

Phonons: Thermal PropertiesPlanck distribution

Consider a particular phonon mode \vec{k}, s with frequency $\hbar\omega_s(\vec{k})$.

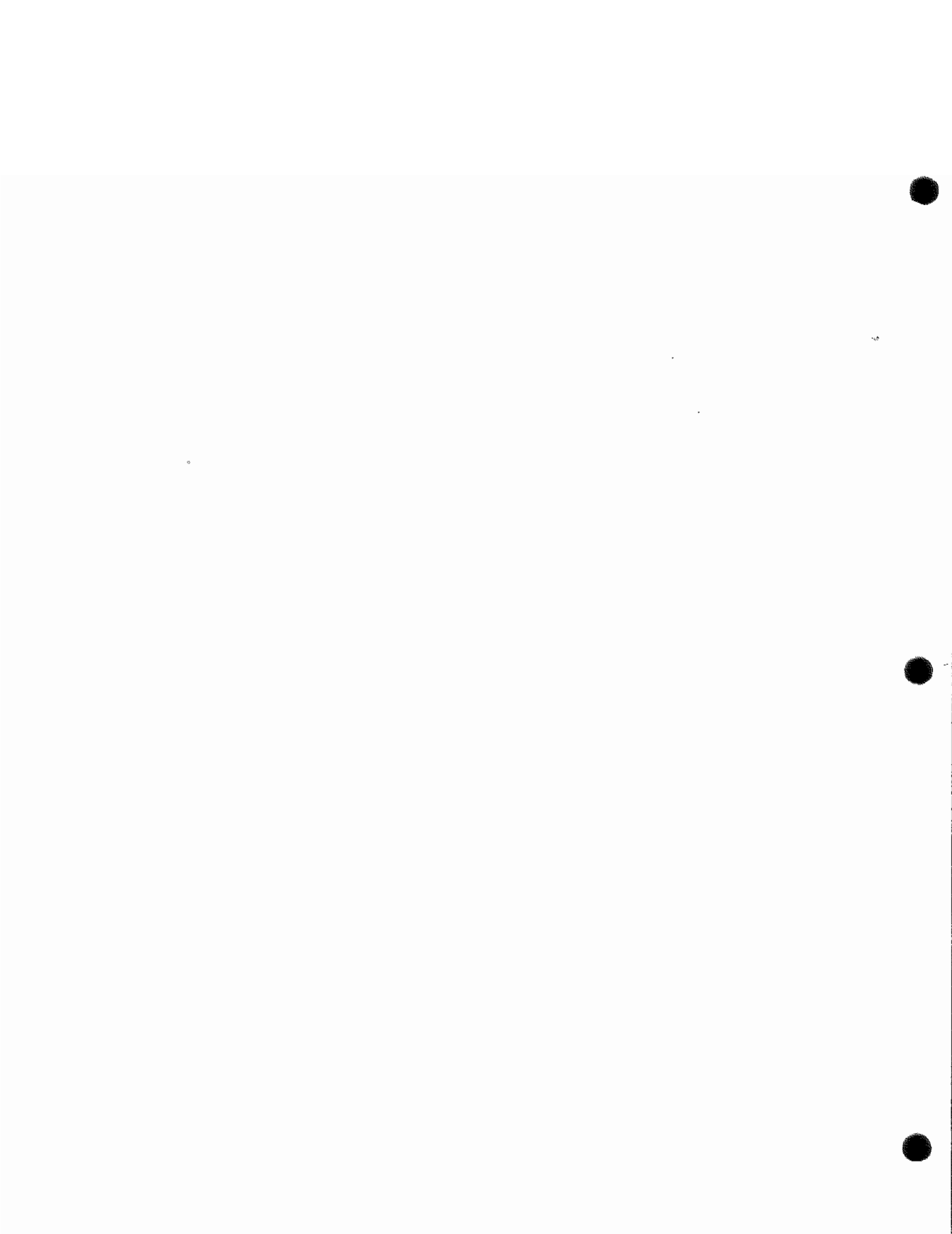
The energy levels are

$$E(n_{\vec{k}s}) = \hbar\omega_s(\vec{k}) \left(n_{\vec{k}s} + \frac{1}{2} \right)$$

