Supplementary Lecture Notes (see for example: [redacted] (1) Maradudin, Montroll & Weiss: "Theory of Lattice Dynamics in the Harmonic approximation" – Seitz & Turnbull (Eds) Series on "SOLID STATE PHYSICS")

General Theory of Lattice Dynamics in 3 Dimensions (one atom / primitive cell)

Let $u_{l,\alpha}$ denote the displacement of the atom in the l^{th} unit cell in the α-direction ($\alpha = 1,2,3$ or x,y,z) from equilibrium pos'n

Expand the Potential Energy Function of the Crystal (function of atom positions) in powers of displacements (Taylor Series)

$$\Phi = \Phi_0 + \sum_{l,\alpha} \left(\frac{\partial \Phi}{\partial u_{l,\alpha}}\right)_0 u_{l,\alpha} + \frac{1}{2} \sum_{\substack{ll' \\ \alpha\beta}} \left(\frac{\partial^2 \Phi}{\partial u_{l,\alpha} \partial u_{l'\beta}}\right)_0 u_{l,\alpha} u_{l'\beta} + \dots \quad (1)$$

Φ_0 = Equilibrium Pot'l Energy (all atoms in their equilibrium positions)

$(\ )_0$ means derivatives are to be taken at the equilibrium configuration

$\left[-\left(\frac{\partial \Phi}{\partial u_{l,\alpha}}\right)_0\right]$ is the Force on atom l in the α-direction at equilibrium which must vanish by definition, so second term is zero.]

If we stop at the 3rd term, we neglect cubic & higher order (anharmonic) powers of the displacements → leads to "Harmonic approximation." Call $\left(\frac{\partial^2 \Phi}{\partial u_{l,\alpha} \partial u_{l'\beta}}\right)_0 \equiv \Phi_{\alpha\beta}(\vec{l}, \vec{l}')$

Now consider a situation where we have arbitrary displacements $u_{l,\alpha}$ of the atoms from equilibrium.

Force on atom l in α-direction is $-\left(\frac{\partial \Phi}{\partial u_{l,\alpha}}\right)$ in displaced configuration $= -\sum_{l'\beta} \left\{\frac{1}{2}\left[\Phi_{\alpha\beta}(l,l') + \Phi_{\alpha\beta}(l',l)\right]\right\} u_{l'\beta}$

because a particular $u_{l,\alpha}$ appears twice in the sum of Eq. (1).

By symmetry $\Phi_{\alpha\beta}(l,l') = \Phi_{\alpha\beta}(l',l)$

$$\therefore F_{l,\alpha} = -\sum_{l'\beta} \Phi_{\alpha\beta}(l,l')\, u_{l'\beta} = M \frac{\partial^2 u_{l,\alpha}}{\partial t^2} \quad (2)$$

Now by general running wave solution

$$u_{l,\alpha} = \mathcal{A}\, e_\alpha\, e^{i(\vec{q}\cdot\vec{l} - \omega t)} \quad (3)$$

$\vec{l}$ = position of l^{th} unit cell atom

$\vec{e}$ is unit vector for direction of displacement (polarization vector)

Substituting in Eq. (2), we get

$$-M\omega^2 \mathcal{A} e_\alpha e^{i(\vec{q}\cdot\vec{l} - \omega t)} = -\sum_{l'\beta} \Phi_{\alpha\beta}(l,l')\, \mathcal{A} e_\beta e^{i(\vec{q}\cdot\vec{l}' - \omega t)}$$

Now

$$\text{or } \frac{1}{M}\sum_{l'\beta} \Phi_{\alpha\beta}(\vec{l},\vec{l}')\, e^{i\vec{q}\cdot(\vec{l}'-\vec{l})}\, e_\beta - \omega^2 e_\alpha = 0 \quad (4)$$

Define $\frac{1}{M}\sum_{l'\beta} \Phi_{\alpha\beta}(\vec{l},\vec{l}')\, e^{i\vec{q}\cdot(\vec{l}'-\vec{l})} = D_{\alpha\beta}(\vec{q})$ (5)

