PHYS 342/555
Condensed Matter in a Nutshell

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Lecture room 314 Nielsen

Chapter 7: Phonons

Lecture in pdf format will be available at:

http://www.phys.utk.edu

Our goal is to find the frequency of an elastic wave in terms of the wavevector that describes the wave and in terms of the elastic constants.

Longitudinal and transverse waves. When a wave propagates along one of the high symmetry directions ([100], [110], and [111]), entire planes of atoms move in phase with displacement either parallel or perpendicular to the direction of the wavevector.
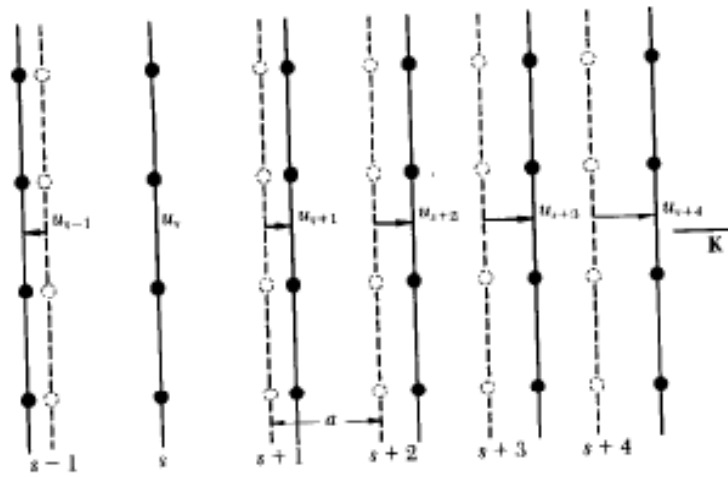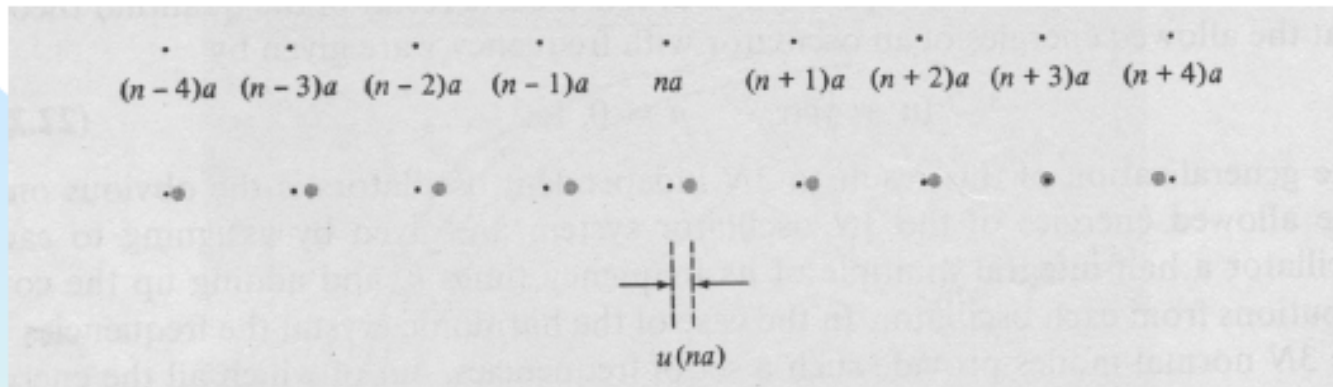
Longitudinal phonon wave
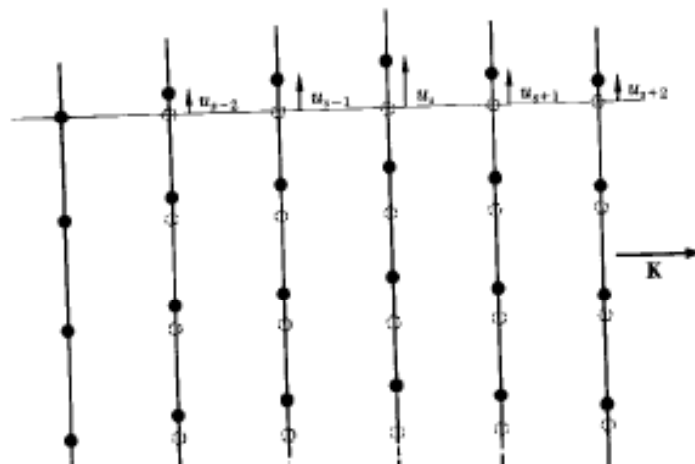
Transverse phonon wave

Normal modes of a 1-D monatomic Bravias Lattice

$(n-4)a$ $(n-3)a$ $(n-2)a$ $(n-1)a$ na $(n+1)a$ $(n+2)a$ $(n+3)a$ $(n+4)a$
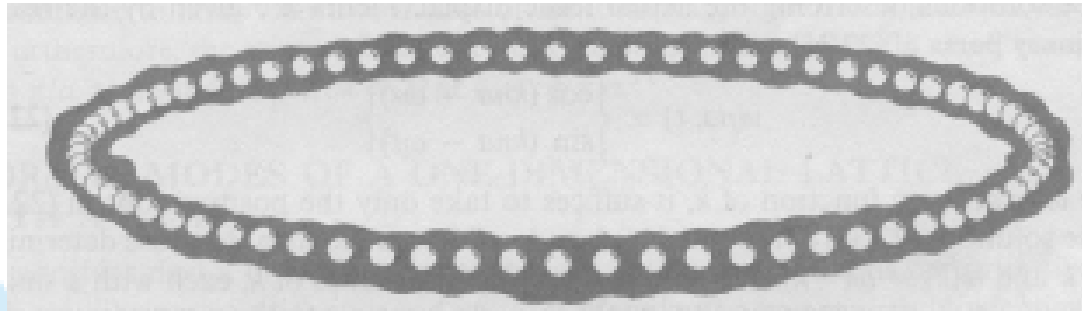
$u(na)$

Consider a set of ions M separated by a distance a,

$\vec{R} = na$ for integral n. Let $u(na)$ be the displacement.

Assuming only neighboring ions interact, we have

$$U^{harm} = \frac{1}{2}C\sum_n \left[u(na) - u([n+1]a)\right]^2,$$

Newton's second law $F = Ma$ or

$$M\frac{du(na)}{dt^2} = -\frac{\partial U^{harm}}{\partial u(na)} = -C\left[2u(na) - u([n-1]a) - u([n+1]a)\right]$$

If the chain of ions has number, N, and N is large, we can join the

two remote ends of the chain back together with

$u([N+1]a) = u(a); u(0) = u(Na).$

This is called Born-von Karman (periodic) boundary condition.

We seek solution of the form: $u(na, t) \propto \exp[i(kna - \omega t)]$.

The periodic condition requires $\exp(ikNa) = 1$,

or $kNa = 2\pi n$, where n is integer, or $k = \dfrac{2\pi n}{Na}$

There are just N values of k yield distinct solutions.

$$M\omega^2 e^{i(kna-\omega t)} = -C\left[2 - e^{-ika} - e^{ika}\right]e^{i(kna-\omega t)} = -2C(1-\cos ka)e^{i(kna-\omega t)},$$

Therefore we have

$$\omega(k) = \sqrt{\frac{2C(1-\cos ka)}{M}} = 2\sqrt{\frac{C}{M}}\,|\sin\frac{1}{2}ka\,|$$
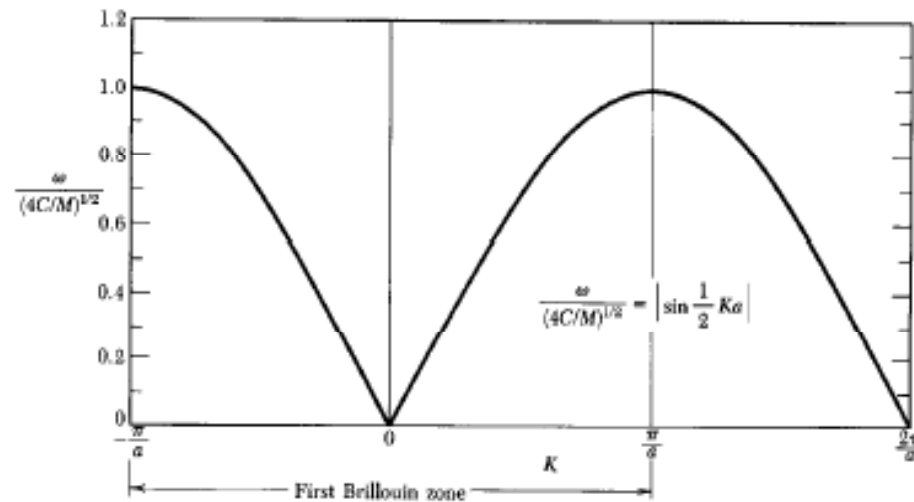
The solutions describing the actual ionic displacements are given by

$$u(na,t) \propto \begin{Bmatrix} \cos(kna - \omega t) \\ \sin(kna - \omega t) \end{Bmatrix}$$

