TSP 2014

1) a) Temperature dependence of internal energy and heat capacity for quantum harmonic oscillator with natural frequency Ω

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

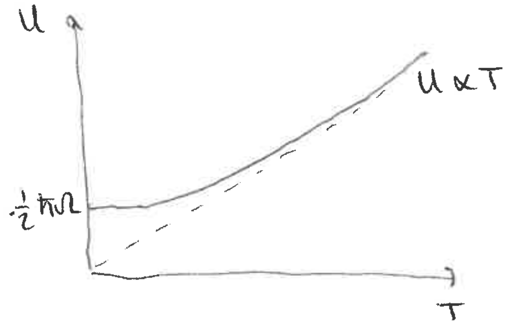
$$Z = \sum_n e^{-\beta E_n} = e^{-1/2\beta\hbar\Omega}\sum_n e^{-\beta n\hbar\Omega} \ldots = \frac{e^{-\beta\hbar\Omega/2}}{1-e^{-\beta\hbar\Omega}}$$

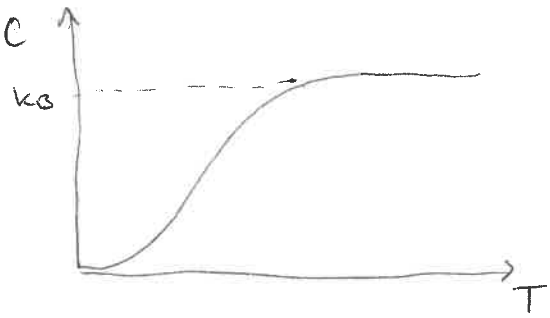
$$\ln Z = -\tfrac{1}{2}\beta\hbar\Omega - \ln[1-e^{-\beta\hbar\Omega}]$$

$$U = -\frac{\partial \ln Z}{\partial\beta} = \tfrac{1}{2}\hbar\Omega + \frac{\hbar\Omega e^{-\beta\hbar\Omega}}{1-e^{-\beta\hbar\Omega}} = \tfrac{1}{2}\hbar\Omega + \frac{\hbar\Omega}{e^{\beta\hbar\Omega}-1}$$

high T (low β): $U \sim \tfrac{1}{2}\hbar\Omega + \frac{1}{\beta} \sim k_B T$

low T (high β): $U \sim \tfrac{1}{2}\hbar\Omega$





b) $p = a(V)T + b(V)$

Show that C_V is independent of volume

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

$$\frac{\partial C_V}{\partial V} = T\frac{\partial}{\partial V}\left.\frac{\partial S}{\partial T}\right|_V = T\frac{\partial}{\partial T}\left.\frac{\partial S}{\partial V}\right|_T = T\frac{\partial}{\partial T}\left.\frac{\partial p}{\partial T}\right|_V$$

$$\left.\frac{\partial p}{\partial T}\right|_V = a(V) \Rightarrow \frac{\partial C_V}{\partial V} = T\frac{\partial a(V)}{\partial T} = 0$$

c) Derive equation of state and molar heat capacity at const. V of a classical ideal gas from $Z_1 \propto V T^{3/2}$

$$Z_N = \frac{1}{N!} Z_1^N \propto V^N T^{3N/2}$$

$$F = -k_B T \ln Z = -k_B T \left[N \ln V + \frac{3}{2} N \ln T \right] + \ldots$$

$$p = -\frac{\partial F}{\partial V}\Big|_{T,N} = \frac{N k_B T}{V}$$

$$U = F + TS$$

$$S = -\frac{\partial F}{\partial T}\Big|_{V,N} = k_B \left[N \ln V + \frac{3}{2} N \ln T \right] + \frac{3}{2} N k_B$$

$$U = \frac{3}{2} N k_B T$$

$$C_V = \frac{\partial U}{\partial T}\Big|_V = \frac{3}{2} N k_B$$

3) Average occupation number for quantum state with energy ϵ

Fermions : $\langle n_k \rangle = \dfrac{1}{e^{\beta(\epsilon-\mu)} + 1}$

Bosons : $\langle n_k \rangle = \dfrac{1}{e^{\beta(\epsilon-\mu)} - 1}$

non-degenerate limit $\epsilon - \mu >> k_B T$

both $\langle n_k \rangle \rightarrow e^{-\beta(\epsilon-\mu)}$ (~ Maxwell-Boltzmann)

