2661

SECOND PUBLIC EXAMINATION

Honour School of Physics Part A: 3 and 4 Year Courses

Honour School of Physics and Philosophy Part A

A1: THERMAL PHYSICS

TRINITY TERM 2013

Wednesday, 12 June, 9.30 am – 12.30 pm

Answer **all** *of Section A and* **three** *questions from Section B.*

For Section A start the answer to each question on a **fresh page.**
For Section B start the answer to each question in a **fresh book.**

A list of physical constants and conversion factors accompanies this paper.

The numbers in the margin indicate the weight that the Examiners expect to assign to each part of the question.

Do NOT turn over until told that you may do so.

Section A

$p(x) - p(x+dx) = (k\,dx)\,p(x)$

1. The Clausius inequality states:

For any closed cycle $\oint \frac{đQ}{T} \leq 0$*, where the equality necessarily holds for reversible cycles.*

Define the symbols $đQ$ and T. Write down the thermodynamic definition of entropy and, starting from the Clausius inequality or otherwise, show that it is a function of state. [5]

$dS = \frac{dQ_{rev}}{T}$ $\quad dQ = C\,dT$

2. (a) 1 kg of silver at 0°C is brought into contact with a large heat reservoir at 100°C. When the silver has reached 100°C what is the change in the entropy of (i) the silver, (ii) the reservoir, and (iii) the universe?

(b) If, instead, the silver is heated from 0°C to 100°C by operating a reversible heat engine between the silver and the reservoir, what is now the change in the entropy of (i) the silver, (ii) the reservoir, and (iii) the universe? [6]

[The specific heat of silver is 2.3×10^2 J kg^{-1} K^{-1}.]

$(1-k\,dx)$ $\quad \frac{dp}{dx} = -kx \quad p(x)$

3. The probability that a molecule in a dilute gas undergoes a collision in a small distance dx is $k\,dx$ with k constant. Show that the probability that a molecule has not collided after travelling a distance x is

$$p(x) = e^{-kx}$$

$k\,dx \quad \frac{dp}{p} = -k\,dx$

and relate k to the mean free path of the gas. State a typical value of the mean free path for a molecule in air at room temperature and atmospheric pressure. $\frac{dp}{dx} = -kp\,dx$ [7]

4. Use kinetic theory to obtain an expression for the pressure (force per unit length exerted on a line) of an isotropic, *two-dimensional* gas in terms of an appropriate average over the velocity distribution. [6]

5. A two-level system has energy levels 0 and Δ. Draw a carefully labelled sketch of (i) the mean energy and (ii) the specific heat as a function of temperature. [6]

6. If all the solar power falling on earth was absorbed by the oceans, estimate how long it would take for them to evaporate, stating the assumptions you make.
[The specific heat of water is 4.2×10^3 J kg^{-1} K^{-1} and the latent heat of water is 2.3×10^6 J kg^{-1}. The solar constant, defined as the solar power per unit area, at a distance from the sun equal to the radius of the earth's orbit, is 1370 Wm^{-2}.] [5]

7. A point P is chosen at random from inside the sphere $x^2 + y^2 + z^2 = 1$. r is the distance of P from the origin. Find the mean and variance of r. [5]

$r \quad \frac{\int r\,dV}{\int dV}$

Section B

8. State the theorem of equipartition of energy, explaining what is meant by the classical limit. [3]

Show that the single particle partition function describing the translational motion of a perfect, classical gas of molecules of mass m occupying a volume V at temperature T is

$$Z_1 = V\left(\frac{mk_\mathrm{B}T}{2\pi\hbar^2}\right)^{3/2} .$$

Derive an expression for the mean kinetic energy of a gas molecule and relate your answer to the equipartition theorem. [7]

A quantum harmonic oscillator has energy levels $(n+\frac{1}{2})\hbar\omega,\ \ n = 0, 1, 2\ldots.$ Derive a formula for the mean energy of the oscillator, E, in terms of $x = \hbar\omega/k_\mathrm{B}T$. State the condition on x for which the equipartition theorem holds, and find E in this limit. [6]

Explain why the high temperature specific heat of an insulating solid is close to $3R$ per mole. Suggest physical effects that might lead to deviations from this value as the temperature is increased. [4]

9. One mole of a van der Waals gas has an equation of state

$$(P + \frac{a}{V^2})(V - b) = RT ,$$

where P, V, and T are the pressure, volume and temperature of the gas.

Explain why the van der Waals equation of state is often a better model of a real gas than the perfect gas equation of state, including the motivation for introducing the parameters a and b. [4]

Plot the isotherms of the van der Waals gas on a P–V diagram, labelling the critical point, and the two-phase coexistence region. Explain what would happen to a fluid in a closed container prepared at a pressure and volume lying within the coexistence curve. [5]

For the van der Waals gas:

(a) find expressions for the pressure, volume and temperature at the critical point in terms of the parameters a and b. [5]

(b) by considering the entropy as a function of T and V, or otherwise, show that the difference between the specific heats at constant pressure and constant volume is

$$C_P - C_V = R\left\{1 - \frac{2a(V-b)^2}{V^3RT}\right\}^{-1} .$$

[6]

$dS(T,V) = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$

$\therefore \frac{1}{T}(C_P - C_V) = \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$

10. Starting from the grand partition function, show that the mean occupation number of a non-interacting Bose gas is

$\xi = \frac{\hbar^2 k^2}{2m} - 2\mu_B B$

$$\bar{n}_i = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1}$$

$(\xi + 2\mu_B B) =$

and that, as long as the temperature is not too low, the number density of the bosons can be written

$$\frac{N}{V} = \frac{(2m)^{3/2}}{4\pi^2\hbar^3} \int_0^\infty \frac{\epsilon^{1/2}\, d\epsilon}{e^{\beta(\epsilon - \mu)} - 1} \,. \tag{1}$$

[6]

State how the value of the chemical potential changes as the gas is cooled at constant density. Hence, or otherwise, argue that equation (1) can no longer hold below a temperature T_c given by

$$\frac{N}{V} = C \left(\frac{m k_B T_c}{\hbar^2} \right)^{3/2}$$

finite $\mu \neq 0$ $\bar{n}_0 \neq N$ $\therefore$ Not occupied

where C is a numerical factor that you need not evaluate. [6]

For $T < T_c$, derive an expression for the number density of particles in the ground state of the Bose gas. [5]

Explain briefly, with examples, what is meant by a Bose condensate. [3]

11. The Laplace transform of a function $f(x)$ is defined as

$$\bar{f}(s) = \int_0^\infty f(x) e^{-sx}\, dx.$$

Find the Laplace transform of

(i) $\frac{df}{dx}$

(ii) $x f(x)$

in terms of $\bar{f}(s)$ and its derivative. [6]

Show that the Laplace transform of a function $g(x)$ which is equal to unity between $x = 0$ and $x = a$, and zero otherwise is

$$\bar{g}(s) = \frac{1}{s}(1 - e^{-sa})$$

$\frac{1}{s^2} - \frac{2}{s^2} e^{-sa} + \frac{1}{s^2} e^{-2sa}$

and find the Laplace transform of $xg(x)$. [4]

The function $h(x)$ is defined by

$$h(x) = \int_0^x g(y) g(x - y)\, dy.$$

Show that $h(x) = x$ for $0 < x < a$ and find expressions for $h(x)$ for $a < x < 2a$ and $x > 2a$. (You may find it helpful to plot $g(y)g(x-y)$ as a function of y.) Hence calculate $\bar{h}(s)$ directly from the definition of the Laplace transform, and show that it is equal to $\bar{g}(s)^2$. [10]

A1 2013 First Attempt

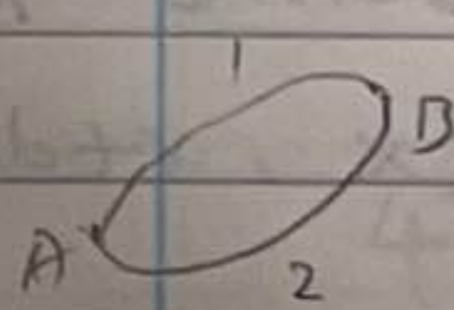
1. $\text{đ}Q$ is the infinitesimal ~~change of~~ amount of heat enters the system at each ~~pomo~~ point with temperature T

T is the temperature

Entropy $S = \frac{\text{đ}Q_{rev}}{T}$

Clausius inequality $\oint \frac{\text{đ}Q}{T} \leq 0$ takes equality if process is reversible $\rightarrow \oint \frac{\text{đ}Q_{rev}}{T} = 0$