Since ω is an even founction of k, solutions determined by k and $-\omega(k)$ are identical to those determined by $-k$ and $\omega(k) = \omega(-k)$. There are N distinct values of k, each with a unique frequency $\omega(k)$, so we have $2N$ independent solutions.
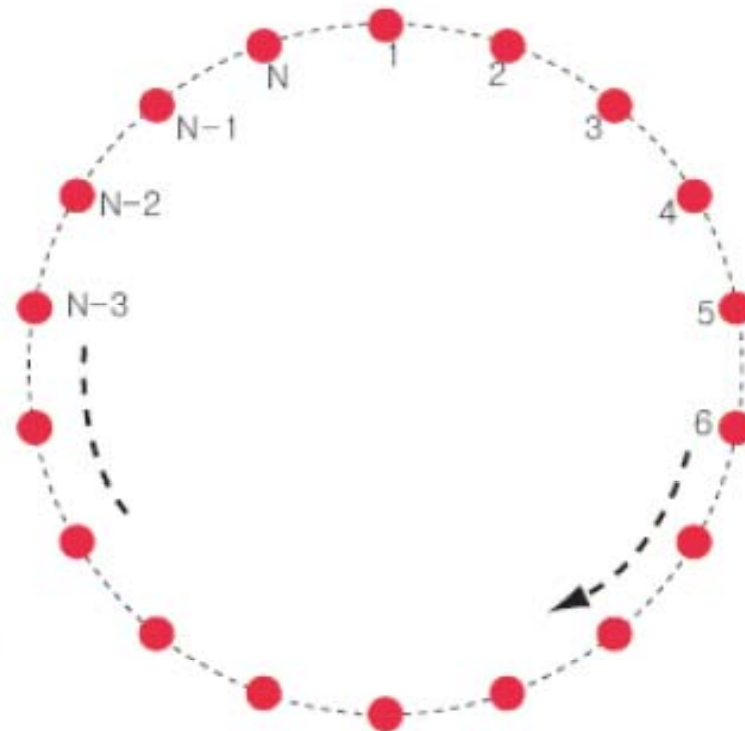
First Brillouin zone

$$\frac{\omega}{(4C/M)^{1/2}} = \left| \sin \frac{1}{2} Ka \right|$$

First Brillouin zone

The boundary of the first Brillouin zone lies at $k = \pm \pi / a$. The slope of ω versus k is zero at the zone boundary:
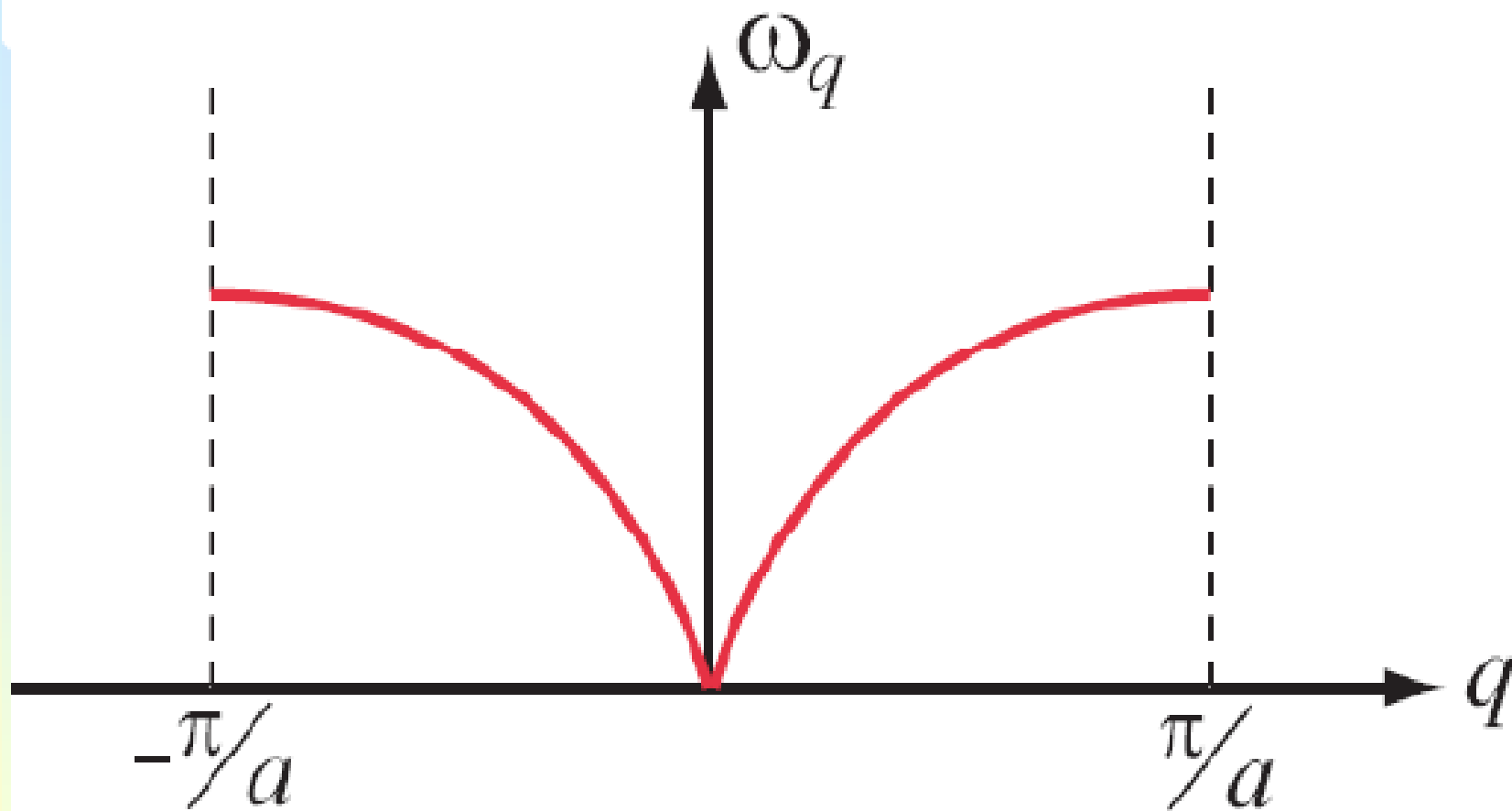
$$d\omega^2 / dk = (2Ca/M)\sin ka = 0.$$

