



Chapter 5
Phonons II
Thermal Properties

Phonon Heat Capacity

$\langle n_{\mathbf{k},\mathbf{p}} \rangle$ is the thermal equilibrium occupancy of phonon wavevector \mathbf{K} and polarization \mathbf{p} ,

$$\text{Total energy at } k_B T, \quad U = \sum_{\mathbf{k}} \sum_{\mathbf{p}} \langle n_{\mathbf{k},\mathbf{p}} \rangle \hbar \omega$$

$$\langle n \rangle = \frac{1}{\exp(\hbar \omega / k_B T) - 1}, \quad \text{Plank Distribution function} \quad (2)$$

For large T , $\hbar \omega / k_B T \ll 1$
i.e. large x ,

$$\langle n \rangle = k_B T / \hbar \omega \propto T$$

$$\mathcal{E} = \hbar \omega / [\exp(\hbar \omega / k_B T) - 1]$$

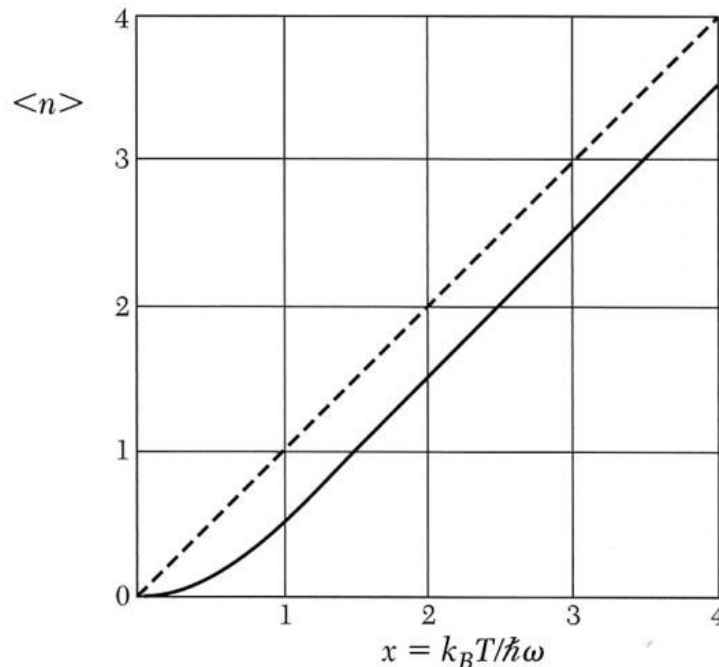


Fig. 1

Quantization of Elastic Waves

- The energy of lattice vibration is quantized.
- The quantum of energy called a **phonon**, and the quantum number is denoted as ***n***.
- The elastic waves in crystals are made of **phonons**.
- Thermal vibration in crystals are thermally excited **phonons**.

The energy of an elastic mode of angular frequency ω is

$$\epsilon = \left(n + \frac{1}{2} \right) \hbar \omega \quad (27)$$

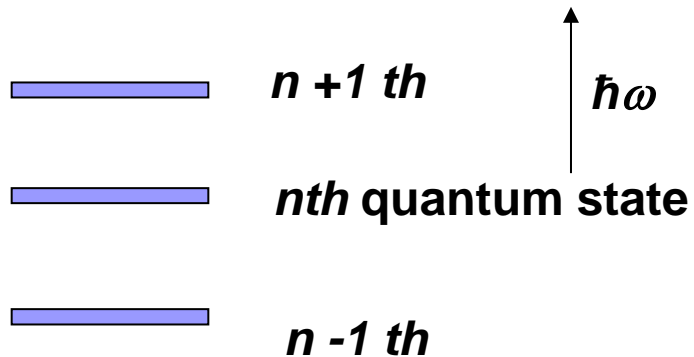
When the mode is excited to quantum number ***n***, that is,

When the mode is occupied by ***n*** phonons.

The term **$\frac{1}{2} \hbar \omega$ is the zero point energy** of the mode.

Plank Distribution :

Consider a situation where we have a set of identical oscillators in thermal equilibrium,



Compare the energy difference $\hbar\omega$ of the two adjacent quantum states to the thermal excitation energy $k_B T$

The ratio of the number of oscillators in their **(n+1)th** quantum state of excitation to the number in **nth** quantum state is

$$N_{n+1}/N_n = \exp(-\hbar\omega/\tau) , \quad \tau \equiv k_B T \quad \text{The Boltzmann factor} \quad (3)$$

$$N_n = N_0 \exp(-n\hbar\omega/\tau)$$

The ratio of the number of oscillators in the **nth** quantum state to the total number of oscillators is

$$\frac{N_n}{\sum_{s=0}^{\infty} N_s} = \frac{\exp(-n\hbar\omega/\tau)}{\sum_{s=0}^{\infty} \exp(-s\hbar\omega/\tau)} . \quad (4)$$

We compute the average excitation quantum number n of an oscillator to be

$$\langle n \rangle = \frac{\sum_s s \exp(-s\hbar\omega/\tau)}{\sum_s \exp(-s\hbar\omega/\tau)} . \quad (5)$$

We let $x = \exp(-\hbar\omega/k_B T)$, and $\tau = k_B T$, the denominator becomes

$$\sum_s x^s = \frac{1}{1-x} ;$$

Then, the numerator is

$$\sum_s s x^s = x \frac{d}{dx} \sum_s x^s = \frac{x}{(1-x)^2} , \quad (6)$$

$$\langle n \rangle = \frac{x}{1-x} = \frac{1}{\exp(\hbar\omega/\tau) - 1} . \quad \text{Plank Distribution, as the Eq.(2)} \quad (7)$$

Plank Distribution

$\langle n_{\mathbf{k},\mathbf{p}} \rangle$ is the thermal equilibrium occupancy of phonon wavevector \mathbf{K} , and polarization \mathbf{p}

At large T , $\langle n \rangle \sim$ linear in T

From Fig. 1, $\langle n \rangle + \frac{1}{2} \sim (k_B T)/\hbar\omega$

$$\langle n \rangle = \frac{1}{\exp(\hbar\omega/\tau) - 1}, \quad (\langle n \rangle + \frac{1}{2}) \hbar\omega \sim k_B T, \quad (2)$$

as in the classical limit

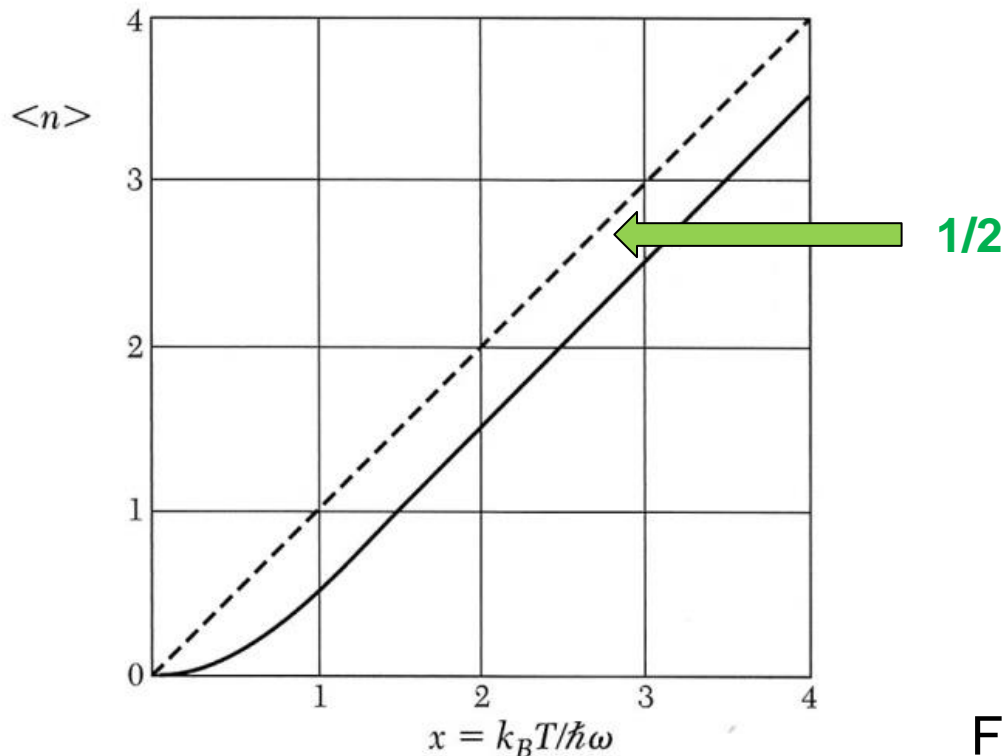


Fig. 1

The total energy of the phonons in a crystal is by summing over all phonon modes **K, p**

$$U_{\text{lat}} = \sum_K \sum_p U_{K,p} = \sum_K \sum_p \langle n_{K,p} \rangle \hbar \omega_{K,p} , \quad (1)$$

indexed by the phonon wave vector **K** ,
and the polarization **p**

We take **$\langle n \rangle$** as the Plank distribution

$$\langle n \rangle = \frac{1}{\exp(\hbar \omega / \tau) - 1} , \quad (2)$$

$$U = \sum_K \sum_p \frac{\hbar \omega_{K,p}}{\exp(\hbar \omega_{K,p} / \tau) - 1} . \quad (8)$$

Contributions from phonons only

Introducing the concept of **$D_p(\omega)$, the density of phonon modes (states)**,
at polarization **p** of frequency in the range from ω to $\omega + d\omega$

$$U = \sum_p \int d\omega D_p(\omega) \frac{\hbar \omega}{\exp(\hbar \omega / \tau) - 1} . \quad \text{Let } X = \hbar \omega / k_B T \quad (9)$$

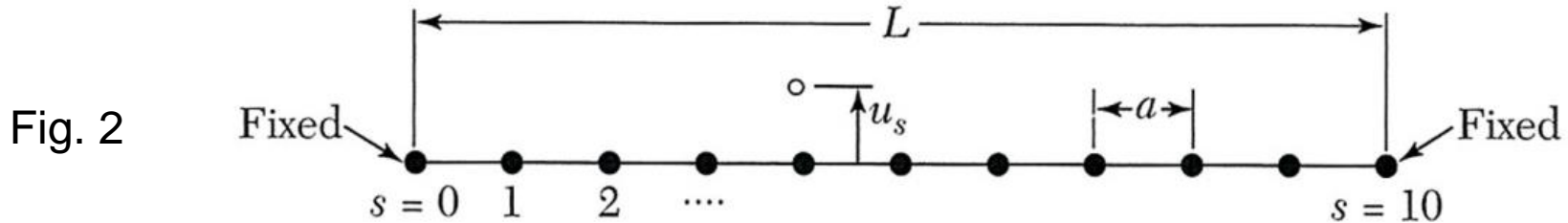
$$C_{\text{lat}} = k_B \sum_p \int d\omega D_p(\omega) \frac{x^2 \exp x}{(\exp x - 1)^2} . \quad (10)$$

**Lattice Heat Capacity
at constant volume**

(1) For the density of states in one dimension :

(A) Fixed Boundary Condition

Consider a 1-dimensional line of $N + 1$ atoms. Considering $N = 10$,
For fixed boundaries, the end atoms $s = 0$, and 10 are held fixed, i.e. $u_s = 0$.



The vibration takes up the form of **a standing wave** with the atomic displacement

$$u_s = u(0) \exp(-i\omega_{K,p}t) \sin sKa, \quad (11)$$

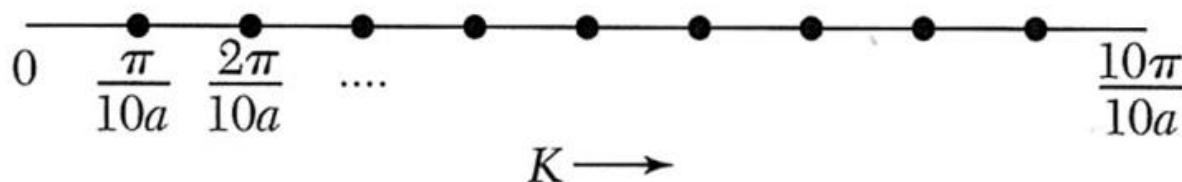
The fixed boundary condition requires that at the end, $u_s = 0$ for $s = 0$ and $s = N$,

→ For $s = 0$, $\sin sKa = 0$.

→ For $s = N$, $NKa = n\pi$, $K = n\pi / Na = n\pi / L$, where $n = 1$ to $N-1$.

$$K = \frac{\pi}{L}, \frac{2\pi}{L}, \frac{3\pi}{L}, \dots, \frac{(N-1)\pi}{L}. \quad (12)$$

Fig. 3



in K space

Showing the $N - 1$ allowed values of K

$$K = \frac{\pi}{L}, \quad \frac{2\pi}{L}, \quad \frac{3\pi}{L}, \dots, \quad \frac{(N-1)\pi}{L}. \quad (12)$$

For $K = \pi/L$,

$$u_s \propto \sin(s\pi a/L) \quad u_s = 0 \text{ for } s = 0 \text{ and } s = N \quad (13)$$

For $K = K_{\max} = N\pi/L = \pi/a$, $u_s = 0$ for each atom, hence this **K** is not a valid solution

There are **$N-1$** allowed values of **K** . And there are **$N-1$** atoms allowed to move.