$$n_{\vec{k}s} = 0, 1, 2, \dots, \infty$$

The partition function is

$$\begin{aligned} Z &= \sum_{n=0}^{\infty} e^{-\beta E(n)} \\ &= \sum_{n=0}^{\infty} e^{-\beta \hbar \omega (n + \frac{1}{2})} \end{aligned}$$



$$Z = e^{-\beta \frac{\hbar \omega}{2}} \sum_{n=0}^{\infty} (e^{-\beta \hbar \omega})^n \quad 2$$

$$= \frac{e^{-\beta \frac{\hbar \omega}{2}}}{1 - e^{-\beta \hbar \omega}} = \frac{1}{2 \sinh(\beta \hbar \omega / 2)}$$

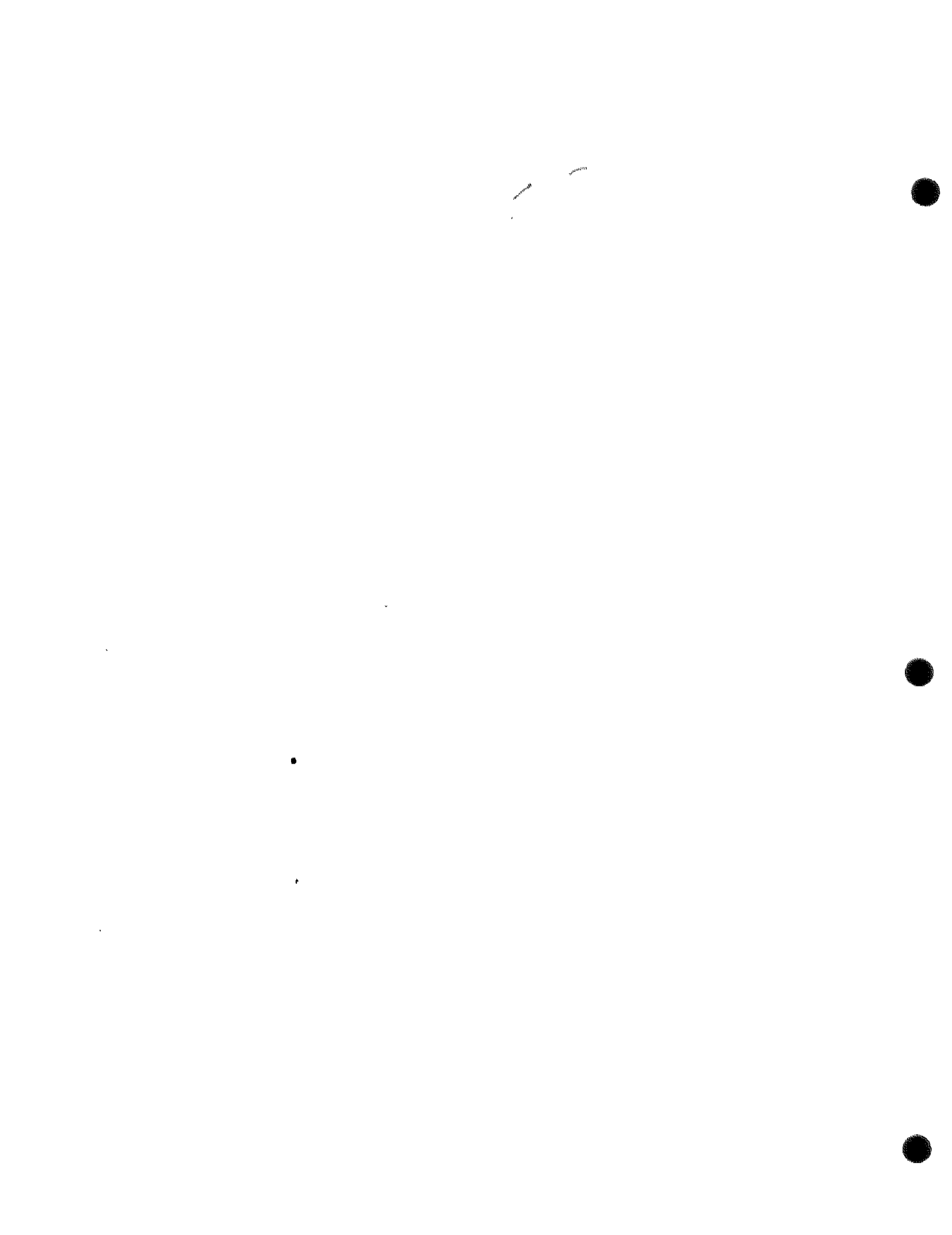
The average number of phonons in the mode is