An arbitrary motion of the chains is determined by specifying the N initial positions and N initial velocities of the ions. Since these can always be fit with a linear combination of the $2N$ independent solutions, we have found a complete solution to the problem.
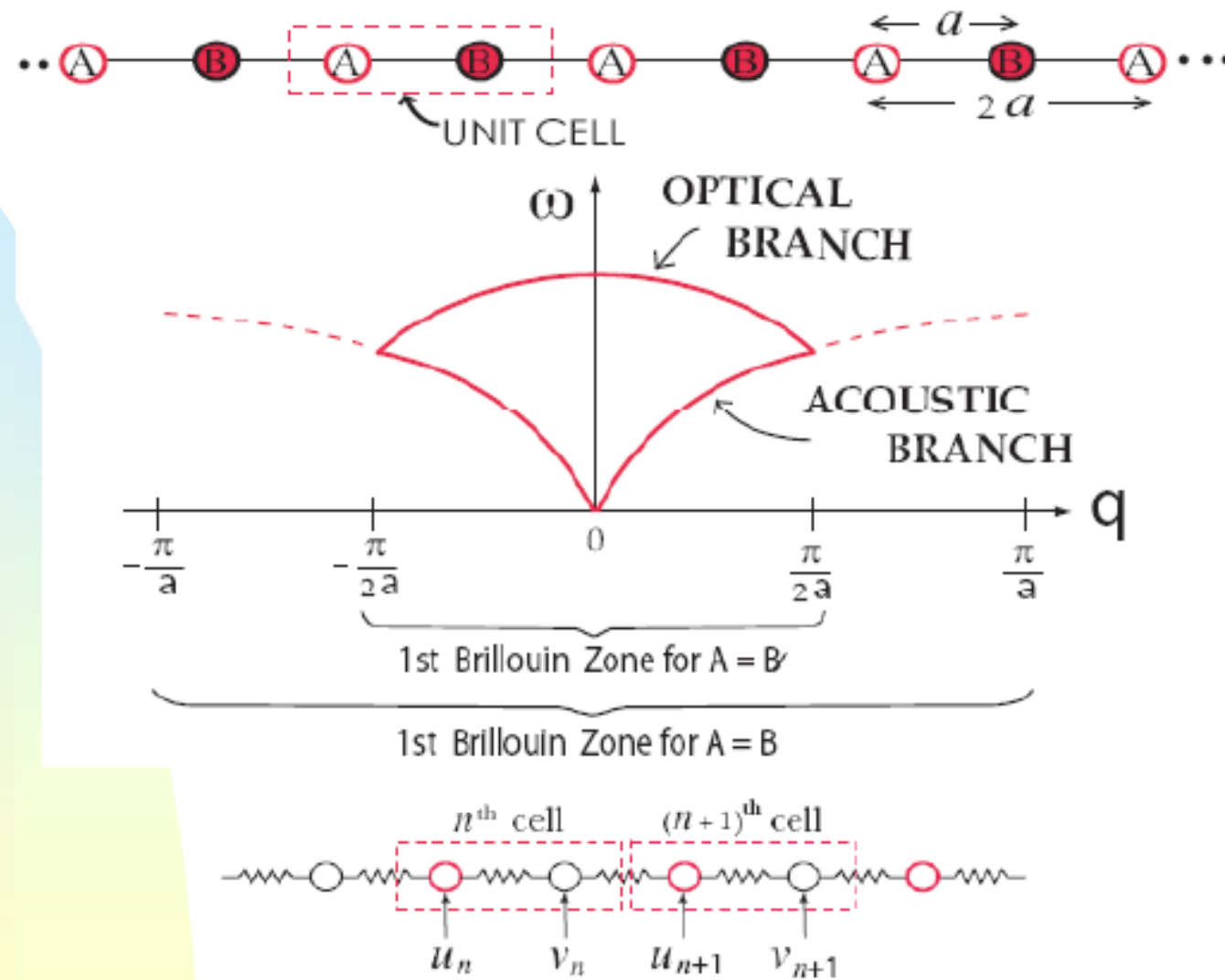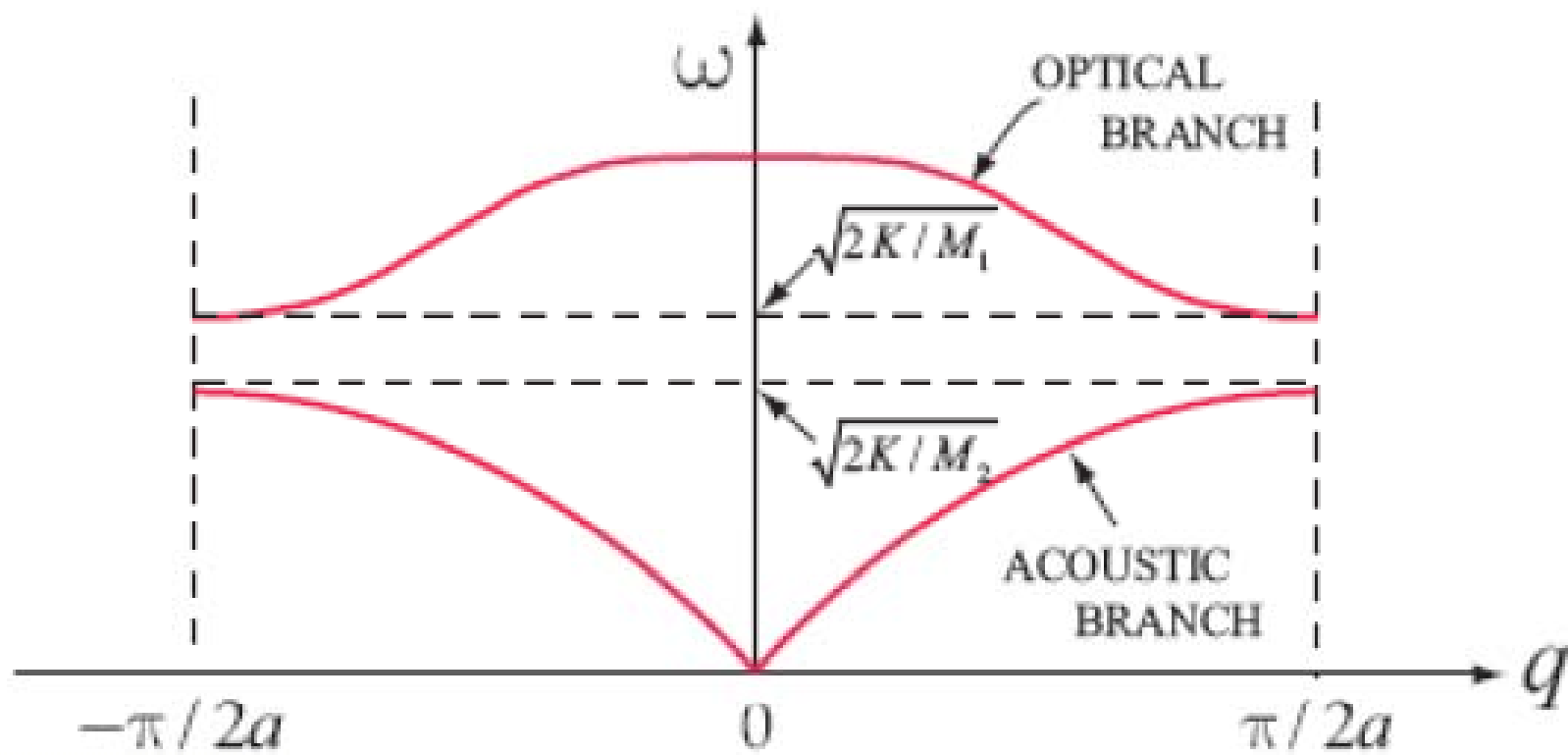
Fig. 2.1. Linear chain of N identical atoms of mass M

2.4 Optical Modes

UNIT CELL

ω OPTICAL BRANCH

ACOUSTIC BRANCH

$-\dfrac{\pi}{a}$ $\qquad$ $-\dfrac{\pi}{2a}$ $\qquad$ 0 $\qquad$ $\dfrac{\pi}{2a}$ $\qquad$ $\dfrac{\pi}{a}$ $\qquad$ q

1st Brillouin Zone for A = B′

1st Brillouin Zone for A = B

n^{th} cell $\qquad$ $(n+1)^{th}$ cell

u_n $\qquad$ v_n $\qquad$ u_{n+1} $\qquad$ v_{n+1}
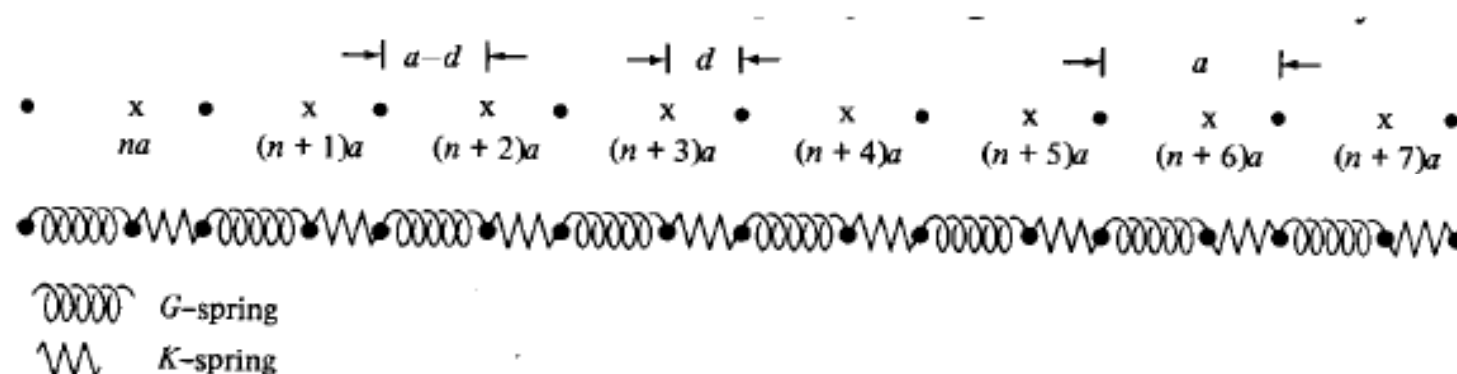
Normal modes of two atoms per primitive basis

The harmonic potential energy is:

$$U^{harm} = \frac{1}{2}K\sum_n\left[u_1(na)-u_2(na)\right]^2 + \frac{1}{2}G\sum_n\left[u_2(na)-u_1([n+1]a)\right]^2$$

where $u_1(na)$ is the displacement around na, $u_2(na)$ the displacement around $na+d$. If $d \le a/2, K \ge G$.

$$M\frac{du_1(na)}{dt^2} = -\frac{\partial U^{harm}}{\partial u_1(na)} = -K\left[u_1(na)-u_2(na)\right]-G\left[u_1(na)-u_2([n-1]a)\right]$$

$$M\frac{du_2(na)}{dt^2} = -\frac{\partial U^{harm}}{\partial u_2(na)} = -K\left[u_2(na)-u_1(na)\right]-G\left[u_2(na)-u_1([n+1]a)\right]$$

We seek solution

$$u_1(na) = \varepsilon_1 \exp[i(kna - \omega t)]$$

$$u_2(na) = \varepsilon_2 \exp[i(kna - \omega t)]$$

Here ε_1 and ε_1 are constants that determines the relative amplitude and phase of the vibration of the ions within each primitive cell.

