Solid State Physics

PHONON HEAT CAPACITY
Lecture 10

A.H. Harker
Physics and Astronomy
UCL

Specific Heats

To recapitulate:

- Lattice vibrations, in the harmonic approximation, described as normal modes of the crystal;

- Each normal mode has the same Hamiltonian as a harmonic oscillator;

- The energy in each normal mode k is $(n_k + \frac{1}{2})\hbar\omega_k$;

Calculate the specific heat, by adding the contributions of all the modes.

- Assume a continuous spread of frequencies/energies

- Find how many normal modes there are in a given range of frequency

- Remember specific heat of harmonic oscillator of frequency ω

- Integrate over ω

4.3 Phonon Density of States

4.3.1 One Dimension - $g(k)$

Take crystal of length L, and impose *periodic boundary conditions*, so that for a wave

$$\exp(ikx) = \exp(ik(x + L)),$$

so

$$\exp(ikL) = 1,$$

or

$$k = n\frac{2\pi}{L},$$

where n is an integer. The allowed states are uniformly distributed in reciprocal space (k-space) with spacing $2\pi/L$.

The density of states is the inverse of the spacing,

$$g(k) = \frac{L}{2\pi}.$$

The number of allowed states with wavevectors between k and $k + \mathrm{d}k$ is $g(k)\,\mathrm{d}k$. Note that if there are N unit cells so that $L = Na$ the total number of allowed states in the Brillouin zone is

$$\int_{-\pi/a}^{\pi/a} g(k)\mathrm{d}k = \frac{L}{2\pi} \times 2\frac{\pi}{a} = \frac{L}{a} = N.$$

The number of allowed states in the Brillouin zone is equal to the number of *unit cells* in the system. N.B. unit cells, not atoms. More atoms $\rightarrow$ more degrees of freedom $\rightarrow$ more branches of the spectrum.

4.3.2 Assumption of Continuous Energy

How closely spaced are the energy levels? Suppose the crystal is 0.01 m long. Then the spacing between k values is $\Delta k = 2\pi/L = 200\pi$ m^{-1}. If the sound wave speed is $v = 5000$ m s^{-1} then on the acoustic branch the minimum angular frequency is 0 and the next is $\Delta\omega = v\Delta k = 5000 \times 200\pi = 10^6\pi$ rad s^{-1}. This is small enough compared with the maximum frequency (about 10^{13} rad s^{-1}) that replacing a sum over discrete frequencies with an integral is a good approximation.

The energy spacing is $\Delta E = \hbar\Delta\omega \approx 3 \times 10^{-28}$ J $= 2 \times 10^{-9}$ eV.

4.3.3 One Dimension: $g(E)$
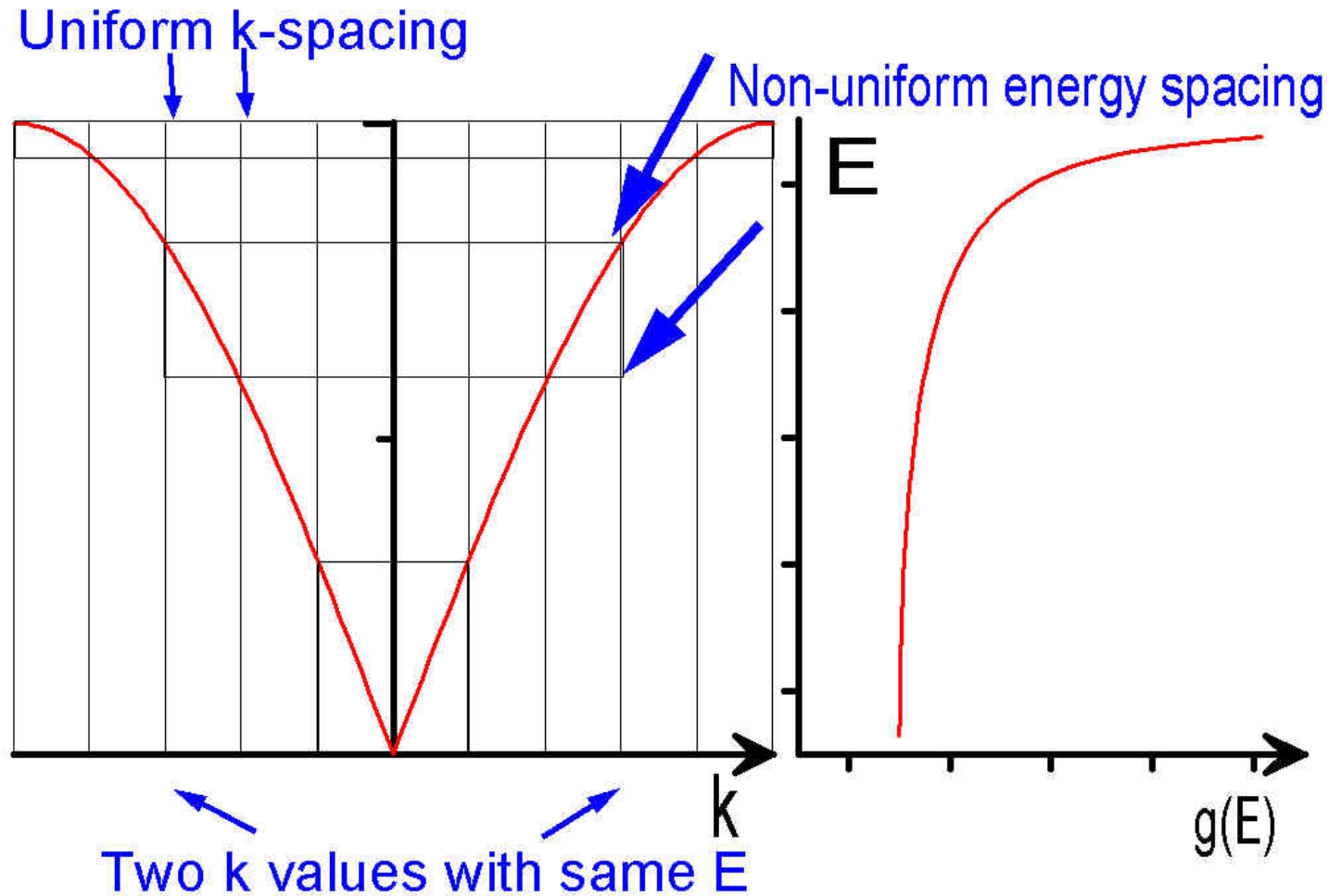
Go from evenly spaced allowed values of k to, in general, unevenly spaced values of energy. Note that positive and negative k have same E.