$$\langle n \rangle = \frac{1}{Z} \sum_{n=0}^{\infty} n e^{-\beta E(n)}$$

$$= \frac{1}{Z} e^{-\beta \frac{\hbar \omega}{2}} \left(- \frac{d}{d(\beta \hbar \omega)} \sum_{n=0}^{\infty} (e^{-\beta \hbar \omega})^n \right)$$

$$= \frac{1}{Z} e^{-\beta \frac{\hbar \omega}{2}} \left(- \frac{d}{d(\beta \hbar \omega)} (1 - e^{-\beta \hbar \omega})^{-1} \right)$$

$$= \frac{e^{-\beta \frac{\hbar \omega}{2}}}{Z} \frac{e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^2} = \frac{e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}}$$



$$\langle n \rangle = \frac{1}{e^{\beta \hbar \omega} - 1}$$

Planck distribution

Thermal energy

$$E = \sum_{\vec{k}, s} \left(\langle n_{\vec{k}s} \rangle + \frac{1}{2} \right) \hbar \omega_s(\vec{k})$$

$$= \sum_{\vec{k}, s} \hbar \omega_s(\vec{k}) \left(\frac{1}{2} + \frac{1}{e^{\beta \hbar \omega_s(\vec{k})} - 1} \right)$$

↑
zero-pt.
energy

↑
thermal
excitations



The total energy of the crystal in thermal equilibrium is

$$E = \underbrace{U_0 + \sum_{\vec{k}s} \frac{\hbar \omega_s(\vec{k})}{2}}_{E_0} + \sum_{\vec{k}s} \frac{\hbar \omega_s(\vec{k})}{e^{\beta \hbar \omega_s(\vec{k})} - 1}$$

- The sum over $\vec{k}s$ runs over all wavevectors in the 1st Brillouin zone, and all branches s . The allowed values of \vec{k} within the 1st BZ are fixed by the boundary conditions. Consider a Bravais lattice generated by the basis vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$, with periodic boundary conditions



imposed on a parallelepiped (5)

with edges $L\vec{a}_1, L\vec{a}_2, L\vec{a}_3$.

The lattice waves

$$\vec{x}(\vec{R}, t) = \vec{E} e^{i(\vec{k} \cdot \vec{R} - \omega t)}$$

must satisfy

$$\vec{x}(\vec{R} + L\vec{a}_i, t) = \vec{x}(\vec{R}, t),$$

which implies

$$L\vec{k} \cdot \vec{a}_i = 2\pi n_i,$$

whence

$$\vec{k} = \frac{n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3}{L}$$

The number of allowed wave vectors in a primitive cell of reciprocal space is $N = L^3$, which

is equal to the total number of primitive cells in the Bravais



lattice. This must be the case, since the # of allowed wavevectors times the number of branches must equal to the # of degrees of freedom of the system. 6

In the limit $N \gg 1$, the sum over \vec{k} can be replaced by an integral

$$\sum_{\vec{k}} \rightarrow \int d^3k = \frac{L^3 |\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)|}{(2\pi)^3} \int d^3k$$

$$= \frac{V}{(2\pi)^3} \int d^3k,$$

where V is the volume of the crystal. Thus, for example,

$$E - \bar{E}_0 = V \sum_{\text{BZ}} \int \frac{d^3k}{(2\pi)^3} \frac{\hbar \omega_s(\vec{k})}{e^{\beta \hbar \omega_s(\vec{k})} - 1}.$$