$\rightarrow \int_A^B \frac{\text{đ}Q_{rev}}{T}$ is path independent



$\rightarrow \int_A^B dS$ is path independent

$\underset{①}{\int_A^B} dS - \underset{②}{\int_A^B} dS = 0$

$= S(B) - S(A) \rightarrow S$ is a function of state

∴ ① = ②

2. (a) (i) $\text{đ}Q = cm\,dT \qquad dS = \frac{\text{đ}Q}{T} = cm\frac{dT}{T}$

$$\Delta S_s = \int dS = cm\int_{T_i}^{T_f} \frac{dT}{T} = cm \ln\frac{T_f}{T_i}$$

$$= (2.3\times10^2)(1)\ln\left(\frac{273+100}{273}\right)$$

$$= \underline{71.8\ \text{J/K}}$$

(ii) $\Delta S_r = -\frac{cm\Delta T}{373\text{K}} = -\frac{2.3\times10^2 \times 1 \times 100\text{K}}{373\text{K}}$

$$= \underline{-61.7\ \text{J/K}}$$

(iii) $\Delta S_u = 71.8\ \text{J/K} - 61.7\ \text{J/K} = \underline{10.1\ \text{J/K}}$

(b) (i) Same as (a) (i) $\Delta S_s = 71.8 \text{ J/K}$

(ii) (iii) ∵ reversible engine ∴ No net change in entropy

→ $\Delta S_r = -71.8 \text{ J/K}$, $\Delta S_u = 0 \text{ J/K}$

3. $p(x)$ = probability not collided ~~after~~ before x

$p(x+dx)$ = Probability not collided ~~after~~ before $x+dx$
= probility not collided before x and not collide between x, $x+dx$

$p(x)(kdx)$ = probability not collided before x but collide between $[x, x+dx]$.

$$\rightarrow \quad p(x) - p(x+dx) = p(x)(k\,dx)$$

$$\rightarrow \quad -dp = pk\,dx \quad \rightarrow \quad \frac{dp}{p} = -k\,dx$$

$$\int_{1}^{p(x)} \frac{dp}{p} = -\int_{0}^{x} k\,dx \quad \rightarrow \quad \ln(p(x)) - \ln(1) = -kx$$

$p(x=0)=1$ start with $x=0$

$$\rightarrow \quad p(x) = e^{-kx}$$

λ = mean free path = mean distance travelled before collision

$\therefore$ ~~$\lambda = \int_0^\infty x\,p(x)\,dx$~~

$u = kx$ $x = \frac{1}{k}u$

$$\lambda = \int_0^\infty x\,p(x)\,k\,dx = k\int_0^\infty x e^{-kx}\,dx = \frac{1}{k}\underbrace{\int_0^\infty u e^{-u}\,du}_{1!}$$

$= \frac{1}{k} \quad \rightarrow \quad \lambda = \frac{1}{k}$

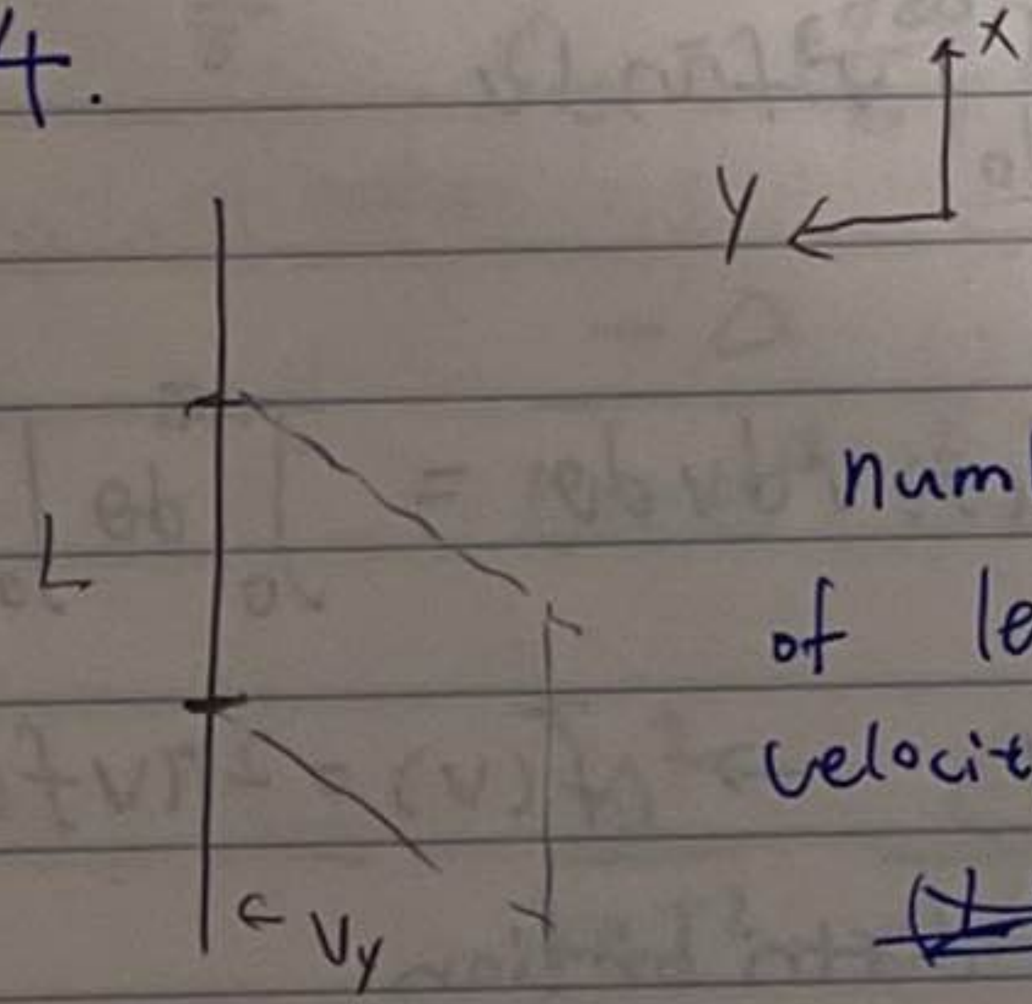
typical collision cross-section $\sigma \sim (10^{-10} m)^2$
$\sim 10^{-20} m^2$

$p = nk_BT \quad n = \frac{p}{k_BT} \sim \frac{(1.01 \times 10^5 Pa)}{(1.38 \times 10^{-23})(300K)} \sim 10^{25} m^{-3}$

typical mean free path

$$\lambda \sim \frac{1}{n\sigma} \sim \frac{1}{10^{-20} \cdot 10^{25}} = 10^{-5} m$$

4.



number of particles colliding on a line of length L in time dt with velocity between $[\vec{v}, \vec{v} + d^2\vec{v}]$ is

~~$(L v_y dt) n$~~

$$L v_y (dt)\, n f(\vec{v})\, d^2\vec{v}$$

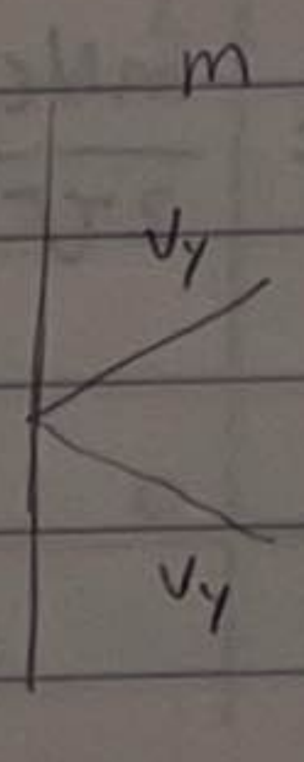
$\therefore$ flux of particles with $[\vec{v}, \vec{v} + d^2\vec{v}]$ is

$P = \frac{dP/dt}{A} \times$ # of particles

$$d\Phi(\vec{v}) = n v_y f(v)\, d^2\vec{v}$$

$n =$ # of particles per area

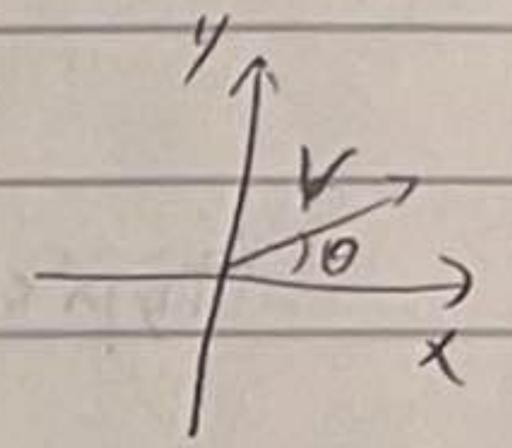
$f(\vec{v}) = f(v)$ is the isotropic ~~speed of~~ velocity distribution



each particle carries a change of momentum $\Delta p = 2mv_y$ to the wall

→ pressure = momentum flux

$$dP(\vec{v}) = 2mv_y \, d\Phi(\vec{v})$$



$$= 2mn\, v_y^2 f(v)\, d^2\vec{v}$$

OR $= 2mn \underbrace{\tfrac{1}{2}}_{\text{half going to the wall}} \langle v_y \rangle^2 = mn\langle v_y\rangle^2 = \frac{1}{2} mn \langle v^2 \rangle$

in polar : $= 2mn\, v^2 \sin^2\theta\, f(v) \cdot v\, dv\, d\theta$

$$= 2mn\, v^3 f(v)\, dv\, \sin^2\theta\, d\theta$$

only forward particles

$$\therefore P = \int dP(\vec{v}) = 2mn \int_0^\infty v^3 f(v)\, dv \underbrace{\int_0^\pi \sin^2\theta\, d\theta}_{\frac{\pi}{2}}$$

$$= \cancel{2mn}\ \pi mn \int_0^\infty v^3 f(v)\, dv$$

Now $\int f(\vec{v})\, d^2\vec{v} = \int f(v)\, v\, dv\, d\theta = \int_0^{2\pi} d\theta \int_0^\infty v f(v)\, dv$

