

## Review - Partition Functions

Quantum  $\ln Z = \pm \sum_i \ln(1 \pm e^{-\beta(\epsilon_i - \mu)})$  + FD  
- BE

$$= \pm \sum_i \ln(1 \pm z e^{-\beta \epsilon_i})$$

Classical

$$\ln Z = \sum_i z e^{-\beta \epsilon_i}$$

sum "i" is over all single particle energy levels  
Let  $E_{\min}$  be the  $\min_i \{\epsilon_i\}$  is smallest single particle energy level

from above we see that quantum result  $\rightarrow$  classical result  
in the limit  $z e^{-\beta E_{\min}}$ , since  $\ln(1 + \delta) \approx \delta$ ,

when  $\delta \ll 1$ ,  $z e^{-\beta E_{\min}} = e^{\beta(\mu - E_{\min})} \ll 1 \Rightarrow \beta(\mu - E_{\min}) \ll 0$

for free part  
particle where  $\epsilon_{\min} = 0$ , chemical potential is negative in the classical limit

## Occupation numbers

quantum  $\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} \pm 1}$  + FD  
- BE

classical  $\langle n_i \rangle = e^{-\beta(\epsilon_i - \mu)}$

we see that quantum  $\rightarrow$  classical for states  $i$

such that  $e^{\beta(\epsilon_i - \mu)} \gg 1 \Rightarrow \beta(\epsilon_i - \mu) \gg 0$

$$\Rightarrow (\epsilon_i - \mu) \gg k_B T$$

Note: Since  $\langle n_i \rangle$  must always be positive, and

for bosons  $\langle n_i \rangle = 1/[e^{\beta(\epsilon_i - \mu)} - 1]$  it therefore follows that we must always have  $(\epsilon_i - \mu) > 0$

for any state  $i$ , for bosons. For free particles the smallest  $\epsilon_i$  is usually  $\epsilon_i = 0$ , so we conclude that  $\mu < 0$  always must hold for bosons (or  $\mu < E_{\min}$ )

## Harmonic Oscillator vs boson

Recall our earlier result for the quantized harmonic oscillator

$$E_n = \hbar\omega(n + 1/2)$$

We found:

$$\begin{aligned} \text{average level of excitation} \rightarrow \langle n \rangle &= \frac{\sum_n e^{-\beta\hbar\omega(n+1/2)} n}{\sum_n e^{-\beta\hbar\omega(n+1/2)}} = \frac{\sum_n e^{-\beta\hbar\omega n} n}{\sum_n e^{-\beta\hbar\omega n}} \\ &= \frac{-\frac{1}{\hbar\omega} \frac{\partial}{\partial \beta} \left( \sum_n e^{-\beta\hbar\omega n} \right)}{\sum_n e^{-\beta\hbar\omega n}} = \frac{-\frac{1}{\hbar\omega} \frac{\partial}{\partial \beta} \ln \left[ \frac{1}{1 - e^{-\beta\hbar\omega}} \right]}{\sum_n e^{-\beta\hbar\omega n}} \\ &= \frac{1}{\hbar\omega} \frac{\partial}{\partial \beta} \ln(1 - e^{-\beta\hbar\omega}) = \frac{1}{\hbar\omega} \frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \end{aligned}$$

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

Compare to occupation number of a boson of energy  $\epsilon$

$$\langle n \rangle = \frac{1}{e^{\beta(\epsilon - \mu)} - 1}$$

We see that average level excitation of the harmonic oscillator has exactly the same form as the average ~~number~~ number of bosons with energy  $\epsilon = \hbar\omega$ , if the boson chemical potential is taken to be  $\mu = 0$ .

⇒ quantized harmonic oscillators obey same statistics as bosons, with  $\mu = 0$

we say that excitation level  $n$  of the oscillator is the same as  $n$  quanta or  $n$  "particles" of excitation.

Applies to: elastic oscillations of a solid  $\leftrightarrow$  "phonons"  
oscillation of electromagnetic waves  $\leftrightarrow$  "photons"

Sound modes in solid

$$\omega = c_s |\vec{k}| \quad c_s = \text{speed of sound}, \vec{k} = \text{wave vector}$$

$$\Rightarrow \text{phonon modes } \langle n_k \rangle = \frac{1}{e^{\beta \hbar c_s k} - 1}$$

electromagnetic waves

$$\omega = c |\vec{k}|, \quad c = \text{speed of light}, \vec{k} = \text{wave vector}$$

$$\text{photon modes } \langle n_k \rangle = \frac{1}{e^{\beta \hbar c k} - 1}$$

Another way to see  $\mu = 0$ . Phonons and photons are not conserved particles - they can be created and destroyed



electron scattered by absorbing a photon

chemical equilib  $\Rightarrow \mu_e + \mu_\gamma = \mu_e \Rightarrow \mu_\gamma = 0$  chemical pot of photon