Since the integrand involves only $\omega_s(\mathbf{k})$, it is often useful to change variables to ω :

$$V \sum_s \int_{\text{BZ}} \frac{d^3k}{(2\pi)^3} = \sum_s \int_0^{\omega_s^{\text{max}}} d\omega D_s(\omega),$$

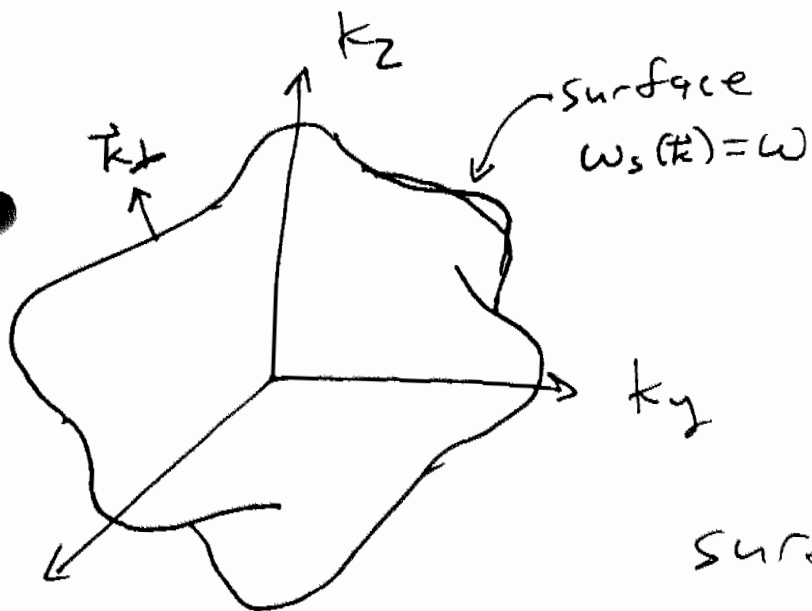
where $D_s(\omega)$ is the density of states for branch s .

How to determine $D_s(\omega)$?
 If the total # of pt-s in the 1st BZ with $\omega_s(\mathbf{k}) \leq \omega$ is $N_s(\omega)$, i.e.,

$$N_s(\omega) = \frac{V}{(2\pi)^3} \int_{\omega_s(\mathbf{k}) \leq \omega} d^3k,$$

then $D_s(\omega) = \frac{dN_s}{d\omega}$.





$D_S(\omega)d\omega$ is the # of states in a thin shell around the surface $\omega_s(\vec{k}) = \omega$.

The thickness δk_{\perp} of the shell satisfies

$$\left| \frac{\partial \omega_s}{\partial k_{\perp}} \right| \delta k_{\perp} = d\omega. \quad \text{Thus}$$

$$D_S(\omega) = \frac{V}{(2\pi)^3} \int_{\omega_s(\vec{k}) = \omega} d^2k \frac{1}{\left| \frac{\partial \omega_s}{\partial k_{\perp}} \right|}$$

↑
group velocity

ω_s may depend in a complicated way on \vec{k} . To make progress, two simple models are often used to describe acoustic



and optical phonons, respectively. (9

• Debye Model

to model acoustic phonons,

let $\omega_s(\mathbf{k}) = v|\mathbf{k}|$, $s=1,2,3$.