$= \int_0^\infty 2\pi v f(v)\, dv \to \tilde{f}(v) = 2\pi v f(v)$

is the speed distribution

in 2-D: $\langle v^n \rangle = \int_0^\infty v^n \tilde{f}(v)\, dv = \int_0^\infty v^n \cdot 2\pi v f(v)\, dv$

$\to \int_0^\infty v^3 f(v)\, dv = \frac{1}{2\pi} \int v^2 (2\pi v f(v))\, dv = \frac{1}{2\pi} \int_0^\infty v^2 \tilde{f}(v)\, dv$

$= \frac{1}{2\pi} \langle v^2 \rangle$

$\to p = \pi mn \frac{1}{2\pi} \langle v^2 \rangle = \underbrace{\frac{1}{2} mn \langle v^2 \rangle} = \frac{mN\langle v^2\rangle}{2V} = \frac{U}{V}$

5. Partition function $Z = e^{-\beta(0)} + e^{-\beta(\Delta)}$

$$= 1 + e^{-\beta\Delta}$$

mean energy $U = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\left(1+e^{-\Delta\beta}\right)$

$$= -\frac{1}{1+e^{-\beta\Delta}}\,\cancel{(-\beta)}\,(-\Delta)\,e^{-\beta\Delta}$$

$$= \frac{\Delta e^{-\beta\Delta}}{1+e^{-\beta\Delta}} = \frac{\Delta}{1+e^{\beta\Delta}} \qquad \left(\beta = \frac{1}{k_B T}\right)$$

Specific heat

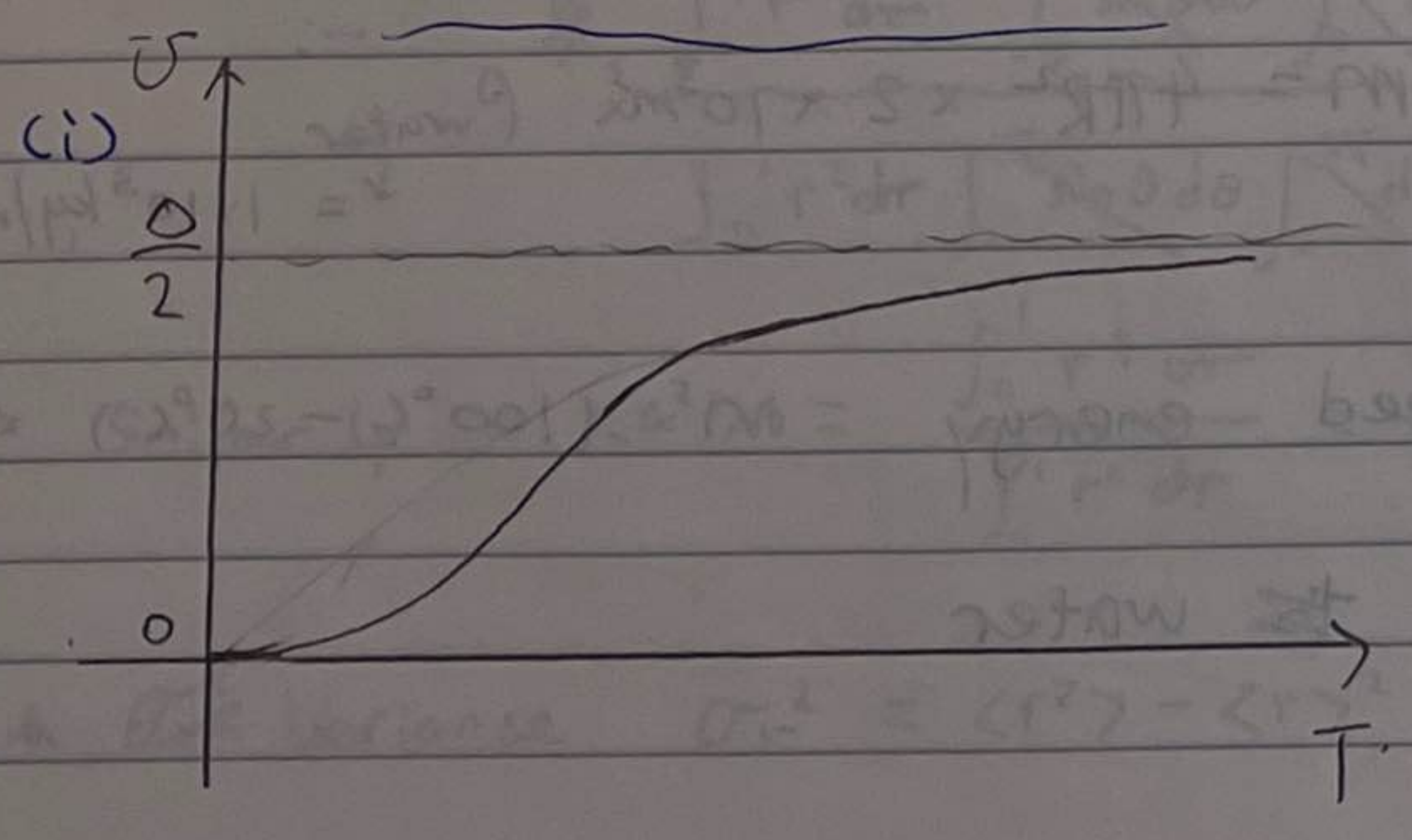
$$C_v = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial \beta}\right)\left(\frac{\partial \beta}{\partial T}\right)$$

$$= \frac{-\Delta}{(1+e^{\beta\Delta})^2}\,(\Delta)\,e^{\beta\Delta}\,\frac{-1}{k_B T^2}$$

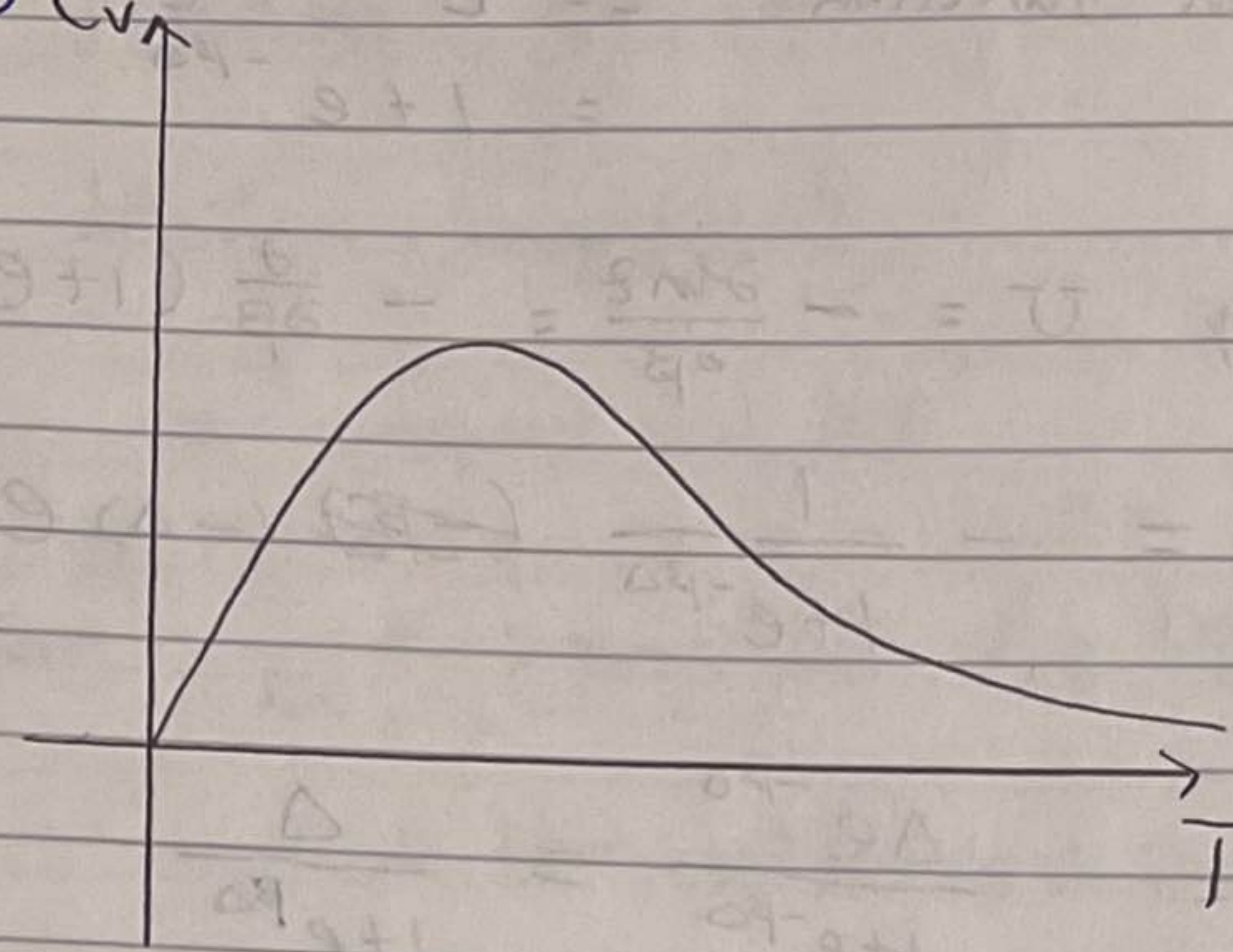
$$= \frac{\Delta^2}{k_B T^2}\,\frac{e^{\beta\Delta}}{(1+e^{\beta\Delta})^2} = \cancel{\frac{\Delta^2 e^{\Delta/k_B T}}{k_B T^2}}$$

