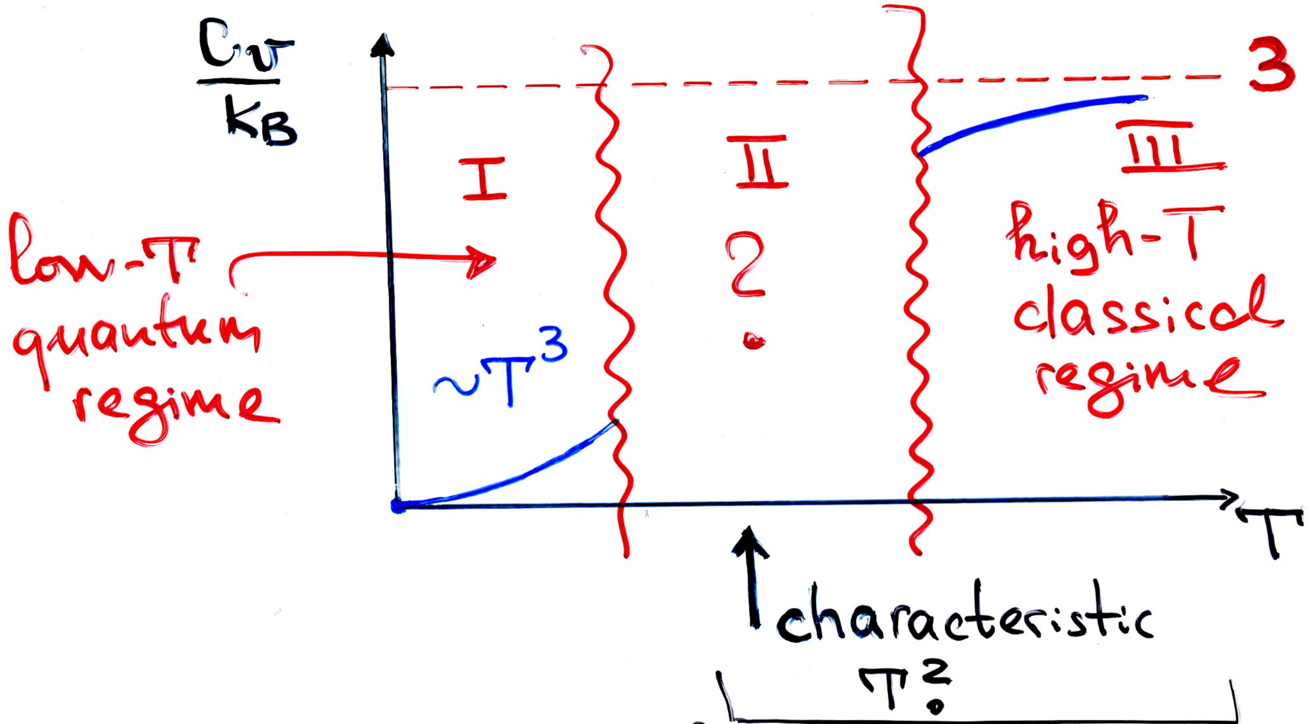
Intermediate-T specific heat:

Debye interpolation (1912)



Debye scheme for all I, II, and III regimes

①. Replace <u>all</u> branches with 3 acoustic branches $\omega = ck$

c is some averaged speed of sound.

②. $$\int\limits_{\vec{k} \in 1BZ} \frac{d^3k}{(2\pi)^3} \dots \longrightarrow \int\limits_{|\vec{k}| < k_D} \frac{d^3k}{(2\pi)^3} \dots$$

radius of Debye sphere

How k_D is chosen?:

: Debye sphere must accommodate all allowed wave vectors $\vec{k}$

Monatomic lattice with N ions

1st BZ contains N different $\vec{k}$

$$N = \frac{V \cdot \frac{4\pi}{3} k_D^3}{(2\pi)^3}$$, V crystal volume

ion density

$$n = \frac{1}{6\pi^2} k_D^3 \qquad \boxed{k_D = (6\pi^2 n)^{1/3}}$$

$$\boxed{\omega_D = k_D \cdot c}$$ Debye frequency

$$\boxed{k_B \Theta_D = \hbar \omega_D = \hbar c k_D \sim n^{1/3}}$$

Debye temperature

(thru n and c) characterizes a particular solid

Specific heat

$$C_v = \frac{\partial}{\partial T} 3 \int_0^{k_D} \frac{4\pi k^2 dk}{(2\pi)^3} \cdot \frac{\hbar c k}{\exp\left(\frac{\hbar c k}{k_B T}\right) - 1}$$