*** For the one dimensional line, there is one mode for each interval,

$$\Delta K = \pi/L$$

*** And the number of modes per unit range of **K** is **L/π** for **$K < \pi/a$** , and it is zero for **$K > \pi/a$** , thus **$D(K) = dN/dK = L/\pi$**

(B) Periodic Boundary Conditions :

For an bounded medium, and require the solutions be periodic over a large distance L , namely, $u(sa) = u(sa + L)$, where $L = Na$.

We use the **traveling (running) wave solution**

$$U_s = u(0) \exp [i(sKa - w_k t)]$$

The periodic boundary condition leads to

$$\exp(isaK) = \exp(isaK + iKL), \text{ then } \exp(iKL) = 1,$$

$$KL = \pm 2n\pi, \quad K = \pm 2n\pi / L, \quad n \text{ is integer from } 0, \text{ to } N$$

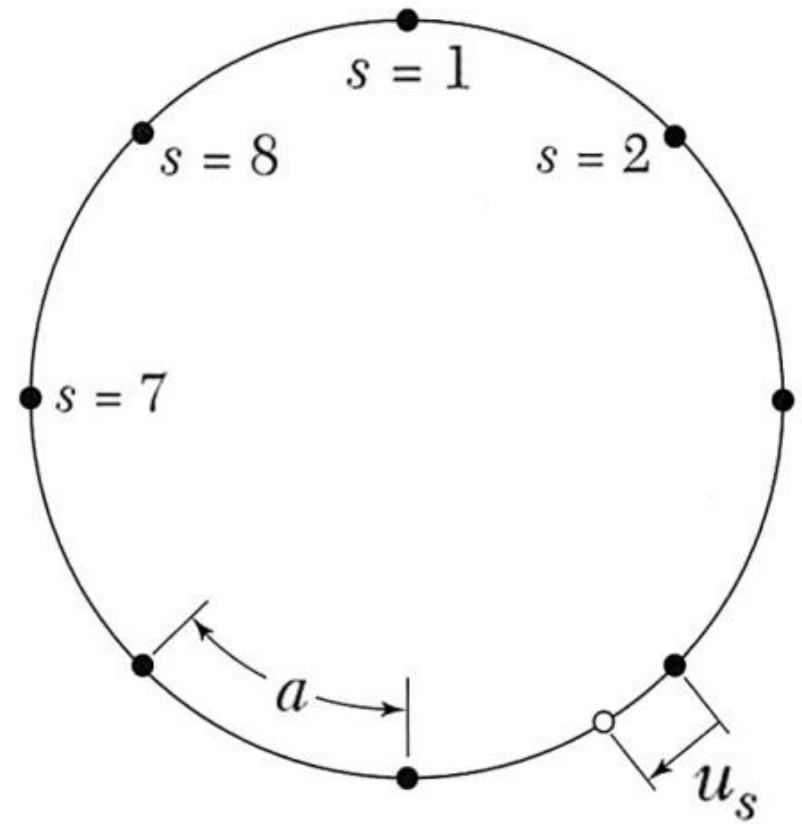
$$K = 0, \quad \pm \frac{2\pi}{L}, \quad \pm \frac{4\pi}{L}, \quad \pm \frac{6\pi}{L}, \quad \dots, \quad \frac{N\pi}{L} \quad (N\pi/Na = \pi/a) \quad (14)$$

There is one mode for every interval $\Delta K = 2\pi/L$.

For periodic boundary conditions, the number of modes per unit range of K is $dN/dK = L/2\pi$ for $-\pi/a < K < \pi/a$, and is zero otherwise.

$$D_1(\omega) d\omega = \frac{L}{\pi} \frac{dK}{d\omega} d\omega = \frac{L}{\pi} \cdot \frac{d\omega}{d\omega/dK} \quad \begin{array}{l} \text{For the fixed boundary condition} \\ \text{Group velocity } v_g \end{array} \quad (15)$$

Figure 4 Consider N particles constrained to slide on a circular ring. The particles can oscillate if connected by elastic springs. In a normal mode the displacement u_s of atom s will be of the form $\sin sKa$ or $\cos sKa$: these are independent modes. By the geometrical periodicity of the ring the boundary condition is that $u_{N+s} = u_s$ for all s , so that NKa must be an integral multiple of 2π . For $N = 8$ the allowed independent values of K are $0, 2\pi/8a, 4\pi/8a, 6\pi/8a$, and $8\pi/8a$. The value $K = 0$ is meaningless for the sine form, because $\sin s0a = 0$. The value $8\pi/8a$ has a meaning only for the cosine form, because $\sin (s8\pi a/8a) = \sin s\pi = 0$. The three other values of K are allowed for both the sine and cosine modes, giving a total of eight allowed modes for the eight particles. Thus the periodic boundary condition leads to one allowed mode per particle, exactly as for the fixed-end boundary condition of Fig. 3. If we had taken the modes in the complex form $\exp(isKa)$, the periodic boundary condition would lead to the eight modes with $K = 0, \pm 2\pi/Na, \pm 4\pi/Na, \pm 6\pi/Na$, and $8\pi/Na$, as in Eq. (14).



Periodic Boundary Condition for a 1-D Lattice

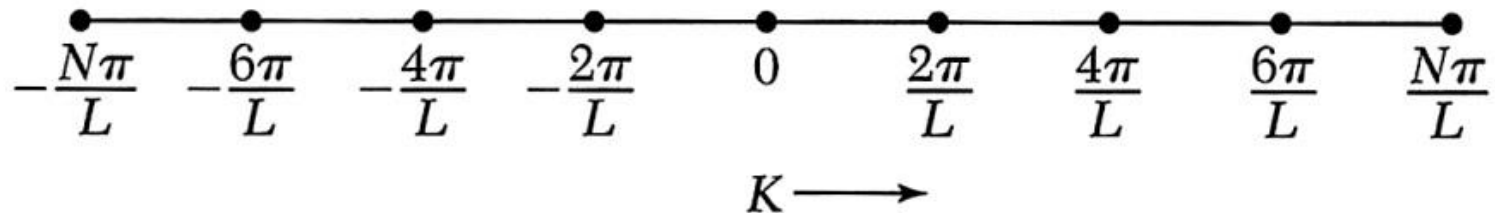


Figure 5 Allowed values of wavevector K for periodic boundary conditions applied to a linear lattice of periodicity $N = 8$ atoms on a line of length L . The $K = 0$ solution is the uniform mode. The special points $\pm N\pi/L$ represent only a single solution because $\exp(i\pi s)$ is identical to $\exp(-i\pi s)$; thus there are eight allowed modes, with displacements of the s th atom proportional to 1, $\exp(\pm i\pi s/4)$, $\exp(\pm i\pi s/2)$, $\exp(\pm i3\pi s/4)$, $\exp(i\pi s)$.

$$\text{Exp}(\pm isKa)$$

For a 2D square lattice

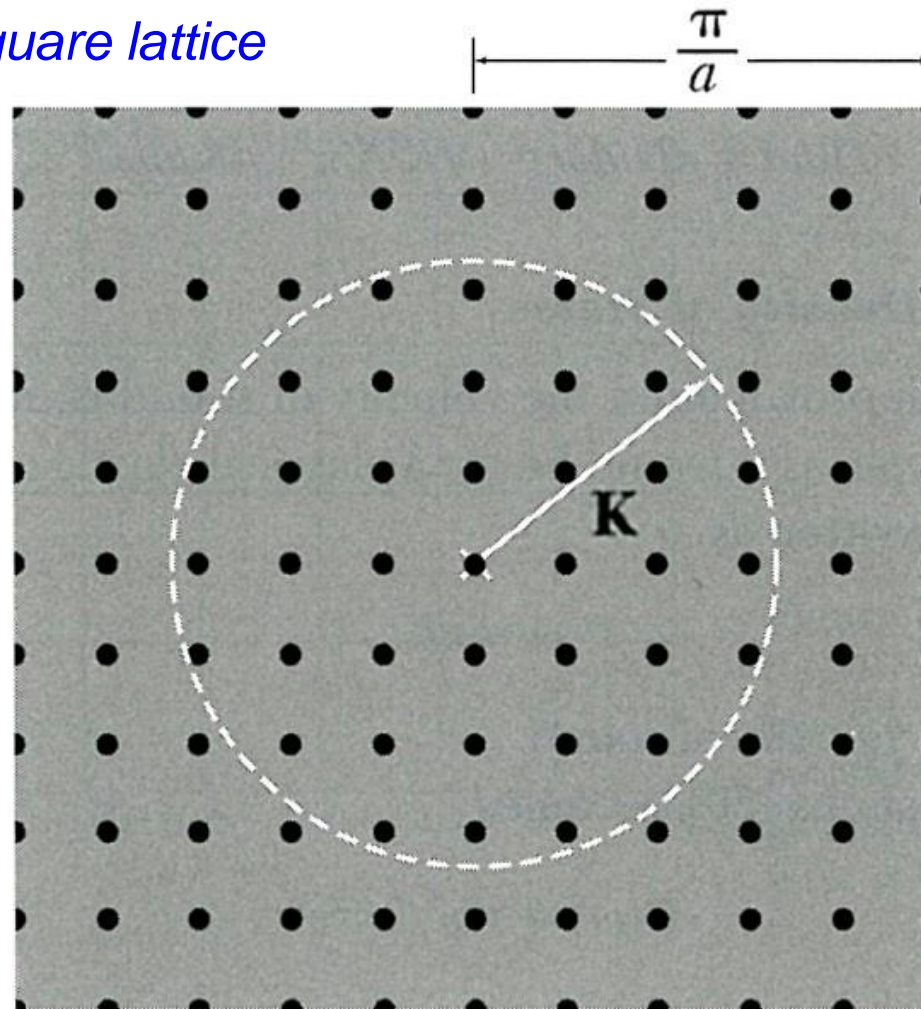


Fig. 6

Figure 6 Allowed values in Fourier space of the phonon wavevector K for a square lattice of lattice constant a , with periodic boundary conditions applied over a square of side $L = 10a$. The uniform mode is marked with a cross. There is one allowed value of K per area $(2\pi/10a)^2 = (2\pi/L)^2$, so that within the circle of area πK^2 the smoothed number of allowed points is $\pi K^2 (L/2\pi)^2$.

(2) For the density of States in 3D:

Considering N^3 primitive cells each of edge L

$$\exp[i(K_x x + K_y y + K_z z)] \equiv \exp\{i[K_x(x + L) + K_y(y + L) + K_z(z + L)]\} , \quad (16)$$

$$K_x, K_y, K_z = 0 ; \quad \pm \frac{2\pi}{L} ; \quad \pm \frac{4\pi}{L} ; \quad \dots ; \quad \frac{N\pi}{L} . \quad (17)$$

There is one allowed value of K per volume of $(2\pi/L)^3$ or

$$\left(\frac{L}{2\pi}\right)^3 = \frac{V}{8\pi^3} \quad \text{Allowed value of } K \text{ per unit volume of } K \text{ space.} \quad (18)$$

For a volume of a sphere of radius of K , the total number of modes of wavevectors less than K is

$$N = (L/2\pi)^3 (4\pi K^3/3) \quad \text{---} \quad dN/dK \quad (19)$$

The density of states for each polarization is

$$\begin{aligned} D(\omega) &= dN/d\omega = (VK^2/2\pi^2)(dK/d\omega) . \\ &= (dN/dK) / (dK/d\omega) \end{aligned} \quad (20)$$

Debye Model for Density of States

In the Debye approximation, the velocity of sound is taken as a constant. v is the velocity of sound, this usually applies for small ω and small K , such as for the acoustic mode for an elastic continuum.

$$\omega = vK , \quad (21)$$

From Eq. 19 $N = (V\omega^3)/6\pi^2v^3$

$$D(\omega) = V\omega^2/2\pi^2v^3 . \quad (22)$$

In **the Debye model**, we define a maximum cutoff frequency ω_D , and a maximum cutoff wavevector K_D

From Eq. 19 $\omega_D^3 = 6\pi^2v^3N/V$. (23)

$$K_D = \omega_D/v = (6\pi^2N/V)^{1/3} . \quad (24)$$

The thermal energy of phonons in a crystal is

$$U = \int d\omega D(\omega) \langle n(\omega) \rangle \hbar\omega = \int_0^{\omega_D} d\omega \left(\frac{V\omega^2}{2\pi^2v^3} \right) \left(\frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1} \right) , \quad (25)$$

