

Phonon Interactions and Thermal Conductivity

A term paper for 22.51

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Chapter 1

Basic Lattice Dynamics

Consider a 3D crystal with r atomic species. Denote the unit cells by L and atom type by S , $S = 1..r$. The position vector is \mathbf{R}_S^L , and the atomic displacement

$$u_\alpha \left(\begin{smallmatrix} L \\ S \end{smallmatrix} \right) = R_\alpha \left(\begin{smallmatrix} L \\ S \end{smallmatrix} \right) - R_\alpha^0 \left(\begin{smallmatrix} L \\ S \end{smallmatrix} \right) \quad (1.1)$$

where α denotes Cartesian components. For convenience's sake, sometime we contract (α, L, S) into a single index m , $u_m = u_\alpha \left(\begin{smallmatrix} L \\ S \end{smallmatrix} \right)$.

Near equilibrium, the total crystalline potential energy $V(q^N)$ could be expanded into

$$V(q^N) = \frac{1}{2} \Phi_{mn} u_m u_n + \frac{1}{6} \Phi_{mm'm''} u_m u_{m'} u_{m''} + \dots \quad (1.2)$$

where

$$\Phi_{mn} = \left. \frac{\partial^2 V(q^N)}{\partial u_\alpha \left(\begin{smallmatrix} L \\ S \end{smallmatrix} \right) \partial u_\beta \left(\begin{smallmatrix} L' \\ S' \end{smallmatrix} \right)} \right|_{q_0^N} \quad (1.3)$$

$$\Phi_{mm'm''} = \frac{\partial^3 V(q^N)}{\partial u_\alpha \binom{L}{S} \partial u_{\alpha'} \binom{L'}{S'} \partial u_{\alpha''} \binom{L''}{S''}} \bigg|_{q_0^N} \quad (1.4)$$

For a crystal, Φ 's will only depend on relative distances between unit cells:

$$\Phi_{\alpha\beta} \binom{LL'}{SS'} = \Phi_{\alpha\beta} \binom{L-L'}{SS'}, \Phi_{\alpha\beta\gamma} \binom{LL'L''}{SS'S''} = \Phi_{\alpha\beta\gamma} \binom{L-L'', L'-L''}{SS'S''}, \dots \quad (1.5)$$

and by exchanging the order of differentiation, there is

$$\Phi_{\alpha\beta} \binom{LL'}{SS'} = \Phi_{\beta\alpha} \binom{L'L}{S'S}, \quad \text{i.e.,} \quad \Phi_{mn} = \Phi_{nm} \quad (1.6)$$

and thus

$$\Phi_{\alpha\beta} \binom{L}{SS'} = \Phi_{\beta\alpha} \binom{-L}{S'S} \quad (1.7)$$

From the translational and rotational invariance of the interaction potential, there must be

$$\sum_{L', S'} \Phi_{\alpha\beta} \binom{LL'}{SS'} = 0 \quad (1.8)$$

$$\sum_{L', S'} \Phi_{\alpha\beta} \binom{LL'}{SS'} R_\gamma^0 \binom{L'}{S'} = \sum_{L', S'} \Phi_{\alpha\gamma} \binom{LL'}{SS'} R_\beta^0 \binom{L'}{S'} \quad (1.9)$$

For instance, Eq(1.9) could be proved by considering a virtual rotation in direction \mathbf{n} for small angle $\delta\theta$, so the displacement of each atom is $\mathbf{n} \times \mathbf{R}^0 \binom{L'}{S'} \delta\theta$. Consider the force on atom (L, S) , it's

$$\begin{aligned} F_\alpha \binom{L}{S} &= - \sum_{L', S', \beta} \Phi_{\alpha\beta} \binom{LL'}{SS'} (\epsilon_{\beta\sigma\gamma} n_\sigma R_\gamma^0 \binom{L'}{S'}) \delta\theta \\ &= - \frac{1}{2} \sum_{L', S', \beta} [\Phi_{\alpha\beta} \binom{LL'}{SS'} R_\gamma^0 \binom{L'}{S'} - \Phi_{\alpha\gamma} \binom{LL'}{SS'} R_\beta^0 \binom{L'}{S'}] \epsilon_{\beta\sigma\gamma} n_\sigma \delta\theta \end{aligned} \quad (1.10)$$

Since $F_\alpha \binom{L}{S}$ should be zero for any \mathbf{n} , it's obvious that Eq(1.9) must be satisfied.

Consider mass-scaled quantities

$$v_m = \sqrt{M_S} u_\alpha \binom{L}{S} \quad (1.11)$$

and

$$D_{mn} = \frac{\Phi_{mn}}{\sqrt{M_S M_{S'}}}, \quad D_{mm'm''} = \frac{\Phi_{mm'm''}}{\sqrt{M_S M_{S'} M_{S''}}}, \quad \dots \quad (1.12)$$

We are concerned with the diagonalization of D_{mn} , i.e., finding a unitary matrix that

$$D_{mn} = U_{mk}^\dagger \omega_k^2 U_{kn}, \quad \text{where} \quad U_{mk}^\dagger U_{kn} = \delta_{mn} \quad (1.13)$$

In doing this, we should know the fact that by using irreducible basis functions $\{\exp(i\mathbf{q} \cdot \mathbf{r})\}$ of the translational group we can easily block-diagonalize this $3rN \times 3rN$ matrix into N $3r \times 3r$ matrices (only functions with the same \mathbf{q} in the first B.Z. can couple to each other through the Hamiltonian). This means we can label our normal coordinates of the crystal by k , which is the contraction of two indices ($\mathbf{q}j$):

$$V_n^k = V_\alpha^{\mathbf{q}j} \binom{L}{S} = \frac{1}{\sqrt{N}} \exp(i\mathbf{q} \cdot \mathbf{R}(L)) e_\alpha^{\mathbf{q}j}(S) \quad (1.14)$$

such that

$$\sum_n V_n^{k*} V_n^{k'} = \sum_{\alpha, L, S} V_\alpha^k \binom{L}{S}^* V_\alpha^{k'} \binom{L}{S} = \delta_{kk'} \quad (1.15)$$

Here $j(1..3r)$ denote the phonon branch, by which polarization vector $e_\alpha^{\mathbf{q}j}(S)$ is specified. For Eq(1.15) to be correct, $e_\alpha^{\mathbf{q}j}$'s for the same \mathbf{q} should be orthonormal to each other,

$$\sum_{\alpha, S} e_\alpha^{\mathbf{q}j}(S)^* e_\alpha^{\mathbf{q}j'}(S) = \delta_{jj'} \quad (1.16)$$

Also, since $\{k\}$ form a complete basis set, there should be completeness relation

$$\sum_k V_n^{k*} V_n^k = \delta_{nn'} \quad (1.17)$$

To block diagonalize D_{mn} , there should be

$$D_{mn}V_n^k = \omega_k^2 V_m^k \quad (1.18)$$

so

$$\sum_{\beta, L', S'} \frac{\Phi_{\alpha\beta}^{(L-L')}(SS')}{\sqrt{M_S M_{S'}}} \exp(i\mathbf{q} \cdot \mathbf{R}(L')) e_\beta^k(S') = \omega_k^2 \exp(i\mathbf{q} \cdot \mathbf{R}(L)) e_\alpha^k(S) \quad (1.19)$$

$$\sum_{\beta, L', S'} \frac{\Phi_{\alpha\beta}^{(L-L')}(SS')}{\sqrt{M_S M_{S'}}} \exp(-i\mathbf{q} \cdot \mathbf{R}(L - L')) e_\beta^k(S') = \omega_k^2 e_\alpha^k(S) \quad (1.20)$$