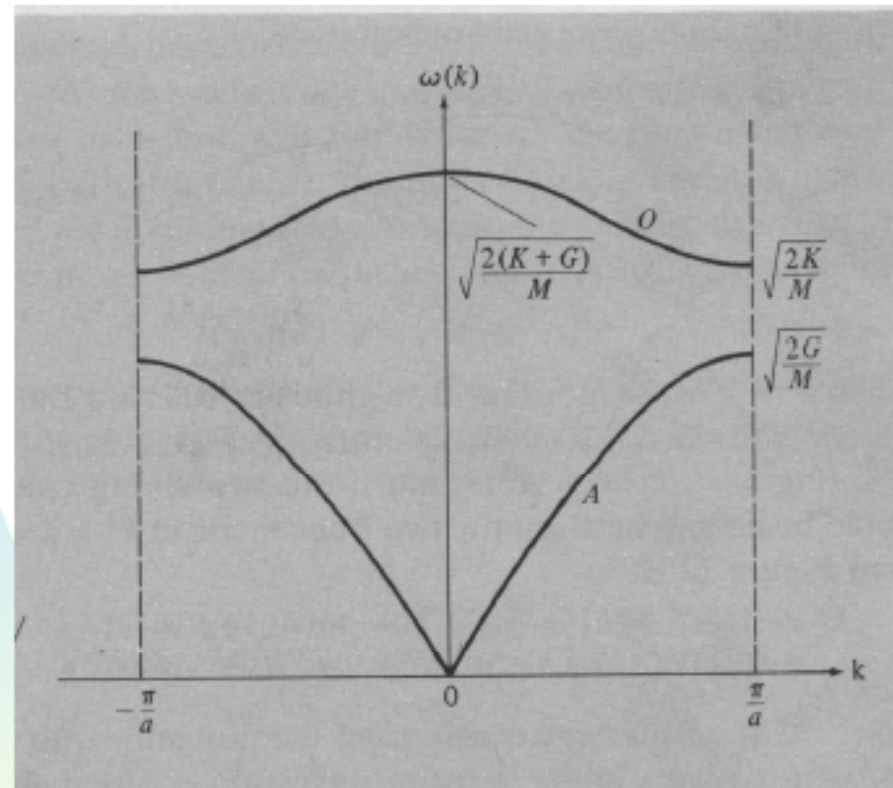$$[M\omega^2 - (K+G)]\varepsilon_1 + (K + Ge^{-ika})\varepsilon_2 = 0$$

$$[M\omega^2 - (K+G)]\varepsilon_2 + (K + Ge^{-ika})\varepsilon_1 = 0$$

This pair of homogeneous equations will have a solution, if the determinant of the coefficients vanishes:

$$[M\omega^2 - (K+G)]^2 - |K + Ge^{-ika}|^2 = 0$$

Two solutions: $\omega^2 = \dfrac{K+G}{M} \pm \dfrac{1}{M}\sqrt{K^2 + G^2 + 2KG\cos ka}$

with $\dfrac{\varepsilon_1}{\varepsilon_2} = \mp\dfrac{K + Ge^{-ika}}{|K + Ge^{-ika}|}$

$\omega(k)$

$\sqrt{\dfrac{2(K+G)}{M}}$

$\sqrt{\dfrac{2K}{M}}$

$\sqrt{\dfrac{2G}{M}}$

O

A

$-\dfrac{\pi}{a}$

0

$\dfrac{\pi}{a}$

k

For each of the N values of k there are thus two solutions, leading to a total of $2N$ normal modes. The two ω vs k curves are two branches of the dispersion relation. Acoustic and optical branches.

Case 3 $K \gg G$ To leading order in G/K we have

$$\omega = \sqrt{\frac{2K}{M}}[1 + O(G/K)], \varepsilon_1 \approx -\varepsilon_2$$

$$\omega = \sqrt{\frac{2G}{M}}\left|\sin\frac{1}{2}ka\right|[1 + O(G/K)], \varepsilon_1 \approx \varepsilon_2$$

The optical branch now has a frequency that is independent of k, to leading order in G/K, and equal to the vibrational frequency of a single diatomic molecule composed of two mass M ions connected by a spring K. The acoustic branch is just that for a linear chain of atoms of mass $2M$ coupled by the weak spring G.

An acoustic mode is one in which all ions within a primitive cell move essentially in phase and the dynamics are dominated by the interaction between cells; an optical mode is one in which the ions within each primitive cell are executing molecular vibratory mode.

Case 4 $K = G$

In this case we are really dealing with a monatomic Bravais lattice of lattice constant $a/2$.

Optical mode

Acoustical mode
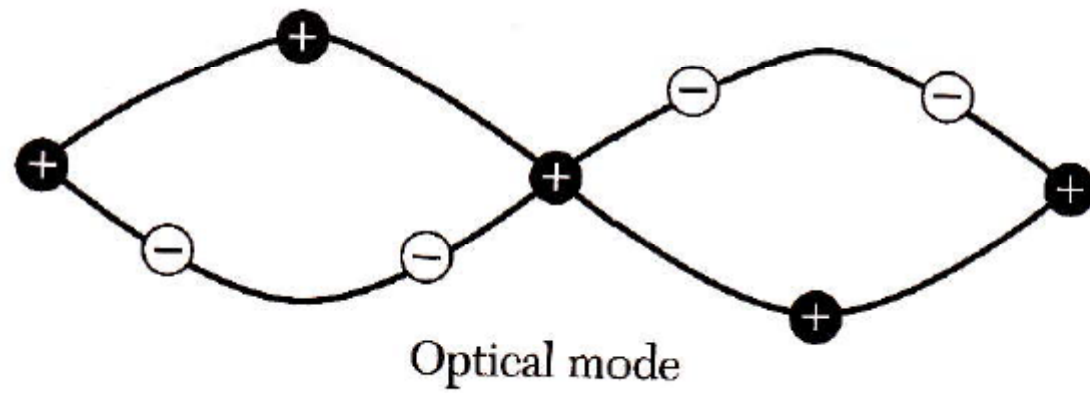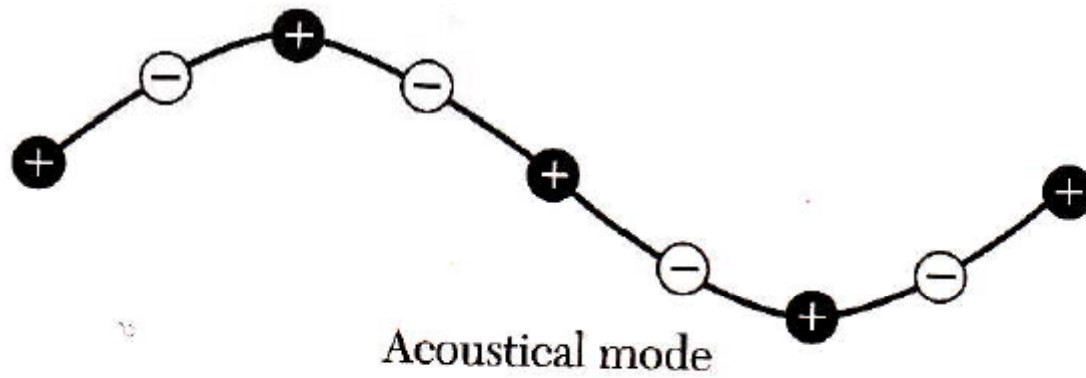
Consider a longitudinal wave

$$u_s = u\cos(\omega t - sKa)$$

which propagates in a monoatomic linear lattice of atoms of mass M, spacing a, and nearest neighbor interaction C.

(a) Show that the total energy of the wave is

$$E = \frac{1}{2}M\sum_s (du_s/dt)^2 + \frac{1}{2}C\sum_s (u_s - u_{s+1})^2$$

where s runs over all atoms.

(b) By substitution of u_s in this expression, show that the time-average total energy per atom is

$$\tfrac{1}{4}M\omega^2 u^2 + \tfrac{1}{2}C(1 - \cos Ka)u^2 = \tfrac{1}{2}M\omega^2 u^2 ,$$

where in the last step we have used the dispersion relation (9) for this problem.

Quantization of elastic waves

The energy of a lattice vibration is quantized and called a phonon. Thermal vibrations in crystals are thermally excited phonons with energy

$E = (n + \frac{1}{2})\hbar\omega$ when the mode is excited to quantum # n.

We can quantize the mean square phonon amplitude.

$u = u_0 \cos kx \cos \omega t$.

The kinetic energy density is $\frac{1}{2}\rho(\frac{\partial u}{\partial t})^2$, where ρ is the mass density. In a crystal of volume V, the average kinetic energy is:

$$\frac{1}{2}\rho V \omega^2 \langle \cos kx \sin \omega t \rangle^2 = \frac{1}{8}\rho V \omega^2 u_0^2 = \frac{1}{2}(n + \frac{1}{2})\hbar\omega,$$

ω should be positive

Phonon momentum

A phonon of wavevector $\vec{k}$ will interact with photons, neutrons & electrons as if it has momentum $\hbar\vec{k}$. Howver, a phonon does not carry physical momentum.

Physical moment: $p = M(d/dt)\sum u \exp(ikna) = M\dfrac{du}{dt}\dfrac{1-e^{ikNa}}{1-e^{ika}}$

Note that periodic condition requires $e^{ikNa} = 1$, this means $p = 0$. At $k = 0$, $p = MN(du/dt)$.

