

Problem set 1 - Liquids

① perfect gas: $U=U(T)$, $dT=0$ $V_1 \rightarrow V_2 = 2V_1$

a). $dT=0 \rightarrow dU=0$ $\Delta U=0$, as $U=U(T)$ only.

$$b). dS = \frac{dq_{rev}}{T} = \frac{pdv}{T} = \frac{nRT}{VT} \cdot dV$$

$$dU = dq_{rev} + dw = 0 \rightarrow dq = -dw = pdv$$

$$\Delta S = \int_{V_1}^{V_2} nR \frac{1}{V} dV = nR \ln \frac{V_2}{V_1} = nR \ln 2$$

$$c). \Delta S = nR \ln 2 = S_2 - S_1$$

$$\downarrow nR = Nk$$

$$Nk \ln 2 = k \ln \Omega_2 - k \ln \Omega_1$$

$$k \ln 2^N = k \ln \frac{\Omega_2}{\Omega_1} \Rightarrow \frac{\Omega_2}{\Omega_1} = 2^N$$

N molecules \rightarrow per molecule the number of ways to realise a given configuration doubles \leftarrow

$$\text{e.g. } N=1 \quad \frac{\Omega_2}{\Omega_1} = 2$$

\rightarrow as $V_2 = 2V_1$

$$\text{for } N \text{ mlc} \rightarrow 2 \cdot 2 \cdot 2 \dots 2 = 2^N$$

\Rightarrow so number of ways to realise config increases by factor 2^N .

$$d). dA = -SdT - pdv + \mu dn = \underbrace{\left(\frac{\partial A}{\partial T}\right)_{v,n}}_{-S} dT + \underbrace{\left(\frac{\partial A}{\partial v}\right)_{T,n}}_{-p} dv + \underbrace{\left(\frac{\partial A}{\partial n}\right)_{T,v}}_{\mu} dn$$

$$\left(\frac{\partial S}{\partial v}\right)_{T,n} = \frac{\partial}{\partial v} (S)_{T,n} = \frac{\partial}{\partial v} \left(-\frac{\partial A}{\partial T}\right)_{v,n} = + \left(\frac{\partial}{\partial T} \left(\frac{\partial A}{\partial v}\right)_{T,n}\right)_{v,n}$$

$$\left(\frac{\partial S}{\partial v}\right)_{T,n} = \left(\frac{\partial p}{\partial T}\right)_{v,n}$$

\leftarrow total diff.
order of diff.
is arbitrary.

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial P}{\partial T}\right)_{V,n}$$

$$P = \frac{nRT}{V} \rightarrow \left(\frac{\partial P}{\partial T}\right)_{V,n} = \frac{nR}{V}$$

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_{T,n} = \frac{nR}{V} \quad (\text{from Maxwell relation})$$

$$\int_{S(V_1)}^{S(V_2)} dS = nR \int_{V_1}^{V_2=2V_1} \frac{1}{V} dV = nR \ln \frac{V_2}{V_1} = nR \ln 2$$

$$\rightarrow \Delta S = nR \ln 2.$$

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$$\textcircled{2} \quad d\mu = -S_m dT + V_m dp$$

a) in equil.: $\mu^\alpha = \mu^\beta \rightarrow d\mu^\alpha = d\mu^\beta$

$$\Rightarrow -S_m^\alpha dT + V_m^\alpha dp = -S_m^\beta dT + V_m^\beta dp$$

$$\underbrace{(S_m^\beta - S_m^\alpha)}_{\Delta S_m} dT = \underbrace{(V_m^\beta - V_m^\alpha)}_{\Delta V_m} dp \Rightarrow \frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

b) $\Delta S_m = \Delta_{trs} S$ & $\Delta V_m = \Delta_{trs} V$

$$\frac{dp}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V} = \frac{\Delta_{trs} H}{T \Delta_{trs} V} \quad \left(ds = \frac{dq_{rev}}{T} \stackrel{cst P}{=} \frac{dH}{T} \rightarrow \Delta S = \frac{\Delta H}{T} \right)$$