$$= k_B\left(\frac{\Delta}{k_B T}\right)^2 \frac{e^{\Delta/k_B T}}{(1+e^{\Delta/k_B T})^2}$$

(i)



(ii)



6. total amount of energy reaching Earth in ~~#~~ time interval Δt is

$$E = \pi R^2 S_0 \Delta t \qquad (R = \text{radius of earth})$$

→ Assume is entirely covered by water

→ Assume average depth of water is 2km

→ Assume temperature of water is $20^\circ C$

Total mass of water:

$$m = 4\pi R^2 \times 2 \times 10^3 m^3 \times \rho_{water}$$
$$\rho_{water} = 1 \times 10^3 \, kg/m^3$$

We need energy $m \times (100^\circ C - 20^\circ C) \times 4.2 \times 10^3 \, J/kg_{\cdot}K$ to boil ~~to~~ water amount of ~~water~~ energy to turn the boiling ocean into vapour is

$$m \times L = m \times (2.3 \times 10^6 \ J/kg)$$

$$\therefore \ \pi R^2 S_0 \Delta t = 4\pi R^2 (2\times10^3 \times 1\times10^3)[(100-20)\times 4.2\times10^3 + 2.3\times10^6].$$

$S_0 = 1370 \ W/m^2$

$$\therefore \ \Delta t = \frac{4 \times 2\times10^3 \times 10^3 \times (4.2\times80 + 2300)\times10^3}{1370}$$

$$\approx \cancel{1.6\times10^5 \ s} \quad \underline{1.5\times10^{10} s} \approx \underline{500 \text{ years}}$$

7. probability density of finding the point inside a volume ~~r, r+dr~~ $d\tau$ is $p(r,\theta,\phi) = 1$ (unnormalised) because P is chosen at random

$$\rightarrow \quad \langle r \rangle = \frac{\int r \, d\tau}{\int d\tau} = \frac{\int r \, r^2 \sin\theta \, d\theta \, d\phi \, dr}{\int r^2 \sin\theta \, d\theta \, d\phi \, dr}$$

$$= \frac{\int_0^1 r^3 dr \ \cancel{\int_0^\pi \sin\theta \, d\theta} \ \cancel{\int_0^{2\pi} d\phi}}{\int_0^1 r^2 dr \ \cancel{\int_0^\pi \sin\theta \, d\theta} \ \cancel{\int_0^{2\pi} d\phi}} = \frac{\cancel{\frac{1}{3}}\frac{1}{4}}{\cancel{\frac{1}{2}}\frac{1}{3}} = \cancel{\frac{2}{3}}\ \underline{\frac{3}{4}}$$

$$\text{Similarly} \quad \langle r^2 \rangle = \frac{\int_0^1 r^4 dr}{\int_0^1 r^2 dr} = \frac{\cancel{\frac{1}{4}}\frac{1}{5}}{\cancel{\frac{1}{2}}\frac{1}{3}} = \cancel{\frac{1}{4}}\ \frac{3}{5}$$

$$\text{Variance} \quad \sigma_r^2 = \langle r^2 \rangle - \langle r \rangle^2 = \cancel{\tfrac{1}{2} - \tfrac{4}{9}} = \cancel{\tfrac{1}{18}}$$

$$\frac{3}{5} - \frac{9}{16} = \underline{\frac{3}{80}}$$

8. ~~是~~ Equipartition of energy: If the energy of system ~~Is~~ consists of n quadratic ~~mode~~ modes, then n = degree of freedom, and the mean energy of the system is equal to

$$\langle E \rangle = \frac{n}{2} k_B T \quad \rightarrow T = \text{temperature}$$

Classical limit: The system of particles is hot and dilute $T \to \infty$, $\frac{N}{V} \to 0$ so we can integrate over continuous energy rather than having to sum discrete ~~energy~~. energies.

perfect classical gas: $\varepsilon = \frac{\hbar^2 k^2}{2m}$.

density of states $g(k)\,dk = \frac{V}{2\pi} k^2 dk$

$\therefore$ Partition function for single particle

$$Z_1 = \int dk\, g(k)\, e^{-\beta\varepsilon} = \int_0^\infty dk \frac{V}{2\pi^2} k^2 e^{-\frac{\beta\hbar^2}{2m}k^2}$$

$$= \frac{V}{2\pi^2}\left(\frac{2m}{\beta\hbar^2}\right)^{3/2} \underbrace{\int_0^\infty du\, u^2 e^{-u^2}}_{\frac{\sqrt{\pi}}{4}}$$

$$= \frac{V}{(4\pi)^{3/2}}\left(\frac{2mk_BT}{\hbar^2}\right)^{3/2}$$

$$= V\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}$$

$$Z_1 = V\left(\frac{m}{2\pi\hbar^2}\right)^{3/2}\beta^{-3/2} \qquad \ln Z_1 = \ln\left(V\left(\frac{m}{2\pi\hbar^2}\right)^{3/2}\right) - \frac{3}{2}\ln(\beta)$$

$$\therefore \quad \langle E_1\rangle = -\frac{\partial \ln Z_1}{\partial \beta} = +\frac{3}{2}\frac{1}{\beta} = \frac{3}{2}k_BT$$

Equipartition theorem :

degree of freedom $= n = 3$ (3 translational d.o.f)

$$\therefore \quad \langle E_1\rangle = \frac{n}{2}k_BT = \frac{3}{2}k_BT \rightarrow \text{consistent.}$$

Quantum harmonic oscillator :

$$Z_1 = \sum_{n=0}^{\infty}\exp(-\beta(n+\tfrac{1}{2})\hbar\omega)$$

$$= \exp(-\tfrac{1}{2}\beta\hbar\omega)\sum_{n=0}^{\infty}\exp(-n\beta\hbar\omega)$$

$$= \exp(-\tfrac{1}{2}\beta\hbar\omega)\left(1+\exp(-\beta\hbar\omega)+\exp(-2\beta\hbar\omega)+\cdots\right)$$

$$= \exp(-\tfrac{1}{2}\beta\hbar\omega)\frac{1}{1-\exp(-\beta\hbar\omega)}$$

$$= \frac{\exp(-\frac{1}{2}\beta\hbar\omega)}{1-\exp(-\beta\hbar\omega)} \qquad \left(\beta = \frac{1}{k_BT}\right) \qquad x = \frac{\hbar\omega}{k_BT} = \beta\hbar\omega$$

$$= \frac{\exp(-\frac{x}{2})}{1-\exp(-x)} = \frac{1}{\exp(\frac{x}{2})-\exp(-\frac{x}{2})} = \frac{1}{2\sinh(\frac{x}{2})}$$

$$\langle E \rangle = -\frac{\partial \ln Z_1}{\partial \beta} \cancel{= -\hbar\omega \frac{\partial \ln Z_1}{\partial x} = \hbar\omega \frac{\cosh(\frac{x}{2})}{(2\sinh(\frac{x}{2}))^2}}$$

$$\cancel{= \frac{1}{4}\hbar\omega \frac{\cosh(\frac{x}{2})}{\sinh^2(\frac{x}{2})}}$$

