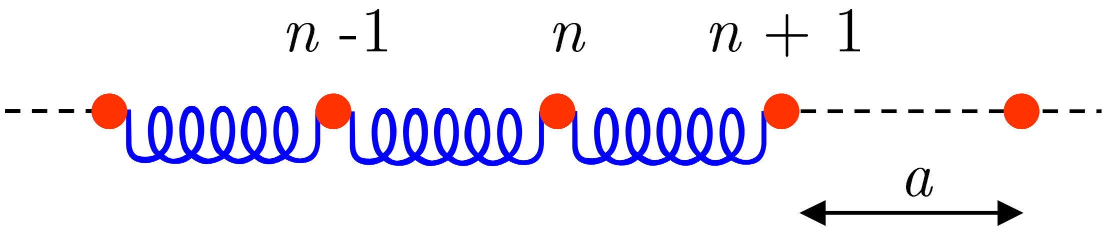
Vibrations in a Solid



Consider displacements δ from equilibrium:

$$m\ddot{\delta} = \lambda\left(\delta_{n+1} - \delta_n\right) + \lambda\left(\delta_{n-1} - \delta_n\right)$$

$$+ \text{ weaker terms } \sim \left(\delta_{n+2} - \delta_n\right)$$

Insoluble coupled problem – Try normal mode approach:

$$\delta \propto \mathrm{e}^{\mathrm{i}(kx-\omega t)}$$

$$\therefore \delta_n = \mathrm{Re}\,\eta \mathrm{e}^{\mathrm{i}(kna-\omega t)}$$

$$\text{So } -m\eta\omega^2\mathrm{e}^{\mathrm{i}kna}$$

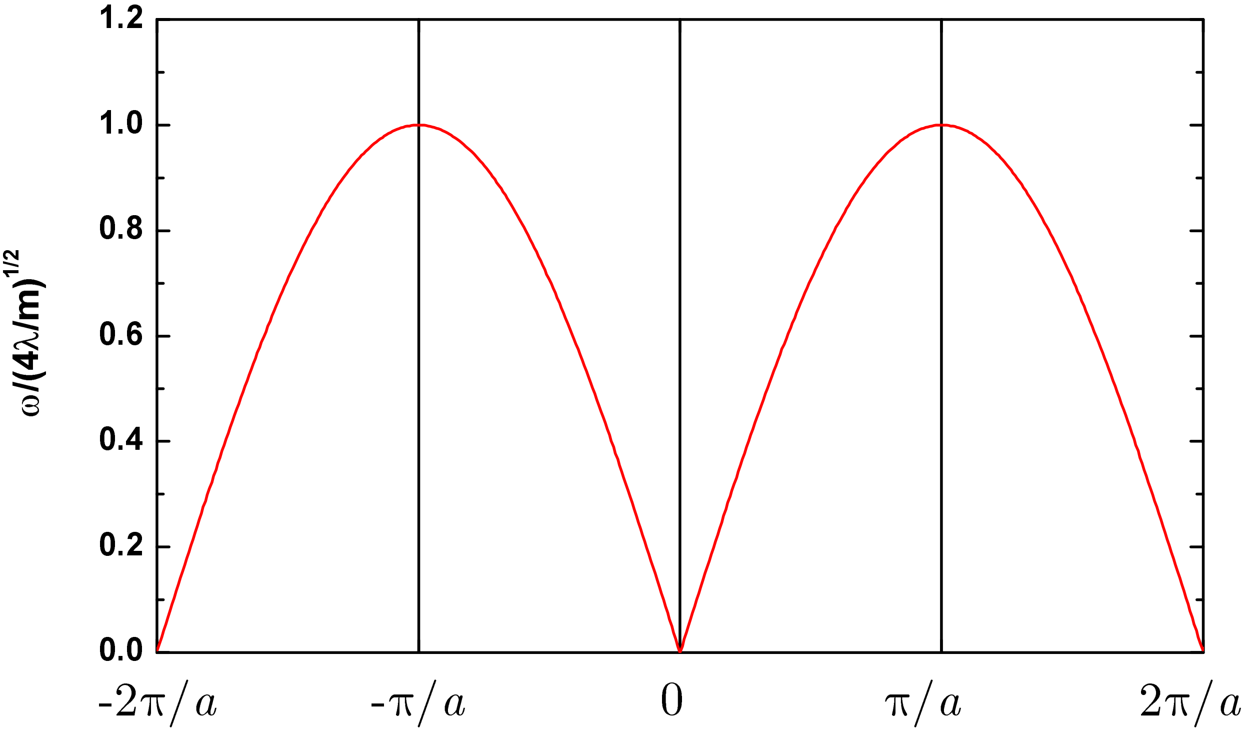
$$= \lambda\left[\eta\mathrm{e}^{\mathrm{i}(n+1)ka} + \eta\mathrm{e}^{\mathrm{i}(n-1)ka} - 2\eta\mathrm{e}^{\mathrm{i}kna}\right]$$

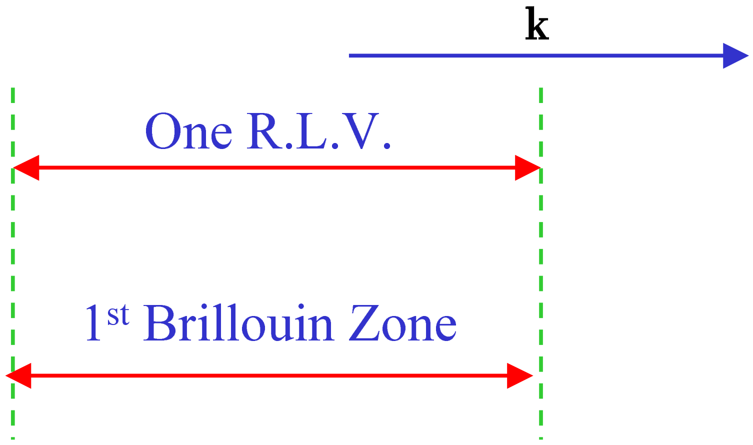
$$\therefore -\frac{m\omega^2}{\lambda} = \mathrm{e}^{\mathrm{i}ka} + \mathrm{e}^{-\mathrm{i}ka} - 2 = 2\cos ka - 2$$

$$= -4\sin^2\frac{ka}{2}$$

Therefore:

$$\boxed{\omega(k) = 2\sqrt{\frac{\lambda}{m}}\sin\frac{ka}{2}}$$





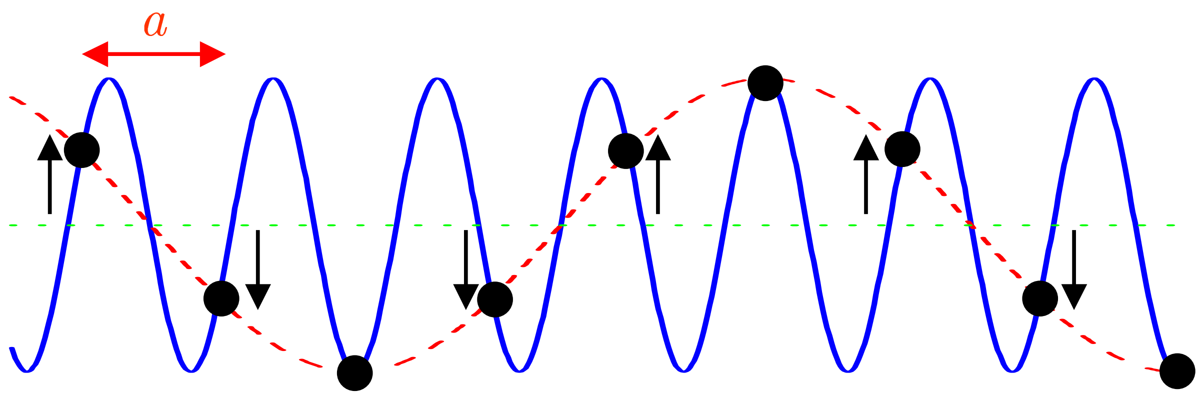
One R.L.V.

