Problem Sheet 4.

1. a)

$$Z = e^{-\epsilon/k_BT} + 1 + e^{\epsilon/k_BT}$$

b) $$F = -k_BT \ln Z$$

$$= -k_BT \ln\left(1 + e^{\epsilon/k_BT} + e^{-\epsilon/k_BT}\right).$$

c) $$p(E=0) = \frac{1}{Z}$$

$$= \frac{1}{1 + e^{\epsilon/k_BT} + e^{-\epsilon/k_BT}}.$$

If $\epsilon = k_BT \Rightarrow p(E=0) = \frac{1}{1+e+e^{-1}} \simeq 0.245.$

d) $$\langle E \rangle = \sum_i p_i E_i$$

$$= \frac{1}{Z}\left(\epsilon e^{-\epsilon/k_BT} + 0 - \epsilon e^{+\epsilon/k_BT}\right).$$

$$= \epsilon \frac{e^{-\epsilon/k_BT} - e^{+\epsilon/k_BT}}{1 + e^{\epsilon/k_BT} + e^{-\epsilon/k_BT}}$$

$$= -2\epsilon \frac{\sinh(\epsilon/k_BT)}{1 + 2\cosh(\epsilon/k_BT)}$$

As $T \to \infty$

we can use the Taylor expansion $e^x \simeq 1 + x + \dots$

$$\langle E \rangle \simeq \frac{\epsilon\left(1-\epsilon/k_BT - \left(1+\epsilon/k_BT\right)\right)}{1 + 1 + \epsilon/k_BT + 1 - \epsilon/k_BT}$$

$$\simeq -\frac{2\epsilon^2}{k_BT} \cdot \frac{1}{3}.$$

$\therefore$ as $T \to \infty$ $\langle E \rangle \to 0$ like $\frac{1}{T}$.

e) At low temperatures $T \to 0$ & $e^{\epsilon/k_BT} \to \infty$; $e^{-\epsilon/k_BT} \to 0$

Hence

$$\langle E \rangle \simeq -\frac{\epsilon \; e^{\epsilon/k_BT}}{e^{\epsilon/k_BT}} \simeq -\epsilon.$$

f) $\frac{\epsilon}{k_B} \cong 724.29\,K.$

i) $T = 10K$ $\Rightarrow$ not enough thermal energy to excite system so $\frac{C_V}{k_B} \simeq 0.$

ii) $T = 1000K$ $\Rightarrow$ thermal energy is comparable to level spacing so $\frac{C_V}{k_B} \sim 1.$

iii) $T = 10^6 K$ $\Rightarrow$ all levels equally occupied so $\frac{C_V}{k_B} \simeq 0.$

g) i) The energies are displaced by $+\epsilon$, so the average energy

$$\langle E \rangle \longrightarrow \langle E \rangle + \epsilon .$$

ii) The additive constant has no effect on the heat capacity. (we differentiate the energy & $\frac{d\epsilon}{dT} = 0$).

2.

3ϵ	1
2ϵ	3
ϵ	3
0	1

$$Z = 1 . e^{0} + 3 . e^{-\epsilon/k_B T} + 3 . e^{-2\epsilon/k_B T} + e^{-3\epsilon/k_B T}$$

$$= \left(1 + e^{-\epsilon/k_B T}\right)^3$$

$$F = -N k_B T \ln Z$$

N particles
$\Rightarrow N \times$ 1 particle free energy

$$= -N k_B T \ln \left(1 + e^{-\epsilon/k_B T}\right)^3$$

$$= -3 N k_B T \ln \left(1 + e^{-\epsilon/k_B T}\right) .$$

3. $$Z = e^{aT^3V}.$$

$$\Rightarrow \quad F = -k_B T \ln Z = -k_B T \ln\left(e^{aT^3V}\right)$$
$$= -k_B T \cdot (aT^3V) = -ak_B T^4 V$$

$$F = U - TS$$
$$\Rightarrow \quad dF = -S\,dT - p\,dV \quad \text{for a gas}$$

$$\Rightarrow \quad S = -\frac{\partial F}{\partial T} \quad \& \quad p = -\frac{\partial F}{\partial V}$$