## Specific Heat of a Solid - Ionic Contribution Debye Model

Classical Law of Dulong & Petit

$6N$  harmonic degrees of freedom -  $\left\{ \begin{array}{l} 3N \text{ momenta} \\ 3N \text{ normal coords} \end{array} \right.$

$$C_V = (6N) \left( \frac{1}{2} k_B \right) = 3Nk_B \quad \Rightarrow \quad \frac{C_V}{V} = 3k_B n \quad n = \frac{N}{V}$$

In QM treatment, the  $3N$  momenta +  $3N$  normal coords can be thought of as  $3N$  harmonic oscillators. These oscillations are the sound waves of vibration in the solid. We can approx their dispersion relation as

$$\omega = c_s |\vec{k}| \quad \vec{k} \text{ is wave vector}$$

3 polarizations:  $S = \left\{ \begin{array}{l} L \text{ longitudinal mode, } \omega \text{ displacement } \parallel \vec{k} \\ T_1, T_2 \text{ transverse modes, } \omega \text{ displacement } \perp \vec{k} \end{array} \right.$  at each  $\vec{k}$

For a solid of volume  $V$ , the only sound modes are those that obey periodic boundary conditions

$$\mu = x, y, z \quad k_\mu L = 2\pi n_\mu \quad n_\mu = 0, 1, 2, \dots \text{ integers}$$
$$\vec{k} = \frac{2\pi}{L} \vec{n} \quad \leftarrow \text{ie } \frac{L}{\lambda} = n \text{ integer}$$

The total number of sound modes = total number of oscillators =  $3N$ . This sets an upper bound on  $|\vec{k}|$

Let the maximum value of  $|\vec{k}|$  be denoted  $k_D$ , called the Debye wave number. Oscillations with  $k > k_D$  would have wavelengths smaller than the spacing between the atoms of the solid and so are not physical

For simplicity we will assume that all 3 polarizations have the same speed of sound  $c_s$ .

Since everything we want to compute depends on  $\vec{k}$  only via  $|\vec{k}| = \omega/c_s$ , it is convenient to define a phonon density of states  $g(\omega)$  as follows.

$g(\omega)d\omega$  is the number of phonon modes with frequencies between  $\omega$  and  $\omega+d\omega$

To count these modes, let  $k = \frac{\omega}{c_s}$  and  $dk = \frac{d\omega}{c_s}$ . Then the number of modes with frequency  $\omega'$  such that  $\omega < \omega' < \omega+d\omega$  is

$$\sum_s \sum_{\vec{k}'} (1) = 3 \sum_{\vec{k}} (1) = 3 \frac{1}{(\Delta k)^3} \int d^3 k' \quad \begin{array}{l} \text{such that} \\ k < |\vec{k}'| < k+dk \end{array}$$

↑ polarizations

$$= 3 \frac{1}{(\Delta k)^3} \int_k^{k+dk} dk' 4\pi (k')^2 = 3 \frac{4\pi}{(\Delta k)^3} k^2 dk$$

$$\Rightarrow \frac{3V}{(2\pi)^3} 4\pi k^2 dk \quad \text{using } \Delta k = \frac{2\pi}{L}$$

$$= \frac{3V}{(2\pi)^3} 4\pi \frac{\omega^2}{c_s^2} \frac{d\omega}{c_s} \quad \text{using } k = \frac{\omega}{c_s}, \quad dk = \frac{d\omega}{c_s}$$

$$= g(\omega) d\omega \quad \Rightarrow \quad \boxed{g(\omega) = \frac{3V}{2\pi^2} \frac{\omega^2}{c_s^3}}$$

Since the total number of modes is  $3N$ , we have

$$3N = \int_0^{\omega_D} d\omega g(\omega) \quad \text{where } \omega_D = c_s k_D \text{ is the "Debye frequency"}$$

$$3N = \frac{3V}{2\pi^2 c_s^3} \int_0^{\omega_D} d\omega \omega^2 = \frac{V}{2\pi^2 c_s^3} \omega_D^3$$

$$\Rightarrow \omega_D = \left[ 6\pi^2 c_s^3 \frac{N}{V} \right]^{1/3} = \left[ 6\pi^2 c_s^3 m \right]^{1/3} \sim m^{1/3}$$

where  $m = \frac{N}{V}$  is the density of atoms in the solid

$$\Rightarrow k_D = \frac{\omega_D}{c_s} = \left[ 6\pi^2 m \right]^{1/3}$$

$\omega_D$  is frequency of most energetic phonons.

Now the average energy due to thermal excitation of phonons is

$$\begin{aligned} \langle E \rangle &= \sum_s \sum_{\vec{k}} \hbar \omega_s(\vec{k}) \left[ \langle n_{s\vec{k}} \rangle + \frac{1}{2} \right] \\ &= \int_0^{\omega_D} d\omega g(\omega) \hbar \omega \left[ \frac{1}{e^{\beta \hbar \omega} - 1} + \frac{1}{2} \right] \end{aligned}$$