Define the 3×3 *dynamical matrix* in \mathbf{q} space to be

$$\mathbf{D}_{(SS')}^{\mathbf{q}} = \frac{1}{\sqrt{M_S M_{S'}}} \sum_L \Phi_{(SS')}^L \exp(-i\mathbf{q} \cdot \mathbf{R}(L)) \quad (1.21)$$

then there would be

$$\sum_{S'} \mathbf{D}_{(SS')}^{\mathbf{q}} \mathbf{e}^k(S') = \omega_k^2 \mathbf{e}^k(S) \quad (1.22)$$

From time-reversal symmetry (conjugate invariance),

$$\mathbf{D}_{(SS')}^{\mathbf{q}} = \mathbf{D}_{(SS')}^{*\mathbf{q}} \quad (1.23)$$

$$\omega_k^2 = \omega_{-k}^2 \quad (1.24)$$

$$\mathbf{e}^k(S) = \mathbf{e}^{-k}(S)^* \quad (1.25)$$

Explicitly written, the $3r \times 3r$ matrix equation is

$$\begin{pmatrix} \mathbf{D}_{(11)}^{\mathbf{q}} & \mathbf{D}_{(12)}^{\mathbf{q}} & \dots & \mathbf{D}_{(1r)}^{\mathbf{q}} \\ \mathbf{D}_{(21)}^{\mathbf{q}} & \mathbf{D}_{(22)}^{\mathbf{q}} & \dots & \mathbf{D}_{(2r)}^{\mathbf{q}} \\ \mathbf{D}_{(31)}^{\mathbf{q}} & . & \dots & . \\ . & . & \dots & . \\ . & . & \dots & . \\ \mathbf{D}_{(r1)}^{\mathbf{q}} & \mathbf{D}_{(r2)}^{\mathbf{q}} & \dots & \mathbf{D}_{(rr)}^{\mathbf{q}} \end{pmatrix} \begin{pmatrix} \mathbf{e}^{\mathbf{q}j}(1) \\ \mathbf{e}^{\mathbf{q}j}(2) \\ \mathbf{e}^{\mathbf{q}j}(3) \\ . \\ . \\ \mathbf{e}^{\mathbf{q}j}(r) \end{pmatrix} = \omega_{\mathbf{q}j}^2 \begin{pmatrix} \mathbf{e}^{\mathbf{q}j}(1) \\ \mathbf{e}^{\mathbf{q}j}(2) \\ \mathbf{e}^{\mathbf{q}j}(3) \\ . \\ . \\ \mathbf{e}^{\mathbf{q}j}(r) \end{pmatrix} \quad (1.26)$$

and with

$$\begin{pmatrix} \mathbf{e}^{\mathbf{q}j}(1)^*, \mathbf{e}^{\mathbf{q}j}(2)^*, \mathbf{e}^{\mathbf{q}j}(3)^*, \dots, \mathbf{e}^{\mathbf{q}j}(r)^* \end{pmatrix} \begin{pmatrix} \mathbf{e}^{\mathbf{q}j'}(1) \\ \mathbf{e}^{\mathbf{q}j'}(2) \\ \mathbf{e}^{\mathbf{q}j'}(3) \\ \vdots \\ \mathbf{e}^{\mathbf{q}j'}(r) \end{pmatrix} = \delta_{jj'} \quad (1.27)$$

Diagonalization complete. We have $3rN$ unit vectors for the crystal now, and thus the unitary matrix $U_{mk}^\dagger = V_k^m$.

• Lagrangian Formulation

Decompose

$$\sqrt{M_S} u_\alpha \binom{L}{S} = v_m = \sum_k Q_k V_m^k \quad (1.28)$$

Since $u_\alpha \binom{L}{S}$ is real, there is

$$Q_k = Q_{-k}^* \quad (1.29)$$

and

$$\dot{v}_\alpha \binom{L}{S} = \sum_k \dot{Q}_k V_m^k = \sum_k \dot{Q}_k^* V_m^{k*} \quad (1.30)$$

the Lagrangian of the crystal then become

$$\begin{aligned} \mathcal{L} &= \sum_m \frac{1}{2} M_S \dot{u}_m^2 - \sum_{mn} \frac{1}{2} u_m \Phi_{mn} u_n \\ &= \sum_m \frac{1}{2} \dot{v}_m^2 - \sum_{mn} \frac{1}{2} v_m D_{mn} v_n \\ &= \sum_{k,k'} \left\{ \sum_m \frac{1}{2} \dot{Q}_k^* V_m^{k*} \dot{Q}_{k'} V_m^{k'} - \sum_m \frac{1}{2} Q_k^* V_m^{k*} D_{mn} Q_{k'} V_n^{k'} \right\} \\ &= \sum_k \frac{1}{2} \dot{Q}_k^* \dot{Q}_k - \frac{1}{2} \omega_k^2 Q_k^* Q_k \end{aligned} \quad (1.31)$$

So

$$P_k = \frac{\partial \mathcal{L}}{\partial \dot{Q}_k} = \dot{Q}_k^* = \dot{Q}_{-k} \quad (1.32)$$

and

$$\begin{aligned} \mathcal{H} &= \sum_k P_k \dot{Q}_k - \mathcal{L} \\ &= \sum_k \frac{P_k^* P_k}{2} + \frac{\omega_k^2}{2} Q_k^* Q_k \\ &= \sum_k \frac{P_{-k} P_k}{2} + \frac{\omega_k^2}{2} Q_{-k} Q_k \end{aligned} \quad (1.33)$$

From here we can see that

$$u_\alpha \binom{L}{S} = \frac{1}{\sqrt{M_S}} \sum_k Q_k \cdot \frac{1}{\sqrt{N}} \exp(i\mathbf{q} \cdot \mathbf{R}(L)) e_\alpha^k(S) \quad (1.34)$$

$$\begin{aligned} p_\alpha \binom{L}{S} &= \sqrt{M_S} \sum_k \dot{Q}_k \cdot \frac{1}{\sqrt{N}} \exp(i\mathbf{q} \cdot \mathbf{R}(L)) e_\alpha^k(S) \\ &= \sqrt{M_S} \sum_k P_{-k} \cdot \frac{1}{\sqrt{N}} \exp(i\mathbf{q} \cdot \mathbf{R}(L)) e_\alpha^k(S) \end{aligned} \quad (1.35)$$

And so the inverse

$$Q_k = \sum_{\alpha, L, S} \sqrt{M_S} u_\alpha \binom{L}{S} \frac{1}{\sqrt{N}} \exp(-i\mathbf{q} \cdot \mathbf{R}(L)) e_\alpha^k(S)^* \quad (1.36)$$

$$P_{-k} = \sum_{\alpha, L, S} \frac{1}{\sqrt{M_S}} p_\alpha \binom{L}{S} \frac{1}{\sqrt{N}} \exp(-i\mathbf{q} \cdot \mathbf{R}(L)) e_\alpha^k(S)^* \quad (1.37)$$

• Second Quantization

Second Quantization is to simply replace all the $u_\alpha \binom{L}{S}, p_\alpha \binom{L}{S}$ in the classical Hamiltonian

$$\mathcal{H} = \sum_{\alpha, L, S} \frac{p_\alpha^2 \binom{L}{S}}{2M_S} + \frac{1}{2} u_\alpha \binom{L}{S} \Phi_{\alpha\beta} \binom{LL'}{SS'} u_\beta \binom{L'}{S'} + \dots \quad (1.38)$$

by operators $\hat{p}_\alpha \binom{L}{S}, \hat{u}_\alpha \binom{L}{S}$. Starting from here is a bit cumbersome, but is much safer.