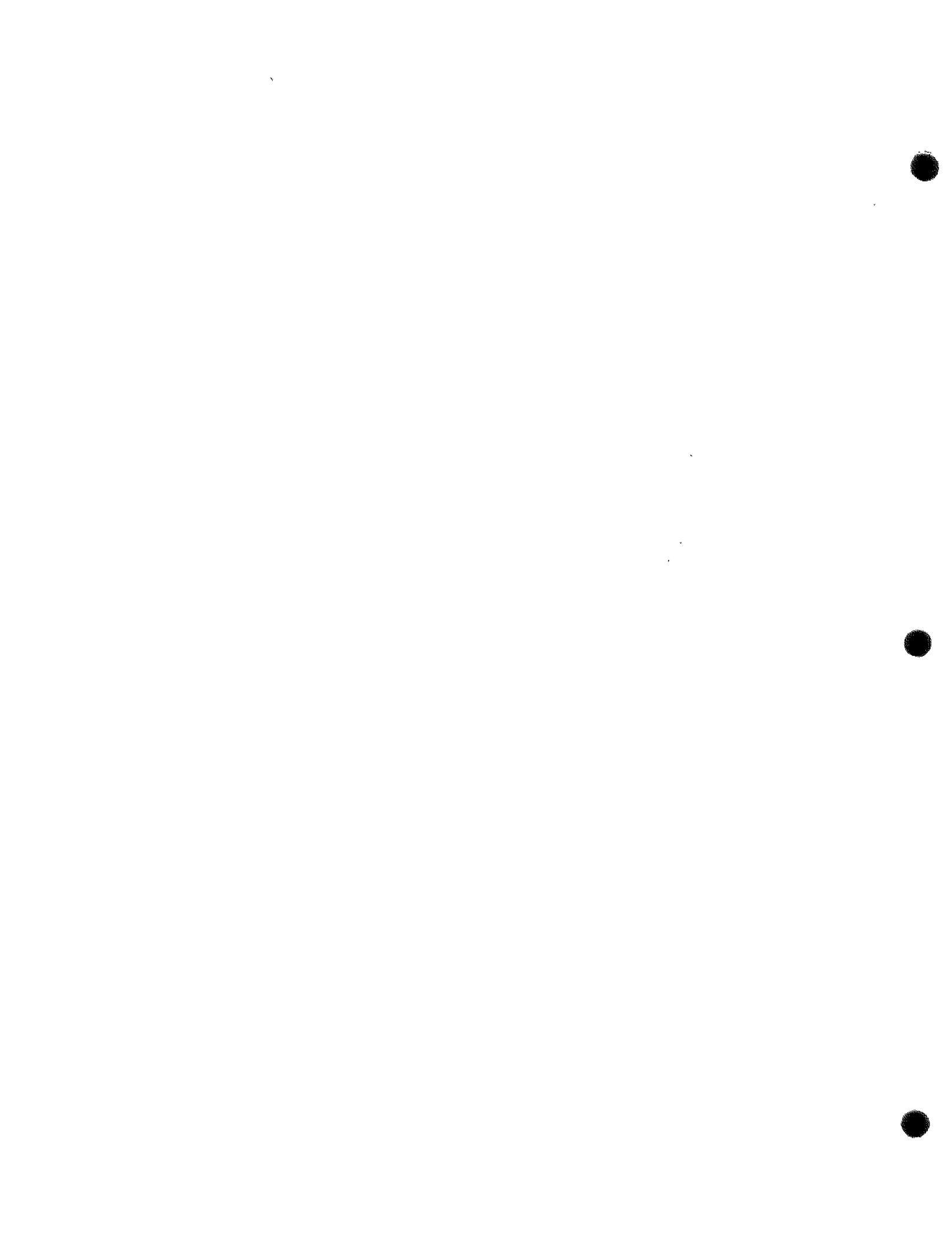
Then the total density of states is

$$D(\omega) = \sum_s D_s(\omega)$$

$$= \frac{3V}{(2\pi)^3} \int_{|\mathbf{k}|=\omega/v} \frac{d^2k}{v}$$

$$= \frac{3V}{(2\pi)^3} 4\pi \left(\frac{\omega}{v}\right)^2 \frac{1}{v}$$

$$D(\omega) = \frac{3V\omega^2}{2\pi^2 v^3}$$



The upper limit ω_{\max} must be chosen to give the correct # of modes

10

$$\int_0^{\omega_{\max}} D(\omega) d\omega = 3N$$

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

$$\frac{V \omega_{\max}^3}{2\pi^2 v^3} = 3N$$

$$\omega_{\max}^3 = 6\pi^2 \frac{N}{V} v^3$$

$$\omega_D = v \left(6\pi^2 \frac{N}{V} \right)^{1/3}$$

"Debye frequency"



$$E - E_0 = \int_0^{\omega_D} \frac{D(\omega) \hbar \omega}{e^{\beta \hbar \omega} - 1} d\omega$$

$$= \frac{3V \hbar}{2\pi^2 v^3} \int_0^{\omega_D} \frac{\omega^3 d\omega}{e^{\beta \hbar \omega} - 1}$$