Specific heat is

$$\begin{aligned} C_V &= \frac{\partial \langle E \rangle}{\partial T} = \int_0^{\omega_D} d\omega g(\omega) \hbar \omega \frac{\partial}{\partial T} \left[ \frac{1}{e^{\beta \hbar \omega} - 1} \right] \\ &= \int_0^{\omega_D} d\omega g(\omega) \hbar \omega \frac{\left( \frac{\hbar \omega}{k_B T^2} \right) e^{\beta \hbar \omega}}{[e^{\beta \hbar \omega} - 1]^2} \\ &= \frac{3V}{2\pi^2 c_s^3} \int_0^{\omega_D} d\omega \omega^2 k_B \left( \frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\beta \hbar \omega}}{[e^{\beta \hbar \omega} - 1]^2} \end{aligned}$$

let  $x \equiv \frac{\hbar \omega}{k_B T} = \beta \hbar \omega$

$$C_V = \frac{3V k_B}{2\pi^2 c_s^3} \left( \frac{k_B T}{\hbar} \right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{[e^x - 1]^2}, \quad x_D = \beta \hbar \omega_D$$

Consider the prefactor of the integral

$$\begin{aligned} \frac{3V k_B}{2\pi^2} \left( \frac{k_B T}{c_s \hbar} \right)^3 &= \frac{3V k_B}{2\pi^2} \left( \frac{k_B T}{k_D c_s \hbar} \right)^3 \underbrace{6\pi^2 m}_{k_D^3} \\ &= 9V k_B m \left( \frac{k_B T}{\hbar \omega_D} \right)^3 \quad \text{where we used} \\ & \quad c_s k_D = \omega_D = c_s [6\pi^2 m]^{1/3} \end{aligned}$$

Define  $\Theta_D \equiv \hbar\omega_D/k_B$  the "Debye temperature"

→ specific heat per volume is

$$\frac{C_V}{V} = 9mk_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} dx \frac{x^4 e^x}{[e^x - 1]^2}$$

$$\text{where } x_D = \beta\hbar\omega_D = \frac{\Theta_D}{T}$$

Now we evaluate the integral in various limits

1) as  $T \rightarrow \infty$ ,  $\Theta_D/T = x_D$  gets very small

⇒ we can expand the integrand for small values of  $x$

$$\frac{x^4 e^x}{[e^x - 1]^2} \approx \frac{x^4}{x^2} = x^2$$

$$\int_0^{x_D} dx x^2 \approx \frac{1}{3} x_D^3 = \frac{1}{3} \left(\frac{\Theta_D}{T}\right)^3$$

$$\text{So } \frac{C_V}{V} = 9mk_B \left(\frac{T}{\Theta_D}\right)^3 \cdot \frac{1}{3} \left(\frac{\Theta_D}{T}\right)^3$$

$$= 3mk_B$$

This is the classical Law of Dulong + Petit!

So classical result remains correct provided

$T \gg \Theta_D$  i.e. high temperature



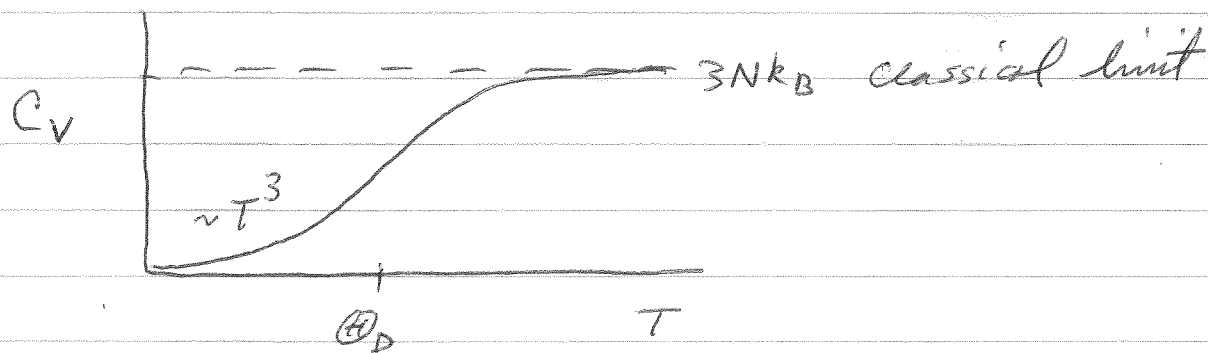
For low  $T \neq 0$ ,  $x_D \rightarrow \infty$

$$\frac{C_V}{V} \approx 9mk_B \left( \frac{T}{\Theta_D} \right)^3 \int_0^\infty dx \frac{x^4 e^x}{(e^x - 1)^2}$$

This integral is just a pure number.  $= \frac{4}{15} \pi^4$

$$\frac{C_V}{V} \approx \frac{12}{5} \pi^4 mk_B \left( \frac{T}{\Theta_D} \right)^3$$

$\propto T^3$  at low temperatures



For common solids,  $\Theta_D \sim 100 - 300 \text{ K}$

so the effects of quantum mechanics on the specific heat of a solid can be seen at room temperature!

Originally, Einstein treated this problem quantum mechanically assuming that all phonon modes had the same  $T$ -independent frequency  $\omega_0$ . This is called the "Einstein-model" and it gives exponentially decreasing  $e^{-\hbar\omega_0/k_B T}$  specific heat at low  $T$ . The Debye model is more physically correct.