Define the density of states in frequency: number of allowed states between ω and $\omega + \mathrm{d}\omega$ is $g(\omega)\,\mathrm{d}\omega$. **This must be the same as the number in the region of k-space containing states in that frequency interval, so in** $0 < k < \pi/a$

$$g(\omega)\,\mathrm{d}\omega = g(k)\,\mathrm{d}k,$$

or

$$g(\omega) = g(k)\frac{dk}{d\omega} = g(k)/\frac{d\omega}{dk}.$$

Allowing also for the states with negative k **we get in one dimension**

$$g(\omega) = 2\,\frac{L}{2\pi}\,\frac{dk}{d\omega}.$$

$$\frac{d\omega}{dk} = v_g,$$

the group velocity of the wave. *Non-dispersive system* v_g **is constant, so**

$$g(\omega) = \frac{L}{\pi v_g} = \text{constant}.$$

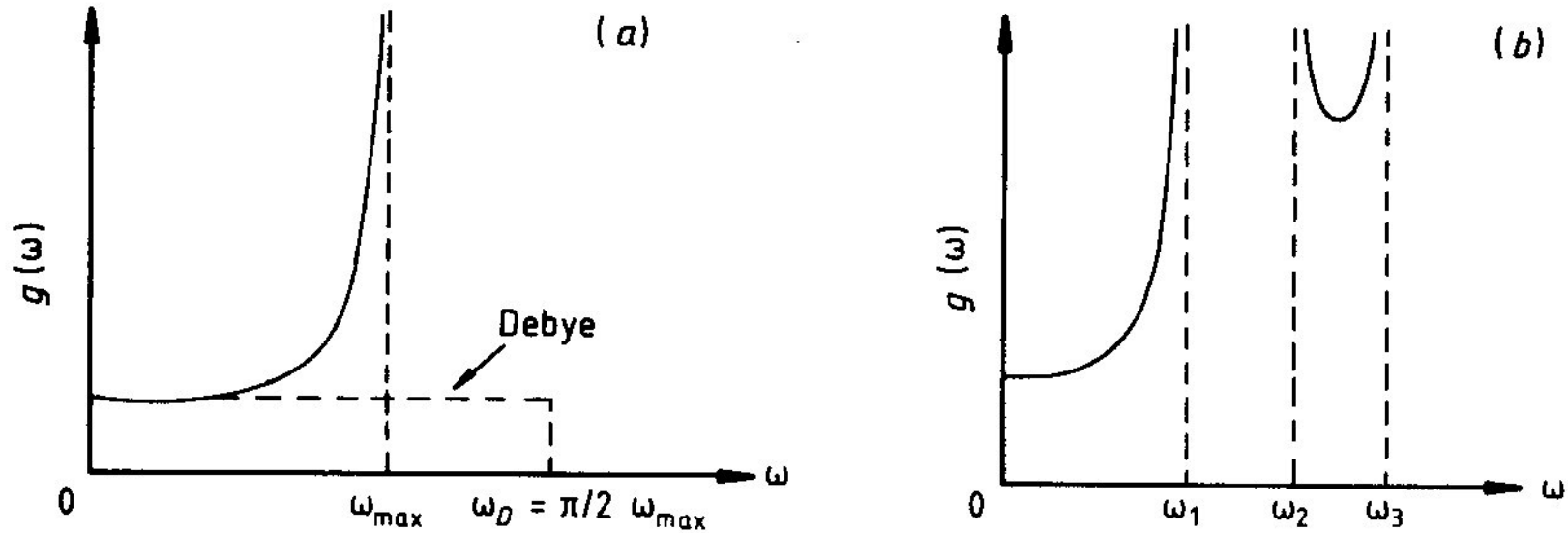*Monatomic chain*

$$\omega = \omega_0 \sin(ka/2),$$

so

$$
\begin{aligned}
v_g &= \frac{a\omega_0}{2}\cos(ka/2) \\
&= \frac{a\omega_0}{2}\sqrt{1 - \sin^2(ka/2)} \\
&= \frac{a\omega_0}{2}\sqrt{1 - \omega^2/\omega_0^2} \\
&= \frac{a}{2}\sqrt{\omega_0^2 - \omega^2}.
\end{aligned}
$$

and then

$$
g(\omega) = \frac{2L}{\pi a\sqrt{\omega_0^2 - \omega^2}}.
$$

One-dimensional density of states for real monatomic structure, non-dispersive system (Debye model), and real diatomic structure.

Note that in one dimension we have singularities whenever the $\omega(k)$ curve is flat.

4.4 Three dimensions – g(E)

Apply periodic boundary conditions along x, y and z. The number of states in the reciprocal space volume $\mathrm{d}k_x\mathrm{d}k_y\mathrm{d}k_z$ is then

$$\frac{L_xL_yL_z}{(2\pi)^3}\ \mathrm{d}k_x\mathrm{d}k_y\mathrm{d}k_z = \frac{V}{8\pi^3}\ \mathrm{d}k_x\mathrm{d}k_y\mathrm{d}k_z,$$

for crystal volume V. Now assume that the crystal is *isotropic* – ω depends only on magnitude of k, not its direction. Then

$$\mathrm{d}k_x\mathrm{d}k_y\mathrm{d}k_z = 4\pi k^2\mathrm{d}k$$

and the number of states with modulus of wavevector between k and $k + \mathrm{d}k$ is

$$g(k)\mathrm{d}k = \frac{V}{8\pi^3}\ 4\pi k^2\mathrm{d}k = \frac{V}{2\pi^2}\ k^2\mathrm{d}k$$

Here we've accounted for all directions, so no extra factor of 2 as in one dimension when going to $g(\omega)$.

But we do have to include all the modes (acoustic, optic, longitudinal, transverse), each with its own dispersion relation, so

$$g(\omega) = \frac{V}{2\pi^2} \sum_s k(\omega_s)^2 / \frac{\mathrm{d}\omega_s}{\mathrm{d}k},$$

where s denotes the mode. *Non-dispersive system* **If we assume that**

$$\omega_s(k) = v_s k,$$

i.e. the sound speed does not depend on frequency, we have

$$k(\omega_s) = \frac{\omega}{v_s},$$

and

$$\frac{\mathrm{d}k}{\mathrm{d}\omega_s} = \frac{1}{v_s},$$

so

$$g(\omega) = \frac{V}{2\pi^2} \sum_s \frac{\omega^2}{v_s^3}.$$

If we define an average sound speed v by

$$\frac{1}{v^3} = \left\langle \frac{1}{v_s^3} \right\rangle,$$

where $\langle \ldots \rangle$ denotes an average. e.g.