The heat capacity at constant volume is

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V$$

$$C_V = \left. \frac{\partial \beta}{\partial T} \frac{\partial E}{\partial \beta} \right|_V = -\frac{1}{k_B T^2} \left. \frac{\partial E}{\partial \beta} \right|_V$$

$$= \frac{3V \hbar^2}{2\pi^2 v^3 k_B T^2} \int_0^{\omega_D} \frac{\omega^4 e^{\beta \hbar \omega} d\omega}{(e^{\beta \hbar \omega} - 1)^2}$$

Change to dimensionless integration

variable! $x = \beta \hbar \omega$

$$\omega = \frac{k_B T}{\hbar} x$$



$$C_V = 9N k_B \left(\frac{T}{\theta}\right)^3 \int_0^{\theta/T} \frac{x^4 e^x dx}{(e^x - 1)^2}$$

$$\theta = \frac{\hbar \omega_D}{k_B} = \text{"Debye temperature"}$$

• Debye T^3 law

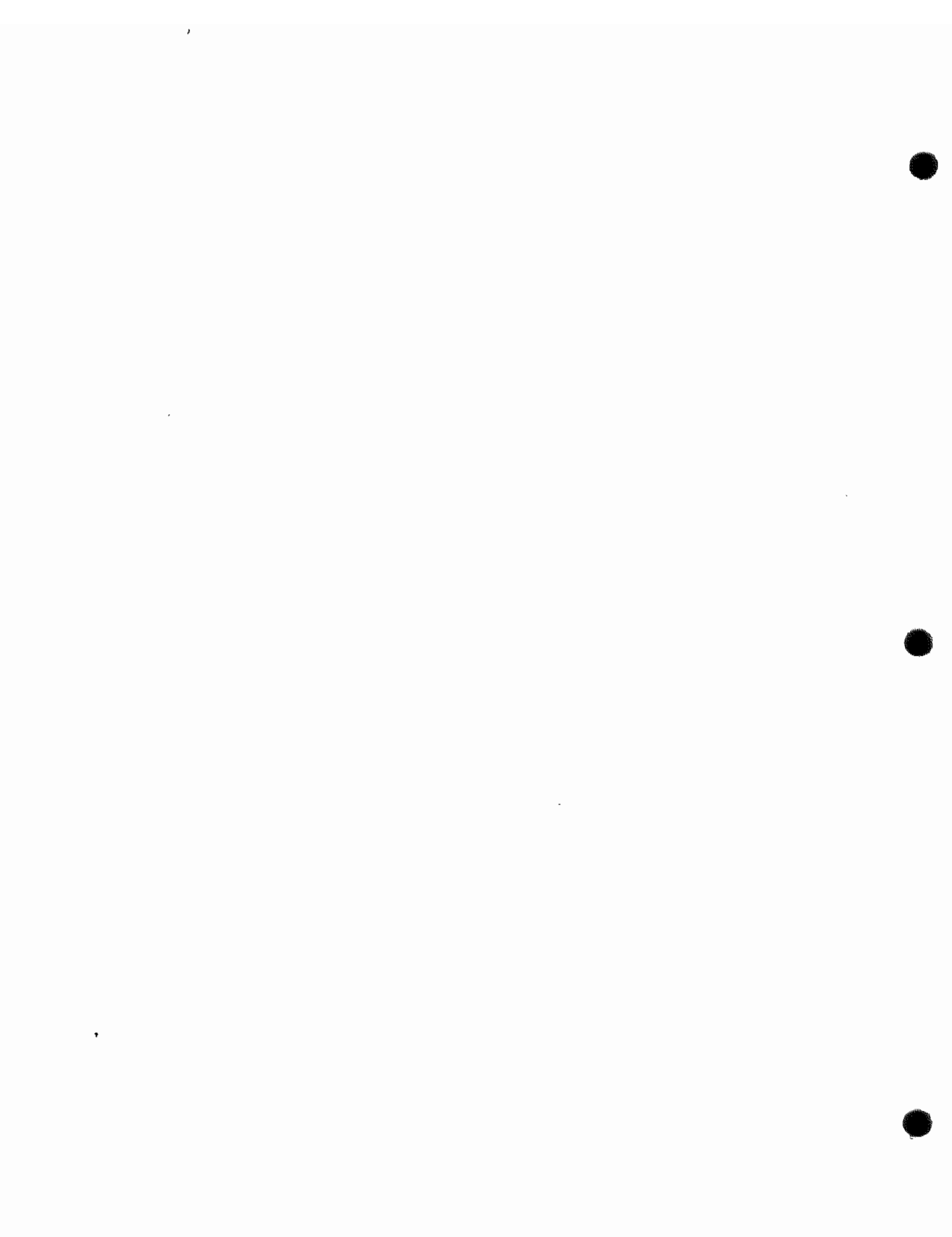
For small temperatures

$T \ll \theta$, the upper limit

$\frac{\theta}{T} \gg 1$. Then

$$C_V \approx 9N k_B \left(\frac{T}{\theta}\right)^3 \underbrace{\int_0^{\infty} \frac{x^4 e^x dx}{(e^x - 1)^2}}_{4\pi^4/15}$$