As $x \ll 1$ $\quad \cosh(\frac{x}{2}) \sim 1$

$\sinh(\frac{x}{2}) \sim \frac{x}{2}$

$$\cancel{\therefore \langle E \rangle = \frac{1}{4}\hbar\omega \frac{1}{(\frac{x}{2})^2} = \frac{\hbar\omega}{x^2}}$$

$$\cancel{=}$$

$$= \frac{\partial}{\partial \beta} \ln\left(2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right)$$

$$= \frac{\cosh(\frac{\beta\hbar\omega}{2})}{\sinh(\frac{\beta\hbar\omega}{2})} \cdot \frac{1}{2}\hbar\omega$$

$\coth(x) = \frac{e^x + e^{-x}}{e^x - e^{-x}}$

$$\underline{= \frac{1}{2}\hbar\omega \coth\left(\frac{\beta\hbar\omega}{2}\right)}$$

$$\rightarrow \underline{E = k_B T \frac{x}{2} \coth\left(\frac{x}{2}\right)}$$

for equipartition theorem to hold

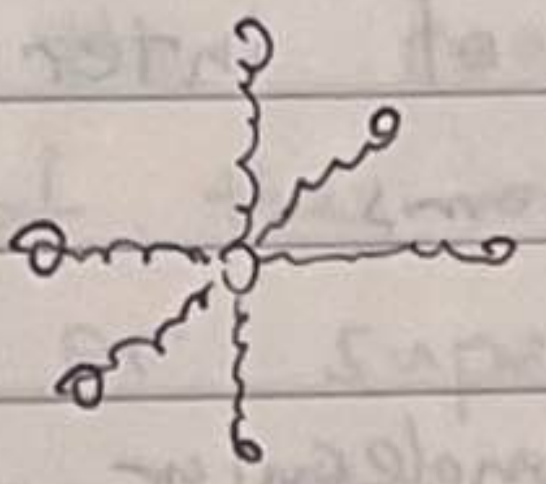
$T \rightarrow \infty$, $\beta \rightarrow 0$ $\therefore \beta\hbar\omega \ll 1 \rightarrow \underline{x \ll 1}$

$$E \rightarrow k_B T \left(\frac{x}{2}\right) \cdot \left(\frac{2}{x}\right) = \underline{k_B T}$$

2 modes, 1 kinetic, 1 potential

$E = \frac{n}{2} k_B T = \frac{2}{2} k_B T = \underline{k_B T} \rightarrow$ consistent.

Consider the lattice ~~joi~~ joined by springs for the solid.



At high temperature, count the modes.

1 atom is connected to 6 ~~spr~~ springs.

~~each~~ 1 spring joins 2 atoms

$\therefore$ in total $6N \div 2 = 3N$ springs.

each spring has 2 modes (1 kinetic, 1 potential)

$\rightarrow$ total degree of freedom $n = 6N$

Equipartition: $\langle E \rangle = \frac{n}{2} k_B T = 3N k_B T$

for ~~1 m~~ 1 mole $N = N_A$

$\therefore \langle E \rangle_1 = 3 N_A k_B T = 3RT$

molar heat capacity $C_1 = \left(\frac{\partial \langle E \rangle_1}{\partial T} \right)_V = 3R$

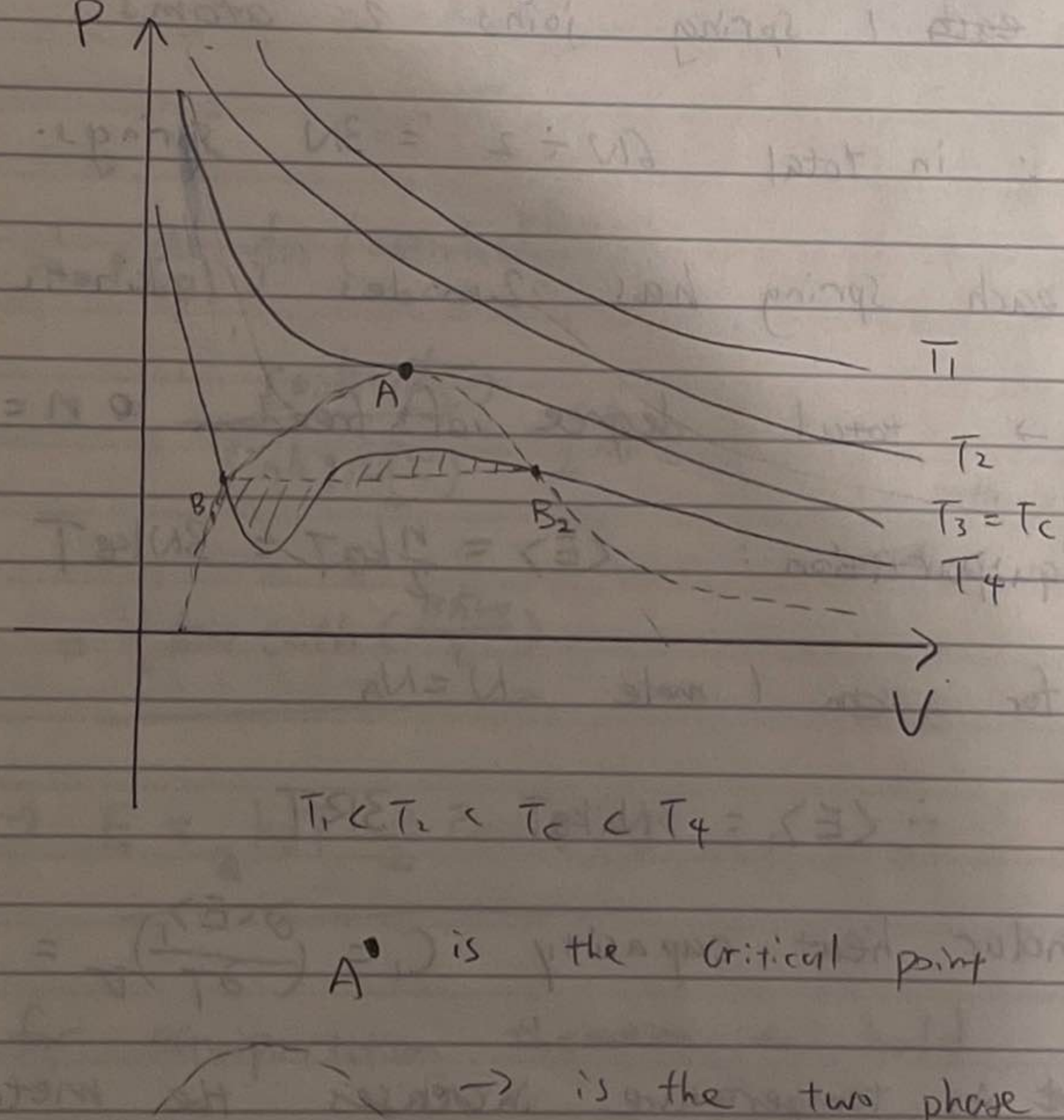
~~At~~ As temperature increases the metal may melt and thus its physical properties change.

Heat capacity may become ~~di~~ different.

9. van der Waals gas is better because it includes the effect of intermolecular forces and finite size of atoms.

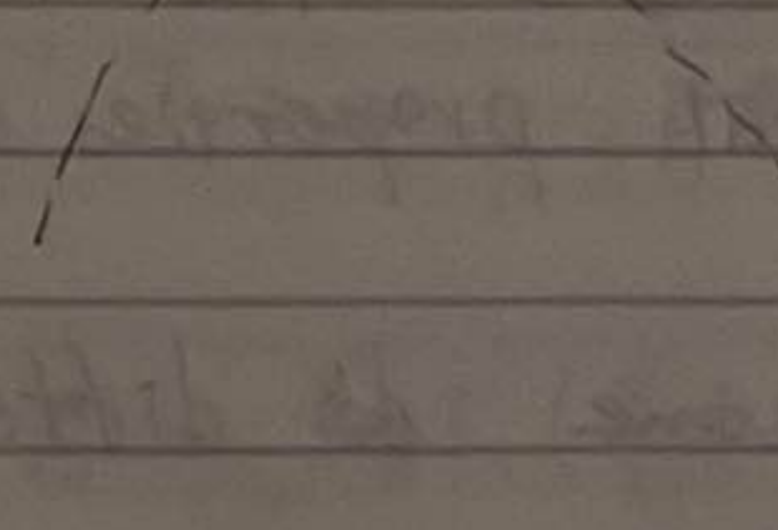
$\frac{a}{V^2}$ → higher intermolecular forces reduce the pressure

b → large atoms increases the volume of gas.



$T_1 < T_2 < T_c < T_4$

A is the critical point



→ is the two phase coexistence region (with shaded area equal).