1^{st} Brillouin Zone

$$\mathbf{v}_g = \nabla_k \omega(\mathbf{k}) = \sqrt{\frac{\lambda a^2}{m}}\cos(ka/2)$$

For long wavelengths, k is small,

$$\therefore\ \omega \approx a\sqrt{\frac{\lambda}{m}}\,k = v_s k\ ,\ v_s =$$ speed of sound



Consider a transverse acoustic wave:

$$\delta(x) = \delta_0 \mathrm{e}^{\mathrm{i}kx}$$

$$\delta(na) = \delta_0 \mathrm{e}^{\mathrm{i}kna} \quad \text{for atom } n$$

Move by 1 R.L.V. $\mathbf{k} \rightarrow \mathbf{k} + \mathbf{G}$

$$\delta(x) = \delta_0 \mathrm{e}^{\mathrm{i}(k+G)x}$$

$$\delta(na) = \delta_0 \mathrm{e}^{\mathrm{i}kna} \mathrm{e}^{\mathrm{i}Gna} = \delta_0 \mathrm{e}^{\mathrm{i}kna}$$

$$\text{since} \quad Gna = \frac{2\pi}{a} na = 2n\pi$$

$$\text{so} \quad |\mathbf{k}|_{\mathrm{max}} = \pm \frac{\pi}{a}$$

$$\therefore \quad \lambda_{\mathrm{min}} = 2a$$

From the above picture we see that where it MATTERS no change has occurred.

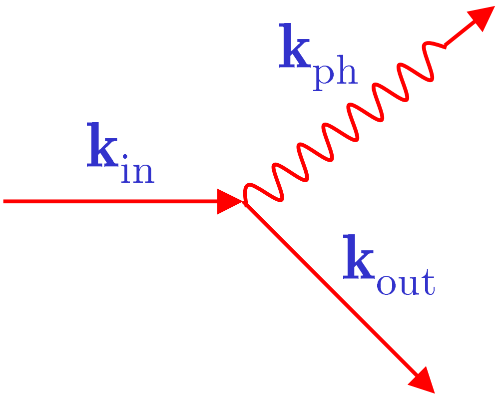
Phonons

Quantize the energy to give:

$$E(\omega) = \left(n_{\mathbf{k}\mathrm{s}} + \frac{1}{2} \right) \hbar \omega_{\mathrm{s}} \left(\mathbf{k} \right)$$

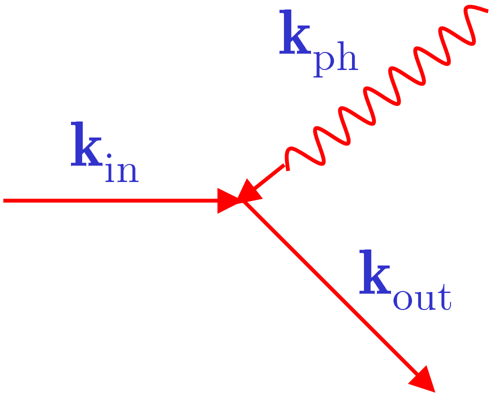
Where $n_{\mathbf{k}\mathrm{s}}$ is the excitation number of a normal mode s. These are phonons i.e. there are $n_{\mathbf{k}\mathrm{s}}$ phonons of type s with wavevector $\mathbf{k}$ present in the crystal.

Measured by Neutron Scattering



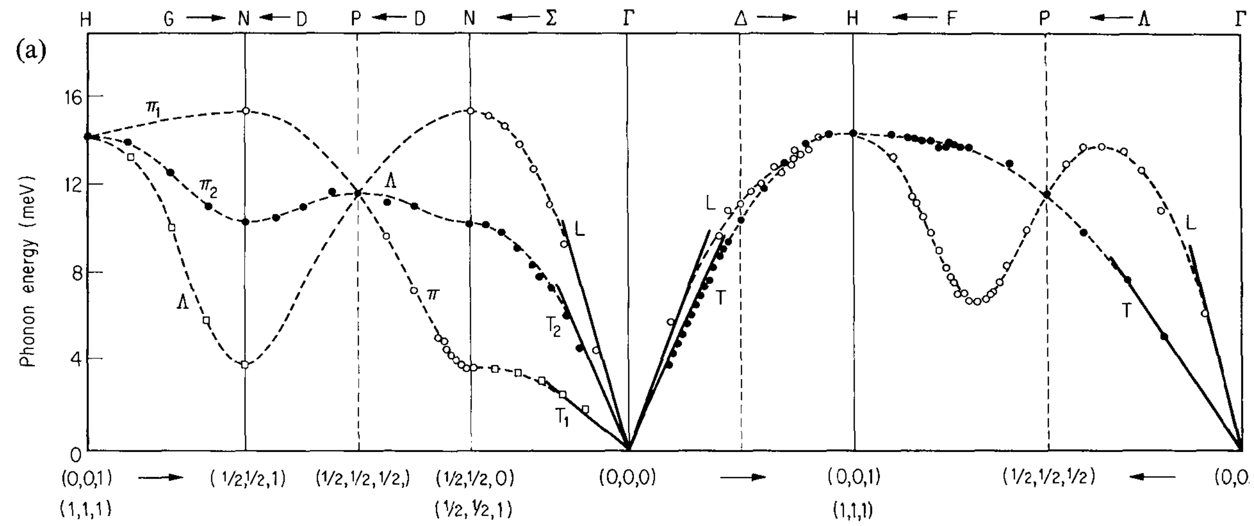
$$\mathbf{k}_{\mathrm{in}} = \mathbf{k}_{\mathrm{out}} + \mathbf{k}_{\mathrm{ph}} \pm \mathbf{G}$$

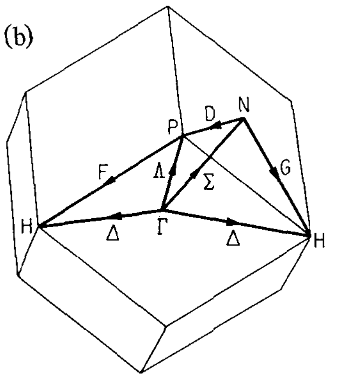
$$E_{\mathrm{in}} = E_{\mathrm{ph}} + E_{\mathrm{out}}$$