$$C_V \underset{T \ll \theta}{=} \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta}\right)^3$$



The T^3 law describes

13

well the low temperature specific heat of insulating crystals for $T \lesssim \theta/50$.

The Debye temperature θ ranges from 38 K in Cs to 2230 K in diamond.

For metals, there is an additional contribution to the low temperature specific heat from the conduction electrons.



For a metal, there are 2

contributions to the specific heat at low temperatures; one from the conduction electrons, $\propto T$, and one from the phonons, $\propto T^3$:

$$\frac{C_V}{Nk_B} = \frac{\pi^2}{2} \frac{T}{T_F} + \frac{12\pi^4}{5} \left(\frac{T}{\theta_D} \right)^3$$

Debye temp.

By plotting $\frac{C_V}{T}$ vs. T^2 , one

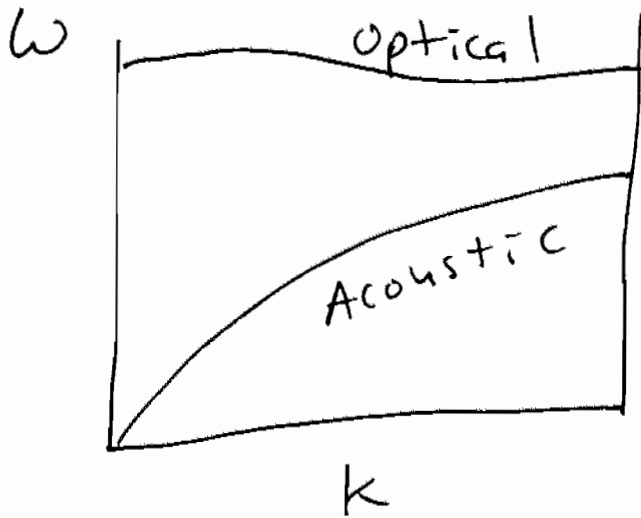
can extract θ_D from the

slope and T_F from the intercept.



Einstein mode)

(14



For an optical phonon, one could approximate $\omega(k) \approx \omega_0$.