ω vs K Dispersion for Monoatomic Lattice

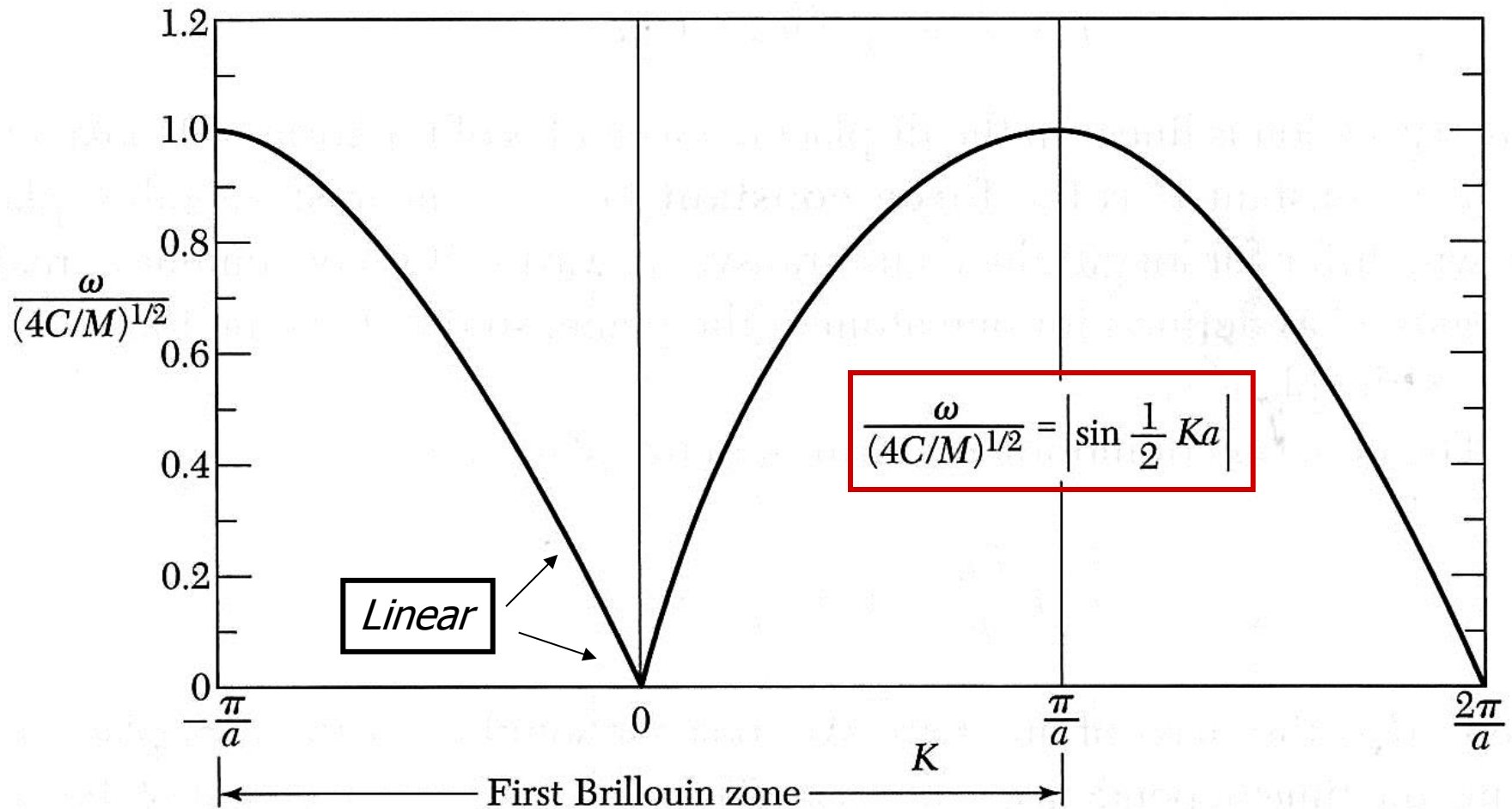


Figure 4 Plot of ω versus K . The region of $K \ll 1/a$ or $\lambda \gg a$ corresponds to the continuum approximation; here ω is directly proportional to K .

Assuming phonon velocity v is independent of polarization for all three direction,
We can multiply a factor of three

$$U = \frac{3V\hbar}{2\pi^2v^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega/\tau} - 1} = \frac{3Vk_B^4T^4}{2\pi^2v^3\hbar^3} \int_0^{x_D} dx \frac{x^3}{e^x - 1} , \quad (26)$$

where $x = \hbar\omega/k_B T$

$$x_D \equiv \hbar\omega_D/k_B T \equiv \theta/T . \quad (27)$$

We Define Debye temperature θ

$\theta = \hbar\omega_D/k_B$, and from eq. 23

$$\theta = \frac{\hbar v}{k_B} \cdot \left(\frac{6\pi^2 N}{V} \right)^{1/3} , \quad (28)$$

The total phonon energy is

$$U = 9Nk_B T \left(\frac{T}{\theta} \right)^3 \int_0^{x_D} dx \frac{x^3}{e^x - 1} , \quad (29)$$

$C_V \equiv (\partial U / \partial T)_V$, By differentiating the eq. (26) w.r.t. T , we get

$$C_V = \frac{3V\hbar^2}{2\pi^2 v^3 k_B T^2} \int_0^{w_D} dw \frac{\omega^4 e^{\hbar\omega/\tau}}{(e^{\hbar\omega/\tau} - 1)^2} = 9Nk_B \left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2} . \quad (30)$$

(1) For large T , x is small, we can expand the integrand, and $\int dx x^2$
 $C_V = 3Nk_B$, since $U = 3Nk_B T$ in the large T limit.

(2) For low T , x_D is approaching to infinity, thus in Eq. (29),

$$\int_0^\infty dx \frac{x^3}{e^x - 1} = \int_0^\infty dx x^3 \sum_{s=1}^\infty \exp(-sx) = 6 \sum_{s=1}^\infty \frac{1}{s^4} = \frac{\pi^4}{15} , \quad (31)$$

$$C_V \cong \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\theta}\right)^3 \cong 234 Nk_B \left(\frac{T}{\theta}\right)^3 , \quad (32)$$