Define \hat{Q}_k, \hat{P}_{-k} through Eq(1.36),Eq(1.37), then

$$\hat{Q}_k = \sum_{\alpha,L,S} \sqrt{\frac{M_S}{N}} \hat{u}_\alpha \binom{L}{S} \exp(-i\mathbf{q} \cdot \mathbf{R}(L)) e_\alpha^k(S)^* \quad (1.39)$$

$$\hat{P}_{-k} = \sum_{\alpha,L,S} \frac{1}{\sqrt{NM_S}} \hat{p}_\alpha \binom{L}{S} \exp(-i\mathbf{q} \cdot \mathbf{R}(L)) e_\alpha^k(S)^* \quad (1.40)$$

If we also define

$$\hat{v}_n = \sqrt{M_S} \hat{u}_n, \quad \hat{w}_n = \frac{1}{\sqrt{M_S}} \hat{p}_n \quad (1.41)$$

then

$$\hat{Q}_k = U_{kn} \hat{v}_n, \quad \hat{P}_{-k} = U_{kn} \hat{w}_n \quad (1.42)$$

and

$$\hat{Q}_k^\dagger = U_{kn}^* \hat{v}_n = \hat{Q}_{-k}, \quad \hat{P}_{-k}^\dagger = U_{kn}^* \hat{w}_n = \hat{P}_k \quad (1.43)$$

Then

$$[\hat{Q}_k, \hat{P}_{k'}] = U_{kn} U_{k'm}^* [\hat{v}_n, \hat{w}_m] = i\hbar \delta_{kk'} \quad (1.44)$$

and obviously

$$[\hat{Q}_k, \hat{Q}_{k'}] = [\hat{P}_k, \hat{P}_{k'}] = 0 \quad (1.45)$$

That's good. However notice that \hat{Q}_k and \hat{P}_k are *not* Hermitian.

Define

$$\hat{a}_k = \frac{1}{\sqrt{2\hbar\omega_k}} (\omega_k \hat{Q}_k + i\hat{P}_{-k}) \quad \hat{a}_k^\dagger = \frac{1}{\sqrt{2\hbar\omega_k}} (\omega_k \hat{Q}_{-k} - i\hat{P}_k) \quad (1.46)$$

$$\hat{a}_{-k} = \frac{1}{\sqrt{2\hbar\omega_k}} (\omega_k \hat{Q}_{-k} + i\hat{P}_k) \quad \hat{a}_{-k}^\dagger = \frac{1}{\sqrt{2\hbar\omega_k}} (\omega_k \hat{Q}_k - i\hat{P}_{-k}) \quad (1.47)$$

Then

$$[\hat{a}_k, \hat{a}_{k'}^\dagger] = \frac{1}{2\hbar\sqrt{\omega_k\omega_{k'}}} (-i\omega_k [\hat{Q}_k, \hat{P}_{k'}] + i\omega_{k'} [\hat{P}_{-k}, \hat{Q}_{-k'}]) = \delta_{kk'} \quad (1.48)$$

$$[\hat{a}_k, \hat{a}_{k'}] = \frac{1}{2\hbar\sqrt{\omega_k\omega_{k'}}}(i\omega_k[\hat{Q}_k, \hat{P}_{-k'}] + i\omega_{k'}[\hat{P}_{-k}, \hat{Q}_{k'}]) = 0 \quad (1.49)$$

$$[\hat{a}_k^\dagger, \hat{a}_{k'}^\dagger] = \frac{1}{2\hbar\sqrt{\omega_k\omega_{k'}}}(-i\omega_k[\hat{Q}_{-k}, \hat{P}_{k'}] - i\omega_{k'}[\hat{P}_k, \hat{Q}_{-k'}]) = 0 \quad (1.50)$$

With this in mind and with Eq(1.42) we have

$$\hat{v}_n = U_{nk}^\dagger \hat{Q}_k, \quad \hat{w}_n = U_{nk}^\dagger \hat{P}_{-k} \quad (1.51)$$

So

$$\begin{aligned} \mathcal{H} &= \sum_n \frac{\hat{w}_n \hat{w}_n}{2} + \sum_{nm} \frac{1}{2} \hat{v}_m D_{mn} \hat{v}_n \\ &= \frac{1}{2} (\hat{P}_{-k}^\dagger (U_{nk}^\dagger)^* U_{nk}^\dagger \hat{P}_{-k'} + \omega_k^2 \hat{Q}_k^\dagger \hat{Q}_k) \\ &= \sum_k \frac{1}{2} (\hat{P}_k^\dagger \hat{P}_k + \omega_k^2 \hat{Q}_k^\dagger \hat{Q}_k) \end{aligned} \quad (1.52)$$

But

$$\begin{aligned} &\sum_k \hbar\omega_k (\hat{a}_k^\dagger \hat{a}_k + \frac{1}{2}) \\ &= \sum_k \hbar\omega_k \left\{ \frac{1}{2\hbar\omega_k} (\omega_k^2 \hat{Q}_{-k} \hat{Q}_k + \hat{P}_k \hat{P}_{-k} - i\omega_k \hat{P}_k \hat{Q}_k + i\omega_k \hat{Q}_{-k} \hat{P}_{-k}) + \frac{1}{2} \right\} \\ &= \sum_k \frac{1}{2} [\hat{P}_{-k} \hat{P}_k + \omega_k^2 \hat{Q}_{-k} \hat{Q}_k] + \hbar\omega_k \left\{ \frac{i}{2\hbar} [\hat{Q}_k, \hat{P}_k] + \frac{1}{2} \right\} \\ &= \sum_k \frac{1}{2} [\hat{P}_k^\dagger \hat{P}_k + \omega_k^2 \hat{Q}_k^\dagger \hat{Q}_k] \end{aligned} \quad (1.53)$$

Compare with Eq(1.52), we see that

$$\mathcal{H} = \sum_k \hbar\omega_k (\hat{a}_k^\dagger \hat{a}_k + \frac{1}{2}) \quad (1.54)$$

Quantization complete. All conclusions of the algebra could be transported onto 3D crystal. Notice that k and $-k$ phonons are entirely decoupled, although they share the same

frequency.