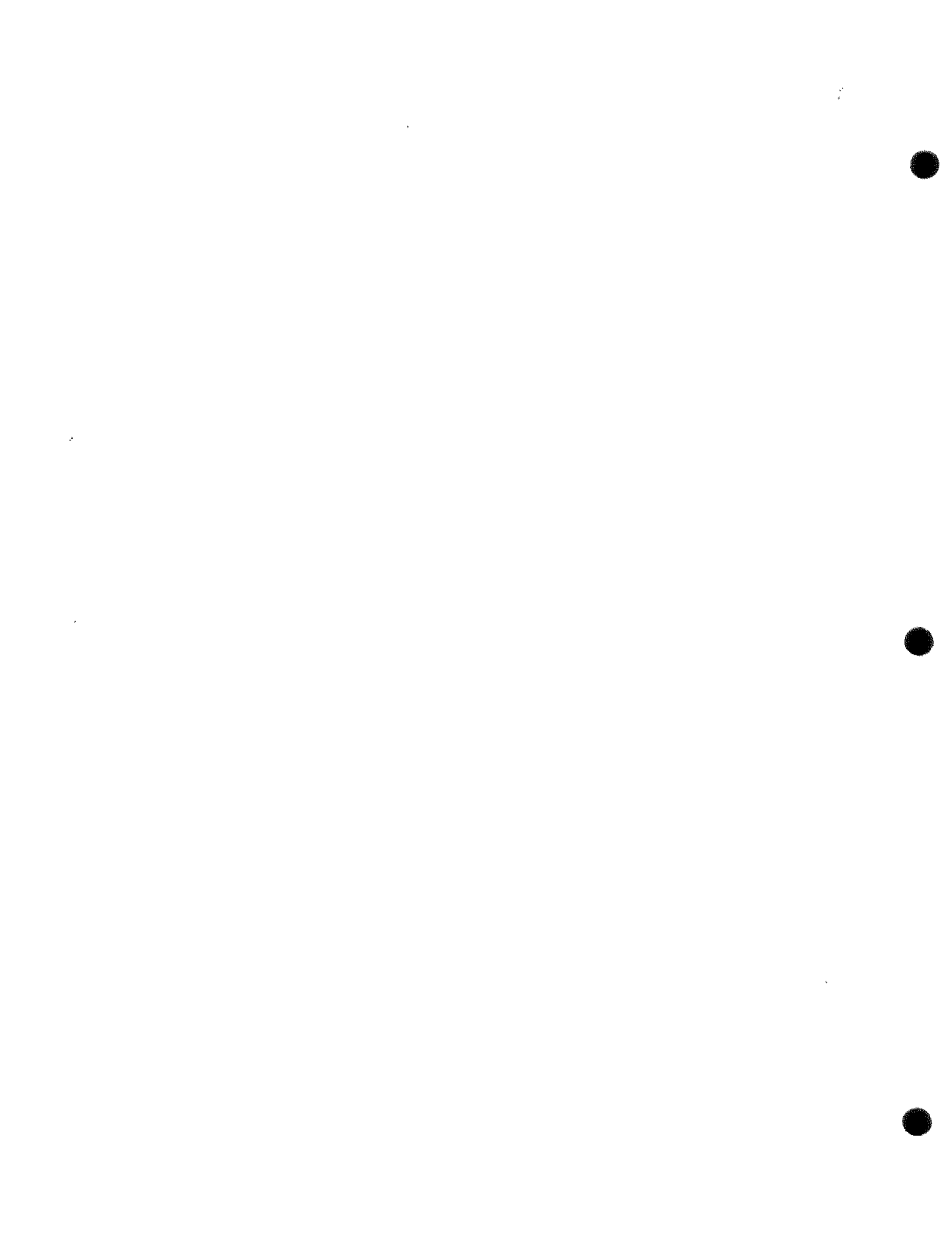
Then $D(\omega) = N \delta(\omega - \omega_0)$

and $E - E_0 = \frac{N \hbar \omega_0}{e^{\beta \hbar \omega_0} - 1}$.

The specific heat is

$$C_V = N k_B \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}$$

where $\theta_E = \hbar \omega_0 / k_B$.



• Law of Dulong and Petit

15

• Quite generally, we have

$$E - E_0 = \sum_s \int_0^{\omega_s^{\max}} \frac{D_s(\omega) \hbar \omega}{e^{\beta \hbar \omega} - 1} d\omega.$$

For very high temperatures

$k_B T \gg \hbar \omega_s^{\max}$, the denominator

becomes $e^{\beta \hbar \omega} - 1 \approx \beta \hbar \omega$,

and

$$E - E_0 \approx k_B T \underbrace{\sum_s \int_0^{\omega_s^{\max}} D_s(\omega) d\omega}_{3N}$$

$$\lim_{T \rightarrow \infty} C_V = \frac{\partial E}{\partial T} \Big|_V = 3N k_B$$

$N = \#$ of atoms