The crystal momentum. If the scattering of the phonon is inelastic, with creation of a phonon of wavevector $\vec{k}$, then
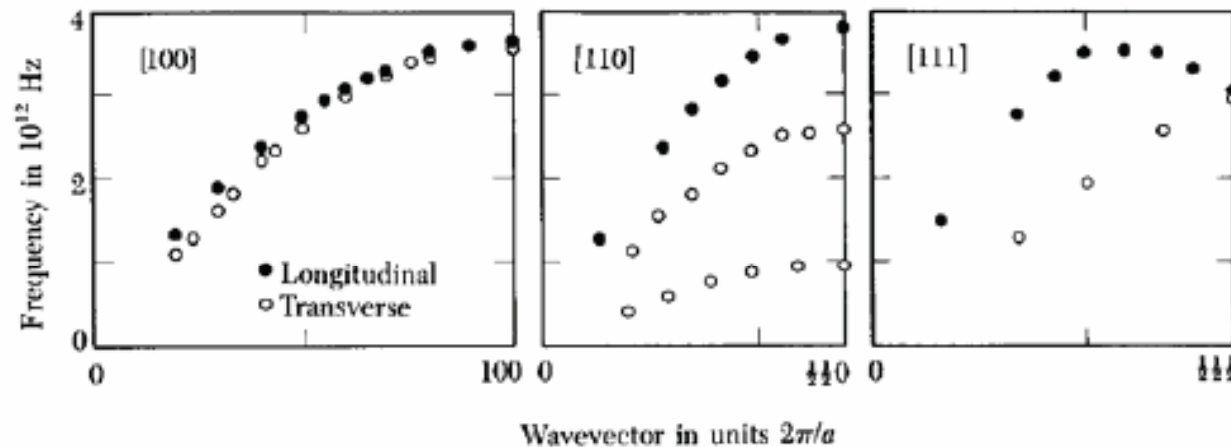
$$\vec{k}_f + \vec{k} = \vec{k}_i + \vec{Q}$$
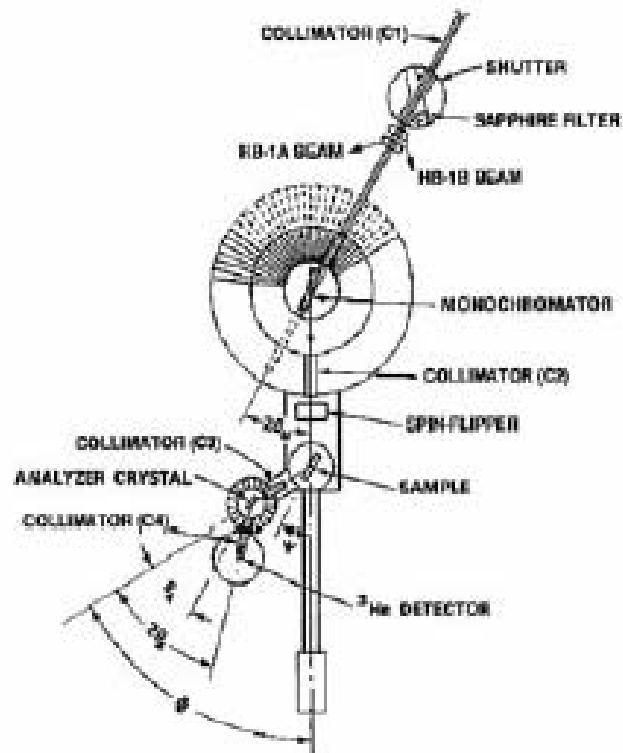
Inelastic scattering of neutrons by phonons

The kinetic energy of the incident neutron is $p^2/2M_n$, where M_n is the mass of the neutron. The momentum of neutron is given by $p = \hbar k = \hbar 2\pi/\lambda$. The conservation of energy requires

$$(\hbar k_i)^2/2M_n = (\hbar k_f)^2/2M_n \pm \hbar\omega,$$

where $\hbar\omega$ is the energy of the phonon created (+) or absorbed (-) in the process.

Wavevector in units $2\pi/a$

Triple Axis Spectrometer

Consider the normal modes of a linear chain in which the force constants between nearest-neighbor atoms are alternately C and $10C$. Let the masses be equal, and let the nearest-neighbor separation be $a/2$. Find $\omega(K)$ at $K = 0$ and $K = \pi / a$. Sketch in the dispersion relation by eye.

Phonons and thermal properties

In quantum theory of specific heat, the total thermal energy of the phonons can be written as the sum of the energies over all phonon modes: $U = \sum_k \sum_p \langle n_{k,p} \rangle \hbar \omega_{k,p}$,

Here $\langle n_{k,p} \rangle$ denotes the thermal equilibrium occupancy of phonons of wavevector k and polarization p. $\langle n_{k,p} \rangle$ is given by the Planck distribution function: $\langle n_{k,p} \rangle = \dfrac{1}{\exp(\hbar\omega/\tau) - 1}$.

The heat capacity is then defined as $C_V \equiv (\dfrac{\partial U}{\partial T})_V$.

catastrophe. Planck's new idea was to assume that the possible energies of the oscillators were quantized, *i.e.*, that oscillators of frequency ν could only have energy

$$\varepsilon_n = nh\nu \qquad n = 0, 1, 2, \ldots$$

where h was a new constant he introduced. Now known as *Planck's constant,* it was determined by fitting the theoretical curve to the experimental data. The average energy per oscillator was calculated from the Maxwell-Boltzmann distribution:

$$\bar{\varepsilon} = \frac{\sum\limits_{n} \varepsilon_n e^{-\varepsilon_n/kT}}{\sum\limits_{n} e^{-\varepsilon_n/kT}}$$

The denominator is called the *partition function,* and is often represented by Z. It is easily evaluated by summing the geometric series:

$$Z = \sum_{n=0}^{\infty} e^{-\varepsilon_n/kT} = \sum_{n=0}^{\infty} e^{-nx} = \frac{1}{1 - e^{-x}} \quad \text{where } x = \frac{h\nu}{kT}$$

The numerator can then be found from the denominator:

$$\sum_{n=0}^{\infty} nh\nu e^{-nx} = h\nu \left(-\frac{dZ}{dx}\right) = \frac{h\nu e^{-x}}{(1 - e^{-x})^2}$$

and the average energy per oscillator is seen to be

$$\bar{\varepsilon} = \frac{h\nu}{e^x - 1} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

Planck distribution function:

Consider a set of identical harmonic oscillators in thermal equilibrium.

The harmonic oscillator has an energy of $(n+\frac{1}{2})\hbar\omega$. Thus the fraction of the total number of oscillators in the nth quantum state is

$$\frac{N_n}{\sum\limits_{s=0}^{\infty} N_s} = \frac{\exp(-n\hbar\omega/\tau)}{\sum\limits_{s=0}^{\infty}\exp(-s\hbar\omega/\tau)}$$

The average excitation quantum # of an oscillator is:

$$\langle n \rangle = \frac{\sum s\exp(-n\hbar\omega/\tau)}{\sum \exp(-s\hbar\omega/\tau)} = \frac{1}{\exp(\hbar\omega/\tau)-1}$$

Normal mode enumeration

The energy of a collection of oscillators in thermal equilibrium

$$U = \sum_k \sum_p \frac{\hbar \omega_{k,p}}{\exp(\hbar \omega / \tau) - 1},$$ If crysal had $D_p(\omega)d\omega$ modes of
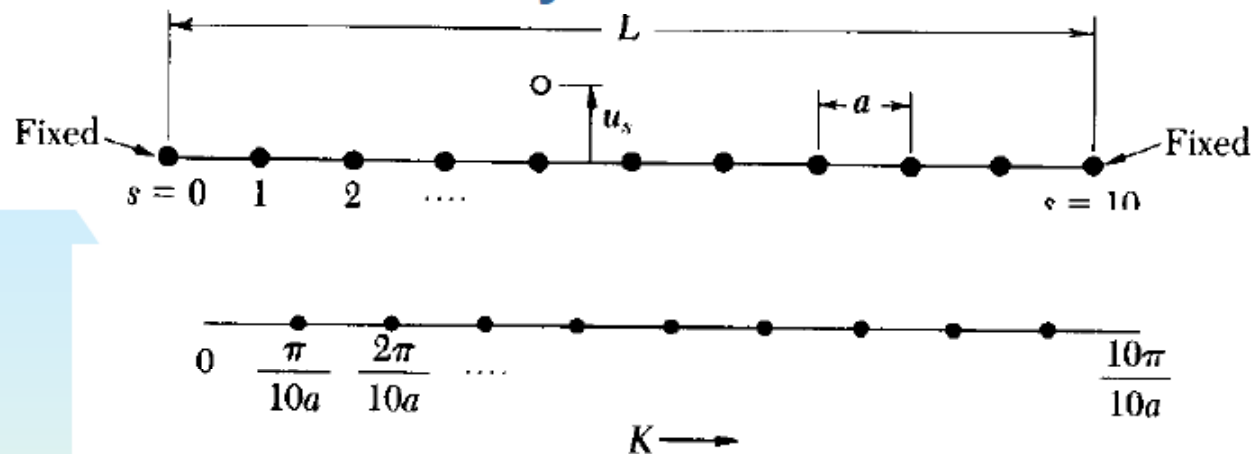
a given plarization p between ω and $\omega + d\omega$.

$$U = \sum_p \int d\omega D_p(\omega) \frac{\hbar \omega}{\exp(\hbar \omega / \tau) - 1},$$ where $D_p(\omega)$ is the number

of modes per unit frequency, called the density of modes or density of states.

