defined by

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

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

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

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

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

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

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

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

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

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

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

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' $(= 1, \ldots, 6)$ 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, $\mathrm{d}\sigma/\mathrm{d}\Omega$, giving the probability that X-rays are scattered into the solid angle $\mathrm{d}\Omega$ is then

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