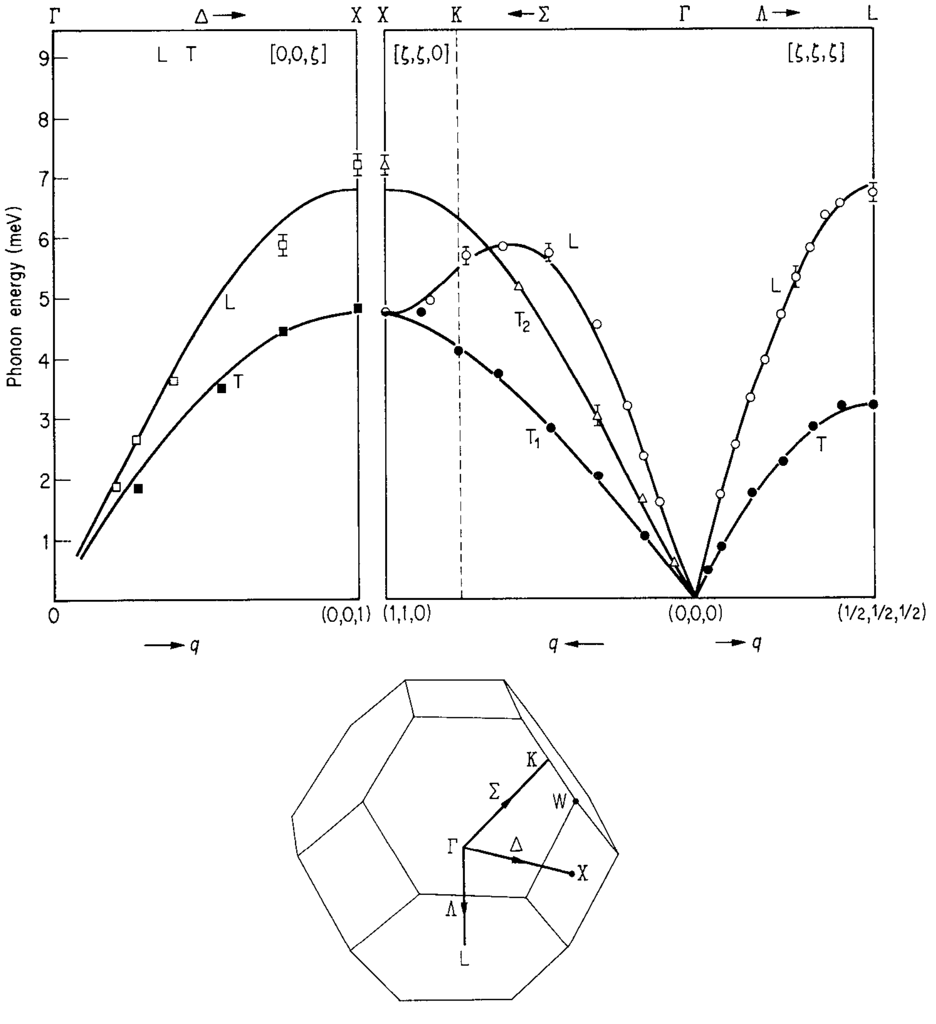
$$\mathbf{k}_{\mathrm{in}} + \mathbf{k}_{\mathrm{ph}} = \mathbf{k}_{\mathrm{out}} \pm \mathbf{G}$$

$$E_{\mathrm{in}} + E_{\mathrm{ph}} = E_{\mathrm{out}}$$





(a) Measured vibrational spectrum of b.c.c. Na at 90 K. Modes which are longitudinal and transverse are marked L and T. (b) The lines where $\boldsymbol{q}$ is measured are shown on the Brillouin zone. (After A. D. B. Woods *et al., Phys. Rev.* **128**, 1112 (1962).)



Measured vibrational spectrum $\hbar\omega(\boldsymbol{q})$ for various directions in the zone of f.c.c. Ne at 4.7 K (after J. A. Leake *et al., Phys. Rev.* **181**, 125 (1969)). The lines of $\boldsymbol{q}$ depicted are shown in a Brillouin zone, with conventional lettering. $\boldsymbol{q}$ is given in units of $2\pi/a$

Allowed values of **k** for excitations

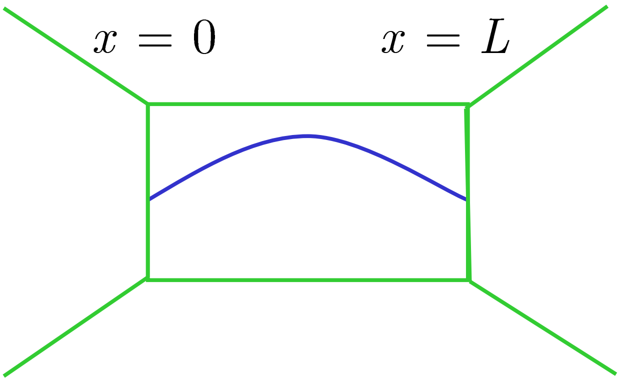
The effect of the size of the specimen:

Photons in a metal box E// = 0 @ walls

Electrons in a potl. well $\Psi = 0$ @ edges

Lattice vibrations in a solid:

Either



No displacement at edge

$$\delta = 0 \text{ @ } x = 0$$

$$\delta = 0 \text{ @ } x = L$$

Try $\delta = \sin kx$

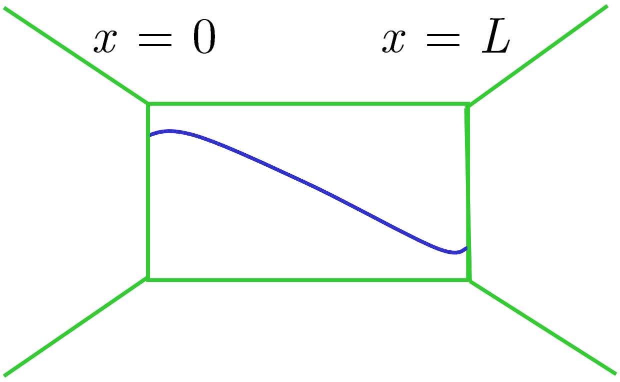
$$\therefore 0 = \sin kL$$

$$\therefore kL = n\pi$$

& $\boxed{k = n\pi / L}$

($n = 0$ or +ve integer)