Bose gas in 3D with $\mu = 0$

Show that $n \propto T^{3/2}$

$$N = \int_0^\infty n(\epsilon) g(\epsilon) \, d\epsilon$$

$$g(\epsilon) = \sigma \frac{4\pi k^2 dk}{(2\pi/L)^3} = \frac{\sigma V}{2\pi^2} k^2 dk$$

$$k = \frac{\sqrt{2m\epsilon}}{\hbar} \Rightarrow k^2 dk = \frac{2m\epsilon}{\hbar^2} \sqrt{\frac{2m}{\hbar^2}} \cdot \frac{1}{2} \epsilon^{-1/2} d\epsilon = \frac{1}{2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2} d\epsilon$$

$$g(\epsilon) = \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2}$$

$$n(\epsilon) = \frac{1}{e^{\beta\epsilon} - 1} \quad \text{for } \mu = 0$$

$$N = \int_0^\infty \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{\epsilon^{1/2} d\epsilon}{e^{\beta\epsilon} - 1}$$

$$x = \beta\epsilon, \quad dx = \beta d\epsilon$$

$$n = \frac{\sigma}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} (k_B T)^{3/2} \int_0^\infty \frac{\sqrt{x}\, dx}{e^x - 1} \qquad \propto T^{3/2}$$

non degenerate gas in 3D

$g(\epsilon) \propto \sqrt{\epsilon}$ (p u vol)

$$\phi = -k_B T \int_0^\infty e^{-\beta(\epsilon-\mu)} g(\epsilon) d\epsilon$$

$$\propto T \int_0^\infty e^{-\beta(\epsilon-\mu)} \sqrt{\epsilon}\, d\epsilon = \frac{T}{\beta^{3/2}} e^{\beta\mu} \int_0^\infty x e^{-x^2} dx \quad \propto T^{5/2} e^{\beta\mu}$$

$$n = -\frac{\partial\phi}{\partial\mu} \quad \propto T^{3/2} e^{\beta\mu}$$

Bose Einstein condensation

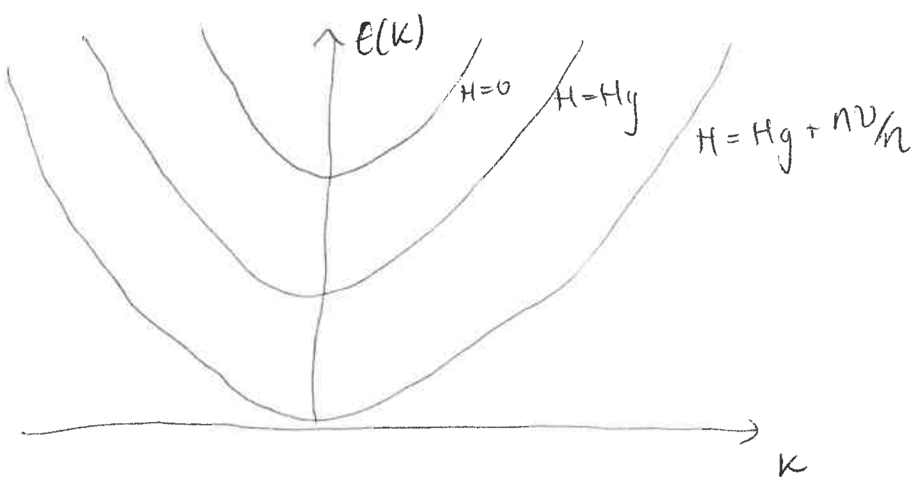
$$N(\epsilon > 0) = \int_0^\infty g(\epsilon) n(\epsilon) d\epsilon = AV T^{3/2}$$

$$N_0 = N(1 - (T/T_c)^{3/2})$$

$$(T/T_c)^{3/2} = \frac{VA}{N} T^{3/2}$$

$$T_c \propto n^{2/3}$$

$$\epsilon(k) = \frac{\hbar^2 k^2}{2m} + \nu n - \eta(H - H_g)$$



For $H > H_c$, part of energy dispersion becomes negative

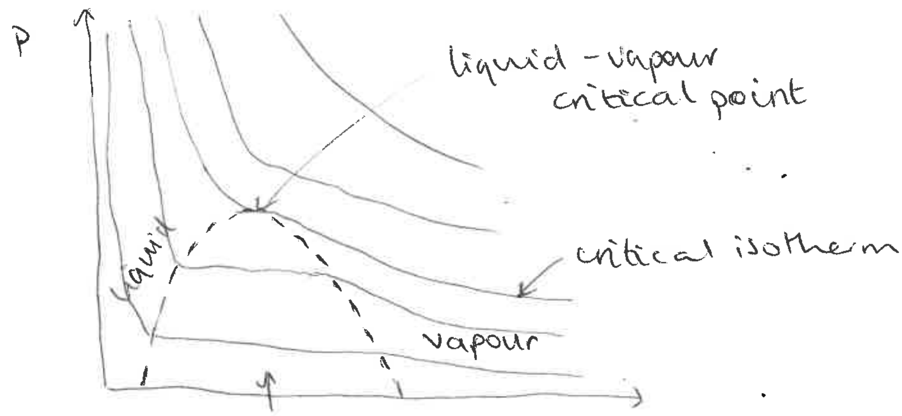
negative energies unphysical

- instead triplons pile up in $\epsilon = 0$ state - Bose-Einstein condensation

$$H_c - H_g = \frac{nv}{\eta}$$

$$n \propto T^{3/2} \Rightarrow H_c - H_g \propto T^{3/2}$$

4) $\left(p + \frac{a}{V^2}\right)(V-b) = RT$ - van der Waals equation of state for one mole of gas