A fluid in a closed container at P and V ~~between~~ within the coexistence curve may first become one of the meta-stable states (~~super~~ superheated liquid or supercooled vapour) depending on whether the fluid starts to be a liquid or a ~~vapour~~ vapour, ~~the~~ but eventually it will separate in ~~to~~ two 2 phases (liquid and vapour) and the 2 phases ~~coex~~ coexist.

(a) → At the critical point $\because \ (P+\frac{a}{V^2})(V-b)=RT$

$$\therefore \quad P = \frac{RT}{V-b} - \frac{a}{V^2}$$

critical point :

$$0 = \left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0$$

$$0 = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2RT_c}{(V_c-b)^3} - \frac{6a}{V_c^4} = 0$$

$$\rightarrow \quad RT = \frac{2a(V_c-b)^2}{V_c^3} = \frac{3a(V_c-b)^3}{V_c^4}$$

$$\rightarrow \quad \frac{3(V_c-b)}{V_c} = 2$$

$$\rightarrow \quad \underline{V_c = 3b}$$

$$\therefore \quad RT_c = \frac{8a}{27b} \quad \rightarrow \quad \underline{T_c = \frac{8a}{27b^2}}$$

$$P_c = \frac{8a}{(27b)\cdot 2b} - \frac{a}{9b^2} = \underline{\frac{a}{27b^2}}$$

(b) $dS(T,V) = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

$\rightarrow \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$

$\rightarrow T\left(\frac{\partial S}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$

$\rightarrow$ maxwell relations, definition of heat capacities

$\rightarrow C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$

$= T\frac{(\partial P/\partial T)_V}{(\partial T/\partial V)_P}$

$(P + \frac{a}{V^2})(V-b) = RT \quad \rightarrow \quad P = \frac{RT}{V-b} - \frac{a}{V^2}$

$\therefore \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}, \quad \cancel{\left(\frac{\partial T}{\partial V}\right)_P =}$

$\rightarrow T = \frac{1}{R}\left(PV + \frac{a}{V} - \frac{ab}{V^2} - Pb\right)$

$\rightarrow \left(\frac{\partial T}{\partial V}\right)_P = \frac{P}{R} - \frac{a}{RV^2} + \frac{2ab}{RV^3}$

$\therefore C_P - C_V = \frac{TR/(V-b)}{\frac{P}{R} - \frac{a}{RV^2} + \frac{2ab}{RV^3}}$

$= \frac{TR/(V-b)}{\frac{1}{R}(P + \frac{a}{V^2}) - \frac{2a(V-b)}{RV^3}}$

$= R\frac{T}{\frac{1}{R}(P+\frac{a}{V^2})(V-b) - \frac{2a(V-b)^2}{V^3 R}}$

$$= R\left[\frac{T}{\frac{1}{R}\cdot RT - \frac{2a(V-b)^2}{V^3R}}\right].$$

$$= R\left[1 - \frac{2a(V-b)^2}{V^3RT}\right]^{-1}$$

10. For Bosons, the grand partition function

$$\mathcal{Z} = \cancel{\prod_i \frac{1}{1-e^{-\beta(\varepsilon_i-\mu)}}} = \sum_{\{n_j\}} e^{-\beta\sum_j n_j(\varepsilon_j-\mu)} = \prod_i \frac{1}{1-e^{-\beta(\varepsilon_j-\mu)}}$$

$$\rightarrow \ln \mathcal{Z} = -\sum_j \ln(1-e^{-\beta(\varepsilon_j-\mu)})$$

The Probability for a given state (set of occupation numbers) to occur is

$$P_\alpha = p(n_1, n_2, \dots) = \frac{1}{\mathcal{Z}} e^{-\beta\sum_i n_i(\varepsilon_i-\mu)}$$

mean occupation for the ith single particle state is:

$$\bar{n_i} = \sum_{\{n_j\}} n_i\, p(n_1, n_2, \dots) = \frac{1}{\mathcal{Z}} \sum_{\{n_j\}} n_i\, e^{-\beta\sum_j n_j(\varepsilon_j-\mu)}$$

sum all possible sets of occupation numbers

sum each element of $\{n_j\}$

$$= -\frac{1}{\beta}\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \varepsilon_i} = -\frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \varepsilon_i}$$

$$\therefore \bar{n_i} = -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_i}\left(-\sum_j \ln\{1 - e^{-\beta(\varepsilon_j - \mu)}\}\right)$$

$$= +\frac{1}{\cancel{\beta}}\sum_j \frac{\cancel{\beta} e^{-\beta(\varepsilon_j - \mu)}}{1 - e^{-\beta(\varepsilon_j - \mu)}}\delta_{ij}$$

$\frac{\partial \varepsilon_j}{\partial \varepsilon_i} = \delta_{ij}$

$$= \cancel{\beta}\ \frac{e^{-\beta(\varepsilon_i - \mu)}}{1 - e^{-\beta(\varepsilon_i - \mu)}} = \frac{1}{e^{\beta(\varepsilon_i - \mu)} - 1}$$

3-D density of states:

$$g(k)\,dk = \frac{V}{2\pi^2}k^2\,dk \qquad \therefore\ \cancel{\ } \varepsilon = \frac{\hbar^2 k^2}{2m}$$

$$\therefore k = \frac{\sqrt{2m\varepsilon}}{\hbar} \qquad \therefore dk = \frac{1}{\hbar}\sqrt{\frac{m}{2\varepsilon}}\,d\varepsilon$$

$$\therefore g(k)\,dk = \frac{V}{2\pi^2}\frac{2m\varepsilon}{\hbar^2}\frac{1}{\hbar}\sqrt{\frac{m}{2\varepsilon}}\,d\varepsilon \equiv g(\varepsilon)\,d\varepsilon$$

$$\rightarrow g(\varepsilon) = \frac{V m^{3/2}}{\sqrt{2}\pi^2\hbar^3}\sqrt{\varepsilon} = \frac{(2m)^{3/2}V}{4\pi^2\hbar^3}\varepsilon^{1/2}$$

$$N = \sum_i \bar{n_i} = \int d\varepsilon\, g(\varepsilon)\, n(\varepsilon)$$

$$= \int_0^\infty \frac{(2m)^{3/2}V}{4\pi^2\hbar^3}\varepsilon^{1/2}\,d\varepsilon\,\frac{1}{e^{\beta(\varepsilon-\mu)} - 1}$$

$$\rightarrow \frac{N}{V} = \frac{(2m)^{3/2}}{4\pi^2\hbar^3}\int_0^\infty \frac{\varepsilon^{1/2}\,d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1}$$

Constant density $\to$ N, V constant

For Bosons, as $T \to 0$ we ~~exp~~ expect all particles to drop to the lowest energy state $\varepsilon_0 = 0$

So $\bar{n}_0 = \frac{1}{e^{\beta(\varepsilon_0 - \mu)} - 1} \to N$ $\to$ ground state macroscopically occupied for small T

$\to \frac{1}{e^{-\beta\mu} - 1} = N$. $e^{-\beta\mu} = 1 + \frac{1}{N}$

$\therefore \mu = -\frac{1}{\beta} \ln(1 + \frac{1}{N}) = -k_B T \ln(1 + \frac{1}{N})$

$T \to 0$, $N \to \infty$ $\to$ $\underline{\mu \to 0 \text{ as } T \to 0}$
$\hookrightarrow$ ~~theire~~ thermodynamic limit

Also for $\bar{n}_i \geq 0$ we require ~~$\mu \geq 0$~~ $\mu \leq 0$

But for ~~certain~~ temperatures $T < T_c$

$$\frac{N}{V} = \frac{(2m)^{3/2}}{4\pi^2 \hbar^2} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{e^{\beta(\varepsilon - \mu)} - 1}$$ gives a μ

that is ~~to~~ > 0 ~~se~~ so it can no longer hold

For $T < T_c$ we need to set $\mu = 0$ ~~and~~
($\because$ as $T \to 0$, ~~$N \to 0$~~ $\mu \to 0$) and then

$$\frac{N_e}{V} = \frac{2m^{3/2}}{4\pi^2 \hbar^2} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{e^{\beta\varepsilon} - 1}$$ gives the

number of excited particles N_e.

the number of ground state particles N_0 is not picked up by the integral because when $\varepsilon = 0$, $\varepsilon^{1/2} = 0$ and the contribution vanishes.