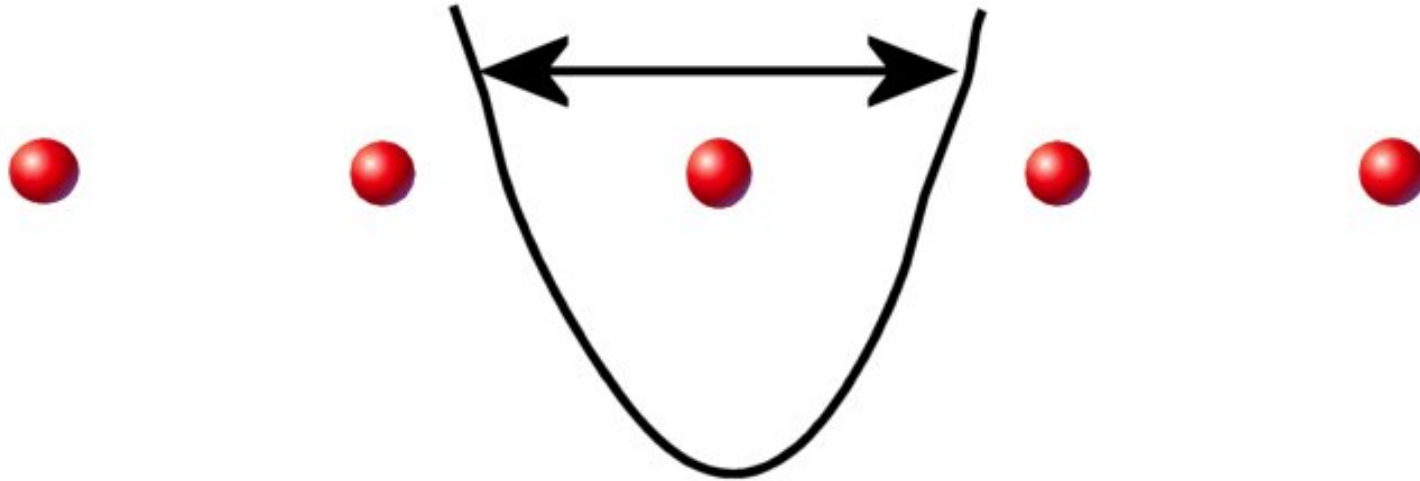$$\frac{1}{v^3} = \frac{1}{3}\left[\frac{1}{v_L^3} + \frac{2}{v_T^3}\right],$$

then

$$g(\omega) = \frac{V}{2\pi^2}\frac{S\omega^2}{v^3}.$$

Here S is the number of branches in the phonon spectrum – 3 for a monatomic 3-D solid.