Important dynamical operators:

$$\hat{Q}_k = \sqrt{\frac{\hbar}{2\omega_k}}(\hat{a}_k + \hat{a}_{-k}^\dagger), \quad \hat{P}_{-k} = -i\sqrt{\frac{\hbar\omega_k}{2}}(\hat{a}_k - \hat{a}_{-k}^\dagger) \quad (1.55)$$

and

$$\begin{aligned} \hat{u}_\alpha^L(S) &= \frac{1}{\sqrt{NM_S}} \sum_k e_\alpha^k(S) \exp(i\mathbf{q} \cdot \mathbf{R}(L)) \hat{Q}_k \\ &= \sum_k \sqrt{\frac{\hbar}{2NM_S\omega_k}} e_\alpha^k(S) \exp(i\mathbf{q} \cdot \mathbf{R}(L)) (\hat{a}_k + \hat{a}_{-k}^\dagger) \\ &= \sum_k \sqrt{\frac{\hbar}{2NM_S\omega_k}} \{e_\alpha^k(S) \exp(i\mathbf{q} \cdot \mathbf{R}(L)) \hat{a}_k + e_\alpha^k(S)^* \exp(-i\mathbf{q} \cdot \mathbf{R}(L)) \hat{a}_k^\dagger\} \end{aligned} \quad (1.56)$$

$$\begin{aligned} \hat{p}_\alpha^L(S) &= \sqrt{\frac{M_S}{N}} \sum_k e_\alpha^k(S) \exp(i\mathbf{q} \cdot \mathbf{R}(L)) \hat{P}_{-k} \\ &= \sum_k -i\sqrt{\frac{\hbar M_S \omega_k}{2N}} e_\alpha^k(S) \exp(i\mathbf{q} \cdot \mathbf{R}(L)) (\hat{a}_k - \hat{a}_{-k}^\dagger) \\ &= \sum_k -i\sqrt{\frac{\hbar M_S \omega_k}{2N}} \{e_\alpha^k(S) \exp(i\mathbf{q} \cdot \mathbf{R}(L)) \hat{a}_k - e_\alpha^k(S)^* \exp(-i\mathbf{q} \cdot \mathbf{R}(L)) \hat{a}_k^\dagger\} \end{aligned} \quad (1.57)$$

Phonons will form bands, as all excitations in a periodic lattice. One important difference between phonon and electron band is that a pure phonon state $|n_k\rangle$ won't carry momentum, which is easily seen from Eq(1.57). A pure electron Bloch state $|\psi_k^n\rangle$ however, does carry the momentum $m_e \mathbf{v}_G$, where \mathbf{v}_G is the group velocity:

$$\mathbf{v}_G = \frac{\partial w_n(\mathbf{q})}{\partial \mathbf{q}} \quad (1.58)$$

• Conservation Laws

We now consider general conservation laws for peoriodic systems, not only under harmonic approximation, but with arbitrary interactions, and with external probes inside the system, say, neutrons or photons. We know that conservation laws are linked closely with some invariance operators, like the conservation of energy with time-translational operator:

$$\hat{U}_\tau = \exp(\frac{\hat{\mathcal{H}}\tau}{i\hbar}) \quad (1.59)$$

Here the infinitesimal generator of \hat{U}_τ is $\hat{\mathcal{H}}$. Since obviously

$$[\hat{U}_\tau, \hat{\mathcal{H}}] = 0 \quad (1.60)$$

as physical laws doesn't depend on the time origin, there is

$$[\hat{\mathcal{H}}, \hat{\mathcal{H}}] = 0 \quad (1.61)$$

which we know directly otherwise. So the measurement of the generator of \hat{U}_τ is conserved, i.e.,

$$\langle \hat{\mathcal{H}} \rangle = \text{const} \quad (1.62)$$

Consider the Hamiltonian of a general crystal,

$$\hat{\mathcal{H}} = \sum_{\alpha, L, S} \frac{\hat{p}_\alpha \binom{L}{S}^2}{2M_S} + V(\{\hat{u}_\alpha \binom{L}{S}\}) + \frac{\hat{P}^2}{2m} + W(\hat{r}, \{\hat{u}_\alpha \binom{L}{S}\}) \quad (1.63)$$

Here \hat{P}, \hat{r} are operators for the external probe, W is its interaction with the crystal. From Eq(1.62) we can see that

$$E_i^{tot} = E_f^{tot}$$

in the case of a photon,

$$\hbar\omega_i + E_i^{xtal} = \hbar\omega_f + E_f^{xtal} \quad (1.64)$$

There are two kinds of spatial translations for a peoriodic system: one is the common real-space translations with arbitrary displacement,

$$\hat{U}_\delta = \exp\left(\frac{i}{\hbar}\left(\sum_{L,S} \hat{p}_S^{(L)} + \hat{P}\right) \cdot \delta\right) \quad (1.65)$$

This means

$$\hat{r} \rightarrow \hat{r} + \delta, \quad \hat{u}_S^{(L)} \rightarrow \hat{u}_S^{(L)} + \delta$$

and obviously

$$[\hat{U}_\delta, \hat{\mathcal{H}}] = 0 \quad (1.66)$$

as the translation of the entire system in space for δ won't change the energy. So,

$$\langle \sum_{L,S} \hat{p}_S^{(L)} + \hat{P} \rangle = \text{const} \quad (1.67)$$

as the law of total momentum conservation. This law isn't so interesting since the recoil of a crystal in a scattering experiment is negligible.

The other one is more subtle, which involves only the translation of *labelings*. Consider the following operation

$$\hat{r} \rightarrow \hat{r} + \mathbf{R}, \quad \hat{u}_S^{(L)} \rightarrow \hat{u}_S^{(L-1)}, \quad \hat{p}_S^{(L)} \rightarrow \hat{p}_S^{(L-1)}$$

with \mathbf{R} being a lattice vector. Obviously, this will also leave the total Hamiltonian invariant, as the incident particle would find itself in the same environment as before. The operator for this translation is

$$\hat{U}_{\mathbf{R}} = \exp\left(\frac{i}{\hbar}(\hat{K} + \hat{P}) \cdot \mathbf{R}\right) \quad (1.68)$$

where

$$\hat{K} = \sum_k \hbar \mathbf{q} (\hat{a}_k^\dagger \hat{a}_k) \quad (1.69)$$

This can be proven in the following way. Since

$$[\hat{a}_k^\dagger \hat{a}_k, \hat{a}_k] = -\hat{a}_k, \quad [\hat{a}_k^\dagger \hat{a}_k, \hat{a}_k^\dagger] = \hat{a}_k^\dagger \quad (1.70)$$

if we define \hat{K} which operates on operators

$$\hat{K} \hat{A} = [\hat{K}, \hat{A}] \quad (1.71)$$

it's obvious that $\hat{a}_k, \hat{a}_k^\dagger$ are the eigenvectors of \hat{K} with eigenvalues $-\hbar \mathbf{q}$ and $\hbar \mathbf{q}$, and so

$$\begin{aligned} & \hat{U}_{\mathbf{R}} \hat{a}_k \hat{U}_{\mathbf{R}}^\dagger \\ = & \exp\left(\frac{i}{\hbar} \hat{K} \cdot \mathbf{R}\right) \hat{a}_k \exp\left(-\frac{i}{\hbar} \hat{K} \cdot \mathbf{R}\right) \\ = & \exp\left(\frac{i}{\hbar} \hat{K} \cdot \mathbf{R}\right) \hat{a}_k \\ = & \exp(-i \mathbf{q} \cdot \mathbf{R}) \hat{a}_k \end{aligned} \quad (1.72)$$

also

$$\hat{U}_{\mathbf{R}} \hat{a}_k^\dagger \hat{U}_{\mathbf{R}}^\dagger = \exp(i \mathbf{q} \cdot \mathbf{R}) \hat{a}_k^\dagger \quad (1.73)$$