Or



No force at edge

$$\frac{d\delta}{dx} = 0 \text{ @ } x = 0$$

$$\& \ x = L$$

Try $\delta = \cos kx$

then $0 = \sin kL$

and again

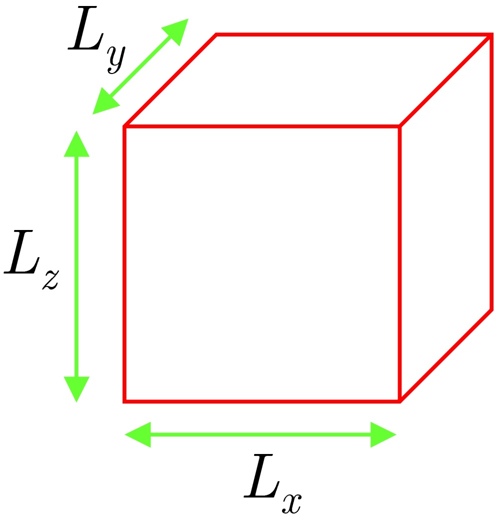
$$\boxed{k = n\pi / L}$$

In Three Dimensions:

$$k_x = \frac{n\pi}{L_x}$$

$$k_y = \frac{n\pi}{L_y}$$

$$k_z = \frac{n\pi}{L_z}$$



$$\therefore\ \mathbf{k} = \mathbf{i}\frac{n\pi}{L_x} + \mathbf{j}\frac{n\pi}{L_y} + \mathbf{k}\frac{n\pi}{L_z}$$

Volume of *k*-space permitted for one *k* point is:

$$\frac{\pi}{L_x}\cdot\frac{\pi}{L_y}\cdot\frac{\pi}{L_z} = \frac{\pi^3}{V_{\mathrm{solid}}}$$

Therefore *k*-space density of states is:

$$\boxed{\frac{V}{\pi^3} \qquad \text{+ve octant only}}$$

Therefore number of states between k and $k+\mathrm{d}k$ is:

$$\frac{4\pi k^2\mathrm{d}k}{8}\times\frac{V}{\pi^3} = \boxed{\frac{V}{2\pi^2}k^2\mathrm{d}k}$$

N.B. This is an entirely general result

What happens when we transform to frequency?

The number of allowed values of **k** for which the phonon frequency is between ω and $\omega+d\omega$ is:

$$D(\omega)\mathrm{d}\omega = \frac{V}{8\pi^3}\int_{\text{shell}} \mathrm{d}^3\mathbf{k}$$

Let dS_ω be an element of area on a surface of constant ω, then:

$$\int_{\text{shell}} \mathrm{d}^3\mathbf{k} = \int \mathrm{d}S_\omega \mathrm{d}k_\perp$$

Where $dk_\perp$ is the perpendicular distance between the surface of constant ω and $\omega+d\omega$. Now:

$$\mathrm{d}\omega = \left|\nabla_k \omega\right| \mathrm{d}k_\perp$$

(by the definition of grad), therefore:

$$D(\omega)\mathrm{d}\omega = \frac{V}{8\pi^3}\int \frac{\mathrm{d}S_\omega}{\left|\nabla_k \omega\right|}\mathrm{d}\omega$$

& $\left|\nabla_k \omega\right| \mathrm{d}k_\perp = v_g =$ group velocity

(which can be zero!)

Vibrational Specific Heat

Classical equipartition (when valid):

N atoms $3N$ vibrational modes

Dulong & Petit (high T limit):

$$\overline{E} = k_{\mathrm{B}}T \,/\, \mathrm{mode}$$

$$\therefore C_{\mathrm{v}} = 3Nk_{\mathrm{B}}$$

Einstein Model

All $3N$ modes of one frequency n, and use Bose-Einstein statistics (good for optical modes).

$$\overline{E} = 3N \, \frac{h\nu}{\mathrm{e}^{h\nu / k_{\mathrm{B}}T} - 1}$$

$$C_{\mathrm{v}} = 3Nk_{\mathrm{B}} \left(\frac{h\nu}{k_{\mathrm{B}}T} \right)^2 \frac{\mathrm{e}^{h\nu / k_{\mathrm{B}}T}}{\left(\mathrm{e}^{h\nu / k_{\mathrm{B}}T} - 1 \right)^2}$$

Debye Model

Deals well with acoustic modes, exact at low T, pretty good at intermediate T, OK at high T.

Assumptions:

1. E vs k for acoustic modes – take linear approximation always ($\omega = kv_{\text{sound}}$)

2. Density in k-space – max. frequency

Number of modes between k and $k + \mathrm{d}k$ is:

$$\frac{V}{2\pi^2} k^2 \mathrm{d}k$$

Which in the Debye approximation becomes:

$$D(\omega) = \frac{V}{2\pi^2} \cdot \frac{3\omega^2}{v_{\mathrm{s}}^3}$$

In total there are $3N$ modes, therefore:

$$3N = \frac{3V}{2\pi^2 v_{\mathrm{s}}^3} \int_0^{\omega_{\max}} \omega^2 \mathrm{d}\omega$$

$$\therefore\ \omega_{\text{max}} = v_{\text{s}}\left[\frac{3N}{V}2\pi^2\right]^{\frac{1}{3}}$$

and define $\boxed{\theta_{\text{D}} = \frac{\hbar\omega_{\text{max}}}{k_{\text{B}}} = \frac{\hbar\omega_{\text{D}}}{k_{\text{B}}}}$

$$\therefore\ E = \frac{3V}{2\pi v_{\text{s}}^3}\int_0^{\omega_{\text{max}}}\omega^2\,\frac{\hbar\omega}{\mathrm{e}^{\hbar\omega/k_{\text{B}}T}-1}\,\mathrm{d}\omega$$

$$= \int_0^{\omega_{\text{max}}} D(\omega)\ n(\omega)\ \hbar\omega\ \mathrm{d}\omega$$

$C_v = \dfrac{\mathrm{d}E}{\mathrm{d}T}$ let $x = \dfrac{\hbar\omega}{k_{\text{B}}T}$

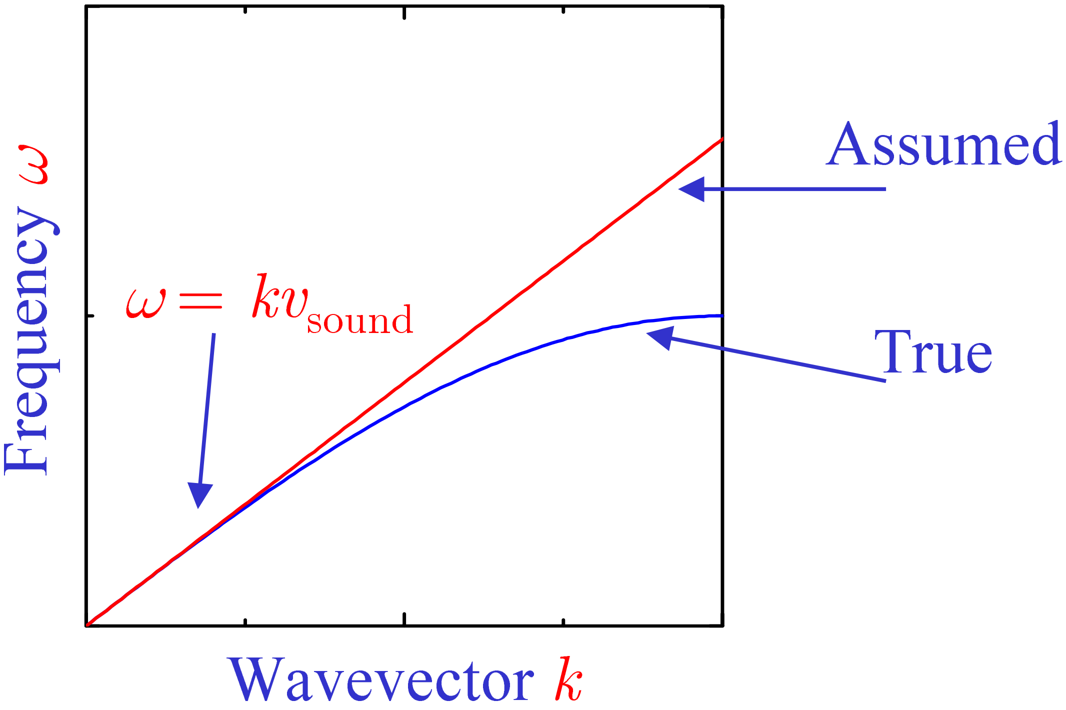
$$E = 9Nk_{\text{B}}T\left(\frac{T}{\theta_{\text{D}}}\right)^3\int_0^{x_{\text{D}}}\frac{x^3}{\mathrm{e}^x-1}\,\mathrm{d}x$$