Assume $x = \hbar \omega / k_B T$. Then $\partial U / \partial T$

$$C_{lat} = k_B \sum_p \int d\omega D_p(\omega) \frac{x^2 \exp(x)}{[\exp(x) - 1]^2}.$$

Density of states in 1D

If each normal vibrational mode of polarization p has the form of a standing wave, where

$$u_s = u(0)\exp(-i\omega_{k,p}t)\sin ska$$

The wavevector k is restricted by the fixed-end boundary conditions to the values

$$k = \frac{\pi}{L}, \frac{2\pi}{L}, \cdots, \frac{(N-1)\pi}{L}$$

For 1D line there is one mode for each interval $\Delta k = \pi / L$, so that the number of modes per unit range of k is L / π for $k \le \pi / a$ and 0 for $k > \pi / a$. The number of modes $D(\omega)d\omega$ in $d\omega$ at ω

$$D(\omega)d\omega = \frac{L}{\pi}\frac{dk}{d\omega}d\omega, \quad d\omega/dk \text{ is the group velocity.}$$
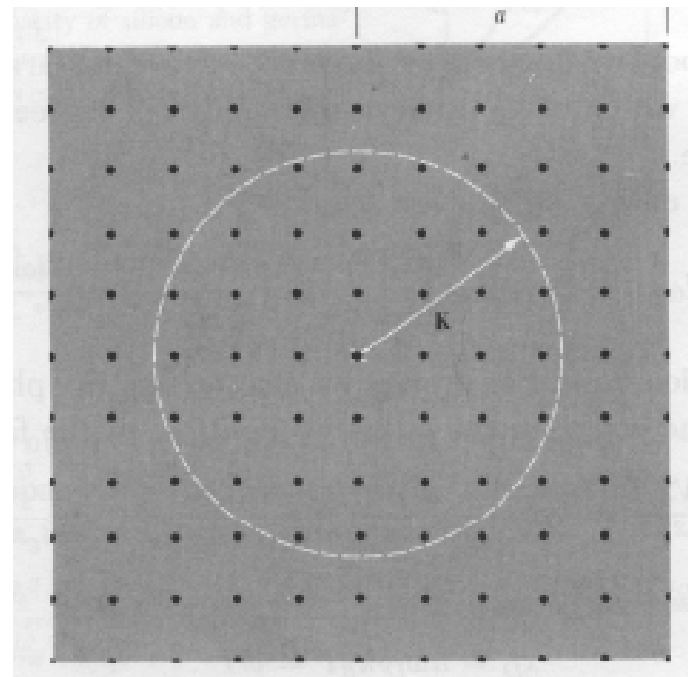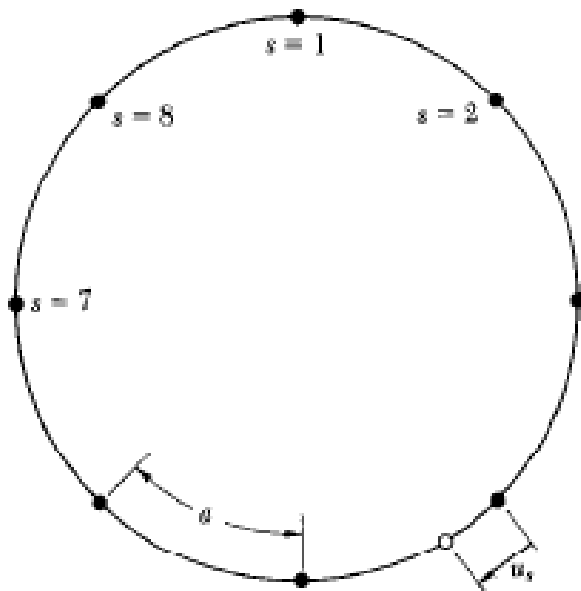
Density of states in three dimensions

In three dimensional lattice with N^3 primitive cells side L, periodic condition requires

$$\exp[i(k_x x + k_y y + k_z z)] \equiv \exp[i(k_x(x+L) + k_y(y+L) + k_z(z+L))]$$

Therefore $k_x, k_y, k_z = 0; \pm \dfrac{2\pi}{L}; \pm \dfrac{4\pi}{L}; \cdots; \pm \dfrac{N\pi}{L}$

There is one allowed value of k per volume $(2\pi/L)^3$ in k space or the total # of modes with wavevector less than k $N = (L/2\pi)^3 (4\pi k^3/3)$. The density of states for each polarization is $D(\omega) = dN/d\omega = (Vk^2/2\pi^2)(dk/d\omega)$

Debye Model for density of states

In the Debye approximation, $\omega = vk$, v is sound velocity.

$$D(\omega) = dN/d\omega = (Vk^2/2\pi^2)(dk/d\omega) = \frac{V\omega^2}{2\pi^2 v^3}.$$

If there are N primitive cells, the total # of acoustic modes is N. The cutoff frequency ω_D is $\omega_D^3 = 6\pi^2 v^3 N/V$.

The cutoff wavevector in k space: $k_D = \omega_D/v = (6\pi^2 N/V)^{1/3}$

The thermal energy is

$$U = \int d\omega D(\omega)\langle n(\omega)\rangle \hbar\omega = \int_0^{\omega_D} d\omega \frac{V\omega^2}{2\pi^2 v^3}\left(\frac{\hbar\omega}{e^{\hbar\omega/\tau}-1}\right)$$

If the phonon velocity is independent of the polarization

$$U = \int_0^{\omega_D} d\omega \frac{3V\omega^2}{2\pi^2 v^3}\left(\frac{\hbar\omega}{e^{\hbar\omega/\tau}-1}\right) = \frac{3Vk_B^4T^4}{2\pi^2v^3\hbar^3}\int_0^{x_D} dx\left(\frac{x^3}{e^x-1}\right),$$

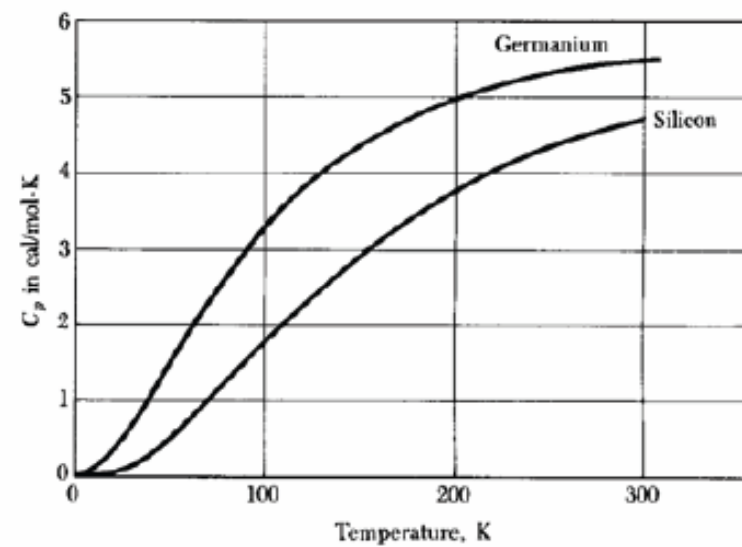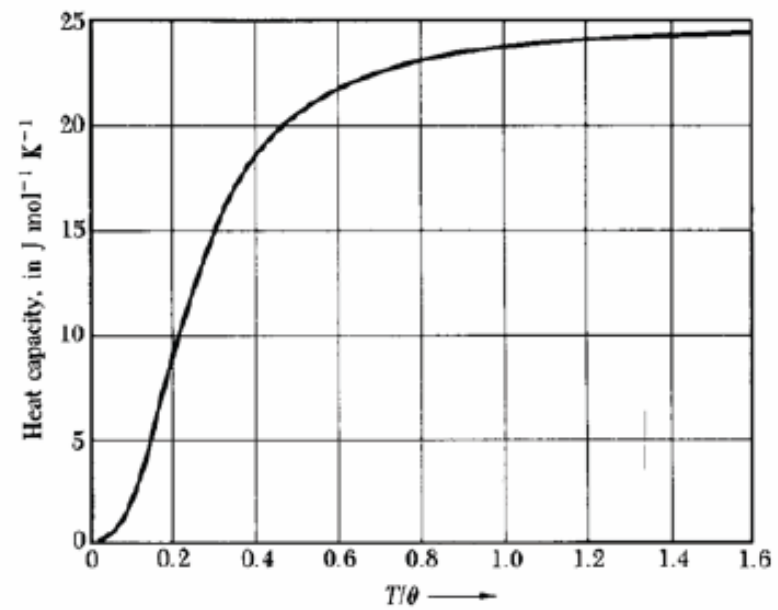where $x \equiv \hbar\omega/\tau \equiv \theta/T$

the Debye temperature θ is $\theta = \dfrac{\hbar v}{k_B}\left(\dfrac{6\pi^2N}{V}\right)^{1/3}$

the total phonon energy $U = 9Nk_BT\left(\dfrac{T}{\theta}\right)^3\int_0^{x_D} dx\left(\dfrac{x^3}{e^x-1}\right),$

the heat capacity $C_V = \dfrac{3V\hbar^2}{2\pi^2v^3k_BT^2}\int_0^{\omega_D} d\omega\left(\dfrac{\omega^4e^{\hbar\omega/\tau}}{(e^{\hbar\omega/\tau}-1)^2}\right)$