The Debye T^3 Law for low temp

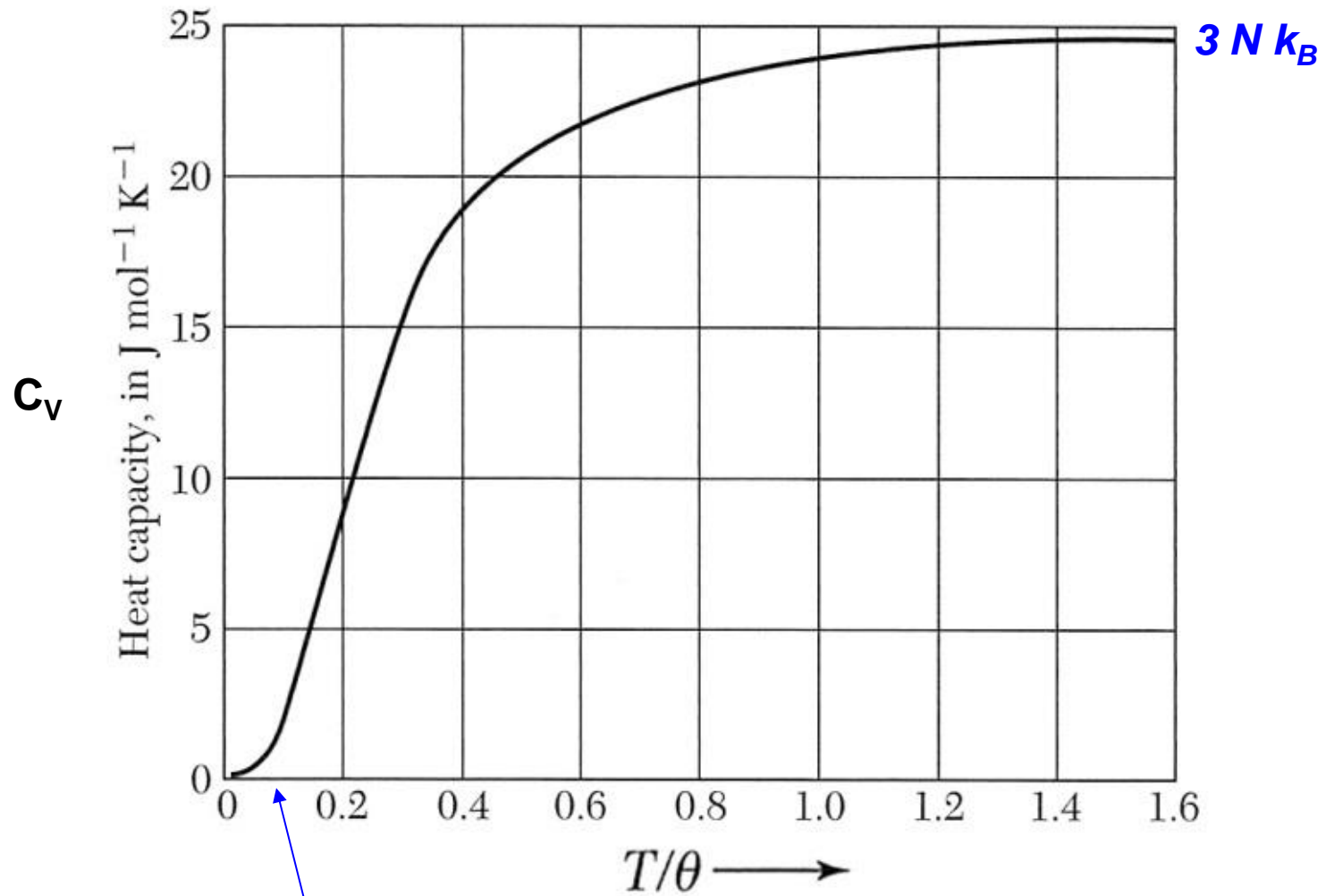


Fig. 7

At $T/\theta < 0.1$, $C_v \sim T^3$ term

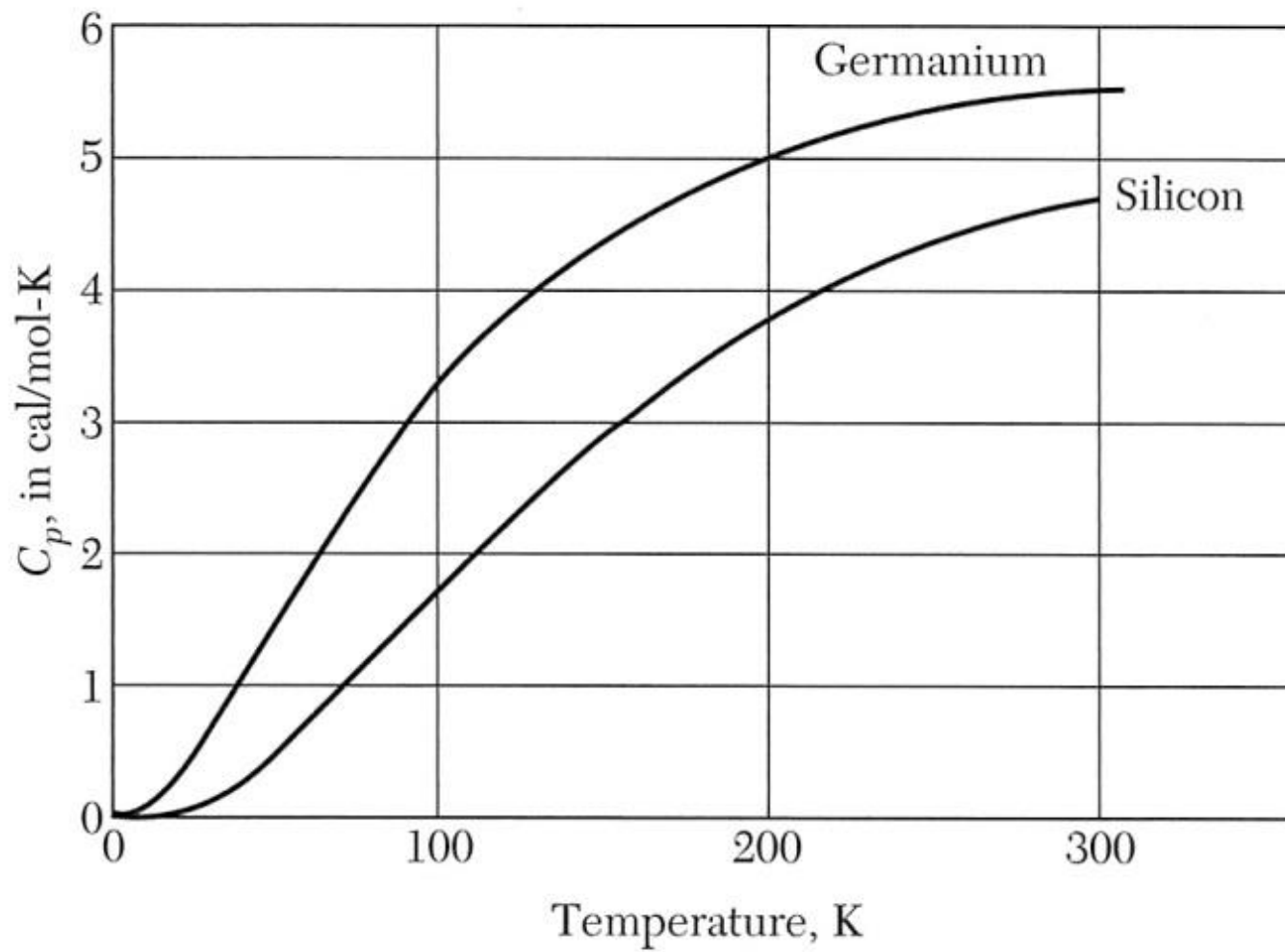


Fig. 8

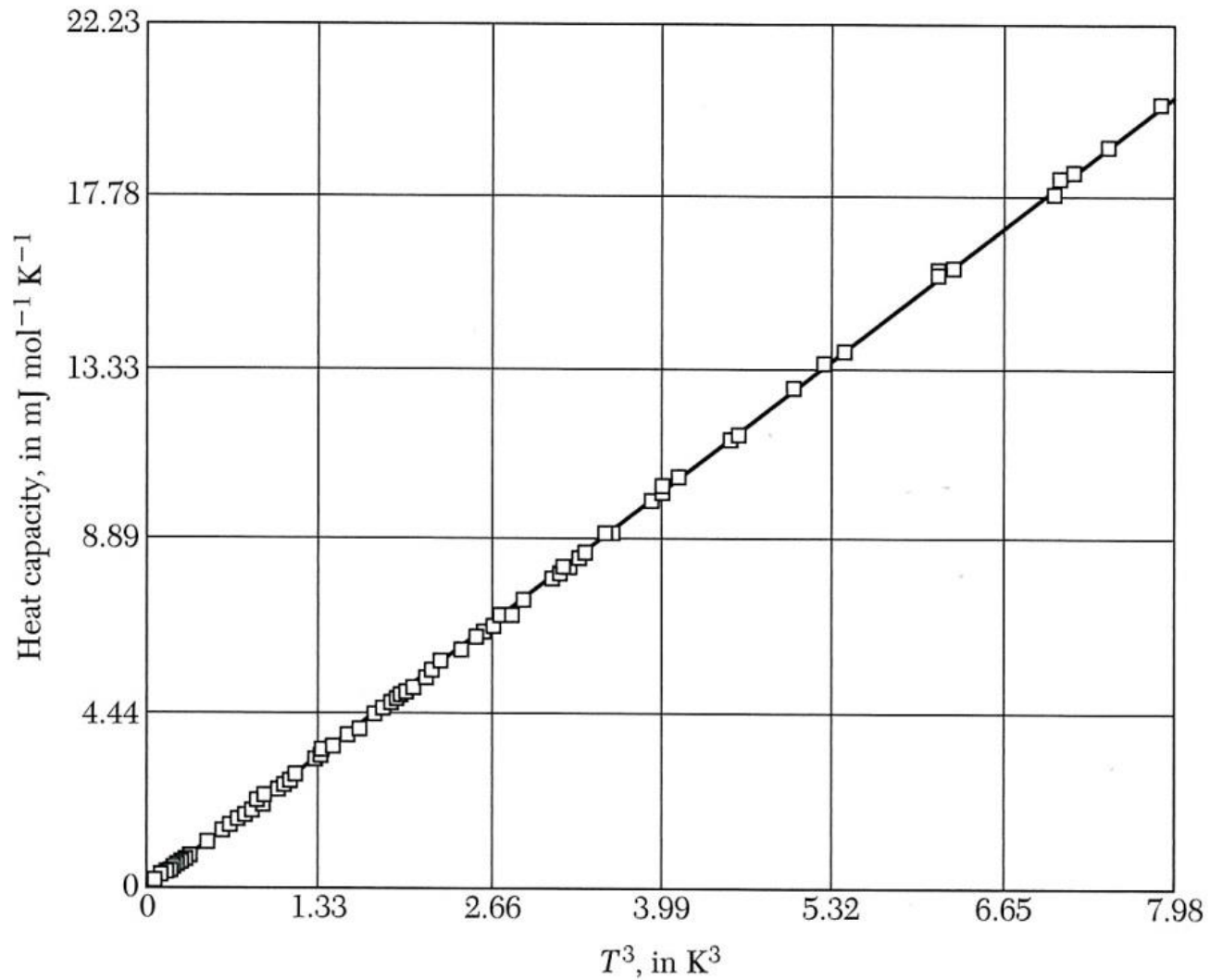
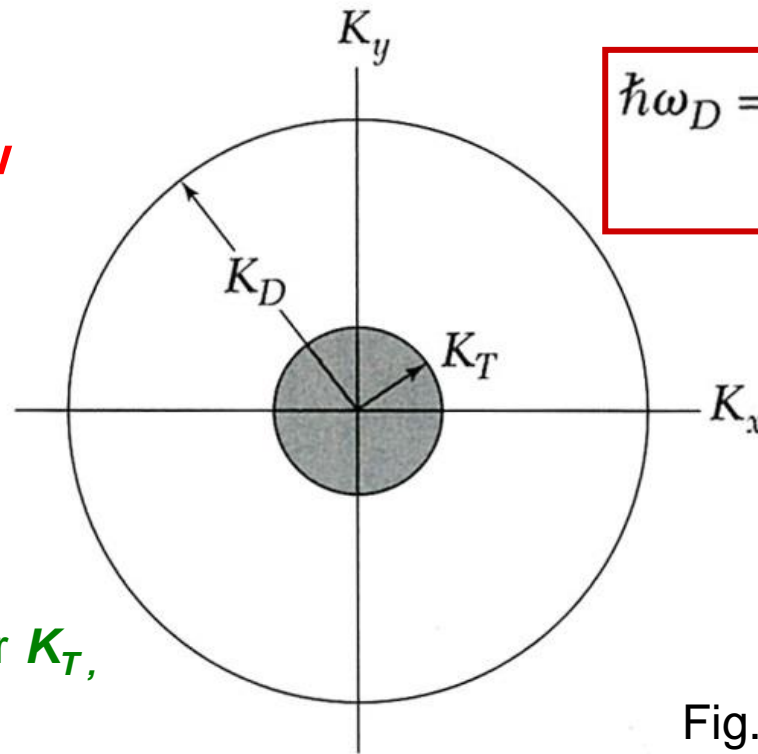


Fig. 9 The low temperature heat capacity of solid Argon linear dependence of T^3

A qualitative approach of deriving the Debye T^3 Law



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

$$\hbar v K_T = k_B T$$

At temp T , the phonons modes are excited to have a wavevector K_T , with thermal energy $k_B T$.

Fig. 10

Of the allowed volume in K space, the fraction occupied by the excited modes is of the order of $(\omega_T/\omega_D)^3$ or $(K_T/K_D)^3$, where K_T is the thermal wavevector defined as $\hbar\omega_T = k_B T$, and $\omega_T = v K_T$.

Hence $\hbar v K_T = k_B T$, and $\hbar v K_D = k_B \theta$, $\Rightarrow K_T/K_D = T/\theta$

Thus the fraction occupied is $(T/\theta)^3$ of the total volume in the K space. For $3N$ modes of energy $k_B T$, we get $U = 3N k_B T (T/\theta)^3$, and $C_V \sim \partial U / \partial T = 12 N k_B (T/\theta)^3$ as the T^3 dependence

Einstein Model of Density of States

$$D(\omega) = N \delta(\omega - \omega_0)$$

We have N oscillators of identical frequency ω_0 ,

$$U = N \langle n \rangle \hbar \omega = \frac{N \hbar \omega}{e^{\hbar \omega / \tau} - 1}, \quad (33)$$

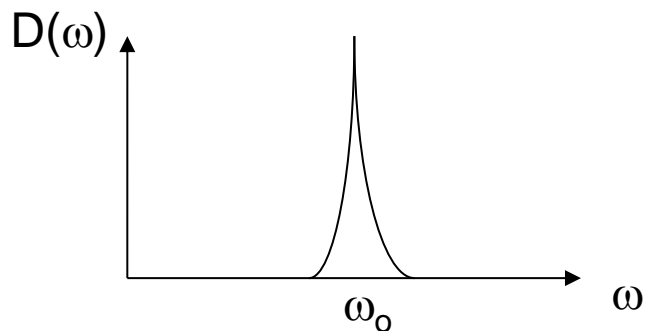
$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = N k_B \left(\frac{\hbar \omega}{\tau} \right)^2 \frac{e^{\hbar \omega / \tau}}{(e^{\hbar \omega / \tau} - 1)^2}, \quad (34)$$

At high T , x is $\ll 1$, $C_V = N k_B$. For 3D, N is replaced by $3N$.

The high T $C_V = 3N k_B$ as the Dulong and Petit value.

At low T , x is $\gg 1$, $C_V = \exp(-\hbar \omega / k_B T)$

= 3



This model usually applies to **optical phonon modes**, where ω is nearly independent of K .

Einstein Model for $D(\omega)$

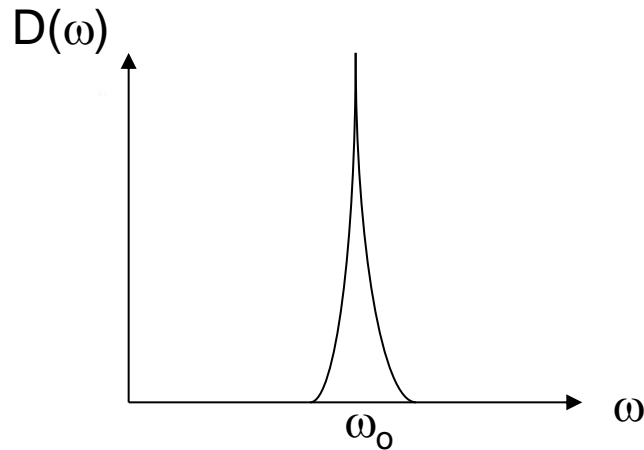
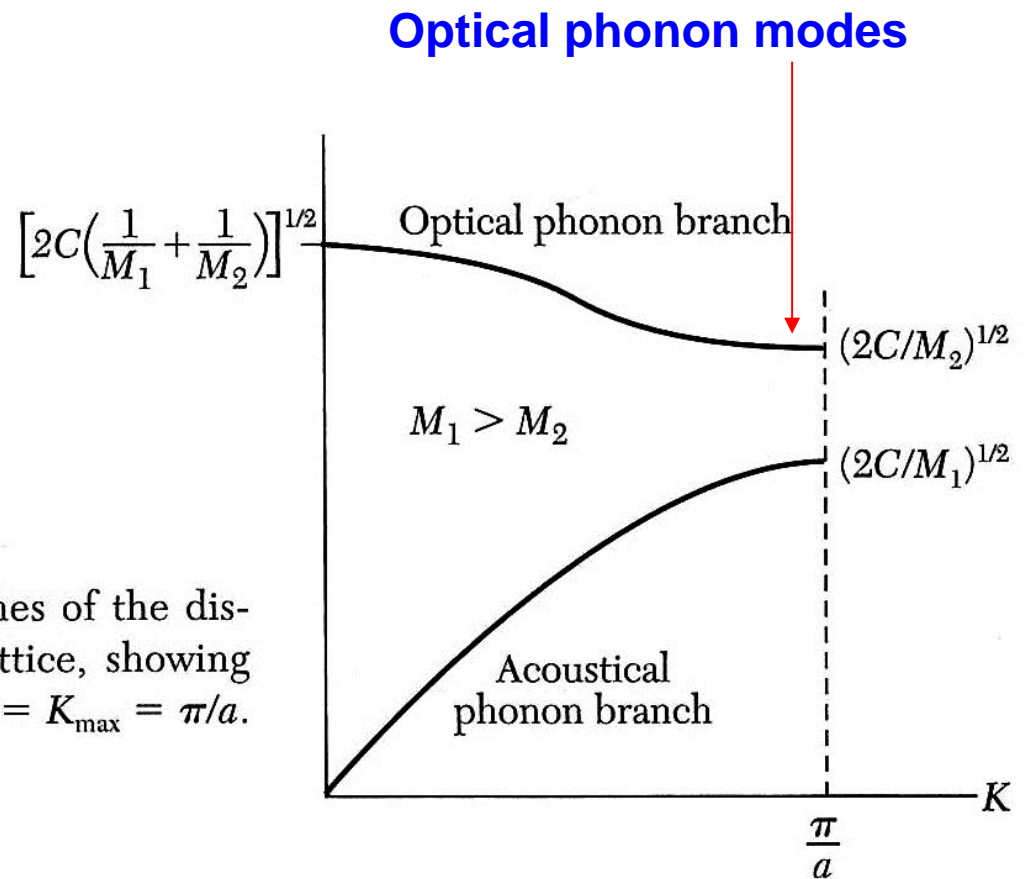


Figure 7 Optical and acoustical branches of the dispersion relation for a diatomic linear lattice, showing the limiting frequencies at $K = 0$ and $K = K_{\max} = \pi/a$. The lattice constant is a .



This model usually applies to optical phonon modes, where ω is nearly independent of K .