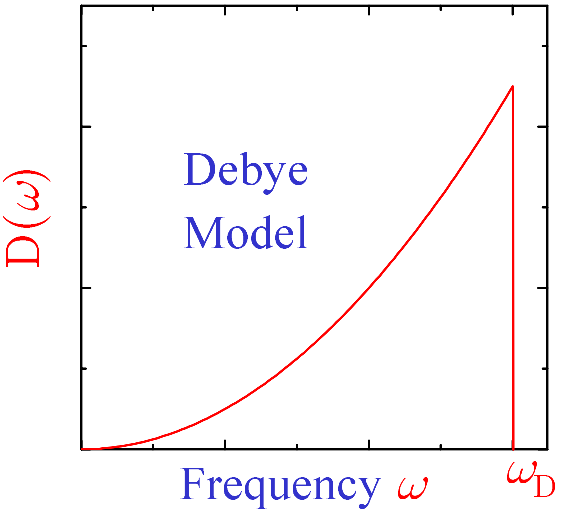
as $T \to 0$ $x_{\text{D}} \to \infty$ & integral $= \dfrac{\pi^4}{15}$

$$\therefore\quad \boxed{C_v = \frac{\mathrm{d}E}{\mathrm{d}T} = \frac{12\pi^4}{5}Nk_{\text{B}}\left(\frac{T}{\theta_{\text{D}}}\right)^3}$$

Here are typical values of θ_D for real materials:

$\theta_D =$	150 K	for	Na
	1860 K	for	C (diamond)
	230 K	for	Ca
	625 K	for	Si
	88 K	for	Pb





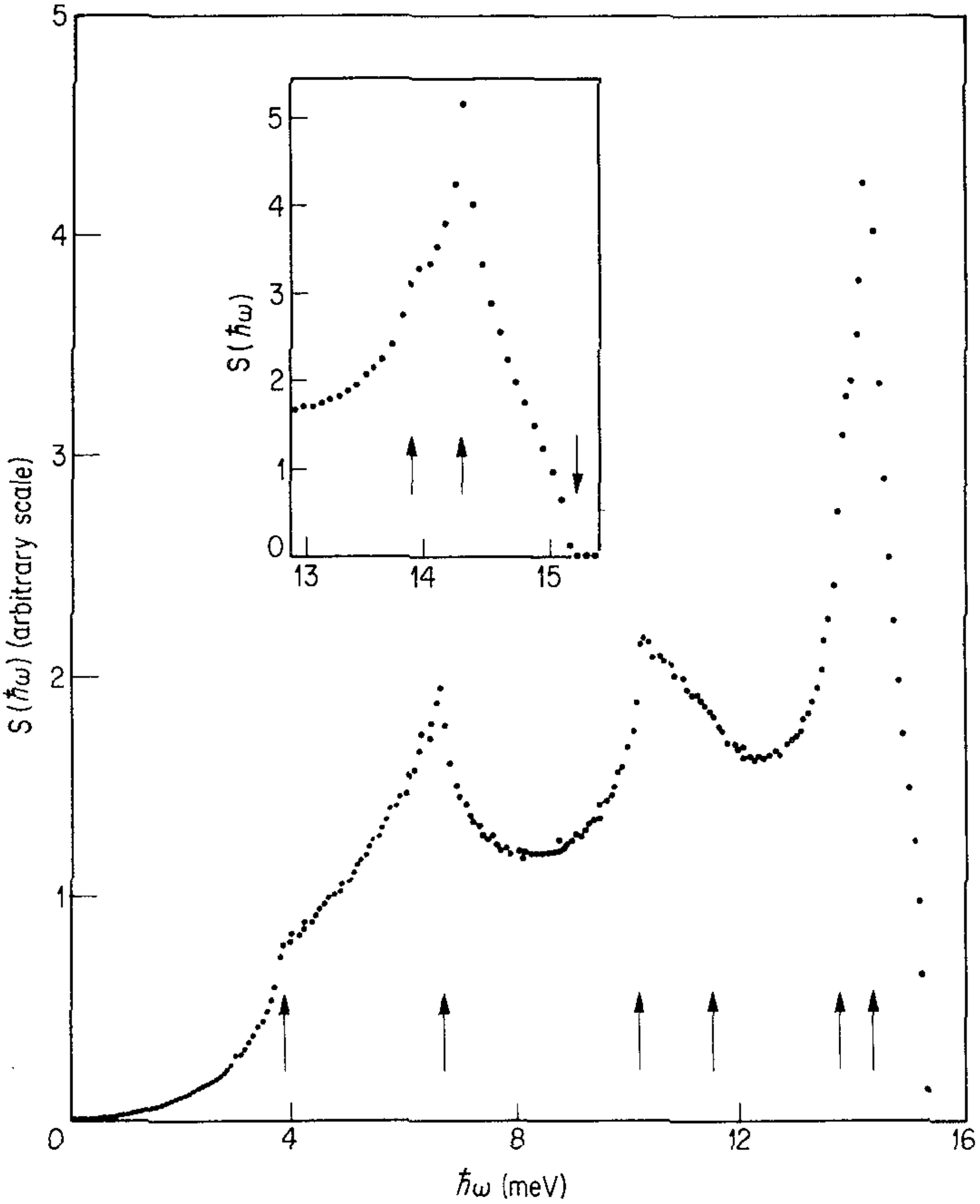


Figure 3.12 Density of modes in Na (after A. E. Dixon *et al., Proc. Phys. Soc.* **81**, 973 (1963)). The arrows indicate critical points—which correspond to points of zero slope in figure 3.11. (For example, the lowest critical point at 4 eV corresponds to the lowest branch at N in figure 3.11. The maximum energy 15.5 meV is also due to a mode at N, the high peak in S just below this due to the flat branch on the zone face N → G → H. H is also a critical point for this upper branch.)