Then from Eq(1.56), Eq(1.57)

$$\hat{U}_{\mathbf{R}} \hat{u}_\alpha \binom{L}{S} \hat{U}_{\mathbf{R}}^\dagger = \hat{u}_\alpha \binom{L-1}{S} \quad (1.74)$$

$$\hat{U}_{\mathbf{R}} \hat{p}_\alpha \binom{L}{S} \hat{U}_{\mathbf{R}}^\dagger = \hat{p}_\alpha \binom{L-1}{S} \quad (1.75)$$

$$\hat{U}_{\mathbf{R}} \hat{r} \hat{U}_{\mathbf{R}}^\dagger = \hat{r} + \mathbf{R} \quad (1.76)$$

And so indeed we have proven $\hat{U}_{\mathbf{R}}$ to be the the operator we descibed. This means the measurement of $\hat{U}_{\mathbf{R}}$ shall always be conserved. Note that although we used $\hat{a}_k, \hat{a}_k^\dagger$ in our derivation, we do not have to be in the harmonic approximation.

Suppose before and after the scattering the incident particle is free, and we are not far from a harmonic crystal such that the instantaneous configuration is represented by a number

state. For $\langle E_q(1.68) \rangle$ to be invariant, also for any lattice vector \mathbf{R} , there must be

$$P_i + \sum_k n_k^i \hbar \mathbf{q} = P_f + \sum_k n_k^f \hbar \mathbf{q} + \mathbf{G} \quad (1.77)$$

where \mathbf{G} is a reciprocal lattice vector. Thus we can define the concept of *crystal momentum*, which is just $\sum_k n_k \hbar \mathbf{q}$. Crystal momentum isn't real momentum. It defines the vibrational phase relation between different labeling but identical atoms, and that, adding the phase factor of the incident particle, should be conserved.

Chapter 2

Basics of Lattice Thermal Conductivity

The thermal conductivity of solids usually consists of two parts: those due to electrons and those due to the lattice. For insulators and semiconductors, the main contribution comes from lattice conduction, and the heat influx

$$\mathbf{J}^q = -\hat{\kappa} \nabla T \quad (2.1)$$

where we had assumed a spatially varying local temperature to be properly defined. κ is generally a 3×3 tensor, but for crystals with point symmetry higher than T_d , it's a scalar.

If a crystal is purely harmonic, κ should be $+\infty$: that's because a purely harmonic crystal cannot support local temperature variance, since all our normal coordinates in the Hamiltonian are of global character. If we heat up the atoms in part of the crystal and let it go, it will automatically do a normal coordinate analysis and the crystal will be homogeneously

vibrating in no time, each normal coordinate independent of other. Thus, for a solid to have finite thermal conductivity/resistivity, there must be anharmonicity of some sort: either it's the higher-order term in the expansion, or defects. The exact solution of these problems are extremely difficult, so usually we treat the crystal as nearly harmonic and do perturbation theories on phonons states.

Another important concept is that of lattice wave packet. When the lattice is under a heat gradient, it can't be described by a single stationary state $|n_{k_1}, n_{k_2}, \dots, n_{k_{3rN}}\rangle$, but should be the linear combination of many such states with time-dependent coefficients, to form a wave packet, localized in some spatial region. It's well known in wave mechanics that such packets will travel in the speed of group velocity,

$$\mathbf{v}_G = \frac{\partial w_j(\mathbf{q})}{\partial \mathbf{q}} \quad (2.2)$$

and so is the energy it carries. Thus, the heat current is

$$\Omega \mathbf{J}^q = \sum_k n_k \hbar \omega_k \mathbf{v}_G \quad (2.3)$$

This picture might work best for lattices with some anharmonicity or defects, so that the packet would be deflected to form a new one before it's too much widely spread. However when the anharmonicity is too much the formula will also break down.

• Boltzmann's equation and the canonical form

There is Boltzmann's equation:

$$\frac{\partial f(k, r)}{\partial t} + \nabla_r \cdot (f(k, r) \mathbf{v}_G(k)) + \text{collision integral} = 0 \quad (2.4)$$

where $f(k, r)$ is the local density distribution of phonon states. The 2nd term is due to the drift of phonons in varying spatial density, the collision integral comes from local transitions between different phonon states, which is the combination of a variety of phonon-defect, phonon-phonon scattering mechanisms.

For a steady state,

$$\frac{\partial f(k, r)}{\partial t} = 0 \quad (2.5)$$

and

$$\nabla_r \cdot (f(k, r) \mathbf{v}_G(k)) = \frac{\partial f(k, r)}{\partial T} \mathbf{v}_G(k) \cdot \nabla_r T \quad (2.6)$$

The exact solution of Eq(2.4) is fairly difficult, so people use variational methods to get approximate solutions.¹ Here it suffices to sketch the basics of the problem. It is convenient to cast Eq(2.4) into a canonical form. Define

$$f(k) = f_0(k) - \Phi_k \frac{\partial f_0(k)}{\partial E_k} \quad (2.7)$$

Since phonons are Bosons with zero chemical potential, in thermal equilibrium there is

$$f_0(k, r) = \frac{1}{\exp(\beta E_k) - 1} \quad (2.8)$$

and so

$$\frac{\partial f_0(k)}{\partial E_k} = -\frac{f_0(k)(1 + f_0(k))}{k_B T} \quad (2.9)$$

Take elastic phonon-defect scattering for example. Here a phonon state k could be scattered into another state k' of the same energy by the defect, with positive transition rate $\mathcal{L}(k, k')$. From the principle of microscopic reversibility, and by verification, there should be

$$\mathcal{L}(k, k') = \mathcal{L}(k', k) \quad (2.10)$$

Then obviously, for a steady state,

$$\begin{aligned} \frac{\partial f(k, r)}{\partial T} \mathbf{v}_G(k) \cdot \nabla_r T &= \text{--collision integral} \\ &= - \int (f(k) - f(k')) \mathcal{L}(k, k') dk' \end{aligned}$$

¹for details see *Electrons and Phonons*, Ziman, 1960

$$\begin{aligned}
&= -\frac{1}{k_B T} \int (\Phi_k - \Phi_{k'}) f_0(k) (1 + f_0(k)) \mathcal{L}(k, k') dk' \\
&= \frac{1}{k_B T} \int (\Phi_{k'} - \Phi_k) \mathcal{P}(k, k') dk'
\end{aligned} \tag{2.11}$$

where we have defined

$$\mathcal{P}(k, k') = f_0(k) (1 + f_0(k)) \mathcal{L}(k, k') \tag{2.12}$$

and in the derivation we have use the fact that since $E_k = E_{k'}$, they have the same occupancy in equilibrium. This is the so called *canonical form* of the Boltzmann's equation.