$$= 9Nk_BT\left(\frac{T}{\theta}\right)^3\int_0^{x_D} dx\left(\frac{x^4e^x}{(e^x-1)^2}\right).$$
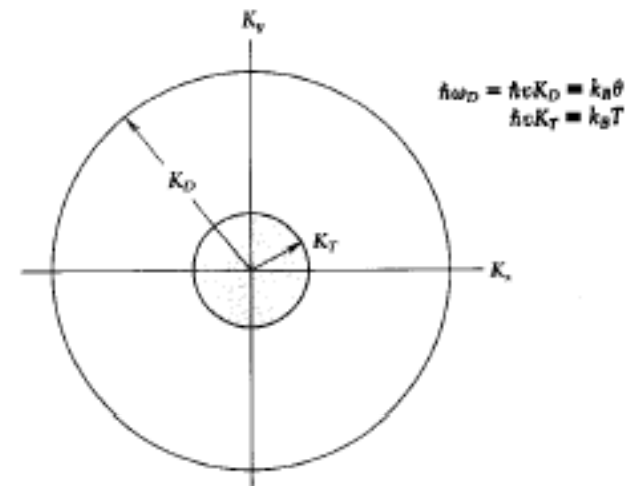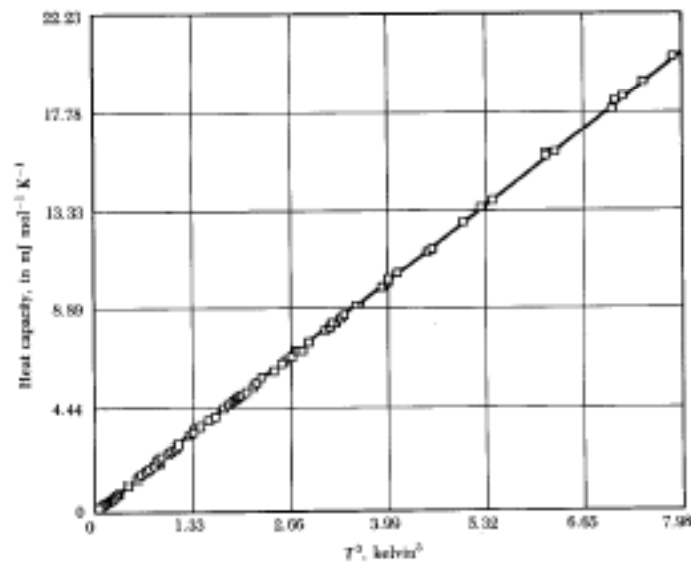
Debye T^3 law

At low temperatures,

$$\int_0^\infty dx \left(\frac{x}{e^x - 1} \right) = \sum_{n=1}^\infty \int_0^\infty x^3 e^{-nx} dx = 6 \sum_{n=1}^\infty \frac{1}{n^4} = \frac{\pi^4}{15},$$

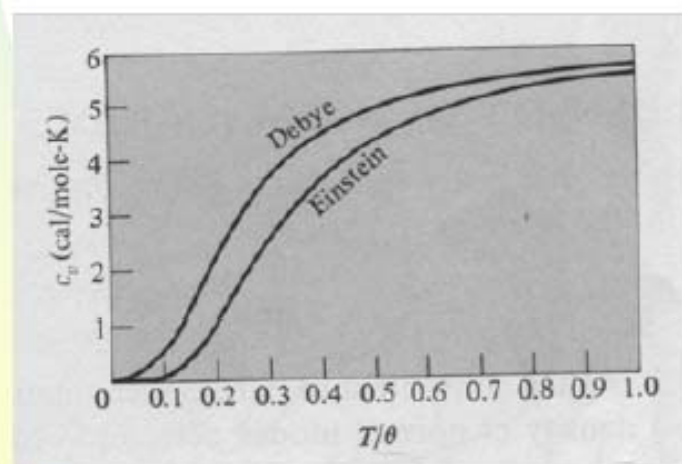the heat capacity $C_V \simeq \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta} \right)^3$.

$$\hbar \omega_D = \hbar v K_D = k_B \theta$$
$$\hbar v K_T = k_B T$$

Einstein models of the density of states

In the case of N oscillators of the same frequency ω_0 in 1D, the Einstein density of states is $D(\omega) = N\delta(\omega - \omega_0)$

$$U = N\langle n \rangle \hbar\omega = \left(\frac{N\hbar\omega}{e^{\hbar\omega/\tau} - 1} \right).$$

The heat capacity $C_V = N\left(\dfrac{\partial U}{\partial T} \right)_V = Nk_B \left(\dfrac{\hbar\omega}{\tau} \right)^2 \dfrac{e^{\hbar\omega}}{(e^{\hbar\omega/\tau} - 1)^2}$

1. **Singularity in density of states.** (a) From the dispersion relation derived in Chapter 4 for a monatomic linear lattice of N atoms with nearest-neighbor interactions, show that the density of modes is

$$D(\omega) = \frac{2N}{\pi} \cdot \frac{1}{(\omega_m^2 - \omega^2)^{1/2}} \cdot$$

where ω_m is the maximum frequency. (b) Suppose that an optical phonon branch has the form $\omega(K) = \omega_0 - AK^2$, near $K = 0$ in three dimensions. Show that $D(\omega) = (L/2\pi)^3 (2\pi/A^{3/2})(\omega_0 - \omega)^{1/2}$ for $\omega < \omega_0$ and $D(\omega) = 0$ for $\omega > \omega_0$. Here the density of modes is discontinuous.

Thermal conductivity

The thermal conductivity coefficient K of a solid is defined as,

$$j_U = -K \frac{dT}{dx},$$ where j_U is the flux of thermal energy, and

x is distance. From the kinetic theory of gases we find

$$K = \frac{1}{3} Cvl = \frac{1}{3} Cv^2\tau,$$ where C is the heat capacity per volume,

v is the average particle velocity, and l is the mean free

path of a particle between collisions, τ^{-1} is the phonon

collision rate.

Table 2 Phonon mean free paths

[Calculated from (44), taking $v = 5 \times 10^5$ cm/sec as a representative sound velocity. The ℓ's obtained in this way refer to umklapp processes.]

Crystal	T, °C	C, in J cm^{-3}K^{-1}	K, in W cm^{-1}K^{-1}	ℓ, in Å
Quartz[a]	0	2.00	0.13	40
	−190	0.55	0.50	540
NaCl	0	1.88	0.07	23
	−190	1.00	0.27	100

[a] Parallel to optic axis.

We give the elementary kinetic theory which leads to (42). The flux of particles in the x direction is $\frac{1}{2}n\langle|v_x|\rangle$, where n is the concentration of molecules; in equilibrium there is a flux of equal magnitude in the opposite direction. The $\langle\cdots\rangle$ denote average value.

If c is the heat capacity of a particle, then in moving from a region at local temperature $T + \Delta T$ to a region at local temperature T a particle will give up energy $c\,\Delta T$. Now ΔT between the ends of a free path of the particle is given by

$$\Delta T = \frac{dT}{dx}\ell_x = \frac{dT}{dx}v_x\tau \ ,$$

where τ is the average time between collisions.

The net flux of energy (from both senses of the particle flux) is therefore

$$j_U = -n\langle v_x^2\rangle c\tau\frac{dT}{dx} = -\tfrac{1}{3}n\langle v^2\rangle c\tau\frac{dT}{dx} \ . \tag{43}$$