(By translational invariance (of crystal) $\Phi_{\alpha\beta}(\vec{l},\vec{l}')$ is function of $(\vec{l}'-\vec{l})$ only, so can choose $\vec{l}$ as origin unit cell $\vec{l}=0$ in Eq. (5)

$$\therefore D_{\alpha\beta}(\vec{q}) = \frac{1}{M}\sum_{\vec{l}} \Phi_{\alpha\beta}(0,\vec{l})\, e^{i\vec{q}\cdot\vec{l}} \quad (6)$$

(Fourier series in 3D)

$[D_{\alpha\beta}(\vec{q})]$ is a (3×3) matrix called the Dynamical Matrix

$\Phi_{\alpha\beta}(0,\vec{l})$ is called the Force Constant Matrix between atoms at $0 \to \vec{l}$. (In general it is a (3×3) matrix – or tensor)

Then Eq. (4) can be written as

$$\sum_\beta D_{\alpha\beta}(\vec{q})\, e_\beta - \omega^2 e_\alpha = 0 \quad \text{(3 equations, one for each } \alpha\text{!)}$$

or $$\sum_\beta \left[D_{\alpha\beta}(\vec{q}) - \delta_{\alpha\beta}\omega^2\right] e_\beta = 0 \quad (7)$$

where the Kronecker delta $\delta_{\alpha\beta} = 1$ if $\alpha = \beta$; $= 0$ if $\alpha \neq \beta$

Eq. (7) represents a set of 3 linear homogeneous equations:

$$(D_{11}(q) - \omega^2)e_1 + D_{12}(\vec{q})\, e_2 + D_{13}(\vec{q})\, e_3 = 0$$

$$D_{21}(\vec{q})\, e_1 + (D_{22}(\vec{q}) - \omega^2)e_2 + D_{23}(\vec{q})\, e_3 = 0$$

$$D_{31}(\vec{q})\, e_1 + D_{32}(\vec{q})\, e_2 + (D_{33}(\vec{q}) - \omega^2)e_3 = 0$$

which implies that e_1, e_2, e_3 have a non-trivial solution if & only

if $$\begin{vmatrix} D_{11}-\omega^2 & D_{12} & D_{13} \\ D_{21} & D_{22}-\omega^2 & D_{23} \\ D_{31} & D_{32} & D_{33}-\omega^2 \end{vmatrix} = 0 \quad (8)$$

→ 3 solutions for ω^2 as a function of $\vec{q}$ → 3 branches of phonon dispersion curves

Eq. (7) may also be written as the matrix equation

$$\underline{\underline{D}}\,\underline{e} = \omega^2 \underline{e} \quad (9)$$

$\underline{\underline{D}}$ is the (3×3) matrix $D_{\alpha\beta}(\vec{q})$, $\underline{e}$ is the vector $\begin{bmatrix} e_1 \\ e_2 \\ e_3 \end{bmatrix}$

Eq. (9) is an example of the Eigenvalue problem in physics.

$(\omega^2)_j$ is one of the 3 eigenvalues of the (3×3) Matrix $\underline{D}$ obtained by solving the determinantal eigenvalue equation (8)

& $\underline{\epsilon}_j$ is the corresponding eigenvector $(j = 1, 2, 3)$

There are 3 eigenvectors — one for each eigenvalue.

By the properties of linear equations & matrices, these eigenvectors are mutually orthogonal, i.e. $\vec{e}_j \cdot \vec{e}_{j'} = \delta_{jj'}$

$$\sum_\alpha e_{j\alpha} e_{j'\beta} = \delta_{jj'}$$ (e.g. longitudinal & transverse polarization vectors but in general direction of $\vec{q}$ polarization vectors will not necessarily be parallel or $\perp$ to $\vec{q}$ (but they will be mutually orthogonal)