This equation must be satisfied for all k 's. If we define X_k to be what's on the left of Eq(2.11), it can be written as

$$X_k = P\Phi_k \tag{2.13}$$

where P is a linear operator, and X_k is a known quantity, once the dispersion curve is known. Further examination will show that \mathcal{P} is a Hermitian operator too. Solution of the inhomogenous integral equation Eq(2.13) can be sought by minimizing the functional

$$\frac{\langle \Phi_k, P\Phi_k \rangle}{\langle \Phi_k, X_k \rangle^2} \propto \frac{1}{\kappa} \tag{2.14}$$

where we have defined the inner product

$$\langle A_k, B_k \rangle = \int A_k B_k dk \tag{2.15}$$

The physical meaning of Eq(2.14) being that nature will facilitate heat conduction, thus maximizing the rate of entropy production, under the constraint of maintaining steady state.

• Relaxation time approximation

One of the most common approximations we make to Eq(2.4) is the *collision time approximation*, where we approximate the collision integral by

$$\text{collision integral} = -\frac{f(k) - f_0(k)}{\tau(k)} = -\frac{\tilde{f}(k)}{\tau(k)} \tag{2.16}$$

irrespective of the distribution of other phonon states. Then at steady state,

$$\frac{\partial f(k, r)}{\partial T} \mathbf{v}_G(k) \cdot \nabla_r T = -\frac{\tilde{f}(k)}{\tau(k)} \quad (2.17)$$

So the heat current is

$$\begin{aligned} \mathbf{J}_k^q &= \hbar \omega_k \tilde{f}(k) \mathbf{v}_G(k) \\ &= \hbar \omega_k \left(-\tau(k) \frac{\partial f(k, r)}{\partial T} \mathbf{v}_G(k) \cdot \nabla_r T \right) \mathbf{v}_G(k) \end{aligned} \quad (2.18)$$

But since

$$\mathbf{J}^q = \sum_k \mathbf{J}_k^q = -\hat{\kappa} \nabla_r T$$

there is

$$\begin{aligned} \hat{\kappa} &= \sum_k \tau(k) \frac{\partial \hbar \omega_k f(k, r)}{\partial T} \mathbf{v}_G(k) \mathbf{v}_G(k) \\ &= \sum_k \tau(k) C_v(k) \mathbf{v}_G(k) \mathbf{v}_G(k) \end{aligned} \quad (2.19)$$

where

$$C_v(k) = \frac{\hbar^2 \omega_k^2}{k_B T^2} f_0(k) (1 + f_0(k)) \quad (2.20)$$

is the heat capacity of phonon-state k .

• Isotope Scattering

Suppose an isotope with extra mass ΔM is situated at (LS) , then

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{V} \quad (2.21)$$

$$\hat{V} = \frac{\hat{p} \binom{L}{S}^2}{2(M_S + \Delta M)} - \frac{\hat{p} \binom{L}{S}^2}{2M_S} = \frac{-\Delta M}{2M_S^2} \hat{p} \binom{L}{S}^2 \quad (2.22)$$

And so, from Eq(1.57), there is

$$\begin{aligned}
\hat{V} &= -\frac{\Delta M}{2M_S^2} \left(\sum_k -i\sqrt{\frac{\hbar M_S \omega_k}{2N}} \mathbf{e}^k(S) \exp(i\mathbf{q} \cdot \mathbf{R}(L)) (\hat{a}_k - \hat{a}_{-k}^\dagger) \right) \\
&\quad \cdot \left(\sum_{k'} i\sqrt{\frac{\hbar M_S \omega_{k'}}{2N}} \mathbf{e}^{k'}(S)^* \exp(-i\mathbf{q}' \cdot \mathbf{R}(L)) (\hat{a}_{k'}^\dagger - \hat{a}_{-k'}) \right) \\
&= -\frac{\Delta M}{2M_S^2} \frac{\hbar M_S}{2N} \sum_{kk'} \mathbf{e}^k(S) \cdot \mathbf{e}^{k'}(S)^* \exp(i(\mathbf{q} - \mathbf{q}') \cdot \mathbf{R}(L)) \\
&\quad \sqrt{\omega_k \omega_{k'}} (\hat{a}_k \hat{a}_{k'}^\dagger - \hat{a}_k \hat{a}_{-k'} - \hat{a}_{-k}^\dagger \hat{a}_{k'}^\dagger + \hat{a}_{-k}^\dagger \hat{a}_{-k'})
\end{aligned} \tag{2.23}$$

Since energy is conserved in 1st-order PT, the $\hat{a}_k \hat{a}_{-k'}, \hat{a}_{-k}^\dagger \hat{a}_{k'}^\dagger$ terms won't survive, also there must be

$$\omega_k = \omega_{k'} \tag{2.24}$$

So,

$$\begin{aligned}
\hat{V} &= -\sum_{kk'} \frac{\hbar \Delta M \omega_k}{4NM_S} \{ \mathbf{e}^k(S) \cdot \mathbf{e}^{k'}(S)^* \exp(i(\mathbf{q} - \mathbf{q}') \cdot \mathbf{R}(L)) \hat{a}_k \hat{a}_{k'}^\dagger \\
&\quad + \mathbf{e}^{k*}(S) \cdot \mathbf{e}^{k'}(S) \exp(-i(\mathbf{q} - \mathbf{q}') \cdot \mathbf{R}(L)) \hat{a}_k^\dagger \hat{a}_{k'} \}
\end{aligned} \tag{2.25}$$

Now, because we are mostly interested in the scattering by a random distribution of isotope defects, we are considering the problem,

$$\begin{aligned}
\hat{V}_{tot} &= -\sum_{kk'} \left(\sum_i \mathbf{A}^k(S) \cdot \mathbf{A}^{k'}(S)^* \exp[i(\mathbf{q} - \mathbf{q}') \cdot \mathbf{R}(L_i)] \right) \hat{a}_k \hat{a}_{k'}^\dagger \\
&\quad + \left(\sum_i \mathbf{A}^{k*}(S) \cdot \mathbf{A}^{k'}(S) \exp[-i(\mathbf{q} - \mathbf{q}') \cdot \mathbf{R}(L_i)] \right) \hat{a}_k^\dagger \hat{a}_{k'}
\end{aligned} \tag{2.26}$$

where

$$\mathbf{A}^k(S) = \sqrt{\frac{\hbar \Delta M \omega_k}{4NM_S}} \mathbf{e}^k(S) \tag{2.27}$$

For a specific scattering process, say, a phonon $k \rightarrow k'$, the matrix element is

$$\begin{aligned}
& \left| \langle n_k - 1, n_{k'} + 1 | \hat{V}_{tot} | n_k, n_{k'} \rangle \right|^2 \\
&= \left| 2 \sum_i \mathbf{A}^k(S) \cdot \mathbf{A}^{k'}(S)^* \exp(i(\mathbf{q} - \mathbf{q}') \cdot \mathbf{R}(L_i)) \right|^2 \\
& \left| \langle n_k - 1, n_{k'} + 1 | \hat{a}_k \hat{a}_{k'}^\dagger | n_k, n_{k'} \rangle \right|^2
\end{aligned} \tag{2.28}$$