Hence $S = 4ak_B T^3 V$ & $p = ak_B T^4$

$$U = F + TS$$
$$= -ak_B T^4 V + T.\,(4ak_B T^3 V)$$
$$= 3ak_B T^4 V.$$

4. $$u(x) = \begin{cases} 0 & 0 < x < L \\ \infty & |x| > L \end{cases}$$

$$Z = \int_{-\infty}^{\infty} e^{-u(x)/k_B T}\,dx = L$$

Hence $F = -k_B T \ln Z = -k_B T \ln L.$

$$p = -\frac{\partial F}{\partial L} = \frac{k_B T}{L}.$$

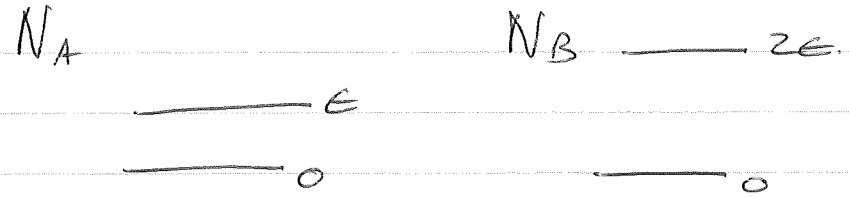
$L = 1\text{nm}$ & $T = 1000\,K$

$\Rightarrow \quad p = 1.38 \times 10^{-11}\ N$

(note in 3-D pressure is F/A $[N m^{-2}]$
2-D pressure is F/L $[N m^{-1}]$
1-D pressure $\equiv F$. $[N.]$)

5.

a)



For atoms of type A

$$Z = 1 + e^{-\epsilon/k_B T}.$$

Hence using $F = -k_B T \ln Z$

$$F_A = -k_B T \ln (1 + e^{-\epsilon/k_B T}) \quad \underline{\text{per atom}}$$

or $F_A = -N_A k_B T \ln (1 + e^{-\epsilon/k_B T})$ for N_A atoms.

Similarly for atoms of type B

$$F_B = -N_B k_B T \ln (1 + e^{-2\epsilon/k_B T}).$$

So in total

$$F = F_A + F_B = -k_B T \left(N_A \ln (1 + e^{-\epsilon/k_B T}) + N_B \ln (1 + e^{-2\epsilon/k_B T}) \right).$$

b) The heat capacity can be got from the free energy as follows:

$$dF = -S\,dT - p\,dV \Rightarrow S = -\left.\frac{\partial F}{\partial T}\right|_V$$

$$C_V = T\left.\frac{\partial S}{\partial T}\right|_V = -T\left.\frac{\partial^2 F}{\partial T^2}\right|_V$$

$$\frac{\partial F}{\partial T} = -k_B\left(N_A \ln\left(1+e^{-\epsilon/k_BT}\right) + N_B \ln\left(1+e^{-2\epsilon/k_BT}\right)\right)$$

$$-\cancel{k_B}T\left(\frac{N_A e^{-\epsilon/k_BT}}{1+e^{-\epsilon/k_BT}}\,\frac{\epsilon}{\cancel{k_B}T^2} + \frac{N_B e^{-2\epsilon/k_BT}}{1+e^{-2\epsilon/k_BT}}\cdot\frac{2\epsilon}{\cancel{k_B}T^2}\right)$$

$$\frac{\partial^2 F}{\partial T^2} = -k_B\left(\frac{N_A e^{-\epsilon/k_BT}}{1+e^{-\epsilon/k_BT}}\,\frac{\epsilon}{k_BT^2} + \frac{N_B e^{-2\epsilon/k_BT}}{1+e^{-2\epsilon/k_BT}}\,\frac{2\epsilon}{k_BT^2}\right)$$

$$-\left(\frac{N_A e^{-\epsilon/k_BT}}{1+e^{-\epsilon/k_BT}}\left(-\frac{\epsilon}{T^2}\right) + \frac{N_B e^{-2\epsilon/k_BT}}{1+e^{-2\epsilon/k_BT}}\left(-\frac{2\epsilon}{T^2}\right)\right).$$