$$= \frac{3\hbar c}{2\pi^2} \frac{\partial}{\partial T} \int_0^{k_D} dk\, k^3 \left[\exp\left(\frac{\hbar c k}{k_B T}\right) - 1\right]^{-1}$$

$$= \frac{3\hbar c}{2\pi^2} \int_0^{k_D} dk\, k^3 \frac{\frac{\hbar c k}{k_B T^2} \exp\left(\frac{\hbar c k}{k_B T}\right)}{\left[\exp\left(\frac{\hbar c k}{k_B T}\right) - 1\right]^2}$$

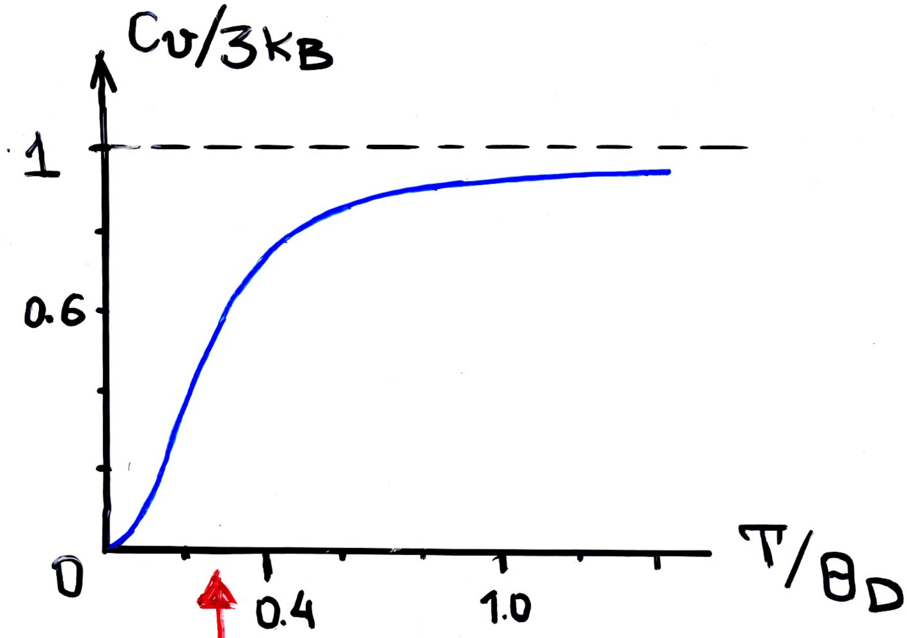
$$k \to x = \frac{\hbar c k}{k_B T}$$

$$C_v = \frac{3}{2\pi^2} k_B \left(\frac{k_B T}{\hbar c}\right)^3 \int_0^{\frac{\hbar c k_D}{k_B T} = \frac{\theta_D}{T}} dx \cdot \frac{x^4 e^x}{\left[e^x - 1\right]^2}$$

$$\theta_D^3 = \left(\frac{\hbar c}{k_B}\right)^3 \cdot 6\pi^2 n$$

$$\boxed{C_v = 9 n k_B \left(\frac{T}{\theta_D}\right)^3 \cdot \int_0^{\frac{\theta_D}{T}} dx \frac{x^4 e^x}{\left[e^x - 1\right]^2}}$$

θ_D is an <u>empirical</u> parameter



In fact $\frac{\Theta_D}{4}$ is characteristic temperature!

$T \ll \frac{1}{4}\Theta_D$ low-temperature regime

$T \gg \frac{1}{4}\Theta_D$ high-temperature regime

	Θ_D (K)		Θ_D (K)
Li	400	Pb	88
Be	1000	Ne	63
Al	394	W	310
C (diamond)	1860		

! 25K

$T_{melting}$ 3683 K!