Here a factor of 2 appears in the module because of the possible interchange of k, k' in Eq(2.26). Since L_i , the position of isotopes, are uncorrelated, the average is

$$4D \left| \mathbf{A}^k(S) \cdot \mathbf{A}^{k'}(S)^* \right|^2 n_k(n_{k'} + 1)$$

where D is the total number of defects. So the transition probability from k to other states is just, by Fermi's Golden rule,

$$W_{k,out} = \frac{2\pi}{\hbar} \sum_{k'} 4D \left| \mathbf{A}^k(S) \cdot \mathbf{A}^{k'}(S)^* \right|^2 n_k(n_{k'} + 1) \delta(\hbar\omega_k - \hbar\omega_{k'}) \tag{2.29}$$

For materials with T_d or higher point symmetry there can be a nice simplification, because then all vectors (x, y, z) belong in whole to a single irreducible representation Γ_{vec} of the point group, and

$$\begin{aligned}
& \sum_{k'} \left| \mathbf{A}^k(S) \cdot \mathbf{A}^{k'}(S)^* \right|^2 \\
&= \sum_{k', \alpha, \beta} A_\alpha^k(S) A_\alpha^{k'*}(S) A_\beta^{k*}(S) A_\beta^{k'}(S) \\
&= \sum_{k', \alpha, \beta} \frac{1}{h} \sum_{\{U\}} A_\alpha^k(S) A_\beta^{k*}(S) A_\alpha^{Uk'*}(S) A_\beta^{Uk'}(S) \\
&= \sum_{k', \alpha, \beta} A_\alpha^k(S) A_\beta^{k*}(S) \frac{1}{h} \left(\sum_{\{U\}} D_{\alpha\alpha'}^{*\Gamma_{vec}}(U) D_{\beta\beta'}^{\Gamma_{vec}}(U) \right) A_{\alpha'}^{k'*}(S) A_{\beta'}^{k'}(S) \\
&= \sum_{k', \alpha, \beta} A_\alpha^k(S) A_\beta^{k*}(S) \frac{1}{h} \frac{h}{d_{vec}} \delta_{\alpha\beta} \delta_{\alpha'\beta'} A_{\alpha'}^{k'*}(S) A_{\beta'}^{k'}(S) \\
&= \sum_{k'} \frac{1}{3} \left| \mathbf{A}^k(S) \right|^2 \left| \mathbf{A}^{k'}(S) \right|^2
\end{aligned} \tag{2.30}$$

For monoatomic crystals, $\mathbf{e}^k(S)$ is a unit vector, so

$$\frac{1}{3} |\mathbf{A}^k(S)|^2 |\mathbf{A}^{k'}(S)|^2 = \frac{1}{3} \left(\frac{\hbar \Delta M \omega_k}{4NM_S} \right)^2 \quad (2.31)$$

If it's not, we can approximate it by

$$\frac{1}{3r^2} \left(\frac{\hbar \Delta M \omega_k}{4NM_S} \right)^2$$

• Exact Solution in Debye Model

Let's assume there is a monoatomic crystal with simple dispersion relations of isotropic elastic medium. Let the sound velocity of transverse and longitudinal wave be c_t , c_l respectively, and the transverse branch is doubly degenerate. In this case,

$$\begin{aligned} & \left. \frac{dn_k}{dt} \right)_{\text{colli}} \\ = & W_{k,in} - W_{k,out} \\ = & \frac{8\pi D}{3\hbar} \sum_{k'} \left(\frac{\hbar \Delta M \omega_k}{4NM_S} \right)^2 [n_{k'}(n_k + 1) - n_k(n_{k'} + 1)] \delta(\hbar\omega_k - \hbar\omega_{k'}) \\ = & \frac{8\pi D}{3\hbar} \left(\frac{\hbar \Delta M \omega_k}{4NM_S} \right)^2 (\bar{n}_k - n_k) \sum_{k'} \delta(\hbar\omega_k - \hbar\omega_{k'}) \end{aligned} \quad (2.32)$$

In the last step we have replaced $n_{k'}$ by the average occupation number \bar{n}_k , which is like collision-time approximation where we ignore the possibility of “group deficiency”.

Inside the summation is just the density of states, which we can replace by integral

$$\begin{aligned} & \sum_{k'} \delta(\hbar\omega_k - \hbar\omega_{k'}) \\ = & \sum_{\text{branches}} \int \frac{\Omega 4\pi k^2 dk}{8\pi^3} \delta(\hbar\omega_k - \hbar\omega_{k'}) \\ = & \frac{\Omega}{2\pi^2} \frac{1}{\hbar} \omega_k^2 \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \end{aligned} \quad (2.33)$$

Combining our results, we have

$$\begin{aligned}
& \left. \frac{dn_k}{dt} \right)_{\text{colli}} \\
= & \frac{8\pi D}{3\hbar} \left(\frac{\hbar \Delta M \omega_k}{4NM_S} \right)^2 \frac{\Omega}{2\pi^2} \frac{1}{\hbar} \omega_k^2 \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) (\bar{n}_k - n_k) \\
= & \frac{D\Omega(\Delta M)^2 \omega_k^4}{12N^2 M^2 \pi} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) (\bar{n}_k - n_k) \tag{2.34}
\end{aligned}$$

It's not surprising that we recover the ubiquitous w^4 laws again, which conforms to the general long-wave *Rayleigh* scattering result of a ball ($ka \ll 1$) stuck in an infinite elastic medium, with higher density.

Chapter 3

3-Phonon Process

In the expansion Eq(1.2) we have ignored the cubic term in harmonic approximation

$$\hat{V}_3 = \frac{1}{6} \Phi_{mm'm''} \hat{u}_m \hat{u}_{m'} \hat{u}_{m''} \quad (3.1)$$

Express it fully in normal coordinates using Eq(1.56), it becomes

$$\begin{aligned} \hat{V}_3 &= \frac{1}{6} \left(\frac{\hbar}{2N} \right)^{\frac{3}{2}} \sum_{\{LS\alpha\}} \Phi_{\alpha\alpha'\alpha''} \binom{LL'L''}{SS'S''} (M_S M_{S'} M_{S''})^{-1/2} \sum_{kk'k''} \frac{e_{\alpha}^k(S) e_{\alpha'}^{k'}(S') e_{\alpha''}^{k''}(S'')}{(\omega_k \omega_{k'} \omega_{k''})^{1/2}} \\ &\quad \exp \left(i[\mathbf{q} \cdot \mathbf{R}(L) + \mathbf{q}' \cdot \mathbf{R}(L') + \mathbf{q}'' \cdot \mathbf{R}(L'')] \right) (\hat{a}_k + \hat{a}_{-k}^{\dagger}) (\hat{a}_{k'} + \hat{a}_{-k'}^{\dagger}) (\hat{a}_{k''} + \hat{a}_{-k''}^{\dagger}) \end{aligned} \quad (3.2)$$

Since the summation is irrelevant with respect to the translation of $(LL'L'')$ as whole, it vanishes unless

$$\mathbf{q} + \mathbf{q}' + \mathbf{q}'' = 0 \quad (3.3)$$


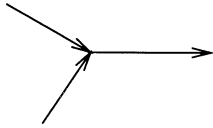
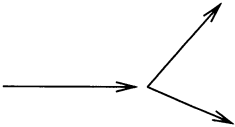

or

$$\mathbf{q} + \mathbf{q}' + \mathbf{q}'' = \mathbf{G} \quad (3.4)$$

where \mathbf{G} is a reciprocal lattice vector. (3.3) is called *normal* or *N-process*, (3.4) is called *Umklapp* or *U-process*.