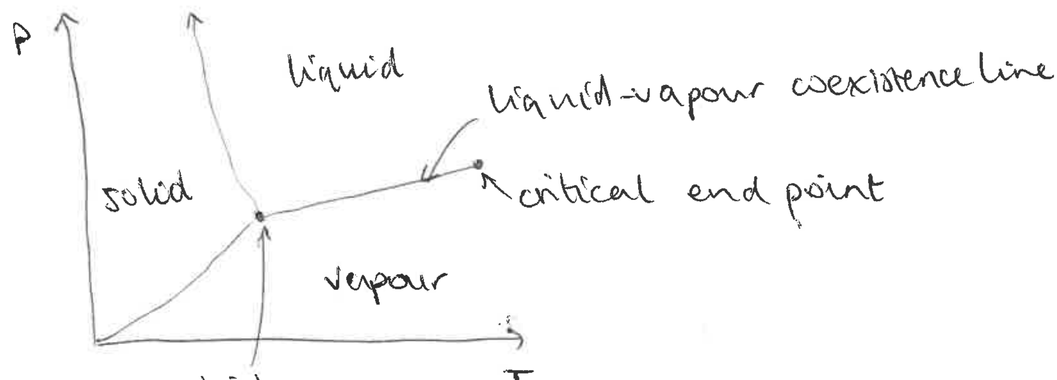
coexistence region
- bounded by dashed line
- in this region liquid and vapour coexist

Constants a and b:

a represents intermolecular attractive forces - reduce velocity of particles near walls of container, reducing pressure at fixed V and T by amount $\propto \frac{1}{V^2}$

b accounts for finite particle size - molecules are excluded from hard core region around other molecules, volume of the gas is corrected for.

p-T phase diagram



triple point
- all 3 phases coexist

find volume, temperature, pressure at critical point

$$\frac{\partial p}{\partial V} = \frac{\partial^2 p}{\partial V^2} = 0 \quad \text{at critical point}$$

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\frac{\partial p}{\partial V} = \frac{-RT}{(V-b)^2} + \frac{2a}{V^3} = 0 \quad ①$$

$$\frac{\partial^2 p}{\partial V^2} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} = 0 \quad ②$$

$$① \div 2 : \quad \tfrac{1}{2}(V_c - b) = \tfrac{1}{3} V_c$$

$$\tfrac{1}{6} V_c = \tfrac{1}{2} b, \quad V_c = 3b$$

$$\frac{2a}{(3b)^3} = \frac{RT_c}{(3b-b)^2} \Rightarrow RT_c = \frac{8a}{27b}$$

$$p_c = \frac{8a}{27b} \cdot \frac{1}{2b} - \frac{a}{9b^2} = \frac{a}{27b^2}$$

Show that variable x at equilibrium undergoes statistical fluctuations with variance

$$\langle (x - \langle x \rangle)^2 \rangle = k_B T / \left(\frac{\partial^2 A}{\partial x^2}\right)$$

$$P(x) \propto \Omega_{tot}(U_{tot}, x)$$

$$S_{tot} = k_B \ln \Omega_{tot}(U_{tot}, x) \Rightarrow P(x) \propto \exp(S_{tot}/k_B)$$

$$dS_{tot} = -dA/T_R \Rightarrow P(x) \propto \exp(-A(x)/k_B T)$$

$$A(x) = A(x_0) + (x - x_0)\frac{\partial A}{\partial x}\Big|_{x_0} + \tfrac{1}{2}(x - x_0)^2 \frac{\partial^2 A}{\partial x^2}\Big|_{x_0}$$

$$\partial A/\partial x|_{x_0} = 0, \quad x_0 = \text{equilibrium value of } x$$

$$P(x) \propto \exp\left(-\frac{(x-x_0)^2}{2k_B T}\frac{\partial^2 A}{\partial x^2}\right)$$

– Gaussian with mean x_0 and variance $\sigma^2 = k_B T / \partial^2 A/\partial x^2$

$$\sigma^2 = \langle (x - \langle x \rangle)^2 \rangle = \frac{k_B T}{\partial^2 A/\partial x^2}$$