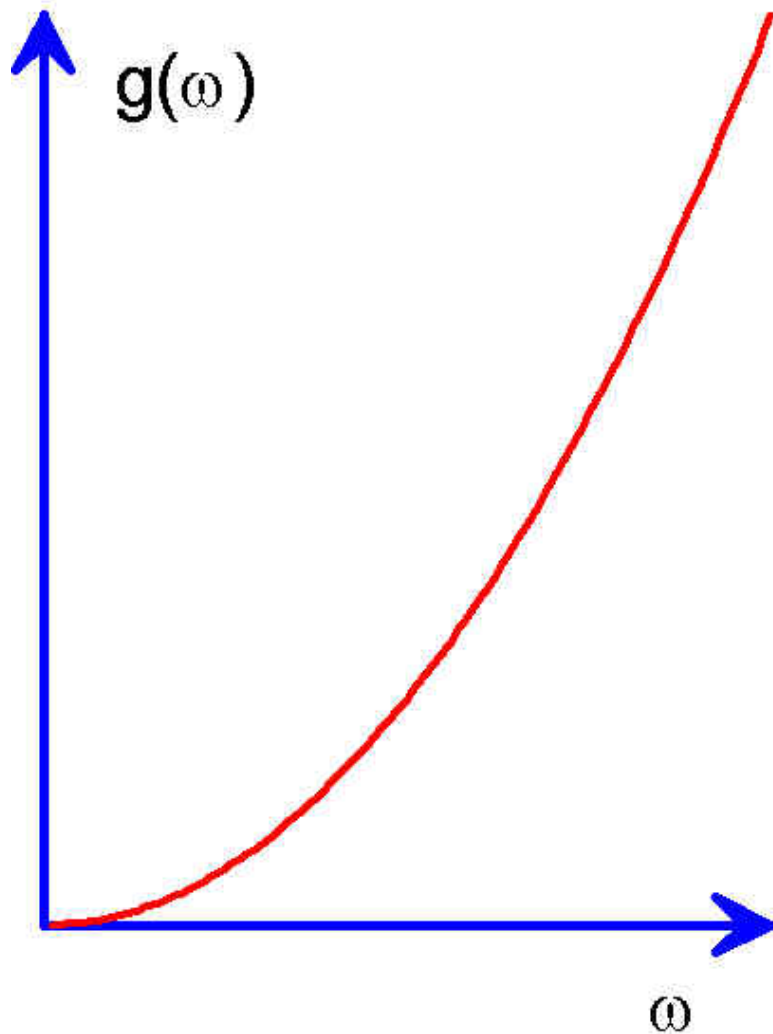## 4.4.1 Special case - single frequency

If we assume (the Einstein model)
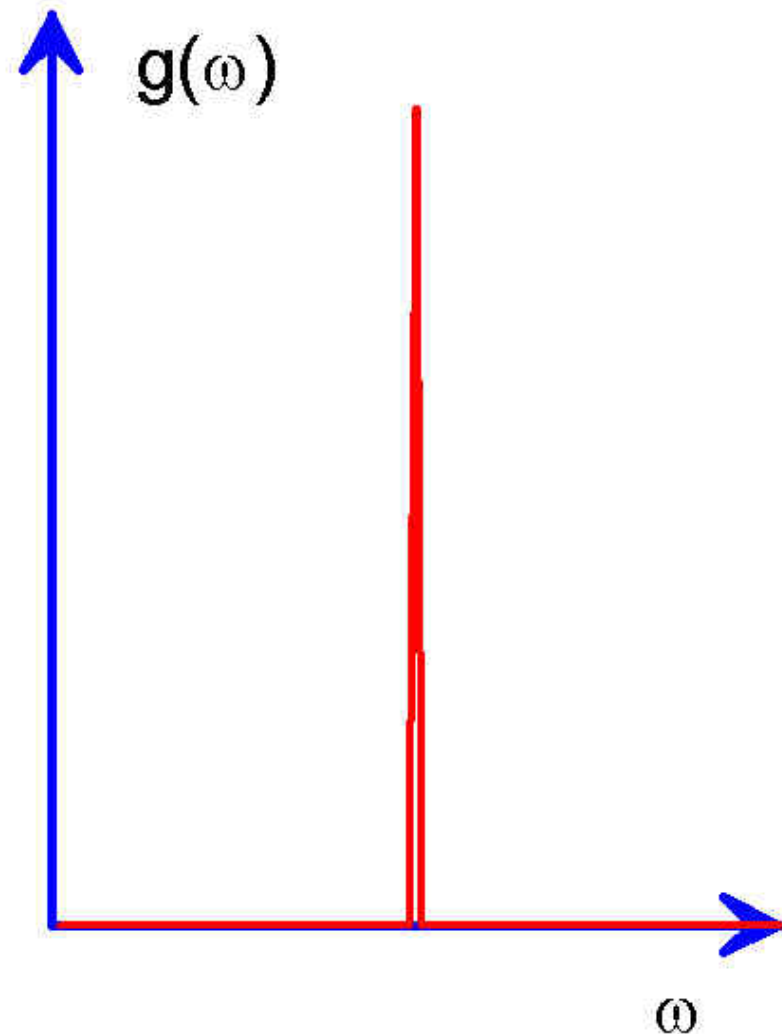
All atoms except one fixed - Einstein model

we get a delta-function density of states.