If, as for phonons, v is constant, we may write (43) as
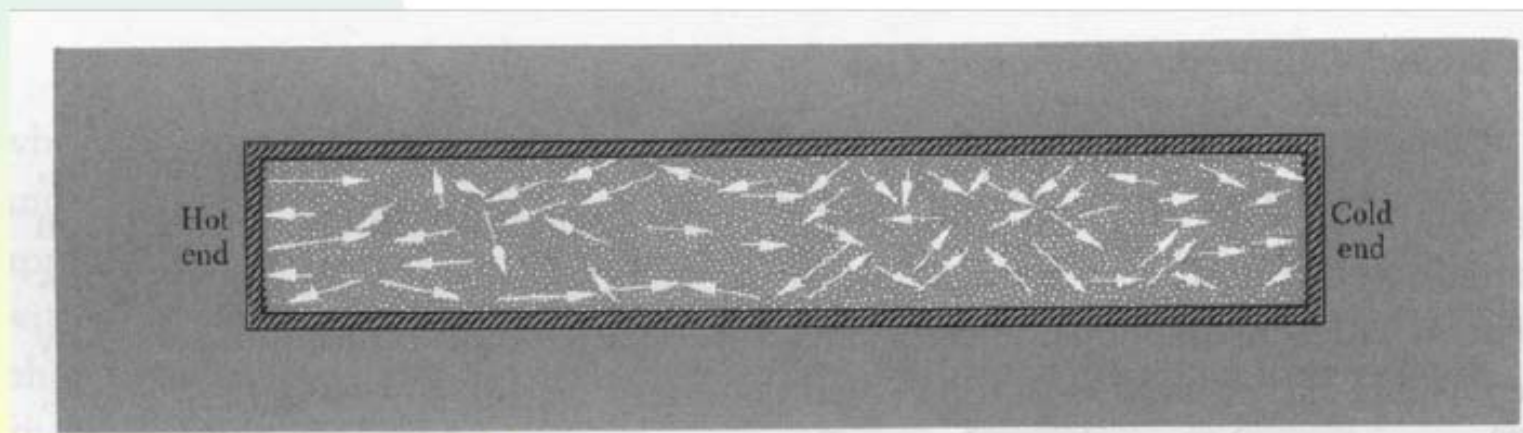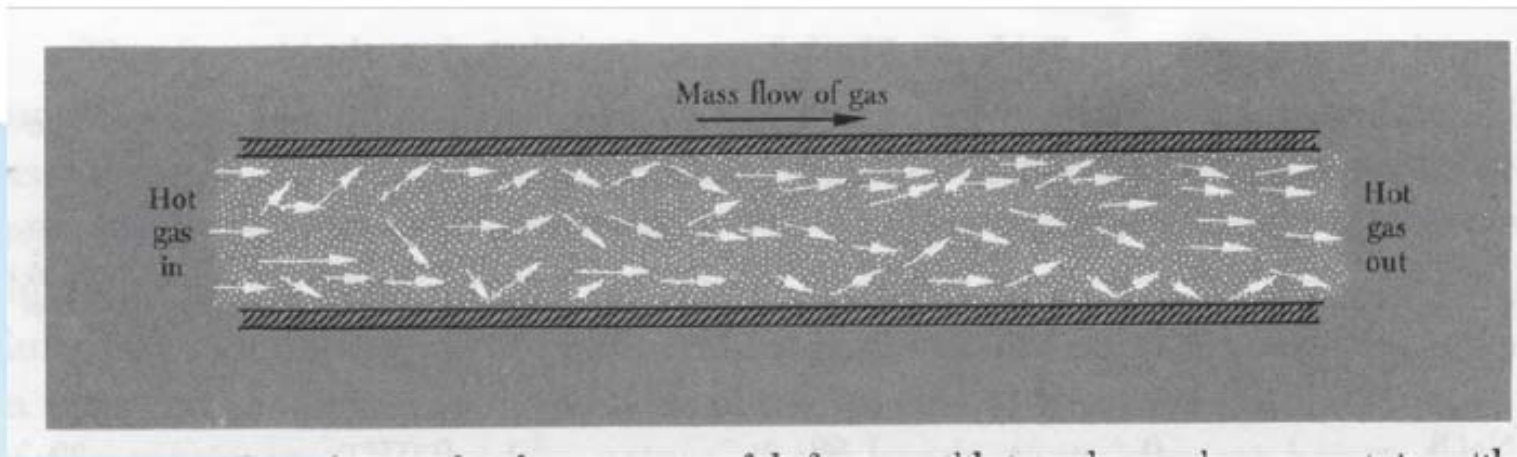
$$j_U = -\tfrac{1}{3}Cv\ell\frac{dT}{dx} \ , \tag{44}$$

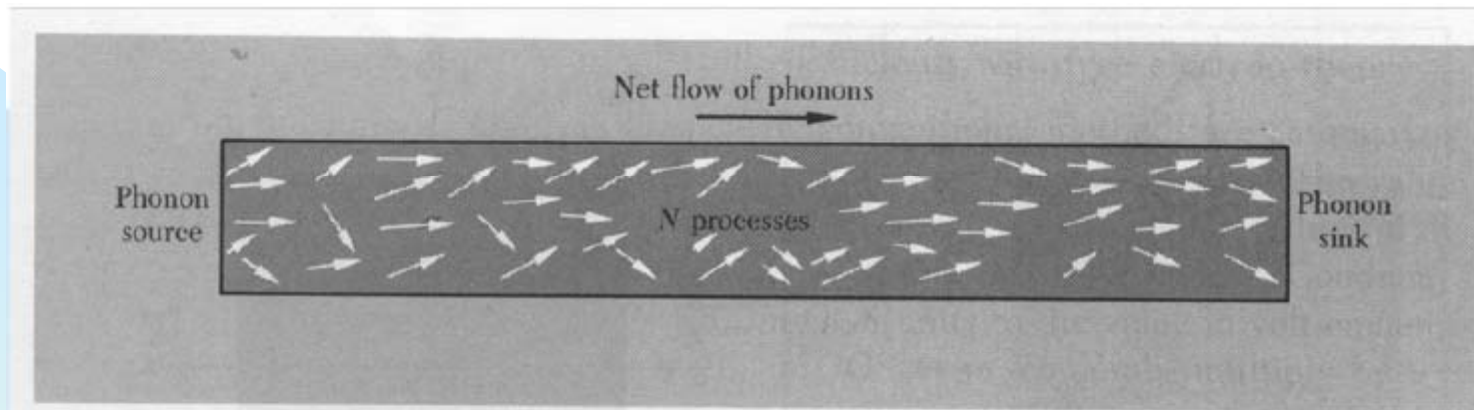with $\ell \equiv v\tau$ and $C \equiv nc$. Thus $K = \frac{1}{3}Cv\ell$.

Case 1 ($T \gg \Theta_D$) At high temperatures the total # of photons present in the crystal is proportional to T because the thermal equilibrium phonon occupation # reduced to:

$$\langle n \rangle = \frac{1}{e^{\hbar\omega/k_B T} - 1} \approx \frac{k_B T}{\hbar\omega}.$$
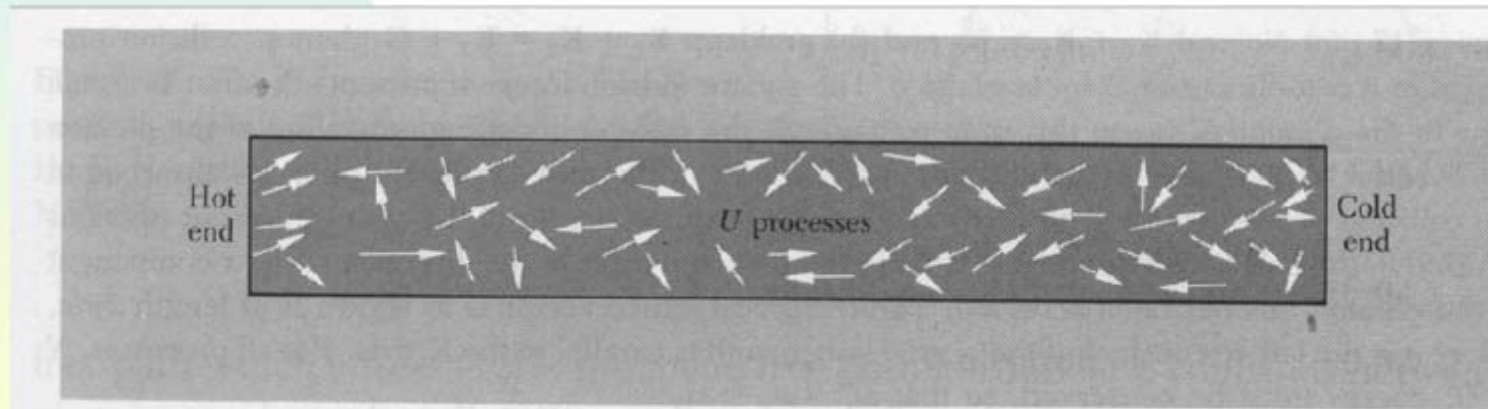
Since a given phonon that contributes to the thermal current is more likely to be scattered the more other phonons there are present to do the scattering, we should expect the relaxation time to decline with increasing temperature. Since at high temperatures C_V is temperature-independent, we should expect the thermal conductivity to decline with increasing temperature, $K \sim 1/T^x$, where x is between 1 and 2.

Case 2 ($T \ll \Theta_D$) At T, only phonons with energy comparable or less than $k_B T$ will have appreciable #. The only collisions occuring with appreciable probability are those that conserve the total crystal momentum exactly. Normal and Umklapp process: A normal process is a phonon collision in which the total initial and final crystal momenta are strictly equal; in an umklapp process they differ by a nonzero reciprocal lattice vector.
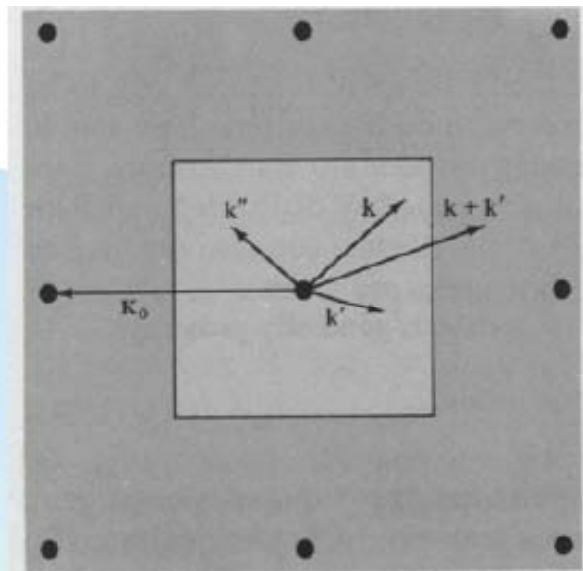
Mass flow of gas

Hot gas in

Hot gas out

Hot end

Cold end

Net flow of phonons

Phonon source — N processes — Phonon sink

$$\vec{k}_1 + \vec{k}_2 = \vec{k}_3$$

Hot end — U processes — Cold end

$$\vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{K}$$

(a)