Multiplying out the terms in Eq(3.2), we have

$$\begin{aligned} & \hat{a}_k \hat{a}_{k'} \hat{a}_{k''}^{[1]} + \hat{a}_{-k}^\dagger \hat{a}_{k'} \hat{a}_{k''}^{[2]} + \hat{a}_k \hat{a}_{-k'}^\dagger \hat{a}_{k''}^{[3]} + \hat{a}_{-k}^\dagger \hat{a}_{-k'}^\dagger \hat{a}_{k''}^{[4]} + \\ & \hat{a}_k \hat{a}_{k'} \hat{a}_{-k''}^\dagger^{[5]} + \hat{a}_{-k}^\dagger \hat{a}_{k'} \hat{a}_{-k''}^\dagger^{[6]} + \hat{a}_k \hat{a}_{-k'}^\dagger \hat{a}_{-k''}^\dagger^{[7]} + \hat{a}_{-k}^\dagger \hat{a}_{-k'}^\dagger \hat{a}_{-k''}^\dagger^{[8]} \end{aligned} \quad (3.5)$$

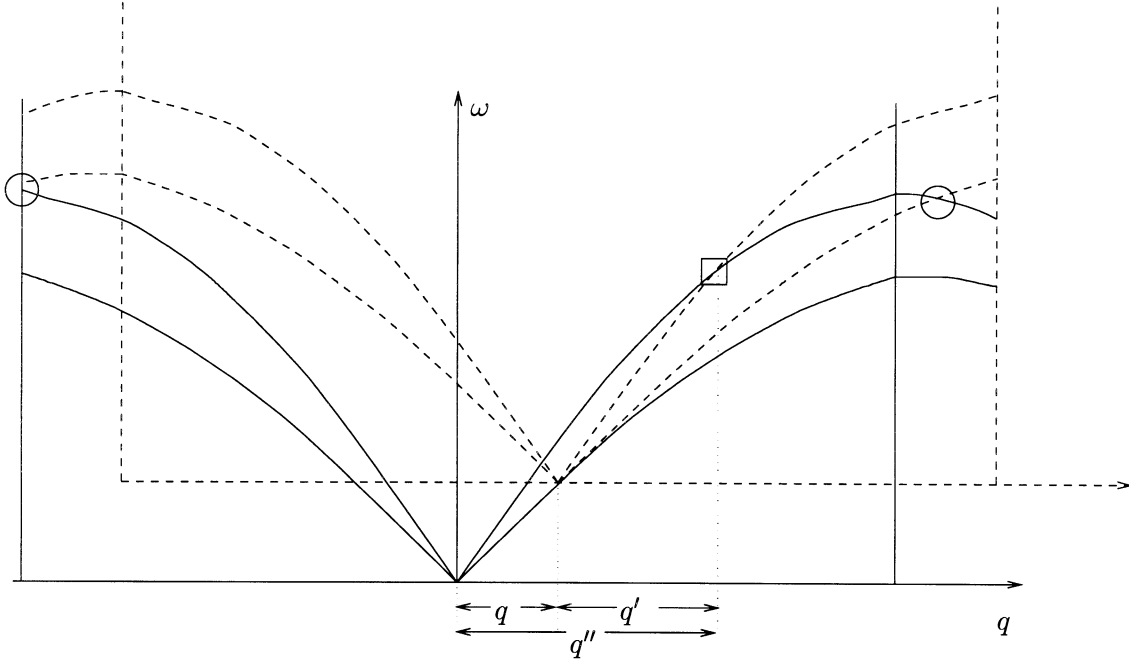
Term number	Graphic Representation
1	
2,3,5	
4,6,7	
8	

If two of the \mathbf{q} 's are fixed, there is only one possible value for the third, either through (3.3)

or (3.4). The conservation of energy further requires that

$$\pm \omega_k \pm \omega_{k'} \pm \omega_{k''} = 0 \quad (3.6)$$

Due to this reason, the terms [1],[8] in Eq(3.5) are not possible in first order process.



Construction for 3-phonon process.
circle: $t+t=l$. square: $t+l=l$

The solutions of Eq(3.6) could be sought from the following graphical construction: First we draw the dispersion curve. If we want to investigate possible interactions concerning (\mathbf{q}, ω) , we just translate the whole dispersion curve onto (\mathbf{q}, ω) , and search for its possible crossing with the old curve: the crossing point on the old coordinates would be (\mathbf{q}'', ω'') , on the new coordinate would be (\mathbf{q}', ω') . Note that the crossing point could be beyond 1st Brillouin zone: if it does, then it's *U-process*, otherwise it's *N-process*. By careful observations of these constructions on a simple Debye model, we arrive at only two possible types of processes:

$$transverse + transverse \rightarrow longitudinal \quad (3.7)$$

$$transverse + longitudinal \rightarrow longitudinal \quad (3.8)$$

For multi-atom systems, we would have $3r - 3$ optical branches. It's generally believed that optical phonons doesn't contribute much to the thermal conductivity because they have less group velocity. Also only one type of process is allowed for Debye model:

$$acoustic + acoustic \rightarrow optical \quad (3.9)$$

3-phonon process constitute the main part of thermal resistivity in a perfect crystal. It is also believed that the *Normal* process is the main part of it. However, if there are *only* N-processes in the system, the thermal resistivity will be infinite, since then the quantity

$$\mathbf{Q} = \sum_k \mathbf{q} f(k) \quad (3.10)$$

would be conserved always. That means once we establish $\mathbf{Q} \neq 0$ in the system, it will continue to be so without the ability to recover true statistical equilibrium, thus having finite heat current (best seen in Debye model) without constant thermal gradient, which implies infinite thermal conductivity. It follows then, that the *Umklapp* process plays a vital role.

We can approximate the thermal conductivity at low temperatures ($T \ll \Theta$) by the following argument: in order for Eq(3.4) to hold, one of the phonon \mathbf{q} must exceed $\mathbf{G}/3$, while smaller than $\mathbf{G}/2$ in order to stay in the 1st B.Z. Since the Debye temperature Θ corresponds to \mathbf{G} , it follows that the probability of existence of such phonon excitation is proportional to

$$\exp(-\gamma\Theta/T) \quad (3.11)$$

with γ between $1/3$ and $2/3$, for the *Umklapp* process to be possible. And thus the thermal conductivity holds the same scaling.