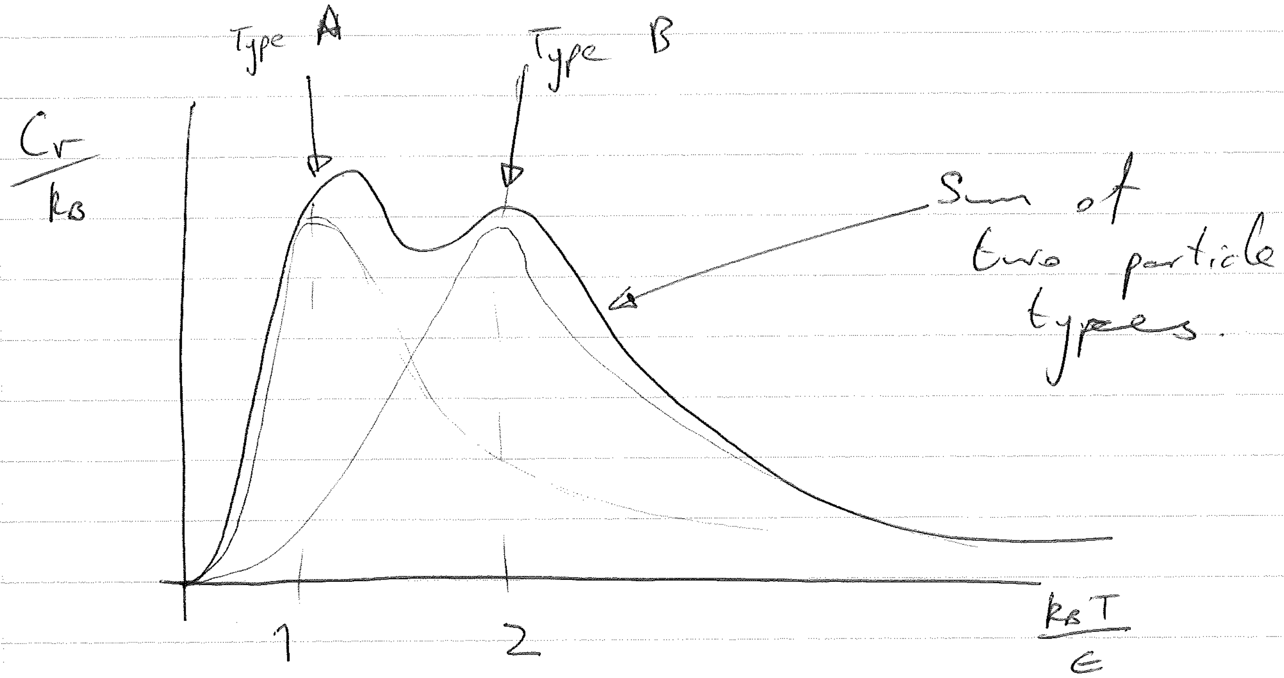
$$-\left(-\frac{N_A\epsilon}{T}\cdot\frac{e^{\epsilon/k_BT}}{\left(1+e^{\epsilon/k_BT}\right)^2}\left(-\frac{\epsilon}{k_BT^2}\right)\right.$$

$$\left.-\frac{2\epsilon}{T}\frac{N_B e^{2\epsilon/k_BT}}{\left(1+e^{2\epsilon/k_BT}\right)^2}\left(-\frac{2\epsilon}{k_BT^2}\right)\right).$$

$$= -\frac{k_B}{T}\,\frac{\epsilon^2}{(k_BT)^2}\left(N_A\frac{e^{\epsilon/k_BT}}{\left(1+e^{\epsilon/k_BT}\right)^2} + \frac{4N_B e^{2\epsilon/k_BT}}{\left(1+e^{2\epsilon/k_BT}\right)^2}\right)$$