Density of states

Waves - linear dispersion

Local oscillators

$g(\omega)$

$g(\omega)$

ω

ω

Debye model

Einstein model

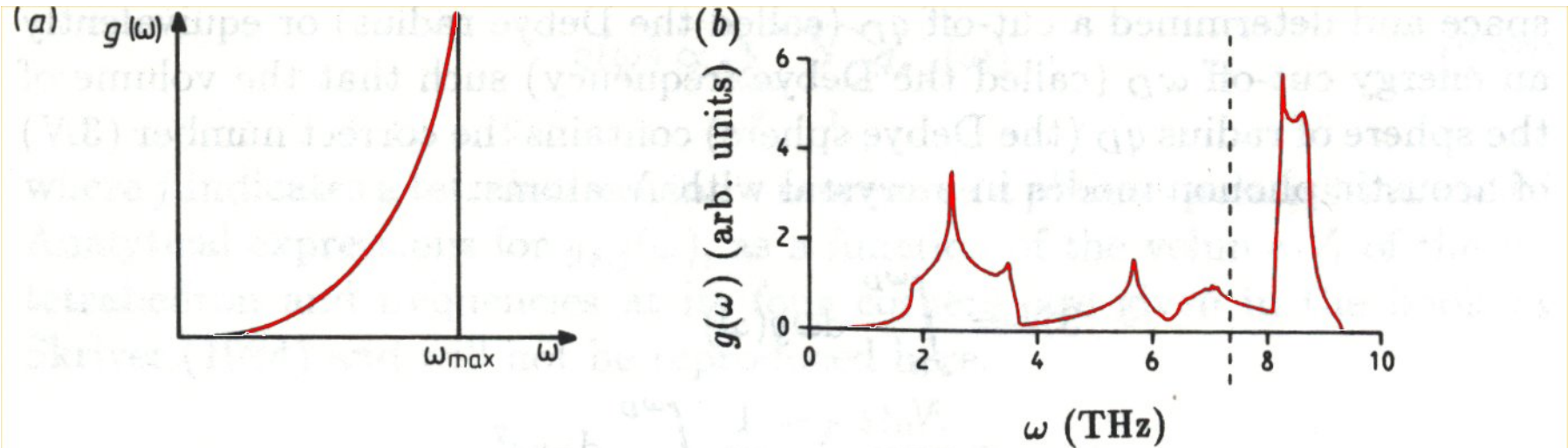N.B. Einstein model can be used as model of narrow optical branch of phonon spectrum.