- Θ_D is a measure of the "stiffness" of the crystal

- Θ_D is an empirical parameter

there is no unique way of choosing Θ_D

usually Θ_D is chosen to fit low-temperature C_v

with exponential accuracy

$$C_v = 9nk_B\left(\frac{T}{\Theta_D}\right)^3 \underbrace{\int_0^{\frac{\Theta_D}{T} \to \infty} dx \, \frac{x^4 e^x}{[e^x - 1]^2}}_{\frac{4\pi^4}{15}}$$

$$\boxed{C_v = \frac{12\pi^4}{5} n k_B \left(\frac{T}{\Theta_D}\right)^3}$$

low-T result

measured $\Rightarrow$ determined

The Einstein model (1907)

<u>All</u> lattice vibrations have a unique frequency ω_E

Specific heat per unit volume

$$C_v = p \cdot n \cdot \left(\frac{\hbar\omega_E}{k_B T}\right)^2 \frac{\exp(\hbar\omega_E/k_B T)}{\left[\exp(\hbar\omega_E/k_B T)-1\right]^2}$$

p: # of branches

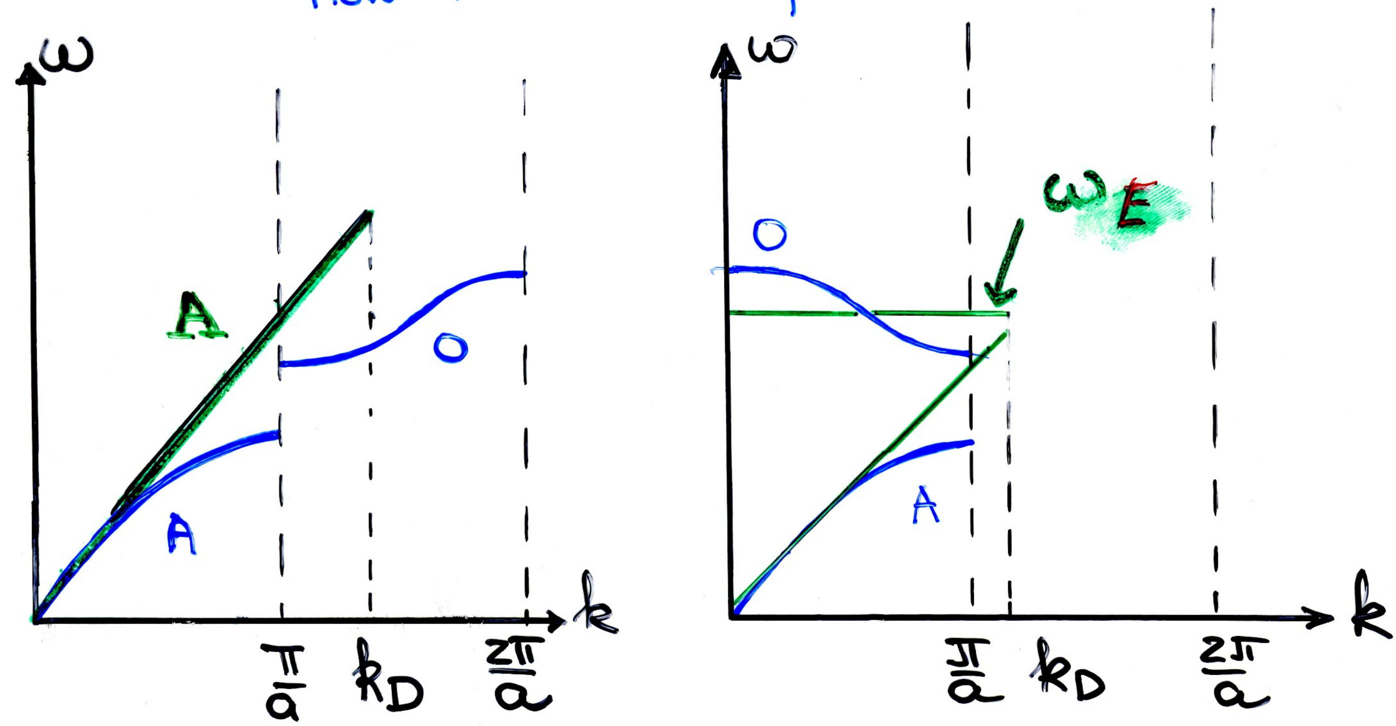
n: ion density

All branches are treated as optical

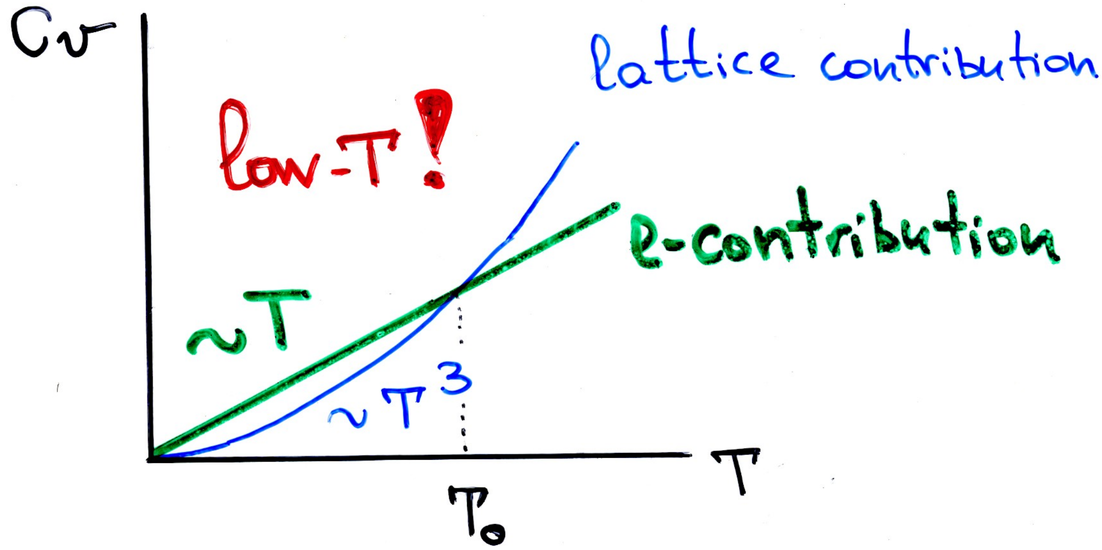
$\Rightarrow$ exp small C_v at $T \ll \hbar\omega_E$

corrected later by Debye

How to include optical branches ?



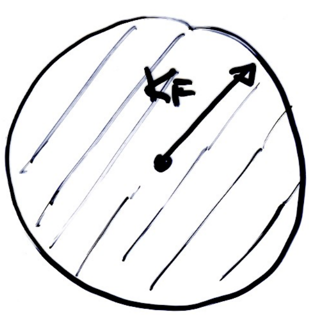
Lattice and Electronic Specific Heat