Hence

$$C_V = k_B \left(\frac{\epsilon}{k_BT}\right)^2 \left(\frac{N_A e^{\epsilon/k_BT}}{(1+e^{\epsilon/k_BT})^2} + \frac{4 N_B e^{2\epsilon/k_BT}}{(1+e^{2\epsilon/k_BT})^2} \right)$$



6. Einstein's theory is based on ~~about~~ the quantum simple harmonic oscillator, so we need to calculate the entropy of an oscillator, then multiply by $3N$.

$$Z = \frac{e^{-\hbar\omega/2k_BT}}{1 - e^{-\hbar\omega/k_BT}} \quad \text{(from lectures).}$$

$$\therefore \quad F = -k_BT \ln Z$$

$$= -k_BT\left(-\frac{\hbar\omega}{2k_BT} - \ln\left(1-e^{-\hbar\omega/k_BT}\right)\right)$$

$$= \underbrace{\frac{\hbar\omega}{2}}_{\text{Zero point energy}} + k_BT \ln\left(1-e^{-\hbar\omega/k_BT}\right)$$

$$S = -\frac{\partial F}{\partial T}$$

$$\Rightarrow S = -k_B \ln\left(1 - e^{-\hbar\omega/k_BT}\right)$$

$$- k_B T \frac{1}{1 - e^{-\hbar\omega/k_BT}} e^{-\hbar\omega/k_BT} \cdot \frac{\hbar\omega}{k_BT^2}$$

$$= -k_B \ln\left(1 - e^{-\hbar\omega/k_BT}\right)$$

$$- \frac{\hbar\omega}{T} \frac{1}{e^{\hbar\omega/k_BT} - 1}$$

per oscillator

or

$$S = -3Nk_B \ln\left(1 - e^{-\hbar\omega/k_BT}\right) - \frac{3N\hbar\omega}{T} \frac{1}{e^{\hbar\omega/k_BT} - 1}$$

for the crystal of N atoms.

As $T \to \infty$ $\quad e^{-\hbar\omega/k_BT} \simeq 1 - \frac{\hbar\omega}{k_BT}$

$$\therefore S \simeq -3Nk_B \ln\left(\frac{\hbar\omega}{k_BT}\right) - \frac{3N\hbar\omega}{\cancel{T}} \frac{k_B\cancel{T}}{\cancel{\hbar\omega}}$$

$$= 3Nk_B \ln\left(\frac{k_BT}{\hbar\omega}\right) - 3Nk_B$$

As $T \to 0$ $\quad e^{-\hbar\omega/k_BT} \to 0 \quad$ & $\ln(1-x) \simeq -x$

$$S \simeq -3Nk_B \left(-e^{-\hbar\omega/k_BT}\right) - \frac{3N\hbar\omega}{T} \cdot e^{-\hbar\omega/k_BT}$$

$$= 3Nk_B e^{-\hbar\omega/k_BT} - \frac{3N\hbar\omega}{T} e^{-\hbar\omega/k_BT} \longrightarrow 0 \text{ as } T \to 0.$$

The mean quantum number $\bar{n} = \langle n \rangle$ is related to the average energy

$$\langle n \rangle = \left(\frac{\langle E \rangle}{\hbar\omega} - \frac{1}{2} \right)$$

Subtract Zero point energy

$$= \frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1} \cdot \frac{1}{\hbar\omega} \quad \text{(from lectures).}$$

$\frac{k_BT}{\hbar\omega}$	0	1	100
$\langle n \rangle$	0	0.58	99.5

7. Debye model

- A crystal, volume V, is modelled as a box that contains sound waves (phonons)

- Thermal energy excites the sound waves & they displace atoms.