Superconductivity

What defines the superconducting state?

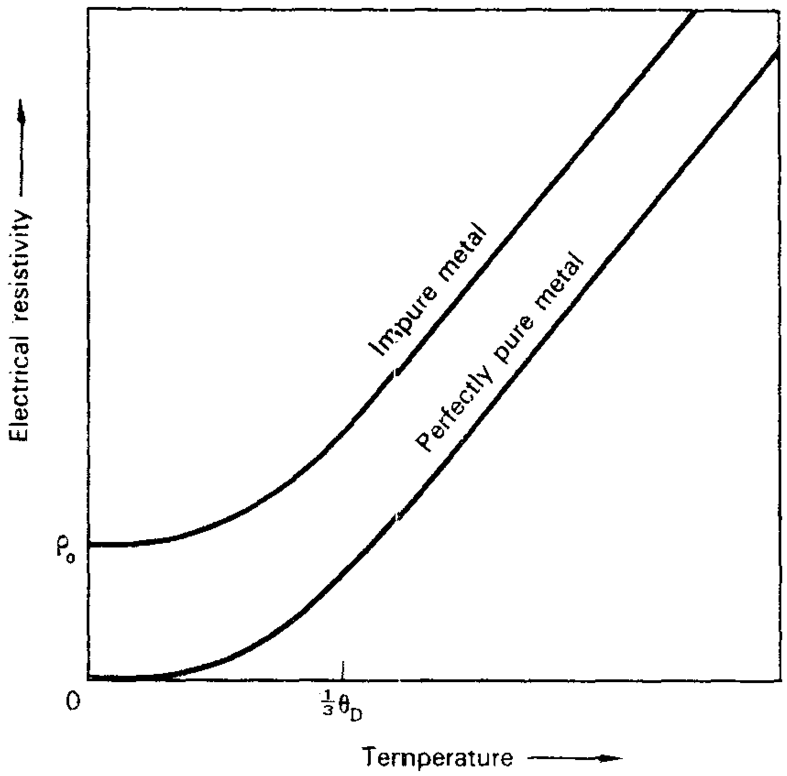
- Complete loss of resistance at a finite temperature

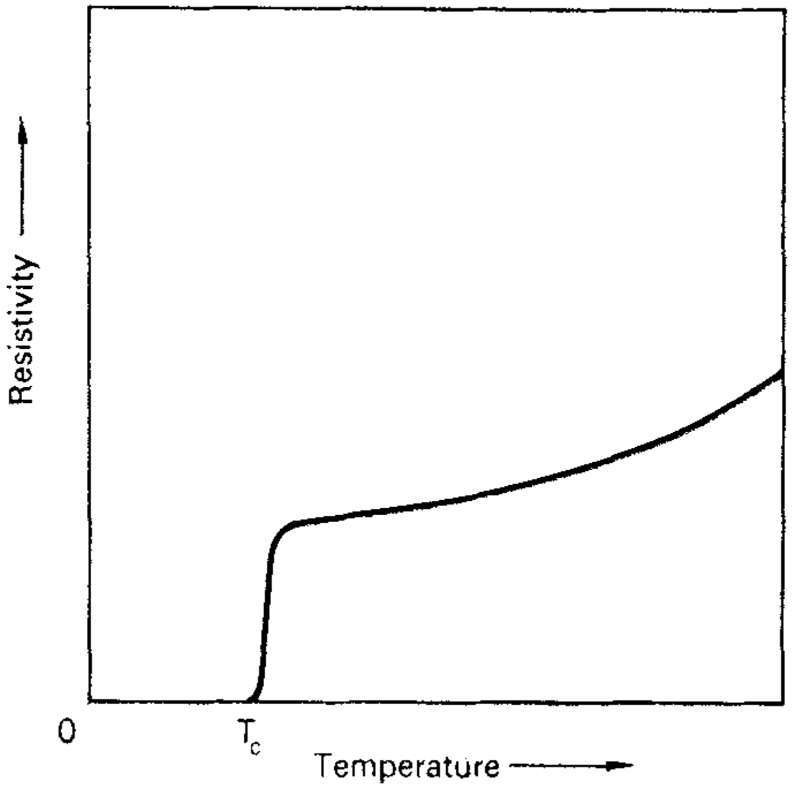
  (discovered by Kamerlingh Onnes at the University of Leiden in 1908)

- Perfect diamagnetism – the Meissner-Ochsenfeld effect

  (discovered in 1933 by Meissner and Ochsenfeld)