Figure   The density of normal modes in a three-dimensional crystal. (a) The Debye model, (b) The density of states for Ge, as calculated with the adiabatic bond charge model (Weber 1977).

Real density of states: complicated structure – no singularities (contrast 1-D), but discontinuities in slope.

15

4.4.2 Quantised Simple Harmonic Oscillator

(Revision of 2B28) For an oscillator of frequency ω in its nth energy level the partition function is

$$
\begin{aligned}
Z &= \sum_{n=0}^{\infty} \exp\left(-\frac{E_n}{k_{\mathrm{B}}T}\right) \\
&= \sum_{n=0}^{\infty} \exp\left(-\frac{(n+1/2)\hbar\omega}{k_{\mathrm{B}}T}\right) \\
&= \frac{1}{2\sinh\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right)} \\
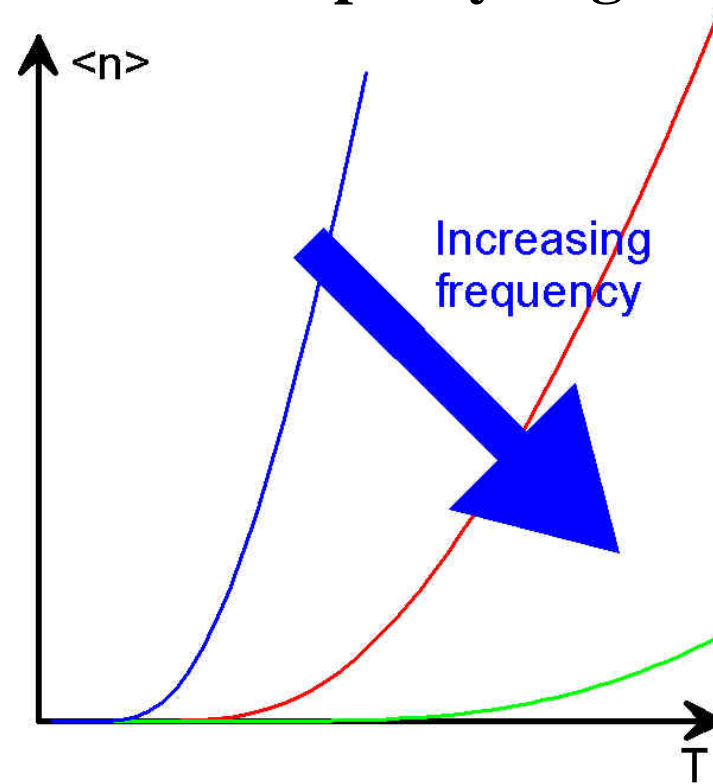&= \frac{1}{2\sinh\left(\frac{\beta\hbar\omega}{2}\right)}
\end{aligned}
$$

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

$$= (\langle n \rangle + \frac{1}{2})\hbar\omega,$$

The crucial result is the mean occupation number of the nth level:

$$\langle n \rangle = \frac{1}{\exp(\hbar\omega/k_{\mathrm{B}}T) - 1},$$
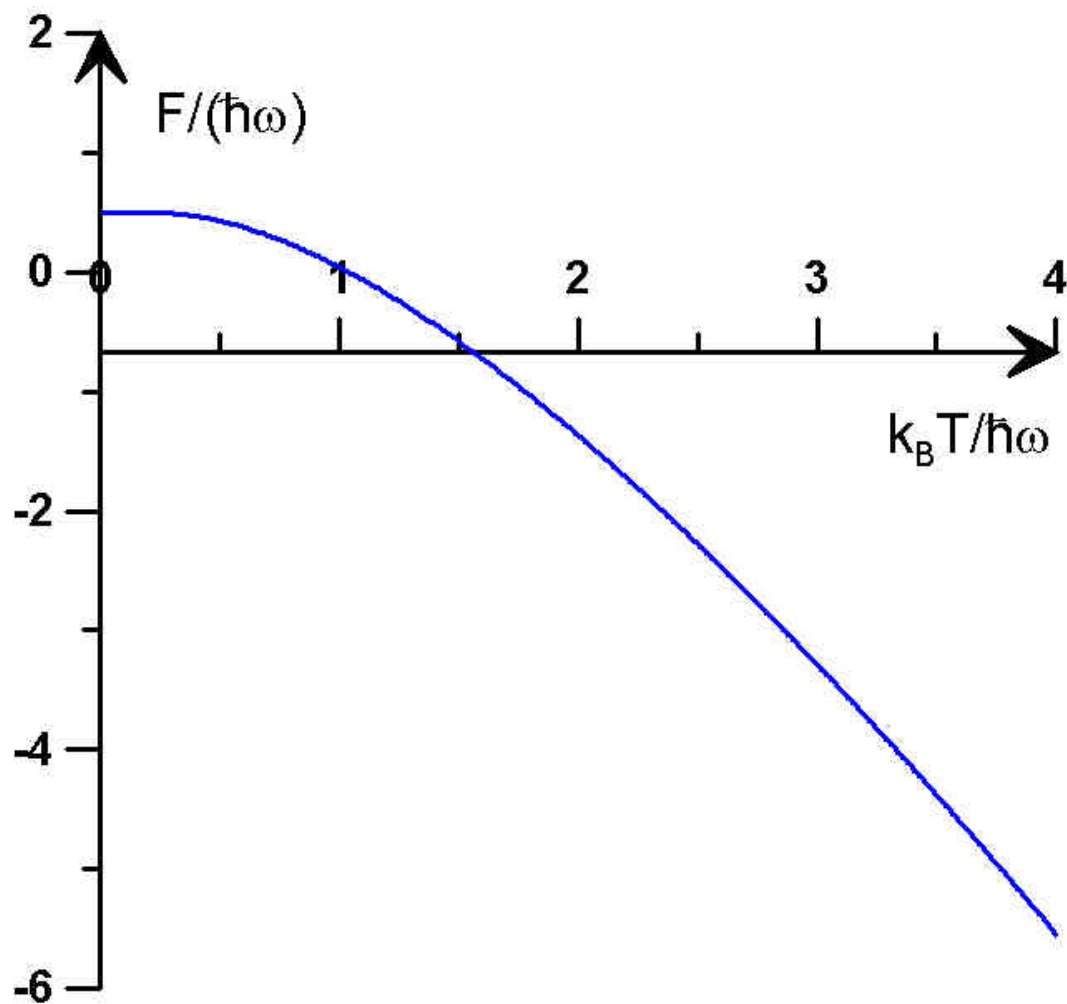
for Bose-Einstein statistics.

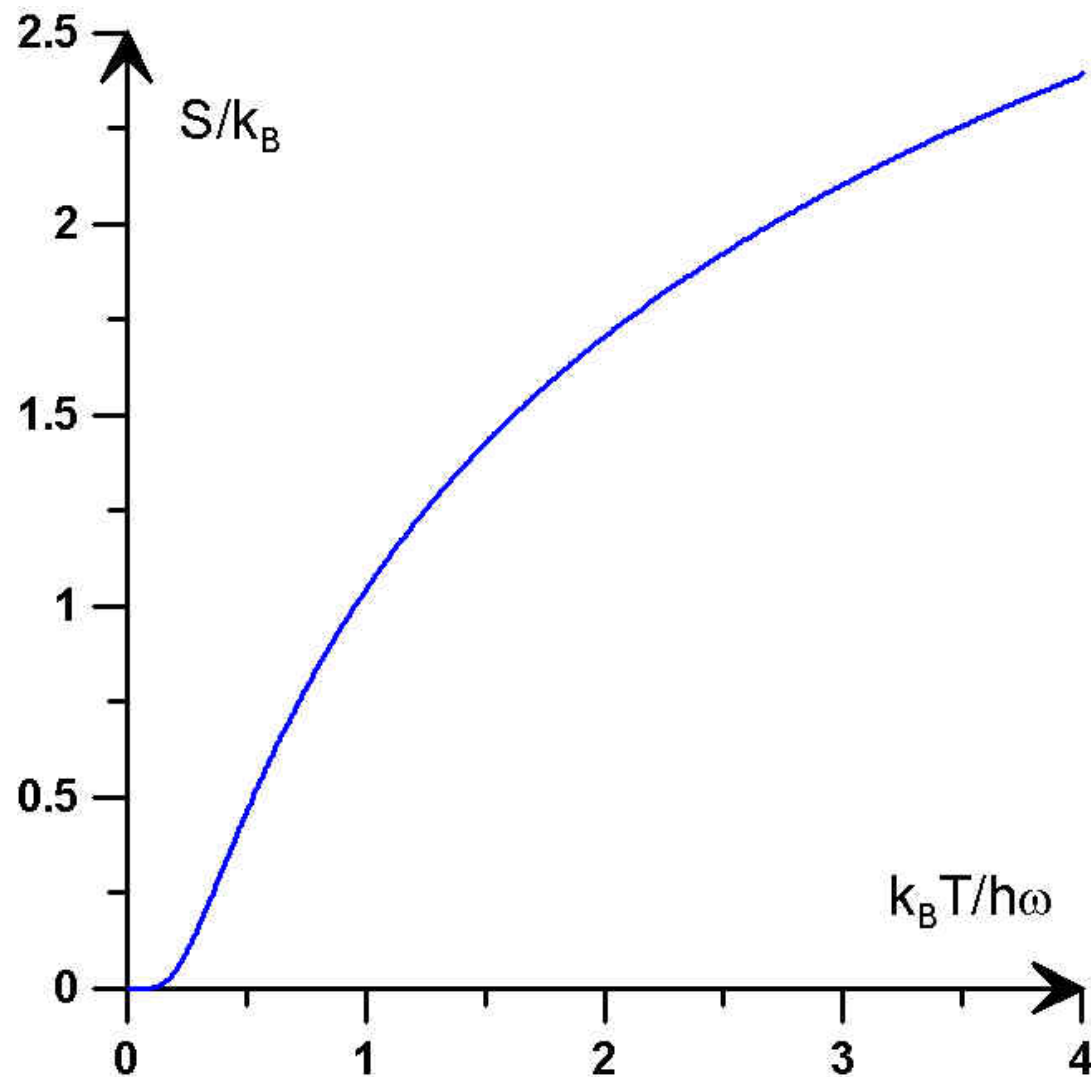# Higher frequency → lower occupancy at given temperature.