- Sound waves are modelled as simple harmonic oscillators.

- Sound waves have dispersion relation

frequency $\rightarrow \omega = s k$ ← wavevector

speed

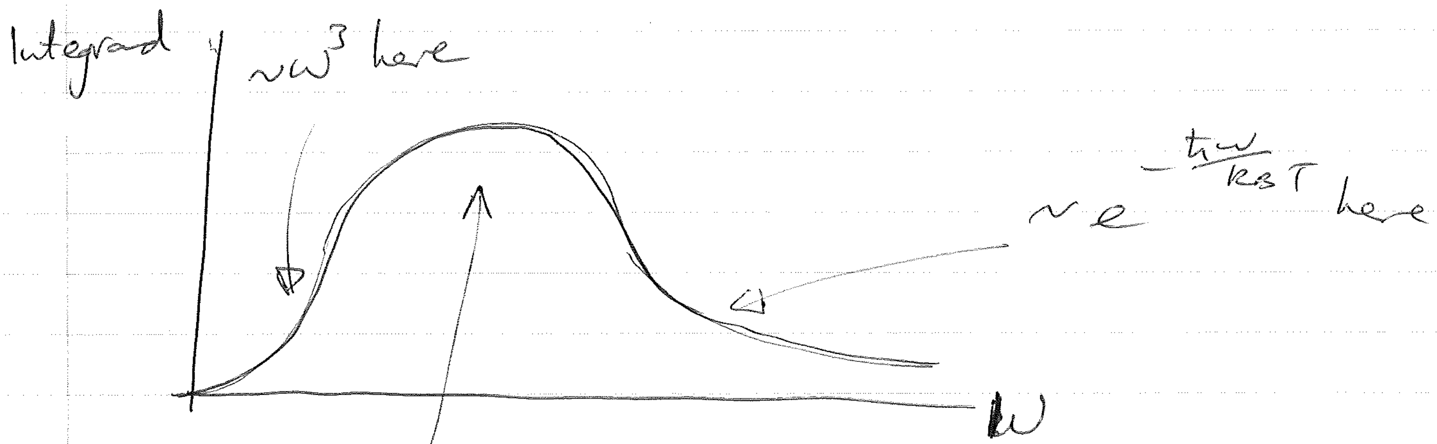
— The density of states for waves in a box is

$$D(\omega) = \frac{V}{2\pi^2}\frac{\omega^2}{s^3}\,d\omega.$$

— A cut off frequency ω_D (the Debye frequency) is used to prevent over counting of the modes — we can only have $3N$ as that's the number of degrees of freedom of N atoms.

Hence

$$C = \int_0^{\omega_D} \underbrace{\frac{V\omega^2}{2\pi^2 s^3}}_{\substack{\text{Density of States} \\ (\#\text{ modes in } \omega \to \omega + d\omega)}} \cdot \underbrace{\frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1}}_{\text{average energy}}\, d\omega$$