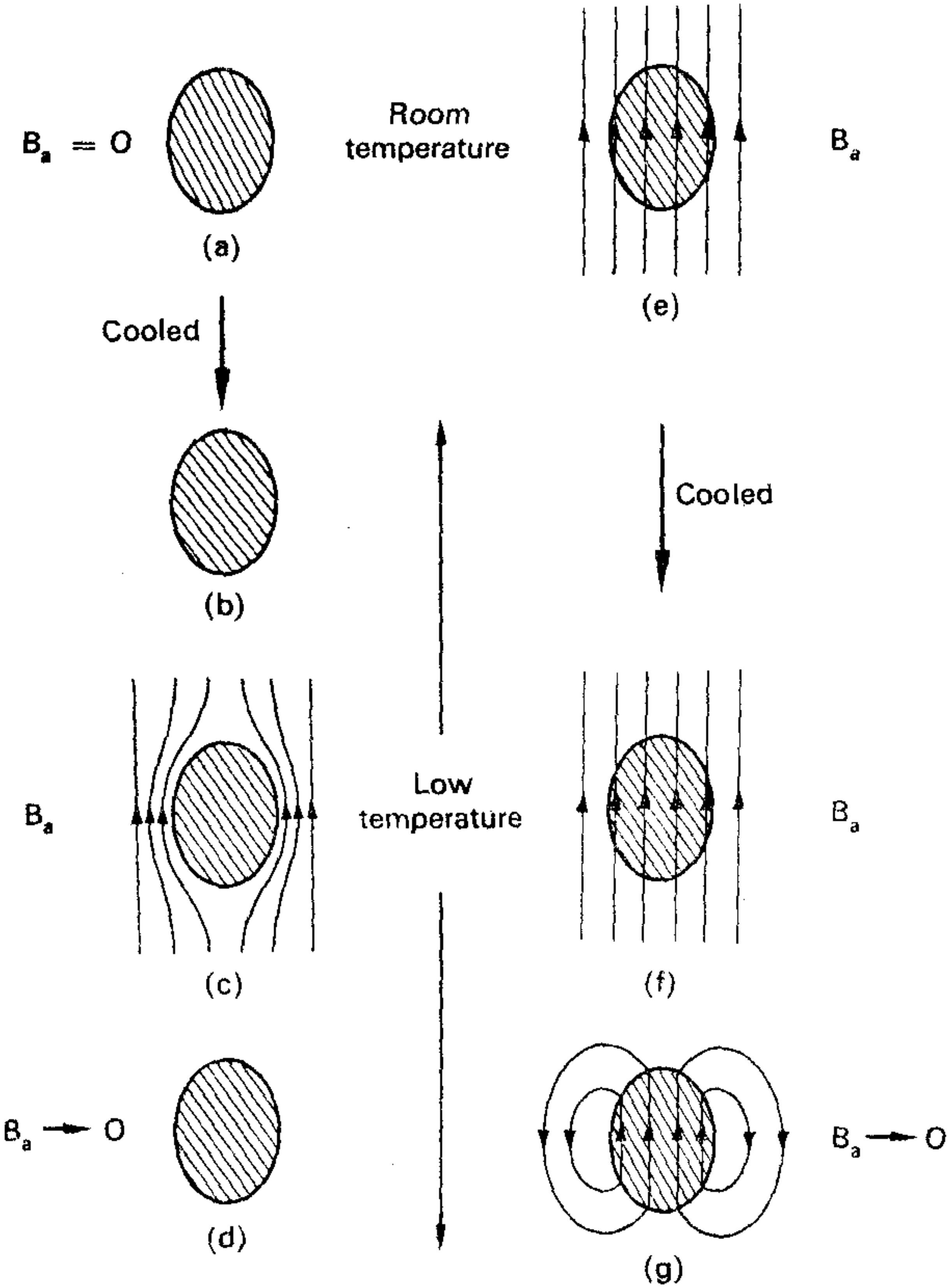
Zero Resistance



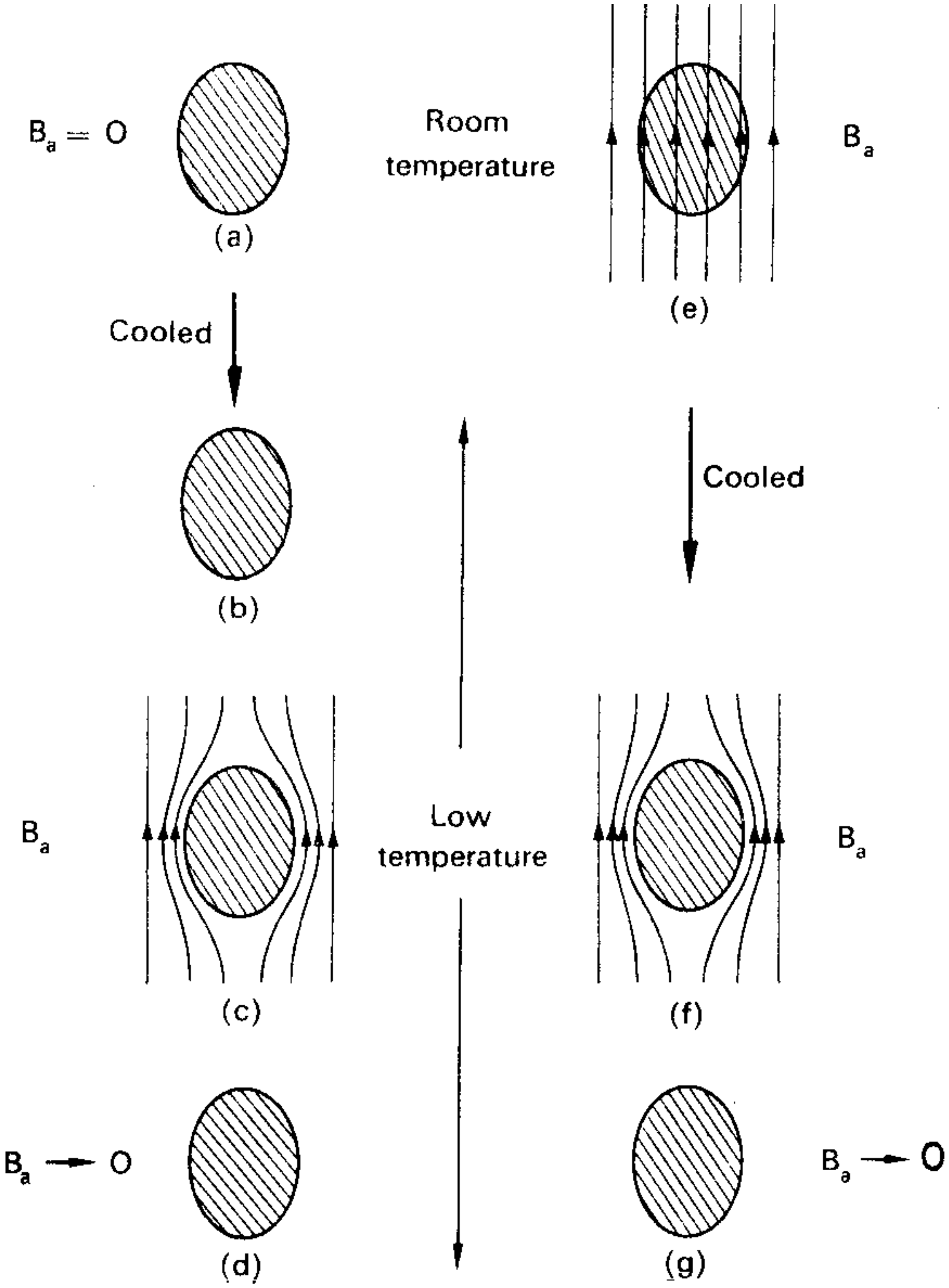


Loss of resistance of a superconductor at low temperatures.

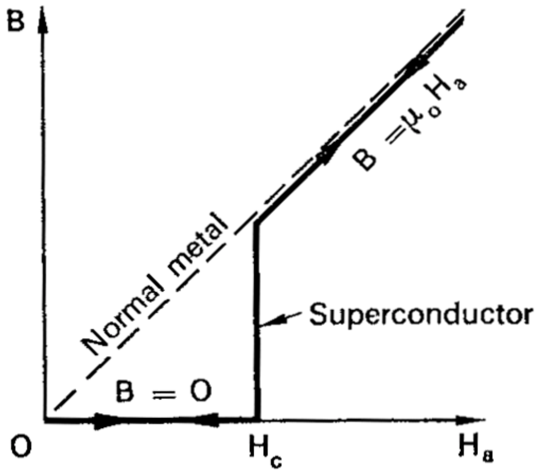
Magnetic Behaviour of a Perfect Conductor