$$T_0 \simeq 0.15 \left(\frac{Z\,\Theta_D}{T_F}\right)^{1/2} \sim \text{few K}$$

valence

Fermi temperature



Fermi-sphere
in $\vec{k}$-space

$$2 \cdot \frac{\frac{4\pi}{3} k_F^3 \cdot V}{(2\pi\hbar)^3} = N_e$$

$$E_F = \frac{\hbar^2 k_F^2}{2m_e} = k_B T_F$$

Typically

$$T_F \sim 10^4\,\text{K} \gg \Theta_D$$

Density of normal modes

$$\frac{1}{V}\sum_{\vec{k}s} Q(\omega_s(\vec{k})) = \frac{1}{V}\sum_{s}\int \frac{V d\vec{k}}{(2\pi)^3} Q(\omega_s(\vec{k}))$$

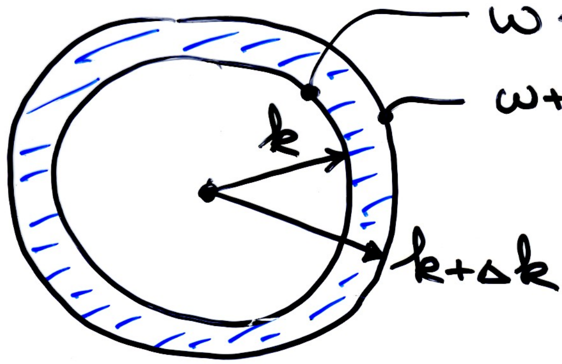
to reduce to $\int_0^\infty \frac{d\omega}{2\pi} g(\omega)\, Q(\omega)$

$$g(\omega) = \sum_s \int \frac{d\vec{k}}{(2\pi)^3} \delta(\omega - \omega_s(\vec{k}))$$

Density Of phonon States

1 Acoustic mode: $\omega = ck$

3D spheres in $\vec{k}$ space



$$\boxed{k = \frac{\omega}{c}}$$

$$\Delta N = \frac{4\pi k^2 \cdot \Delta k \cdot V}{(2\pi)^3}$$

$$dn = d\left(\frac{N}{V}\right) = \frac{1}{2\pi^2}\left(\frac{\omega}{c}\right)^2 d\left(\frac{\omega}{c}\right)$$

$$\boxed{g(\omega) = \frac{\partial n}{\partial \omega} = \frac{\omega^2}{2\pi^2 c^3}}$$