gas involved, we can assume:

$$\left. \begin{array}{l} \textcircled{1} \Delta_{trs} V = V_{m,g} - V_{m,l} \approx V_{m,g} \\ \textcircled{2} \text{assume perfect gas: } V_{m,g} = \frac{RT}{P} \end{array} \right\} \Delta_{trs} \approx \frac{RT}{P}$$

$$\Rightarrow \frac{dp}{dT} = \frac{P \cdot \Delta_{trs} H}{RT^2} \Rightarrow \frac{1}{P} \frac{dp}{dT} = \frac{\Delta_{trs} H}{RT^2} \Rightarrow \frac{d \ln P}{dT} = \frac{\Delta_{trs} H}{RT^2}$$

(liq-vap: $\Delta_{trs} H = \Delta_{vap} H$)

c) $\Delta_{vap} H = 44.0 \text{ kJ mol}^{-1}$

→ need P_2 @ $T_2 = 393 \text{ K}$ & liq-vap equil: Clausius-Clapeyron

→ know: $T_1 = 373 \text{ K}$ @ $P_1 = P^\ominus = 1 \text{ bar}$

$$\int_{P_1=P^\ominus}^{P_2=P} \frac{d \ln P}{dT} = \frac{\Delta_{vap} H}{R} \int_{T_1}^{T_2} \frac{1}{T^2} dT \rightarrow \ln \frac{P}{P^\ominus} = -\frac{\Delta_{vap} H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

assume ΔH indep. of T

$$\ln \frac{P_2}{P^\ominus} = -\frac{44 \cdot 10^3}{8.314} \left(\frac{1}{393} - \frac{1}{373} \right) = 0.722$$

$$P^\ominus = 1 \text{ bar} \rightarrow P_2 = 2.06 \text{ bar}$$

d) solid-liquid equil. $\frac{dp}{dT} = \frac{\Delta S_{SL}}{\Delta S_{SL}V} = \frac{\Delta S_{SL}H}{T \Delta S_{SL}V} = \frac{\Delta S_{fus}H}{T \Delta S_{fus}V}$

(fusion = melting)

$$\int_{P_1}^{P_2} dp = \frac{\Delta S_{fus}H}{\Delta S_{fus}V} \int_{T_1}^{T_2} \frac{1}{T} dT \quad \rightarrow \quad P_2 - P_1 = \frac{\Delta S_{fus}H}{\Delta S_{fus}V} \ln \frac{T_2}{T_1}$$

e). $\Delta S_{fus}H = 6.01 \text{ kJ mol}^{-1}$

ice $T_1 = 273 \text{ K}$ $P_1 = P^{\ominus} = 1 \text{ bar} = 10^5 \text{ Pa}$

water $T_2 = T_{TP}$ $P_2 = 533.29 \text{ Pa}$

\rightarrow temp. @ triple point \rightarrow then $T_2 - T_1$

first: calculate $\Delta S_{fus}V \rightarrow$ use $\rho = \frac{m}{V} \rightarrow V = \frac{m}{\rho}$
mass density

$$\Delta S_{fus}V = \frac{m^*}{\rho_L} - \frac{m^*}{\rho_S} = m^* \left(\frac{1}{\rho_L} - \frac{1}{\rho_S} \right)$$

mass 1 mole H₂O
 18 g mol^{-1}

$$\rho_L = 1 \cdot 10^6$$

$$\rho_S = 0.917 \cdot 10^6 \text{ g m}^{-3}$$

same mass unit!

so: $\Delta S_{fus}V = 18 \cdot \left(\frac{1}{1 \cdot 10^6} - \frac{1}{0.917 \cdot 10^6} \right) = -1.63 \cdot 10^{-6} \frac{\text{m}^3}{\text{mol}}$ (should be -ve)