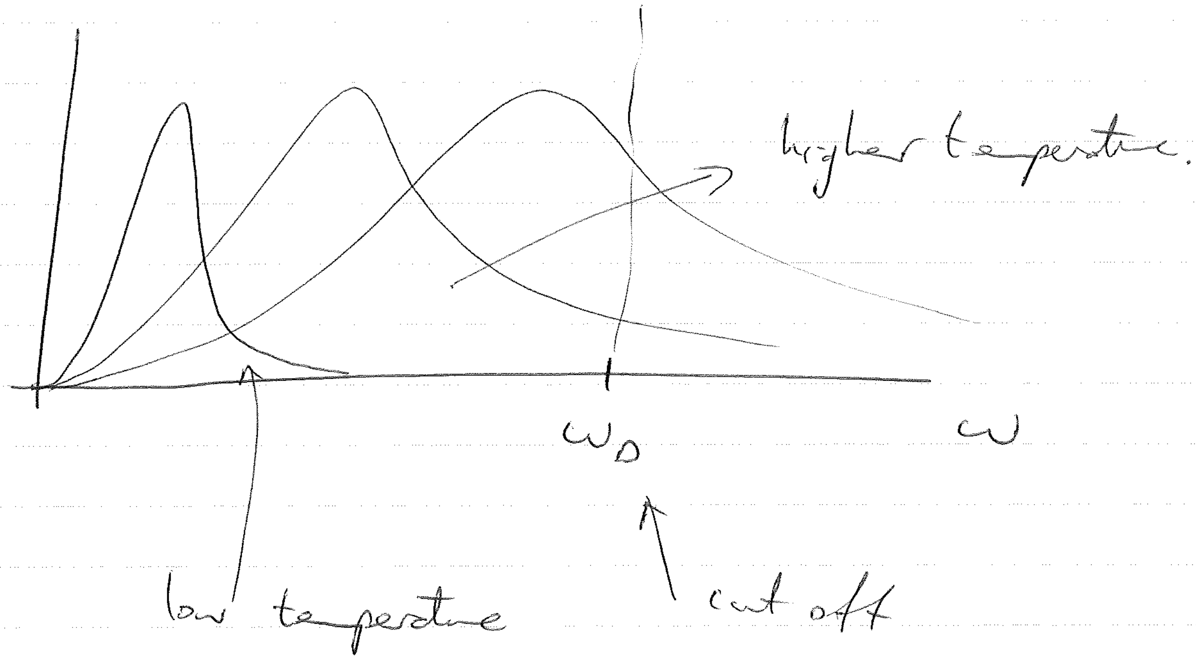


phonons near peak make largest contribution

— There are lots of them (ω^2)

— They have lots of energy.

At different temperatures the cutoff ω_D comes in different places



If $T \ll \Theta_D$ (the Debye temperature) then the cutoff comes at high frequency, so the modes that make the largest contribution are at the peak of the integrand.

$$\Rightarrow \quad \hbar\omega \sim k_B T \sim 7 \text{ meV}.$$

8. $$\langle E \rangle = \sum_i p_i E_i$$

$$= \sum_i \frac{e^{-\beta E_i}}{Z} E_i \quad \text{where } \beta = \frac{1}{k_B T}$$

$$= \frac{1}{Z}\left(\frac{-\partial}{\partial \beta}\right) \sum_i e^{-\beta E_i} = \frac{1}{Z}\left(\frac{-\partial Z}{\partial \beta}\right)$$

$$= -\frac{\partial \ln Z}{\partial \beta}.$$

$$\langle E^2\rangle = \frac{1}{Z}\left(-\frac{\partial}{\partial\beta}\right)\cdot\left(-\frac{\partial}{\partial\beta}\right)Z$$

(Using trick twice).

$$= \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2}$$

$$\langle E^2\rangle - \langle E\rangle^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} - \left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right)^2$$

BUT

$$\frac{\partial^2 \ln Z}{\partial\beta^2} = \frac{\partial}{\partial\beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial\beta}\right)$$

$$= -\frac{1}{Z^2}\left(\frac{\partial Z}{\partial\beta}\right)^2 + \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2}.$$

Just as above.

Hence

$$\langle \Delta E^2\rangle = \frac{\partial^2}{\partial\beta^2}\ln Z.$$

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

$$= -\frac{\partial\langle E\rangle}{\partial\beta} = -\frac{dT}{d\beta}\frac{\partial\langle E\rangle}{\partial T}$$

$$= k_B T^2 C_V \quad \text{since } \frac{d\beta}{dT} = \frac{d}{dT}\left(\frac{1}{k_B T}\right) = -\frac{1}{k_B T^2}.$$