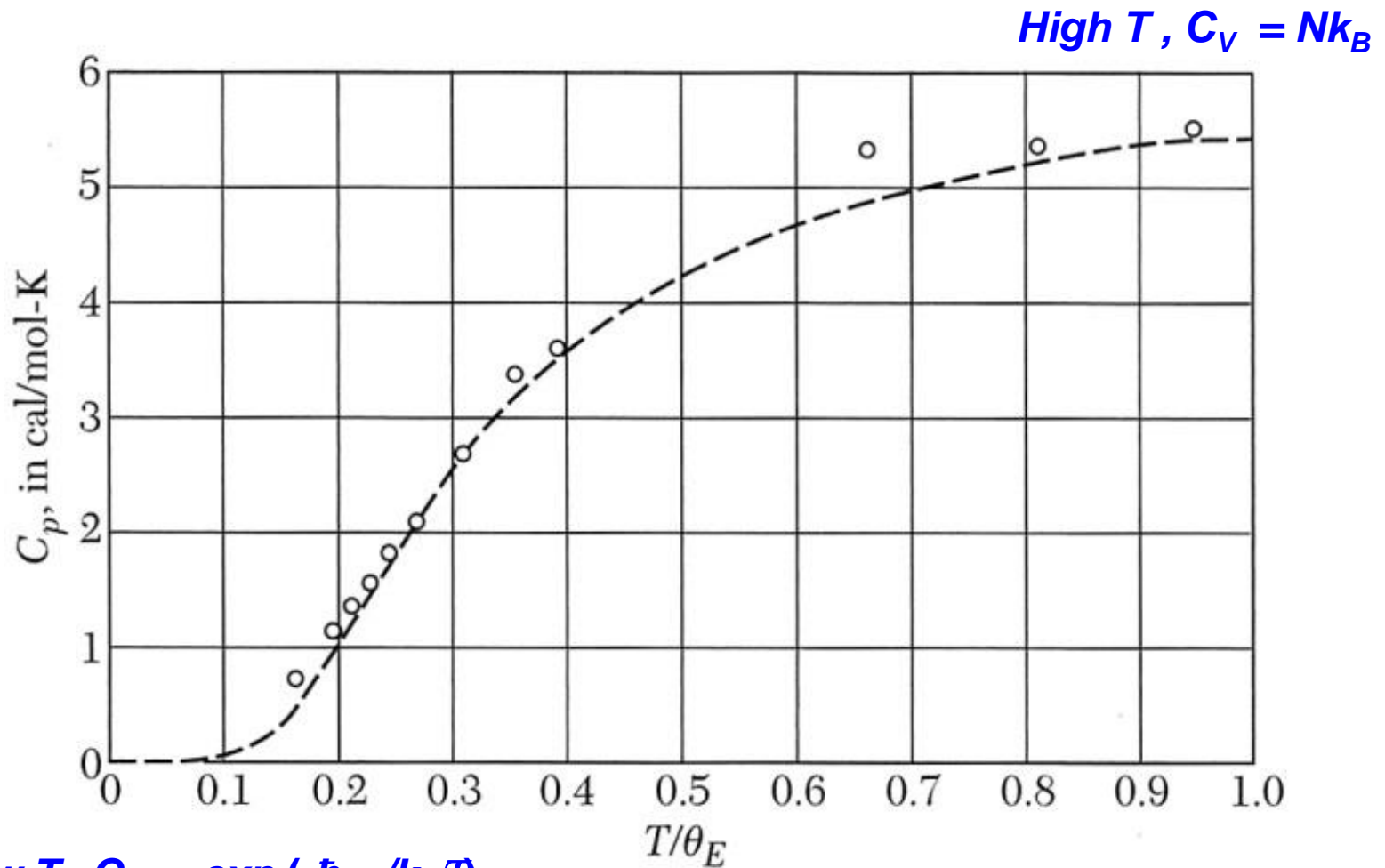


Fig. 11 Experimental C_V vs T/θ for diamond compared to [the Einstein Model](#) in dashed line . $\theta_E = \hbar\omega/K_B = 1320K$

General Expressions for $D(\omega)$:

As the density of states per unit frequency range at a given $\omega(K)$

For phonon frequency between ω and $\omega + d\omega$

$$D(\omega) d\omega = \left(\frac{L}{2\pi} \right)^3 \int_{\text{shell}} d^3K , \quad (35)$$

The integral is extended over the volume of shell in \mathbf{K} space bounded between two surfaces of constant frequency ω , and constant frequency $\omega + d\omega$

The volume between the constant frequency surfaces ω and $\omega + d\omega$ is a right cylinder of base dS_ω and altitude dK_\perp

$$\int_{\text{shell}} d^3K = \int dS_\omega dK_\perp , \quad (36)$$

Where dK_\perp is the perpendicular distance between two constant frequency surfaces, and dS_ω is an element of area of the constant frequency surface of ω in \mathbf{K} space.

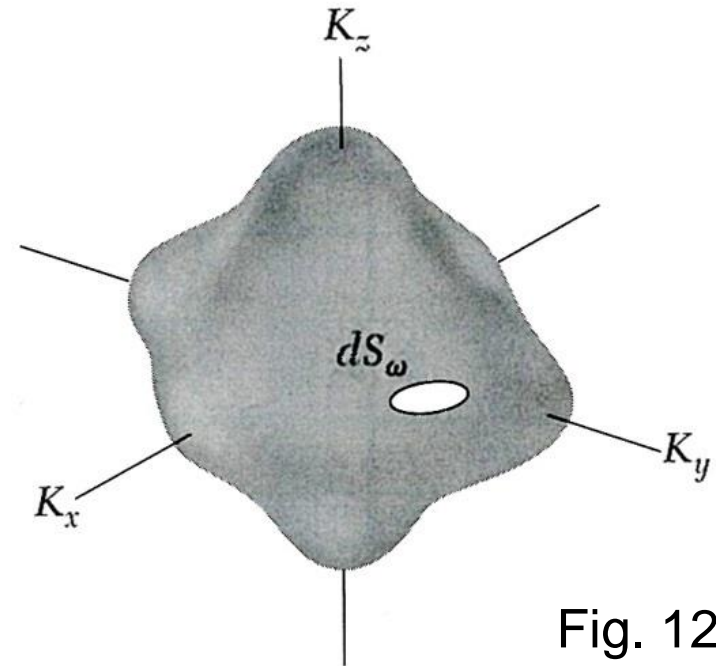
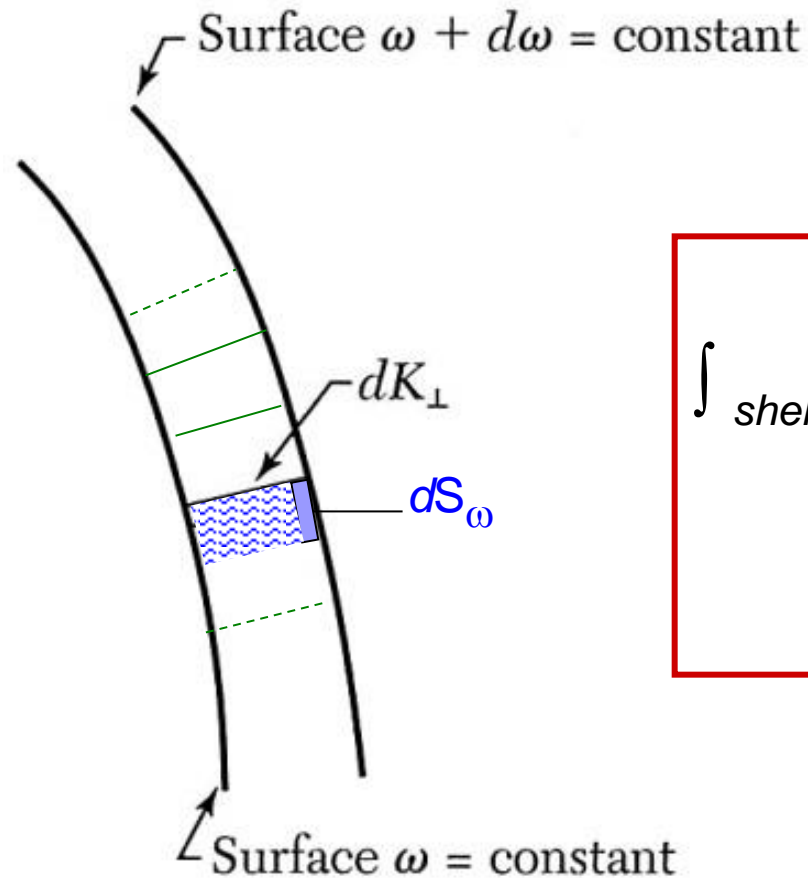


Fig. 12



$$\begin{aligned} \int_{\text{shell}} d^3K &= \int d_{\text{cylinders}} \\ &= \int dS_\omega dK_\perp \end{aligned}$$

Fig. 13

The quantity dK_\perp is the perpendicular distance between two constant frequency surfaces ω , and $\omega + d\omega$

The gradient of ω , which is $\nabla_{\mathbf{K}}\omega$, is also normal to the surface ω constant, and the quantity

$$|\nabla_{\mathbf{K}}\omega| dK_{\perp} = d\omega ,$$

is the difference in frequency between the two surfaces connected by dK_{\perp} . Thus the element of the volume is

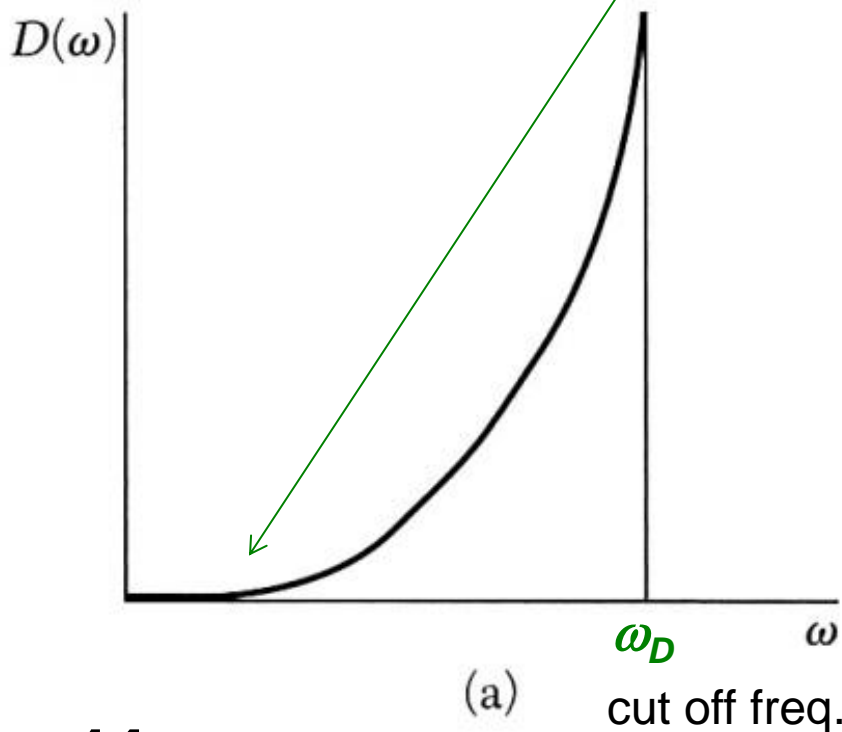
$$dS_{\omega} dK_{\perp} = dS_{\omega} \frac{d\omega}{|\nabla_{\mathbf{K}}\omega|} = dS_{\omega} \frac{d\omega}{v_g} ,$$

where $v_g = |\nabla_{\mathbf{K}}\omega|$ is the magnitude of the group velocity of a phonon. For (35) we have

$$D(\omega) d\omega = \left(\frac{L}{2\pi}\right)^3 \int \frac{dS_{\omega}}{v_g} d\omega .$$

$$\boxed{D(\omega) = \frac{V}{(2\pi)^3} \int \frac{dS_{\omega}}{v_g} .} \quad (37)$$

Debye Model, $\omega = v K$, v is a constant,
It is a good approximation for small ω
and for the **acoustic mode**, $D(\omega) \sim \omega^2$



Near the brillouin zone boundary,
 v_g is approaching to zero, and the
dispersion of ω vs K is very flat.
This leads to a large peak
(singular points) in the $D(\omega)$.