\Rightarrow use: $P_2 - P_1 = \frac{\Delta S_{fus}H}{\Delta S_{fus}V} \ln \frac{T_2}{T_1}$

$$\ln \frac{T_2}{T_1} = (P_2 - P_1) \cdot \frac{\Delta S_{fus}V}{\Delta S_{fus}H} = (533.29 - 10^5) \cdot \frac{-1.63 \cdot 10^{-6}}{6.01 \cdot 10^3} = 2.697 \cdot 10^{-5}$$

$$\frac{T_2}{T_1} = 1.0000269 \rightarrow (T_1 = 273 \text{ K}) : T_2 = 273.007363 \text{ K}$$

$$T_2 - T_1 = 7.37 \cdot 10^{-3} \text{ K}$$

\Rightarrow small difference makes sense, as seal boundary is very steep
 small change in $T \Leftrightarrow$ large change in p .

$$(3) \quad p = \frac{RT}{v-b} - \frac{a}{v^2}$$

a) a : parametrizes the attractive interactions
 b : " " repulsive "

$$b) \quad \left(\frac{\partial p}{\partial v}\right)_T = 0 \quad \& \quad \left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0$$

$$(1): \left(\frac{\partial p}{\partial v}\right)_T = \frac{-RT}{(v-b)^2} + \frac{2a}{v^3} = 0 \rightarrow \frac{2a}{v^3} = \frac{RT}{(v-b)^2}$$

$$(2): \left(\frac{\partial^2 p}{\partial v^2}\right)_T = + \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0 \rightarrow \frac{2a}{v^3} \cdot \frac{3}{v} = \frac{2RT}{(v-b)^3}$$

$$\text{combine: } \frac{RT}{(v-b)^2} \cdot \frac{3}{v} = \frac{2RT}{(v-b)^3} \rightarrow \frac{3}{v} = \frac{2}{v-b}$$

$$\Rightarrow 2v = 3(v-b) = 3v - 3b \rightarrow -v = -3b \Rightarrow \boxed{v_c = 3b}$$

sub back into (1):

$$\frac{2a}{(3b)^2} = \frac{RT}{(3b-b)^2} \rightarrow \frac{2a}{27b^2} = \frac{RT}{4b^2} \rightarrow \boxed{T_c = \frac{8a}{27Rb}}$$

sub back into vld Waals:

$$p_c = \frac{RT_c}{v_c - b} - \frac{a}{v_c^2} = \frac{\cancel{R} \left(\frac{8a}{27Rb}\right)}{(3b-b)} - \frac{a}{(3b)^2} \Rightarrow$$

$$\frac{8a}{27 \cdot 2b^2} - \frac{a}{9b^2} \cdot \frac{2 \cdot 3}{2 \cdot 3} = \frac{8a}{27 \cdot 2 \cdot b^2} - \frac{6a}{27 \cdot 2 \cdot b^2} = \frac{\cancel{8}a}{27 \cdot \cancel{2} \cdot b^2}$$

$$\boxed{p_c = \frac{a}{27b^2}}$$

$$c). \quad a = 0.361 \text{ J m}^3 \text{ mol}^{-2}$$

$$b = 42.9 \cdot 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

$$V_c = 3 \cdot b = 1.29 \cdot 10^{-4} \text{ m}^3 / \text{mol}$$

$$P_c = \frac{a}{27b^2} = \frac{0.361}{27 \cdot (42.9 \cdot 10^{-6})^2} = 7.26 \cdot 10^6 \text{ Pa} = 72.6 \text{ bar}$$

$$T_c = \frac{8a}{27Rb} = \frac{8 \cdot 0.361}{27 \cdot 8.314 \cdot 42.9 \cdot 10^{-6}} = 299.9 \text{ K}$$

comparison is not too bad given
the simplicity of vdW's equation of state.