3 acoustic modes $\omega_s = ck$ $s = 1, 2, 3$

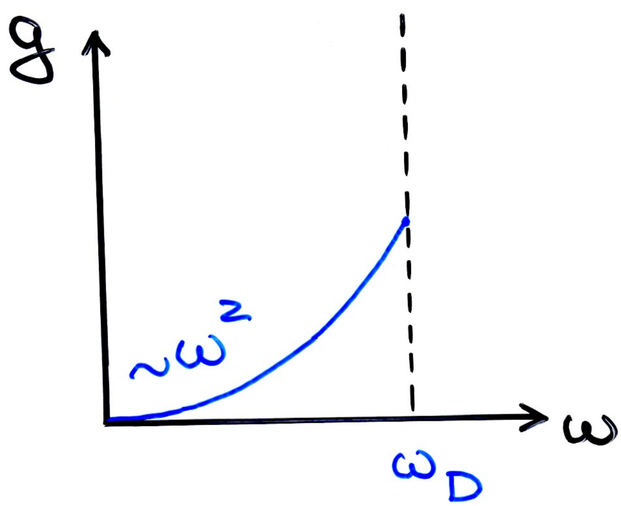
$$g_D(\omega) = 3 \cdot \int_{|\vec{k}|<k_D} \frac{d\vec{k}}{(2\pi)^3} \delta(\omega - ck)$$

in the Debye approximation

$$g_D(\omega) = 3 \int_0^{k_D} \frac{4\pi k^2 dk}{(2\pi)^3} \delta(\omega - ck)$$

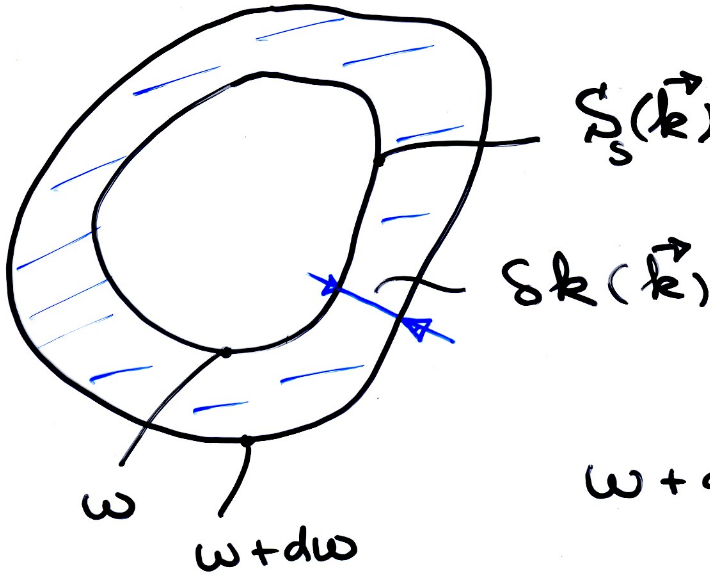
$$\delta\left(c\left(k - \frac{\omega}{c}\right)\right) = \frac{1}{|c|}\delta\left(k - \frac{\omega}{c}\right)$$

$$g_D(\omega) = \begin{cases} 0, & \omega > \omega_D \\ \dfrac{3\omega^2}{2\pi^2 c^3}, & \omega < \omega_D = k_D c \end{cases}$$



Simple isotropic model

Anisotropy $\quad \omega_s = \omega_s(\vec{k})$



$$\omega + d\omega = \omega + |\vec{\nabla}\omega|\,\delta k$$

$$\delta k = \frac{d\omega}{|\vec{\nabla}\omega_s|}$$

$$\frac{dN_s}{V} = g_s(\omega)\,d\omega = \int\limits_{\omega_s(\vec{k})=\omega} \frac{dS_s(\vec{k})\cdot\delta k}{(2\pi)^3}$$

$$\boxed{g_s(\omega) = \int \frac{dS}{(2\pi)^3}\,\frac{1}{|\vec{\nabla}\omega_s(\vec{k})|}}$$

over the surface in $\vec{k}$-space
at which $\omega_s(\vec{k}) = \omega$

$$\left|\vec{\nabla}\omega_s(\vec{k})\right| = \left|\frac{\partial\omega_s(\vec{k})}{\partial\vec{k}}\right|$$ – group velocity

vanishes at: zone boundary

and $\vec{k}=0$ (0 modes)

produce singularities in $g(\omega)$

van Hove singularities

(1953)