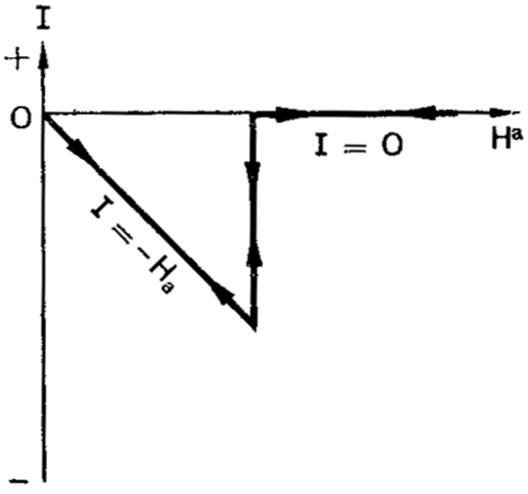
Magnetic Behaviour of a Superconductor



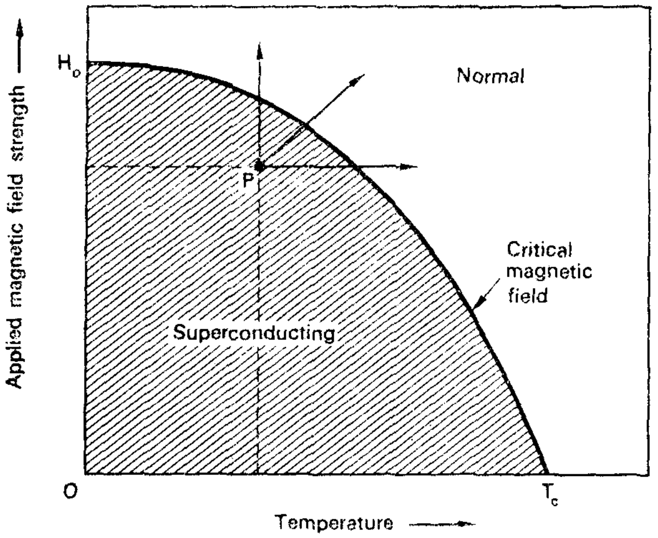
Magnetization and the Critical Field



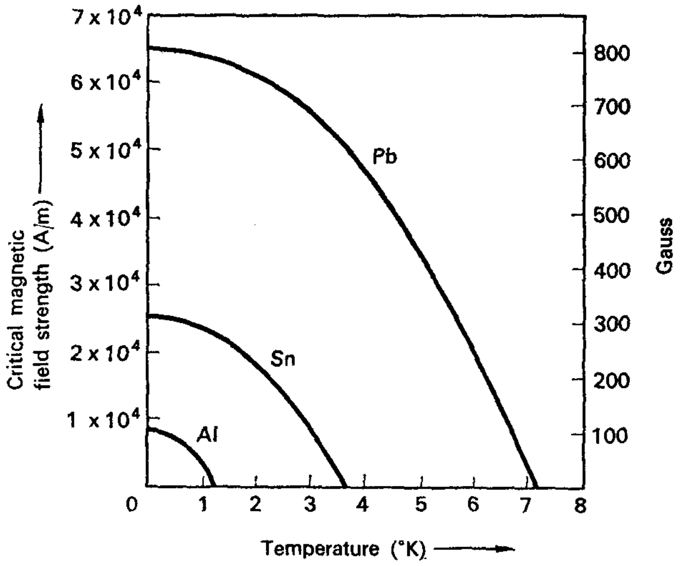
(a)



(b)

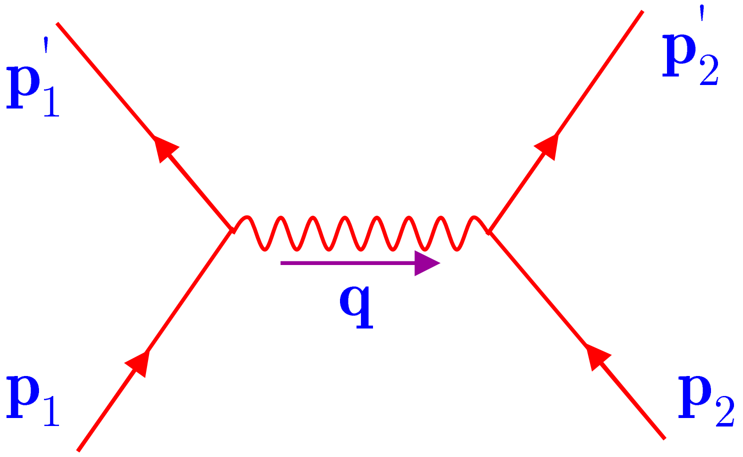


Phase diagram of a superconductor, showing variation with temperature of the critical magnetic field.



Critical fields of some superconductors.

Bardeen-Cooper-Schreiffer Theory



Any successful microscopic theory of superconductivity has to explain the following:

1) SC is bound up with some profound change in the behaviour of the conduction electrons, marked by the appearance of long range order and a gap in their energy spectrum ~ 10^{-4} eV.

2) The xtal. lattice must play a very important part in establishing SC because T_c depends upon the atomic mass (isotope effect).

3) The SC – normal transition is a 2nd order phase change

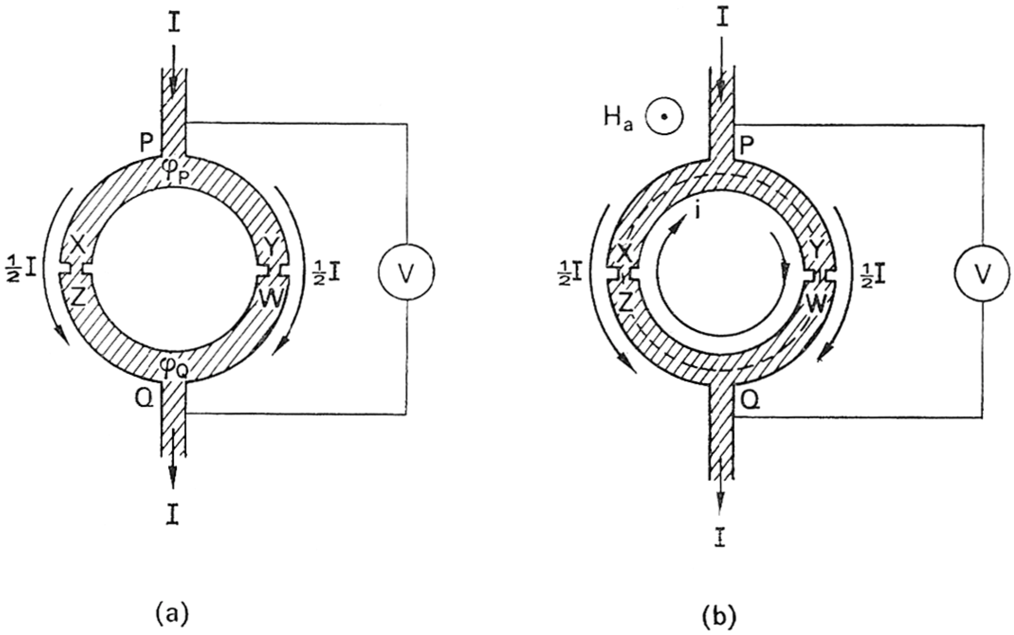
Flux Quantization

Any magnetic flux within a superconductor only exists as multiples of a quantum, the fluxon, Φ_0, given by:

$$\Phi_0 = h/2e = 2.07 \times 10^{-15}\ \text{Wb}$$

The $2e$ in the denominator is strong evidence That the supercurrent is carried by *pairs* of electrons.

Use? Superconducting Quantum Interference Device



Quantum interferometer. (a) No applied magnetic field. (b) With applied magnetic field.