$$d). \quad P = \frac{RT}{V-b} - \frac{a}{V^2} \approx \frac{RT}{V} \left[1 + \underbrace{\left(b - \frac{a}{RT} \right)}_{B(T)} \frac{1}{V} + \dots \right]$$

$$T_B = \text{where } B(T) = 0$$

$$\Rightarrow b - \frac{a}{RT_B} = 0 \quad \rightarrow \quad T_B = \frac{a}{Rb}$$

$$T_B = \frac{0.361}{8.314 \cdot 42.9 \cdot 10^{-6}} = 1012 \text{ K} \quad (\gg T_c = 300 \text{ K})$$

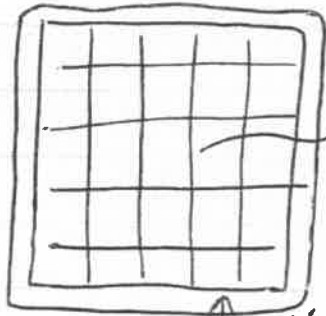
$T_B \gg T_c$ as at $T_B \rightarrow$ gas behaves "ideally", while
at T_c it condenses into liquid \rightarrow so not ideal at all.

"perfect gas behaviour \rightarrow at temp. far above condensation temp,
as we need to be in gas phase: $T_B > T_c$."

$$\text{indeed: } \left. \begin{array}{l} T_c = \frac{8a}{27Rb} \\ T_B = \frac{a}{Rb} \end{array} \right\} T_c = \frac{8}{27} \cdot T_B \rightarrow T_B > T_c$$

Problem Set 1

4. a). no unique answer



N, V, T

thermal insulation

canonical ensemble

- large collection of systems
 - each system replicates the closed isothermal system of interest: N, V, T
 - $Q = \sum_i \exp(-\beta E_i)$ $\beta = \frac{1}{k_B T}$
- ↑
energy of i th state

from $Q \rightarrow$ all thermodynamic $A = -k_B T \ln Q$... etc.
- useful for interacting systems!

b). $\bar{u} = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N, V}$
 $A = -k_B T \ln Q$

c).

$$dA = -SdT - PdV + \mu dN \rightarrow P = - \left(\frac{\partial A}{\partial V} \right)_{N, T}$$

$$\text{so: } P = - \frac{\partial}{\partial V} (-k_B T \ln Q)_{N, T} = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N, T}$$

$$Q = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} (V - Nb)^N \exp\left(-\frac{aN^2}{V k_B T}\right)$$

$$\therefore P = k_B T \frac{\partial}{\partial V} \left\{ \ln \frac{1}{N!} + \frac{3N}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) - \frac{3N}{2} \ln h^2 + N \ln(V - Nb) + \frac{aN^2}{V k_B T} \right\}$$

$$= k_B T \left\{ N \cdot \frac{1}{(V - Nb)} - \frac{aN^2}{k_B T V^2} \right\}$$

$$= \frac{N k_B T}{V - Nb} - a \left(\frac{N}{V} \right)^2 \Rightarrow \text{vd Waals EOS.}$$

$$d). \quad \bar{U} = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N, V}$$

$$= kT^2 \frac{\partial}{\partial T} \left\{ \ln \left(\frac{1}{N!} \right) + \frac{3N}{2} \ln (2\pi m k_B T) - \frac{3N}{2} \ln h^2 + N \ln (V - Nb) + \frac{aN^2}{V k_B T} \right\} =$$

$$= kT^2 \left\{ \frac{3N}{2} \cdot \frac{1}{2\pi m k_B T} \cdot 2\pi m k_B + \frac{-aN^2}{V k_B T^2} \right\} =$$

$$= kT^2 \left\{ \frac{3N}{2T} - \frac{aN^2}{V k_B T^2} \right\} = \frac{3N k_B T}{2} - \frac{aN^2}{V}$$

$$\therefore \frac{\bar{U}}{N} = \frac{3 k_B T}{2} - a \frac{N}{V}$$

independent of b : b accounts for the excluded volume effect & does not affect the energy of interaction between particles.

