\mathbf{q} \cdot \mathbf{r}(L)], \quad (4.1.2.5)$$

where $\mathbf{r}(\kappa)$ is the position of atom κ with respect to the cell origin, L is $l' - l$ and $\mathbf{r}(L)$ is the separation between cells l and l' . The element $D_{\alpha\alpha'}$ is obtained by writing down the $\alpha\alpha'$ component of the force constant between atoms κ, κ' which are L cells apart and multiplying by the phase factor $\exp[i\mathbf{q} \cdot \mathbf{r}(L)]$; this term is then summed over those values of L covering the range of interaction of κ and κ' .

The dynamical matrix is Hermitian and has dimensions $3n \times 3n$. Its eigenvalues are the squared frequencies $\omega_j^2(\mathbf{q})$ of the normal modes and its eigenvectors $\mathbf{e}(j\mathbf{q})$ determine the corresponding pattern of atomic displacements. The frequencies of the modes in three of the branches, j , go to zero as \mathbf{q} approaches zero: these are the acoustic modes. The remaining $3n - 3$ branches contain the optic modes. There are N distinct \mathbf{q} vectors, and so, in all, there are $3N$ acoustic modes and $(3n - 3)N$ optic modes. Thus copper has acoustic modes but no optic modes, silicon and rock salt have an equal number of both, and lysozyme possesses predominantly optic modes.

4.1.2.2. Quantization of normal modes. Phonons

Quantum concepts are not required in solving the equations of motion (4.1.2.4) to determine the frequencies and displacement patterns of the normal modes. The only place where quantum mechanics is necessary is in calculating the energy of the mode, and from this the amplitude of vibration $|A_j(\mathbf{q})|$.

It is possible to discuss the theory of lattice dynamics from the beginning in the language of quantum mechanics (Donovan & Angress, 1971). Instead of treating the modes as running waves, they are conceived as an assemblage of indistinguishable quasi-particles called phonons. Phonons obey Bose–Einstein statistics and are not limited in number. The number of phonons, each with energy $\hbar\omega_j(\mathbf{q})$ in the vibrational state specified by \mathbf{q} and j , is given by

$$n_j(\mathbf{q}) = \{\exp[\hbar\omega_j(\mathbf{q})/k_B T] - 1\}^{-1} \quad (4.1.2.6)$$

and the mode energy $E_j(\mathbf{q})$ by

$$E_j(\mathbf{q}) = \hbar\omega_j(\mathbf{q})[n_j(\mathbf{q}) + (1/2)]. \quad (4.1.2.7)$$

Thus the quantum number $n_j(\mathbf{q})$ describes the degree of excitation of the mode ($j\mathbf{q}$). The relation between $E_j(\mathbf{q})$ and the amplitude $|A_j(\mathbf{q})|$ is

$$E_j(\mathbf{q}) = N\omega_j^2(\mathbf{q})|A_j(\mathbf{q})|^2. \quad (4.1.2.8)$$

Equations (4.1.2.6) to (4.1.2.8) together determine the value of $|A_j(\mathbf{q})|$ to be substituted into equation (4.1.2.3) to give the atomic displacement in terms of the absolute temperature and the properties of the normal modes.

In solving the lattice-dynamical problem using the Born–von Kármán analysis, the first step is to set up a force-constant matrix describing the interactions between all pairs of atoms. This is followed by the assembly of the dynamical matrix \mathbf{D} , whose eigenvalues give the frequencies of the normal modes and whose eigenvectors determine the patterns of atomic displacement for each mode.

Before considering the extension of this treatment to molecular crystals, we shall comment briefly on the less rigorous treatments of Einstein and Debye.

4.1.2.3. Einstein and Debye models

In the Einstein model it is assumed that each atom vibrates in its private potential well, entirely unaffected by the motion of its neighbours. There is no correlation between the motion of different atoms, whereas correlated motion – in the form of collective modes propagating throughout the crystal – is a central feature in explaining the characteristics of the TDS. Nevertheless, the Einstein model is occasionally used to represent modes belonging to flat optic branches of the dispersion relations, with the frequency written symbolically as $\omega(\mathbf{q}) = \omega_E$ (constant).

In the Debye model the optic branches are ignored. The dispersion relations for the remaining three acoustic branches are assumed to be the same and represented by

$$\omega(\mathbf{q}) = \mathbf{v}_s q, \quad (4.1.2.9)$$

where \mathbf{v}_s is a mean sound velocity. The Brillouin zone is replaced by a sphere with radius q_D chosen to ensure the correct number of modes. The linear relationship (4.1.2.9) holds right up to the boundary of the spherical zone. In an improved version of the Debye model, (4.1.2.9) is replaced by the expression

$$\omega(\mathbf{q}) = \mathbf{v}_s(2q_D/\pi) \sin(\pi q/2q_D), \quad (4.1.2.10)$$

which is the same as (4.1.2.9) at $q = 0$ but gives a sinusoidal dispersion relation with zero slope at the zone boundary.

4.1.2.4. Molecular crystals

The full Born–von Kármán treatment becomes excessively cumbersome when applied to most molecular crystals. For example, for naphthalene with two molecules or 36 atoms in the primitive cell, the dynamical matrix has dimensions 108×108 . Moreover, the physical picture of molecules or of groups of atoms, vibrating in certain modes as quasi-rigid units, is lost in the full treatment.

To simplify the setting up of the dynamical matrix, it is assumed that the molecules vibrate as rigid units in the crystal with each molecule possessing three translational and three rotational (librational) degrees of freedom. The motion of these rigid groups as a whole is described by the *external modes* of motion, whereas the *internal modes* arise from distortions within an individual group. The frequencies of these internal modes, which are largely determined by the strong intramolecular forces, are unaffected by the phase of the oscillation between neighbouring cells: the modes are taken, therefore, to be equivalent to those of the free molecule. The remaining external modes are calculated by applying the Born–von Kármán procedure to the crystal treated as an assembly of rigid molecules.

The dynamical matrix $\mathbf{D}(\mathbf{q})$ now has dimensions $6n' \times 6n'$, where n' is the number of molecules in the primitive cell: for naphthalene, \mathbf{D} is reduced to 12×12 . The elements of \mathbf{D} can be expressed in the same form as equation (4.1.2.5) for an atomic system. κ, κ' refer to molecules which are L cells apart and the indices α, α' ($= 1, \dots, 6$) label the six components of translation and rotation. $m(\kappa)$ in equation (4.1.2.5) is replaced by $m_\alpha(\kappa)$ where m_α represents the 3×3 molecular-mass matrix for $\alpha = 1, 2, 3$ and the 3×3 moment-of-inertia matrix referred to the principal axes of inertia for $\alpha = 4, 5, 6$. The 6×6 force-torque constant matrices $\Phi_{\alpha\alpha'}$ are derived by taking the second derivative of the potential energy of the crystal with respect to the coordinates of translation and rotation.

4.1.3. Scattering of X-rays by thermal vibrations

The change of frequency, or energy, of X-rays on being scattered by thermal waves is extremely small. The differential scattering cross section, $d\sigma/d\Omega$, giving the probability that X-rays are scattered into the solid angle $d\Omega$ is then