At $T = T_c$, equation (1) gives $\mu = 0$

$$\therefore \frac{N}{V} = \frac{(2m)^{3/2}}{4\pi^2\hbar^3} \int_0^\infty \frac{\varepsilon^{1/2}\,d\varepsilon}{e^{\beta\varepsilon} - 1}$$

(let $x = \beta\varepsilon$)
$dx = \beta d\varepsilon \rightarrow d\varepsilon = \frac{dx}{\beta}$
$\varepsilon^{1/2} = x^{1/2}\beta^{-1/2}$

$$\rightarrow \frac{N}{V} = \frac{(2m)^{3/2}}{4\pi^2\hbar^3} \underset{= (k_B T_c)^{3/2}}{\beta^{-3/2}} \underbrace{\int_0^\infty \frac{x^{1/2}\,dx}{e^x - 1}}_{= [C\sqrt{2\pi}]}$$

$$\rightarrow \frac{N}{V} = C\left(\frac{m k_B T_c}{\hbar^2}\right)^{3/2}$$

for $T < T_c$

$$N_e = C\left(\frac{m k_B}{\hbar^2}\right)^{3/2} T^{3/2}$$

$$N = C\left(\frac{m k_B}{\hbar^2}\right)^{3/2} T_c^{3/2} \rightarrow \text{always true}$$

$$\therefore \frac{N_e}{N} = \left(\frac{T}{T_c}\right)^{3/2}, \quad N = N_0 + N_e$$

$$\therefore N_0 = N\left(1 - \frac{N_e}{N}\right) = N\left(1 - \left(\frac{T}{T_c}\right)^{3/2}\right)$$

→ Ground state is macroscopically occupied. ~~Example~~: He-4 becomes a ~~supa~~ superfluid at $T < 2.17\,K = T_c$.

11. $\bar{f}(s) = \int_0^\infty f(x) e^{-sx}\, dx$

(i) $\overline{\frac{df}{dx}} = \int_0^\infty \frac{df}{dx} e^{-sx}\, dx$

$= \int_0^\infty (df) e^{-sx} = \left[\frac{f e^{-sx}}{-s}\right]_0^\infty - \int_0^\infty (-s) e^{-sx} f(x)\, dx$

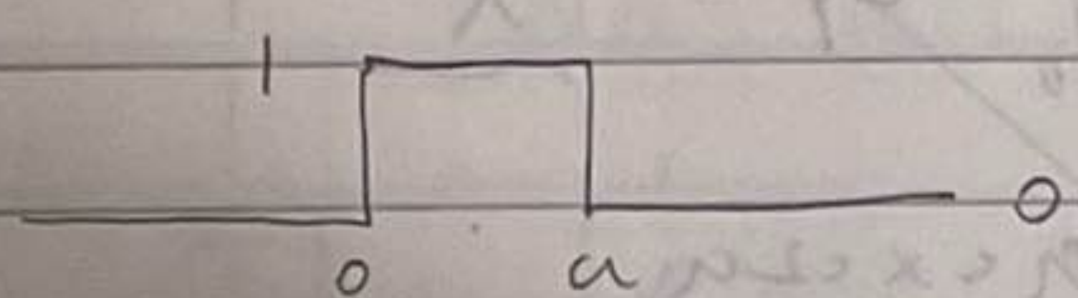
$\cancel{\lim_{x\to\infty} f(x) = 0}$ $\cancel{\lim_{x\to 0} e^{-sx} =}$ $\lim_{x\to\infty} f e^{-sx} \to 0$

(assuming $f \to 0$ as $x \to \infty$)

$= \cancel{f} - f(0) + s\bar{f}(s) = s\bar{f}(s) - f(0)$

(ii) $\overline{xf(x)} = \int_0^\infty x f(x) e^{-sx}\, dx$

$= -\frac{d}{ds}\int_0^\infty f(x) e^{-sx}\, dx = -\frac{d\bar{f}}{ds}$

$g(x) =$ 

$\rightarrow \bar{g}(s) = \int_0^\infty g(x) e^{-sx}\, dx$

$= \int_0^a e^{-sx}\, dx$

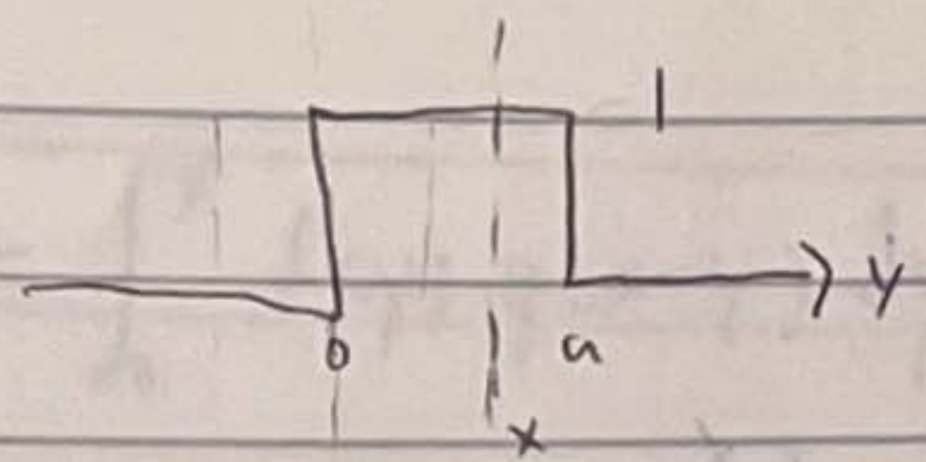
$= -\frac{1}{s}\left[e^{-sx}\right]_0^a = \frac{1}{s}(1 - e^{-sa})$

$\rightarrow \overline{xg}(s) = -\frac{d\bar{g}(s)}{ds} = \frac{-1}{s}\frac{d}{ds}(1 - e^{-sa}) + (1 - e^{-sa})\frac{d}{ds}\left(\frac{1}{s}\right)$

$= -\frac{1}{s}(ae^{-sa}) - (1 - e^{-sa})\left(-\frac{1}{s^2}\right)$

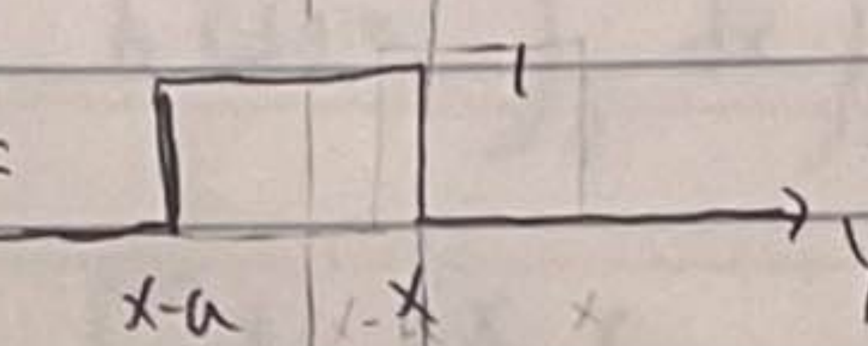
$= \frac{1}{s^2}(1 - e^{-sa}) - \frac{1}{s}(ae^{-sa})$