Integrable in 3D

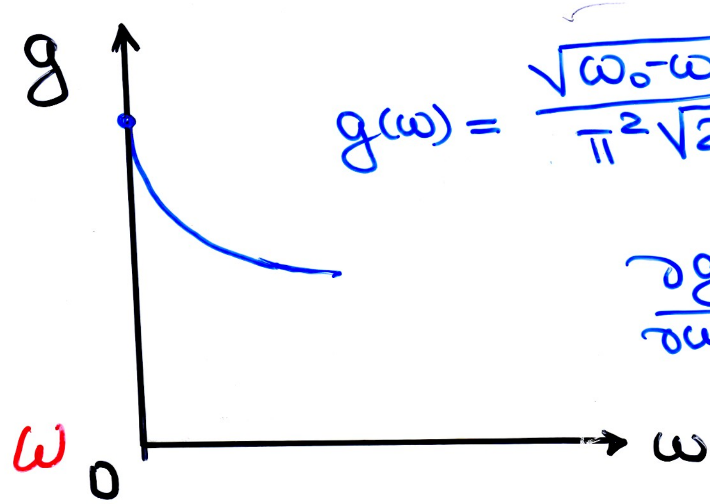
Example:

$$\omega = \omega_0 - \frac{1}{2}\gamma k^2$$ – optical mode $ka \ll 1$

$$\left|\frac{\partial\omega}{\partial k}\right| = \gamma k \qquad g(\omega) = \int\frac{dS}{(2\pi)^3}\cdot\frac{1}{\gamma k}$$

$S:\ \omega(k)=\omega:\ S = 4\pi k^2$

$$g(\omega) = \frac{4\pi k^2}{(2\pi)^3}\cdot\frac{1}{\gamma k} = \frac{1}{2\pi^2\gamma}k \leftarrow k = \sqrt{\frac{2(\omega_0-\omega)}{\gamma}}$$



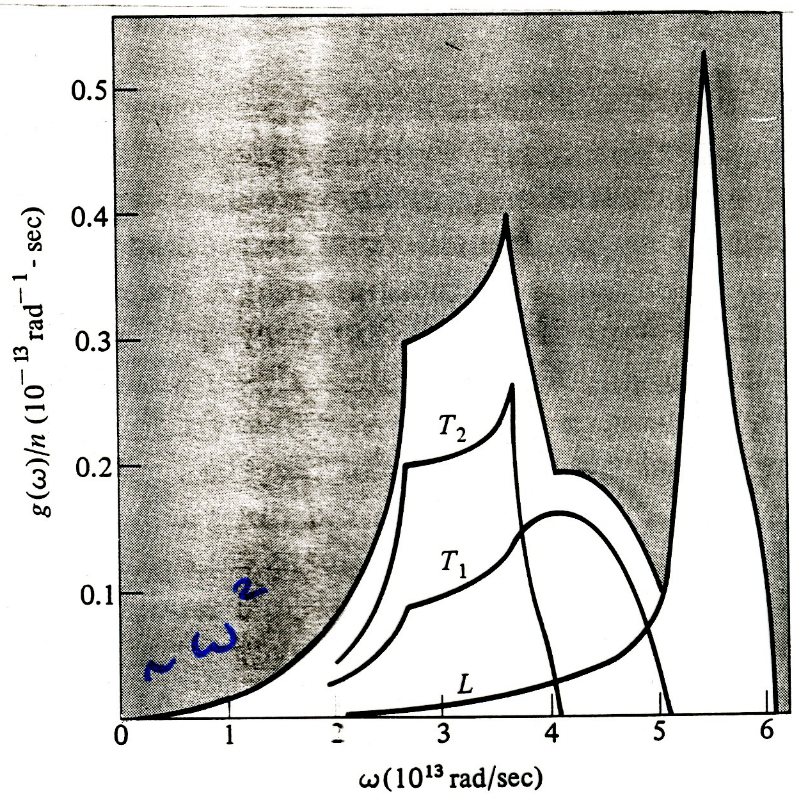
$$g(\omega) = \frac{\sqrt{\omega_0-\omega}}{\pi^2\sqrt{2\gamma^3}}$$

$$\frac{\partial g}{\partial\omega} \sim -\frac{1}{\sqrt{\omega_0-\omega}} \to -\infty$$

16.11

Figure 23.6
Phonon density of levels in aluminum, as deduced from neutron scattering data (Chapter 24). The highest curve is the full density of levels. Separate level densities for the three branches are also shown. (After R. Stedman, L. Almqvist, and G. Nilsson, *Phys. Rev.* **162**, 549 (1967).)

FCC



Example of experimental phonon level density with van Hove sungularities