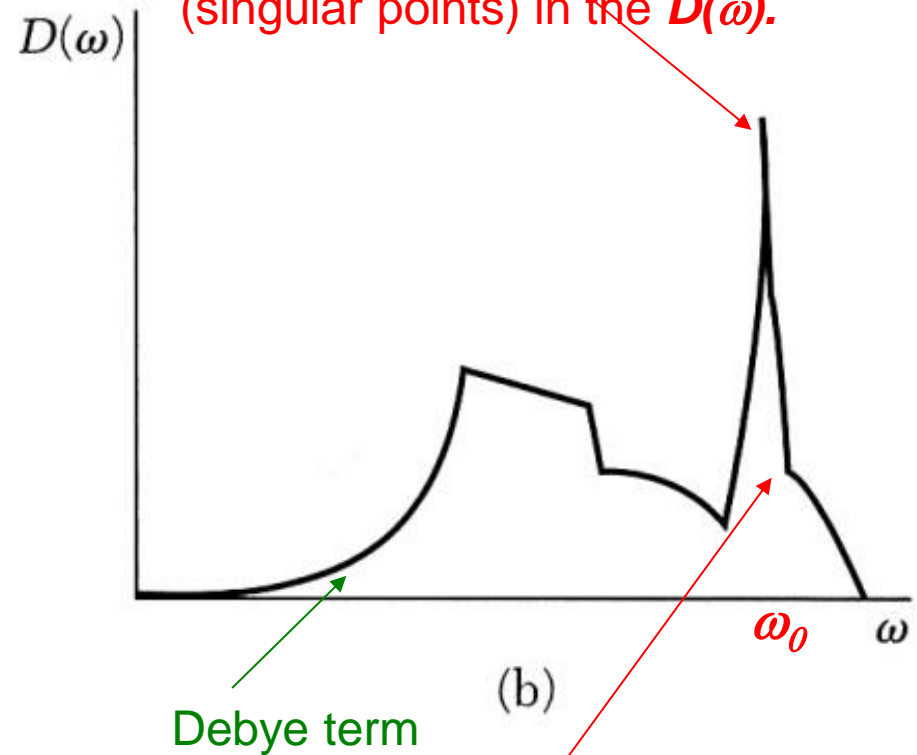


Fig. 14

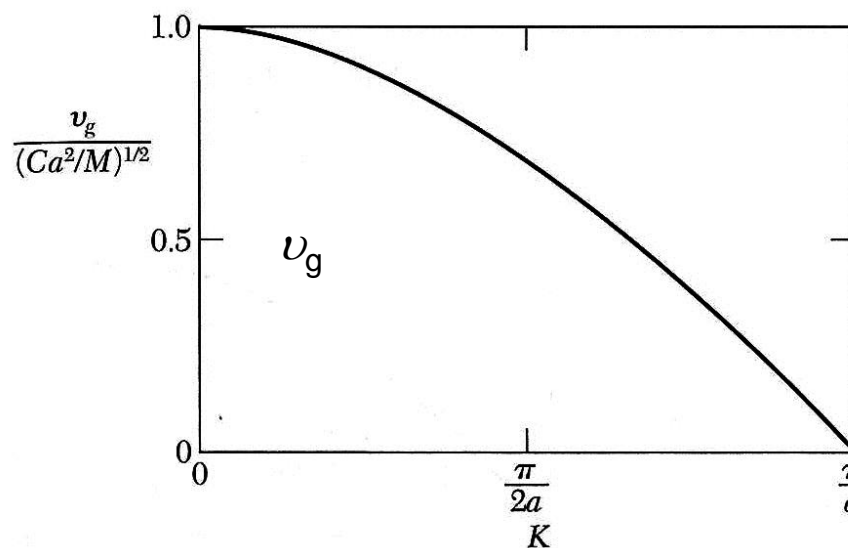
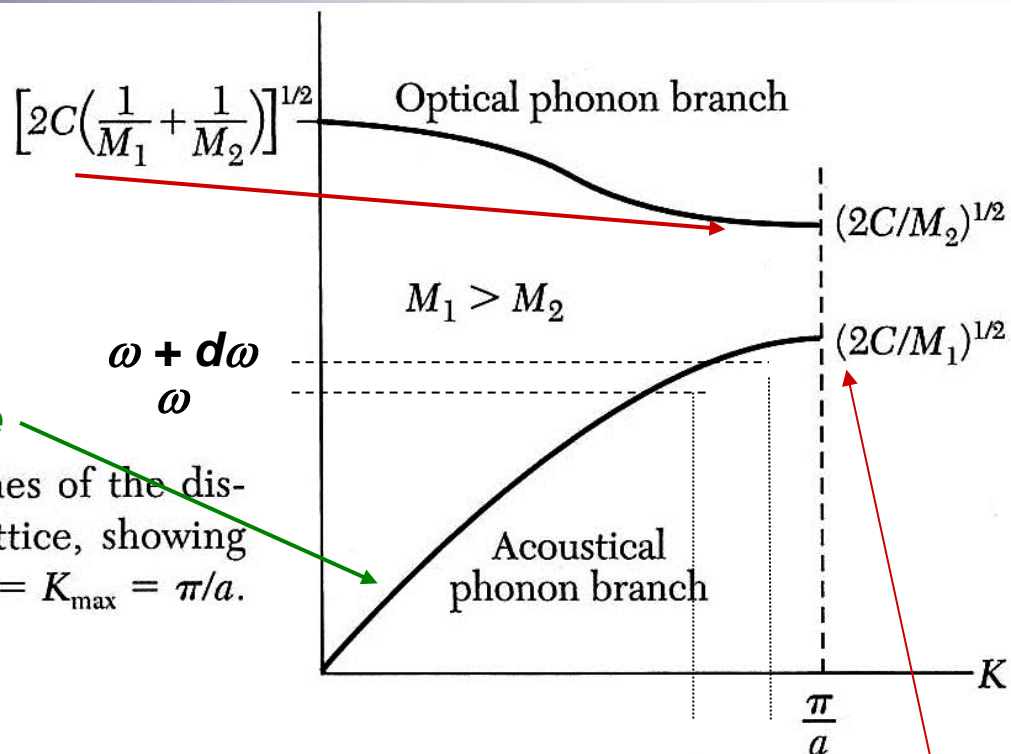
The density of states $D(\omega)$ vs ω for (a) the Debye Solid; (b) the actual solid.
The spectrum for the crystal structure starts as ω^2 , but discontinuity develops at the
singular points ($v_g = 0$)

Also known as the **Van Hove Singularity**

Near the zone boundary, a large population of states in K , i.e. a peak in $D(\omega)$, the corresponding v_g is zero.

$\omega = v_g K$, acoustic mode

Figure 7 Optical and acoustical branches of the dispersion relation for a diatomic linear lattice, showing the limiting frequencies at $K = 0$ and $K = K_{\max} = \pi/a$. The lattice constant is a .



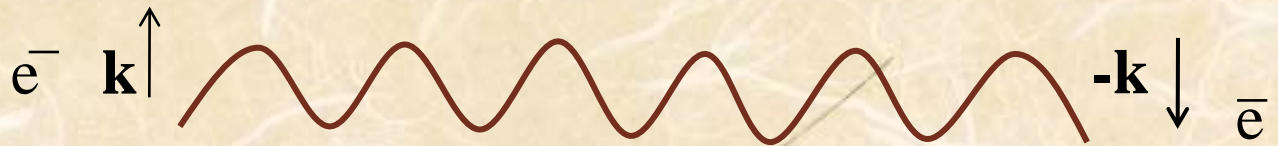
**At zone boundary
 v_g is zero**

Low- T_c Superconductivity Mechanism



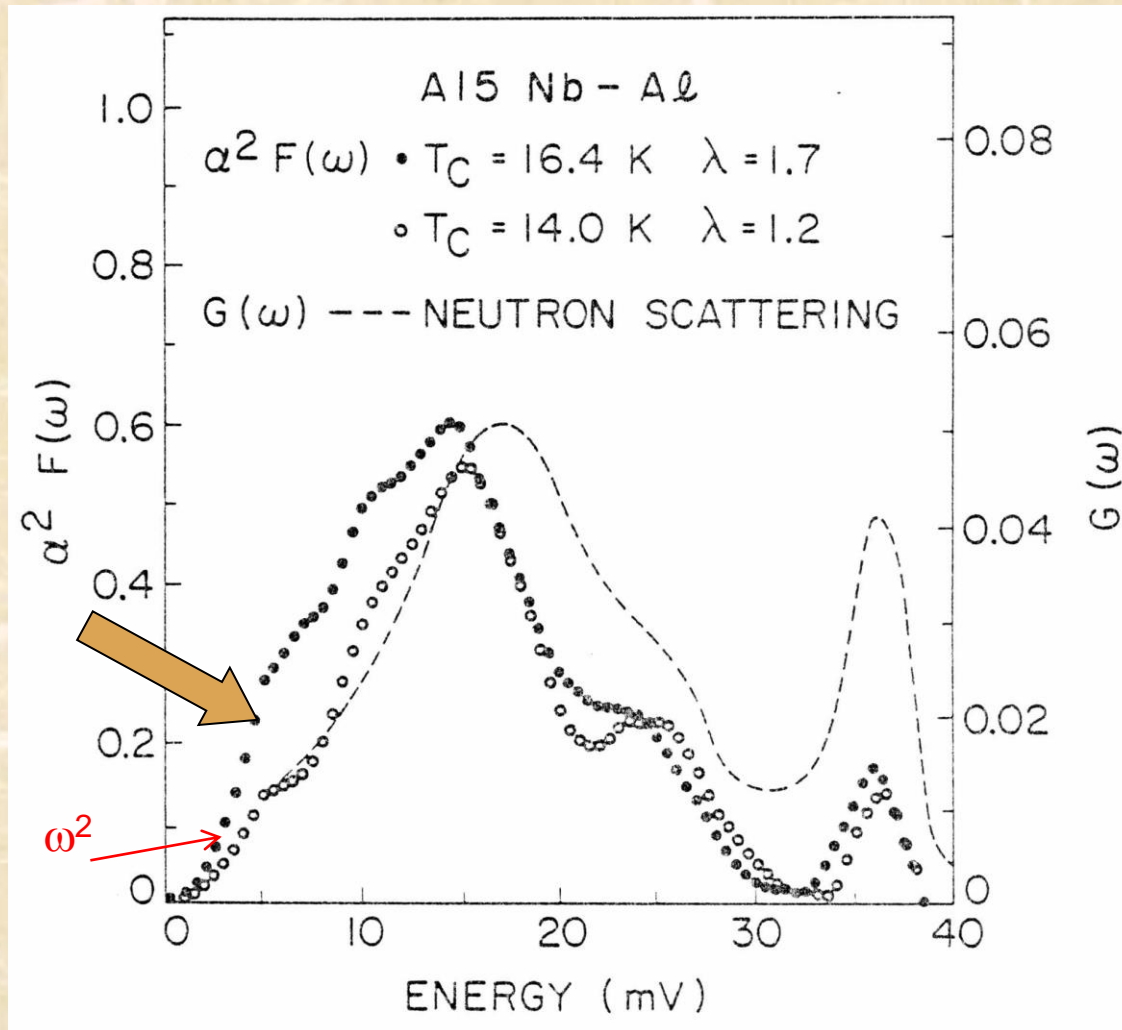
BCS Theory in 1957

Electron phonon coupling



Two electrons are bounded in pairs.

The Electron-Phonon Spectra Function of the Low T_c A-15 Compound Nb_3Al



Harmonic interaction: the quadratic terms of strains. Two lattice waves do not interact, and no thermal expansion, etc.

In real crystals : Anharmonic crystal interactions

The energy includes higher order terms than the quadratic (harmonic) term.

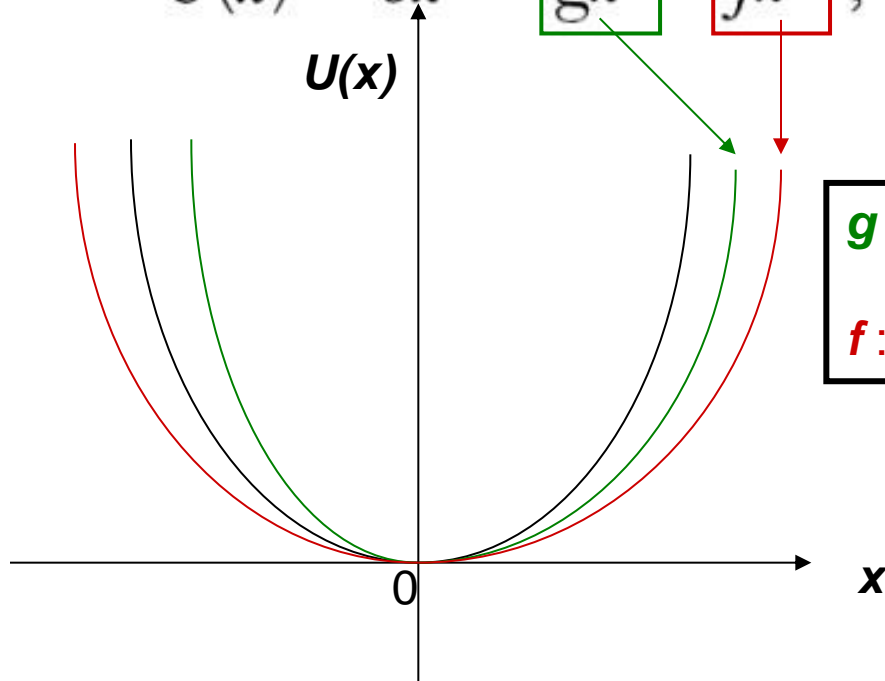
$$U_3 = A e_{xx} e_{yy} e_{zz}$$

Three phonon processes are caused by the third order terms in the lattice potential energy.

Thermal Expansions:

$$U(x) = cx^2 - gx^3 - fx^4, \quad C, f, g \text{ are positive.} \quad (38)$$

Including anharmonic energy terms



g : asymmetry of mutual repulsion interaction

f : softening of the vibration at large x

By using the Boltzmann distribution, we calculate average displacement $\langle x \rangle$ as the ratio of the following two terms:

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} dx x \exp[-\beta U(x)]}{\int_{-\infty}^{\infty} dx \exp[-\beta U(x)]}, \quad \beta = 1/k_B T$$

$$\begin{aligned} \int dx x \exp(-\beta U) &\cong \int dx [\exp(-\beta c x^2)](x + \beta g x^4 + \beta f x^5) = (3\pi^{1/2}/4)(g/c^{5/2})\beta^{-3/2}; \\ \int dx \exp(-\beta U) &\cong \int dx \exp(-\beta c x^2) = (\pi/\beta c)^{1/2}, \end{aligned} \quad (39)$$