Free energy

$$F = -k_{\mathrm{B}} \ln(Z)$$
$$= k_{\mathrm{B}} T \ln \left(\sinh \left(\frac{\hbar \omega}{2 k_{\mathrm{B}} T} \right) \right)$$

Entropy The decrease in free energy with T is due to an increase in entropy. at $p = 0$

$$S = \frac{E - F}{T}.$$

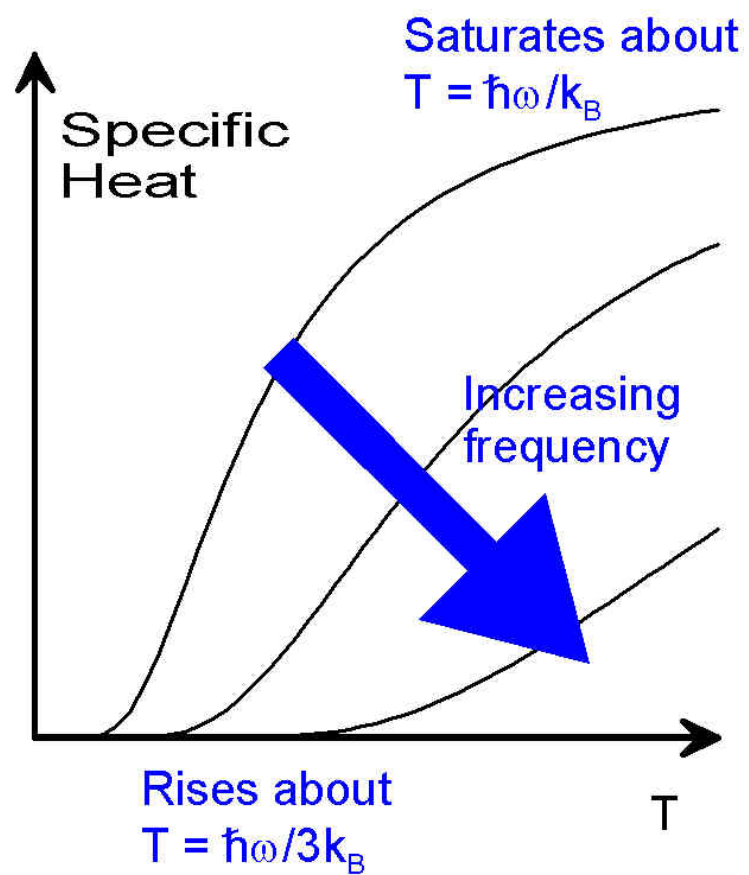**Increase T, increase S: more displacement from equilibrium position**

means more *disorder*.

Specific heat:

$$C = \frac{\partial E}{\partial T}.$$

Specific Heat

Saturates about
T = ℏω/k_B

Increasing
frequency

Rises about
T = ℏω/3k_B

T

- **low T: exponential dependence** $C \propto T^{-2} \exp(-\hbar\omega/k_{\mathrm{B}}T$

- **intermediate** $T \approx \hbar\omega/3k_{\mathrm{B}}$**: steep rise in** C

- **high** $T > \hbar\omega/k_{\mathrm{B}}$**:** C **saturates to classical result,** $C = k_{\mathrm{B}}$ **per oscillator.**

- C **universal function of** T/Θ**, where** $\Theta = \hbar\omega/k_{\mathrm{B}}$