$g(y) =$

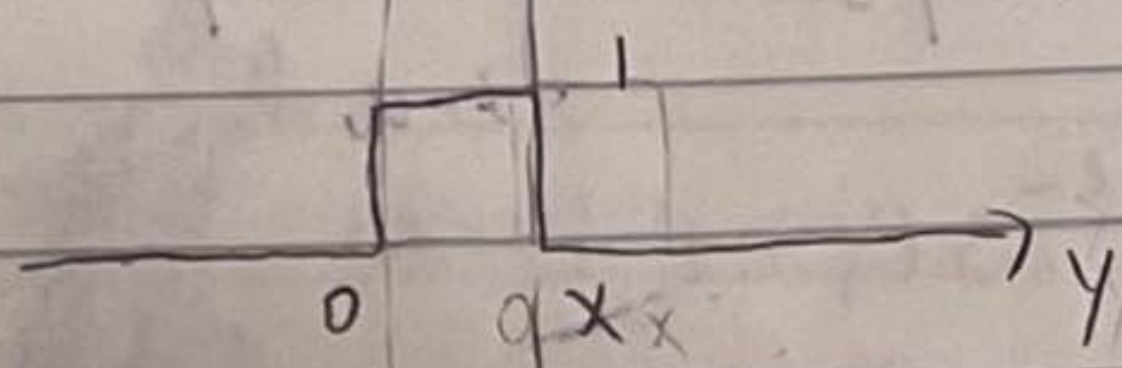


For $0 < x < a$

$g(x-y) =$

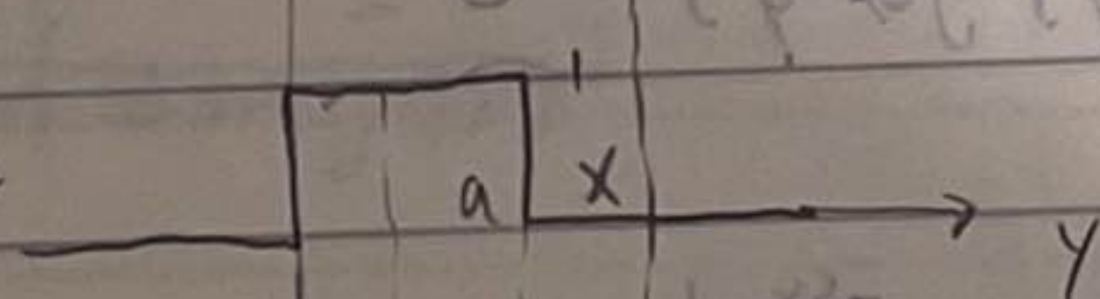


$g(y)\, g(x-y) =$

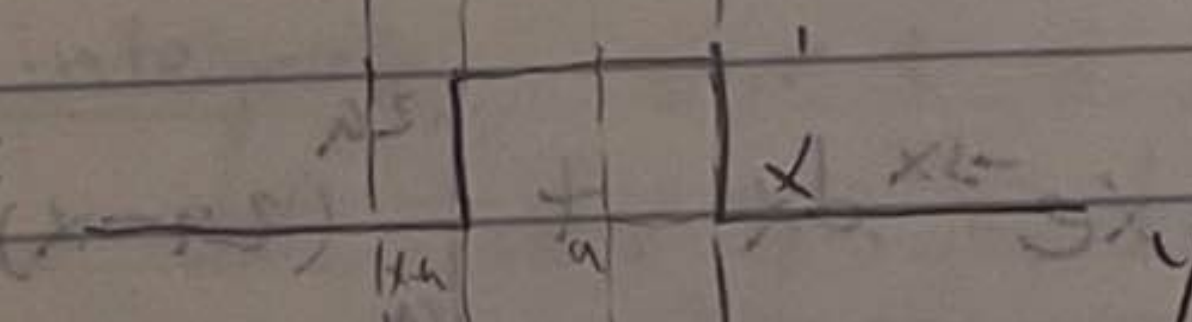


For $a < x < 2a$

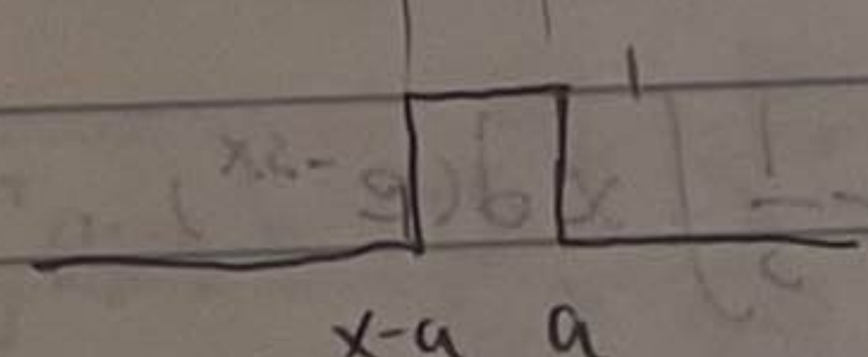
$g(y) =$



$g(x-y) =$

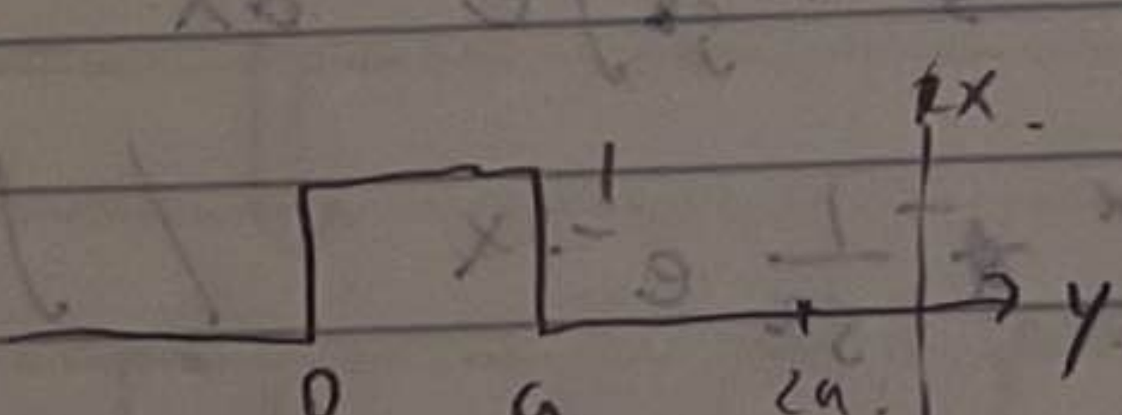


$g(y)\, g(x-y) =$

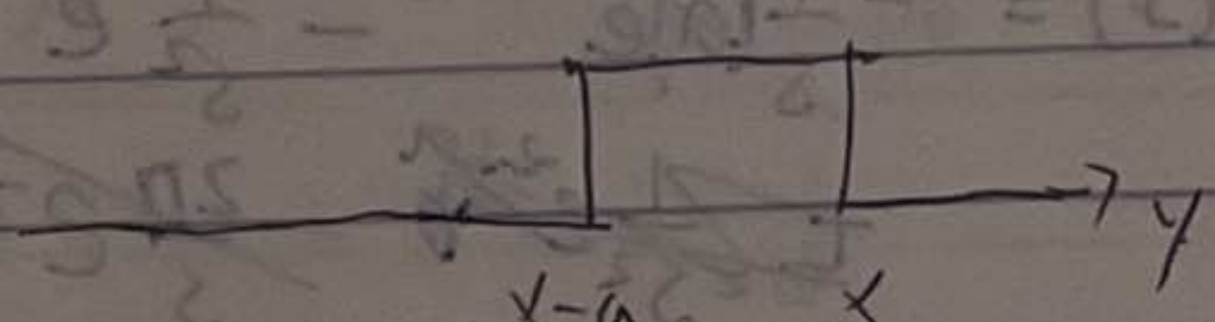


$x > 2a$

$g(y) =$



$g(x-y) =$



$\rightarrow g(y)\, g(x-y) =$

$= 0$

→ For $0 < x < a$.

$$h(x) = \int_0^x dy\, g(y)\, g(x-y) = \int_0^x dy = x$$

→ For $a < x < 2a$

$$h(x) = \int_0^x dy\, g(y)\, g(x-y) = \int_{x-a}^{a} dy = a-(x-a) = 2a-x$$

→ For $x > 2a$

$$h(x) = \int_0^x dy\, g(y)\, g(x-y) = 0$$

$$\therefore \bar{h}(s) = \int_0^\infty h(x) e^{-sx}\, dx$$

$$= \int_0^a x e^{-sx}\, dx + \int_a^{2a} (2a-x) e^{-sx}\, dx$$

$$\int x e^{-sx}\, dx = -\frac{1}{s}\int x\, d(e^{-sx})$$

$$= -\frac{1}{s} x e^{-sx} + \frac{1}{s}\int e^{-sx}\, dx$$

$$= -\frac{1}{s} x e^{-sx} - \frac{1}{s^2} e^{-sx} \qquad / \int e^{-sx}\, dx = -\frac{1}{s} e^{-sx}$$

$$\therefore \bar{h}(s) = \cancel{-\frac{1}{s} a e^{-sa}} - \frac{1}{s^2} e^{-sa} + \frac{1}{s^2}$$

$$- \frac{2a}{s} e^{-2sa} + \cancel{\frac{2a}{s} e^{-sa}}.$$

$$+ \cancel{\frac{1}{s}(2a) e^{-2sa}} + \frac{1}{s^2} e^{-2sa}$$

$$- \cancel{\frac{1}{s} a e^{-sa}} - \frac{1}{s^2} e^{-sa}$$

$$= \frac{1}{s^2}\left(1 - 2e^{-sa} + e^{-2sa}\right) = \left[\frac{1}{s}\left(1 - e^{-sa}\right)\right]^2 = \bar{g}(s)^2$$

$$h(x) = \int_0^x f(y)\, g(x-y)\, dy$$

$$\cancel{\bar{f}(s) =}\ \bar{h}(s) = \int_0^\infty dx \int_0^x dy\, f(y)\, g(x-y)\, e^{-sx}$$

$$= \int_0^\infty dx \int_0^x f(y)\, g(x-y)\, e^{-s(x-y)}\, e^{-sy}\, dy$$

$$= \int_0^\infty dy \int_0^\infty d(x-y)\, g(x-y)\, e^{-s(x-y)} \int_0^\infty f(y)\, e^{-sy}$$

$$\cancel{= \bar{f}(s) * \bar{g}(s)}$$

When integrate w.r.t x, y is held constant

$\therefore$ ~~dx~~ $d(x-y) = dx$

$$\sum_{i=0}^{\infty} \sum_{j=0}^{i} a_{j,i-j} = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} a_{j,i}$$

$a_{j\,i}$

$=$

$$\Downarrow$$

$$\int_0^\infty dx \int_0^x dy = \int_0^\infty dx \int_0^\infty dy$$

$$\downarrow$$

$$= \int_0^\infty dx\, g(x)\, e^{-sx} \int_0^\infty dy\, f(y)\, e^{-sy}$$

$$= \bar{f}(s)\, \bar{g}(s)$$