$$\langle x \rangle = \frac{3g}{4c^2} k_B T \quad (40)$$

$\langle x \rangle$ is linear at higher T , but

$\langle x \rangle$ is ~ 0 at very low T

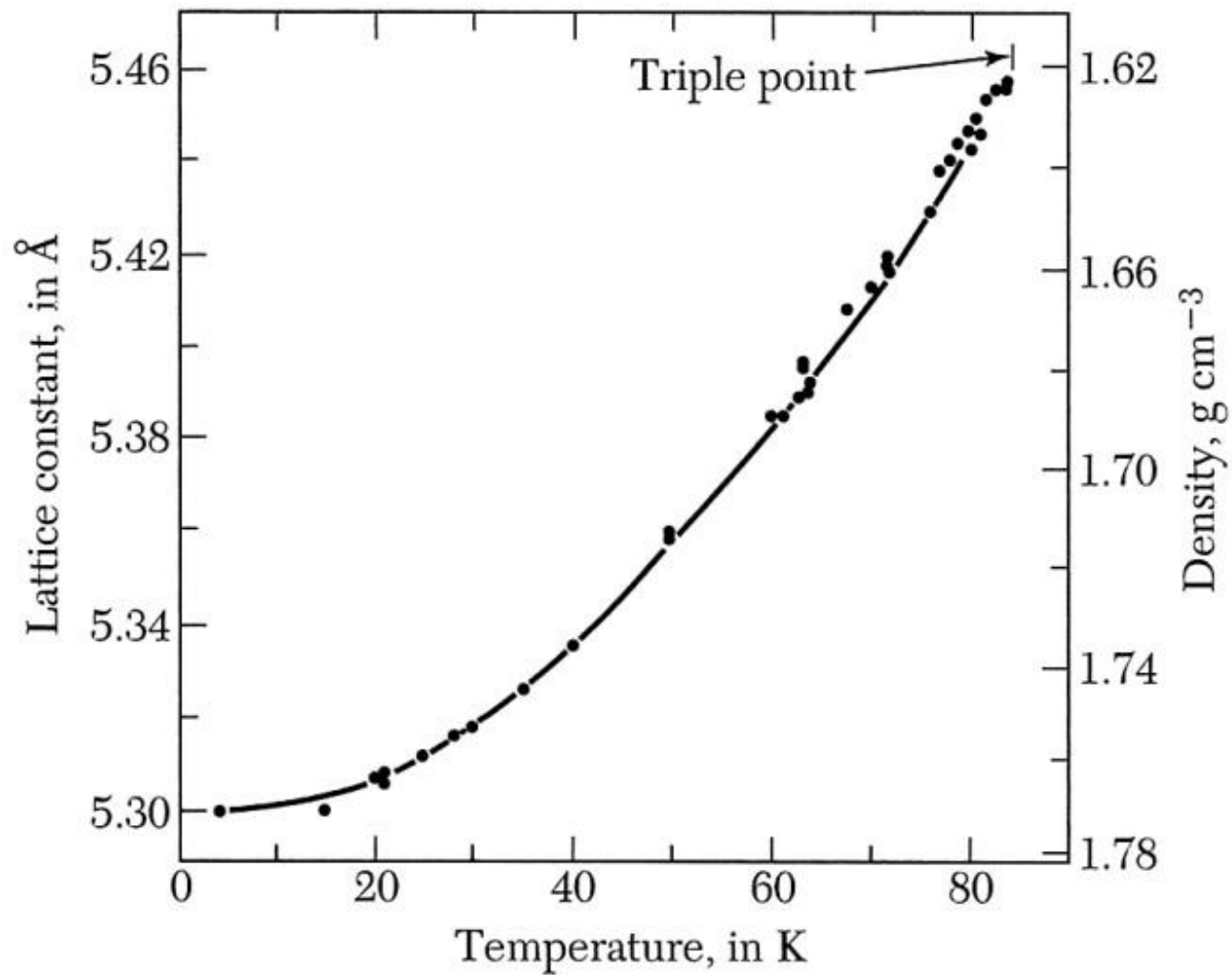


Fig. 15 Lattice constant of **solid Argon** as a function of temperature

THERMAL CONDUCTIVITY

$$j_U = -K \frac{dT}{dx} , \quad \begin{array}{l} j_U \text{ as the flux of thermal energy transmitted} \\ \text{per unit time per unit area.} \end{array} \quad (41)$$

dT/dx is the temperature gradient

The transfer of thermal energy process is not a straight path, but a *random* diffusion process with frequent collisions.

$$j_U = \langle N_f \rangle c \Delta T , \quad \langle N_f \rangle \text{ is the particle flux} = n \langle v_x \rangle \text{ in the } x \text{ direction}$$

Here we introduce

$$\Delta T = dT/dx \ell_x = dT/dx v_x \tau \quad \begin{array}{l} \ell_x \text{ is the mean free path between collisions} \\ \tau \text{ is the average time between collisions} \end{array}$$

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

$$j_U = -\frac{1}{3} C v \ell \frac{dT}{dx} , \quad \text{let } \ell = v \tau , \quad C = n c \quad (44)$$

$$K = \frac{1}{3} C v \ell ,$$

Debye's Expression for K (42)

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	$T, ^\circ\text{C}$	$C, \text{ in } \text{J cm}^{-3}\text{K}^{-1}$	$K, \text{ in } \text{W cm}^{-1}\text{K}^{-1}$	$\ell, \text{ in } \text{\AA}$
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

^aParallel to optic axis.

$$K = \frac{1}{3}Cv\ell ,$$

Thermal Resistivity of Phonon Gas

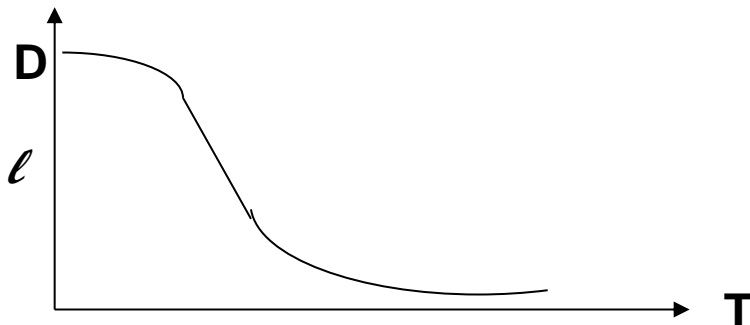
Phonon mean free path ℓ

Geometrical scattering by crystal boundary, and lattice imperfections, etc.

Purely **harmonic** interaction

At low T

ℓ is limited by sample width D



Scatterings by other phonons

Anharmonic interactions with third phonon

At high T , frequency of collisions $\langle f \rangle$

$$\langle f \rangle \propto \langle N \rangle \sim K_B T$$

$$\ell \propto 1/f \propto 1/T$$

(A) For a three phonon collision process: the total momentum of the phonon gas is not changed by such a collision.

$$\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3 \quad \mathbf{G} = 0, \quad \text{the } \underline{N} \text{ process} \quad (45)$$

The total phonon momentum is conserved.

$$\mathbf{J} = \sum_{\mathbf{K}} n_{\mathbf{K}} \hbar \mathbf{K} \quad (46)$$

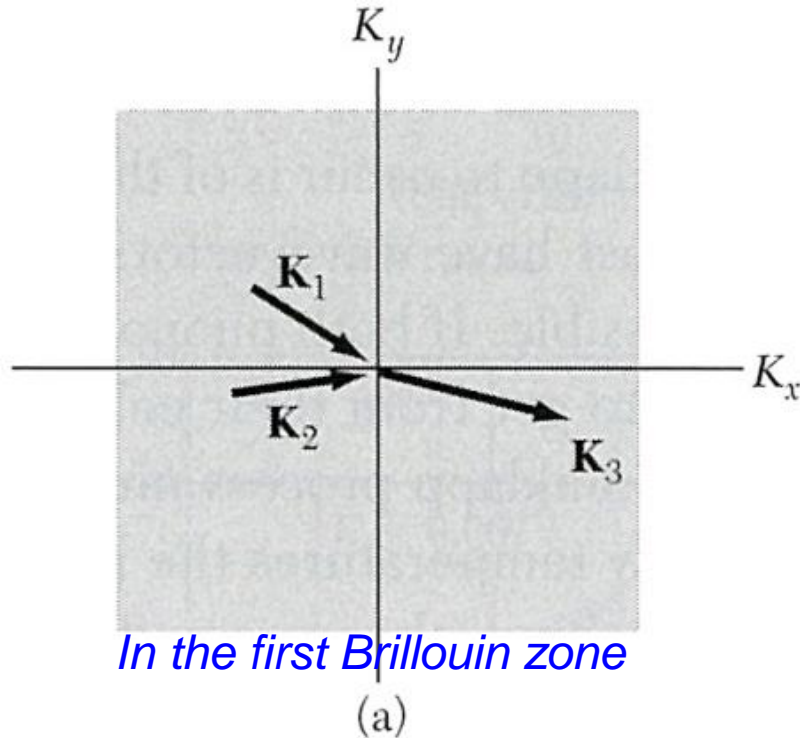
(B) The Umklapp Process: the three phonon process that caused thermal resistivity,

\mathbf{G} is a reciprocal lattice vector,

$$\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3 + \mathbf{G}, \quad \text{the } U \text{ process} \quad (47)$$

The energy of phonons $\mathbf{K}_1, \mathbf{K}_2$ suitable for umklapp to occur is of the order of $\frac{1}{2}k_B\theta$, because each of the phonons 1 and 2 must have wavevectors of the order of $\frac{1}{2}\mathbf{G}$ in order for the collision (47) to be possible.

The Normal process



The Umklapp process

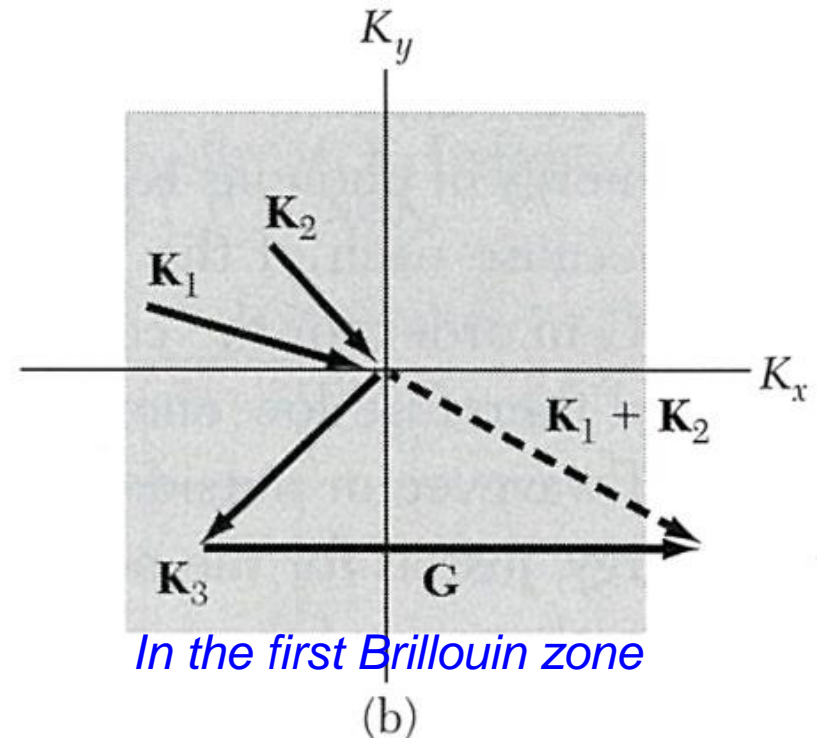


Figure 17 (a) Normal $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3$ and (b) umklapp $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3 + \mathbf{G}$ phonon collision processes in a two-dimensional square lattice. The square in each figure represents the first Brillouin zone in the phonon \mathbf{K} space; this zone contains all the possible independent values of the phonon wavevector. Vectors \mathbf{K} with arrowheads at the center of the zone represent phonons absorbed in the collision process; those with arrowheads away from the center of the zone represent phonons emitted in the collision. We see in (b) that in the umklapp process the direction of the x-component of the phonon flux has been reversed. The reciprocal lattice vector \mathbf{G} as shown is of length $2\pi/a$, where a is the lattice constant of the crystal lattice, and is parallel to the K_x axis. For all processes, N or U , energy must be conserved, so that $\omega_1 + \omega_2 = \omega_3$.

Open end tube

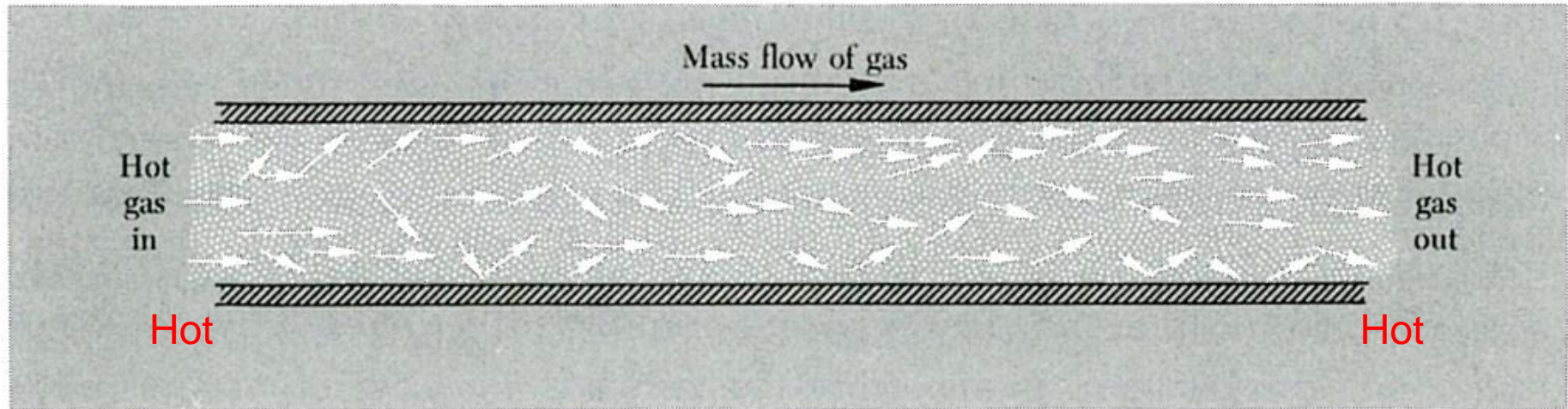


Figure 16a Flow of gas molecules in a state of drifting equilibrium down a long open tube with frictionless walls. Elastic collision processes among the gas molecules do not change the momentum or energy flux of the gas because in each collision the velocity of the center of mass of the colliding particles and their energy remain unchanged. Thus energy is transported from left to right without being driven by a temperature gradient. Therefore the thermal resistivity is zero and the thermal conductivity is infinite.

J_u is finite, $dT/dX = 0$, thus the thermal conductivity K is infinite !

Close end tube

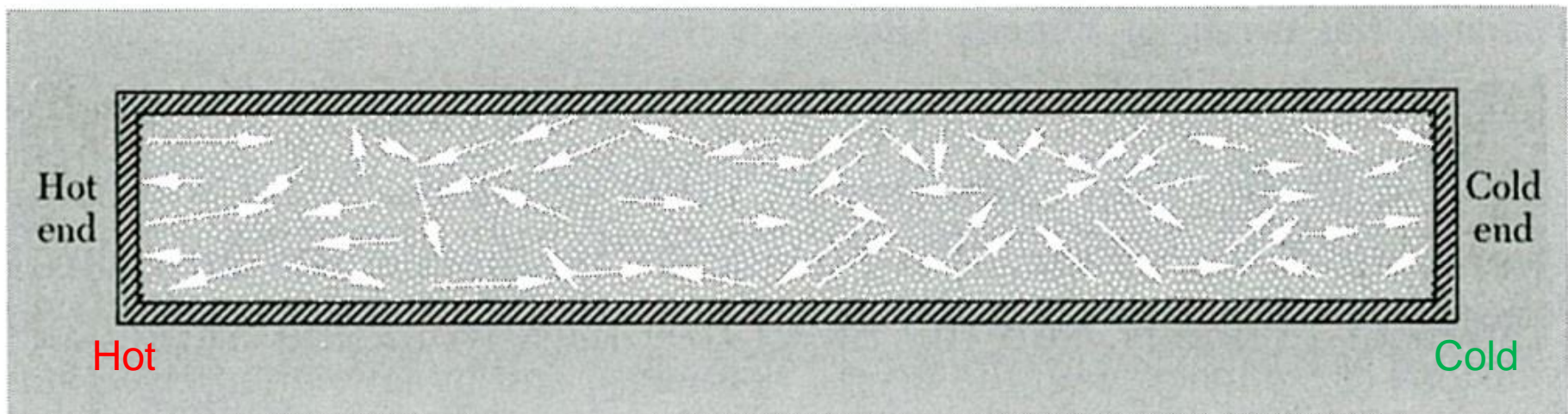


Figure 16b The usual definition of thermal conductivity in a gas refers to a situation where no mass flow is permitted. Here the tube is closed at both ends, preventing the escape or entrance of molecules. With a temperature gradient the colliding pairs with above-average center of mass velocities will tend to be directed to the right, those with below-average velocities will tend to be directed to the left. A slight concentration gradient, high on the right, will be set up to enable the net mass transport to be zero while allowing a net energy transport from the hot to the cold end.

Net energy transfer = J_u is finite



Shine light on

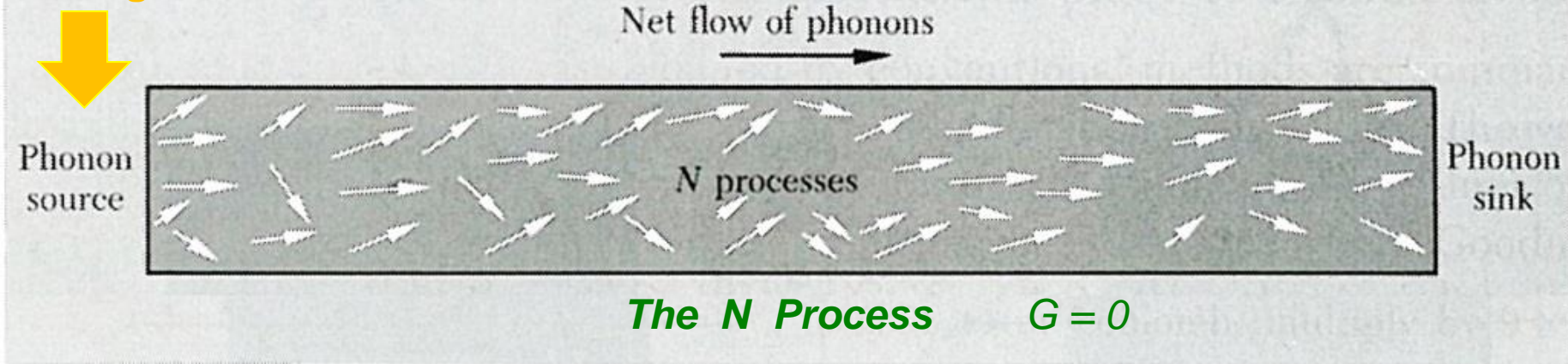


Figure 16c In a crystal we may arrange to create phonons chiefly at one end, as by illuminating the left end with a lamp. From that end there will be a net flux of phonons toward the right end of the crystal. If only N processes ($\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3$) occur, the phonon flux is unchanged in momentum on collision and some phonon flux will persist down the length of the crystal. On arrival of phonons at the right end we can arrange in principle to convert most of their energy to radiation, thereby creating a sink for the phonons. Just as in (a) the thermal resistivity is zero.

The thermal conductivity \mathbf{K} is infinite !

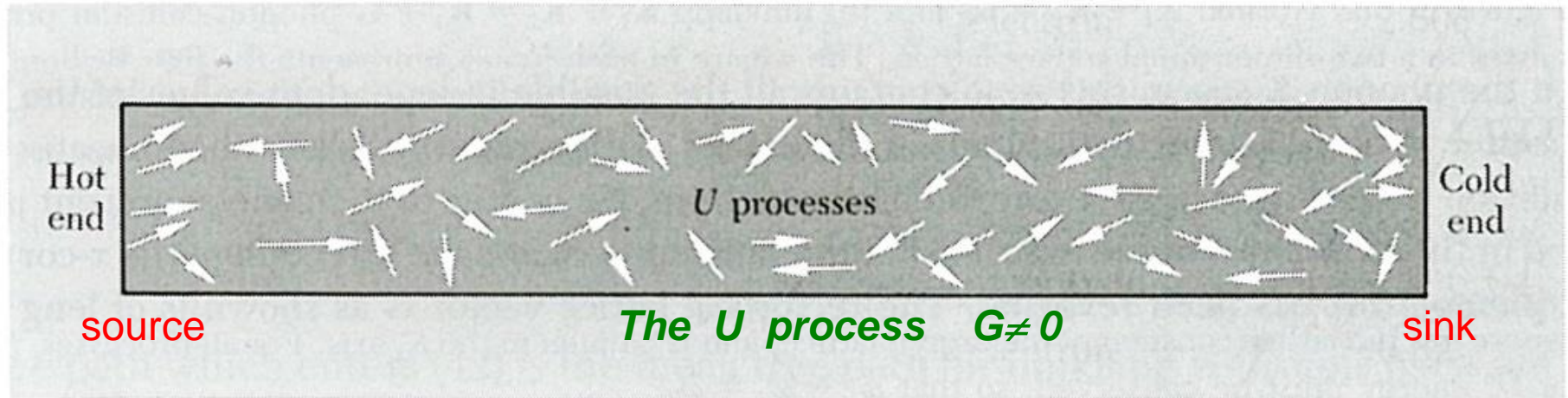


Figure 16d In U processes there is a large net change in phonon momentum in each collision event. An initial net phonon flux will rapidly decay as we move to the right. The ends may act as sources and sinks. Net energy transport under a temperature gradient occurs as in (b).

Net energy transfer


The momentum \mathbf{G} , and the energy are transmitted to the crystal, causing the temperature change.

$$J_u = \text{finite}, \quad dT/dx = \text{finite}.$$

Crystal imperfections:

We must consider scattering by crystal boundaries, the distribution of isotopic masses in natural chemical elements, chemical impurities, lattice imperfections, and amorphous structures.

At high T , $\ell \sim 1/T$, $K \propto 1/T$

At low T , $\ell \sim D$, limited by the sample width

At low T , $C \sim T^3$, $K \propto T^3$

$$K \approx CvD \quad (48)$$

K varies as T^3 at low T , and displays a maximum feature due to the temperature dependence of ℓ .

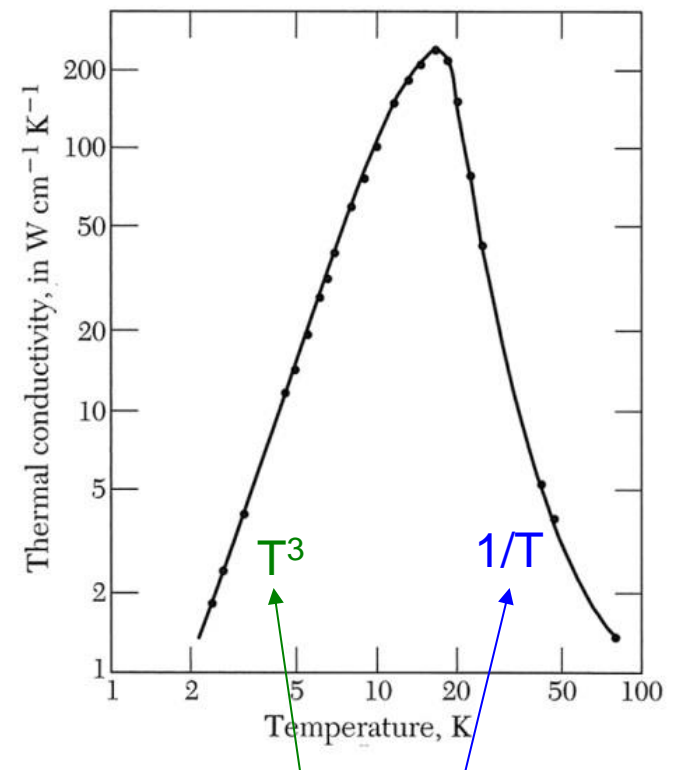
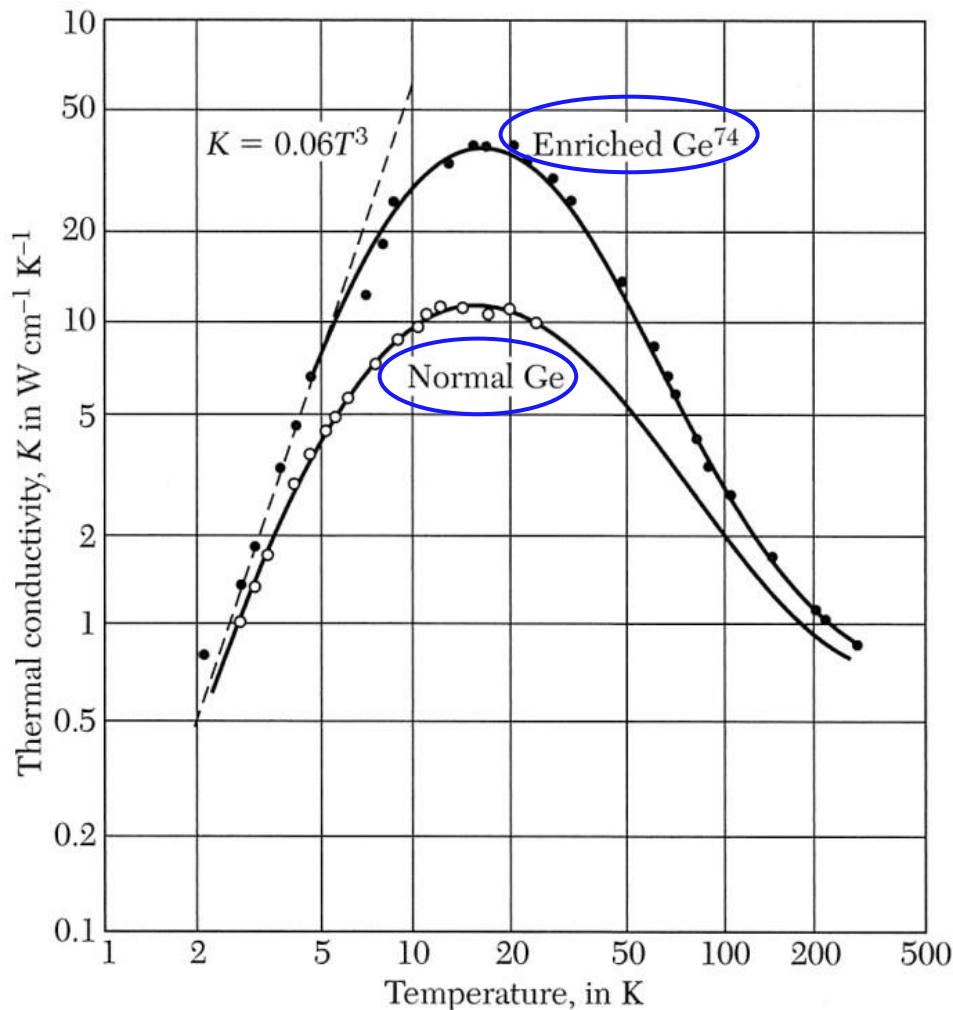


Figure 18 Thermal conductivity of a highly purified crystal of sodium fluoride, after H. E. Jackson, C. T. Walker, and T. F. McNelly.



Ge

Isotope effect increases the thermal conductivity by a factor of 2-3.

Phys. Rev. 110, 773 (1958)

Figure 19 Isotope effect on thermal conduction in germanium, amounting to a factor of three at the conductivity maximum. The enriched specimen is 96 percent Ge^{74} , natural germanium is 20 percent Ge^{70} , 27 percent Ge^{72} , 8 percent Ge^{73} , 37 percent Ge^{74} , and 8 percent Ge^{76} . Below 5 K the enriched specimen has $K = 0.06 T^3$, which agrees well with Casimir's theory for thermal resistance caused by boundary scattering. (After T. H. Geballe and G. W. Hull.)

In an otherwise perfect crystal, the distribution of isotopes of the chemical elements often provides an important mechanism for phonon scattering. The random distribution of isotopic mass disturbs the periodicity of the density as

This leads to a significant increase in thermal conductivity

Age 95,

Age 85