5

$$a). \quad \begin{aligned} E_n &= (n + \frac{1}{2}) h\nu & E_0 = ZPE = \frac{1}{2} h\nu \rightarrow 0 \\ &= E_0 + \Delta E \\ &= \frac{1}{2} h\nu + n h\nu \end{aligned} \quad \rightarrow \text{if } E_0 = 0 \rightarrow E_n = \Delta E = n h\nu$$

$$q_{vib} = \sum_{n=0}^{\infty} e^{-\beta E_n} = 1 + e^{-\beta h\nu} + e^{-2\beta h\nu} + \dots =$$

$$= (1 + (e^{-\beta h\nu})^1 + (e^{-\beta h\nu})^2 + (e^{-\beta h\nu})^3 + \dots)$$

$$(x = e^{-\beta h\nu}) \quad = (1 - e^{-\beta h\nu})^{-1}$$

$$\therefore q_{vib} = (1 - e^{-h\nu/kT})^{-1}$$

$$\left[\begin{aligned} q_{vib} &= \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})h\nu} = e^{-\beta\frac{1}{2}h\nu} + e^{-\beta(\frac{1}{2}+1)h\nu} + e^{-\beta(\frac{1}{2}+2)h\nu} + \dots \\ &= e^{-\beta\frac{1}{2}h\nu} (1 + e^{-\beta h\nu} + e^{-2\beta h\nu} + \dots) \\ &= e^{-\frac{1}{2}\beta h\nu} (1 - e^{-\beta h\nu})^{-1} = e^{-\beta\frac{1}{2}h\nu} (1 - e^{-\beta h\nu})^{-1} \\ &q_{vib} = (1 - e^{-h\nu/kT})^{-1} \end{aligned} \right]$$

ZPE $\rightarrow 0$

b) dist. particles: $Q = q^{3N}$ ($q_x = q_y = q_z \rightarrow q^3$)

$$U(T) = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} = 3NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_{N,V}$$

$$= 3NkT^2 \frac{\partial}{\partial T} \left\{ \ln (1 - e^{-h\nu_E/kT})^{-1} \right\} =$$

$$= 3NkT^2 \cdot -1 \cdot \left\{ \frac{1}{(1 - e^{-h\nu_E/kT})} \cdot -e^{-h\nu_E/kT} \cdot \frac{h\nu_E}{k} \cdot \frac{-1}{T^2} \right\} =$$

$$= 3N h\nu_E \left(\frac{e^{-h\nu_E/kT}}{(1 - e^{-h\nu_E/kT})} \right) \cdot \frac{e^{h\nu_E/kT}}{e^{h\nu_E/kT}} =$$

$$= 3N h\nu_E \left(\frac{1}{e^{h\nu_E/kT} - 1} \right) \rightarrow U(T) = 3N h\nu_E \left(\frac{e^{h\nu_E/kT}}{e^{h\nu_E/kT} - 1} \right)^{-1}$$

$$c) u(T) = 3N h \nu_E (e^{h\nu_E/kT} - 1)^{-1} \quad C_V = \left(\frac{\partial u}{\partial T} \right)_V$$

$$C_V = 3N h \nu_E \frac{\partial}{\partial T} \left\{ (e^{h\nu_E/kT} - 1)^{-1} \right\} =$$

$$= 3N h \nu_E \cdot - (e^{h\nu_E/kT} - 1)^{-2} \cdot e^{h\nu_E/kT} \cdot \frac{-h\nu_E}{kT^2} =$$

$$= 3N \left(\frac{h\nu_E}{k} \right)^2 \cdot \frac{1}{T^2} = 3N \left(\frac{h\nu_E}{T} \right)^2 \cdot \frac{1}{k} \cdot \frac{e^{h\nu_E/kT}}{(e^{h\nu_E/kT} - 1)^2}$$

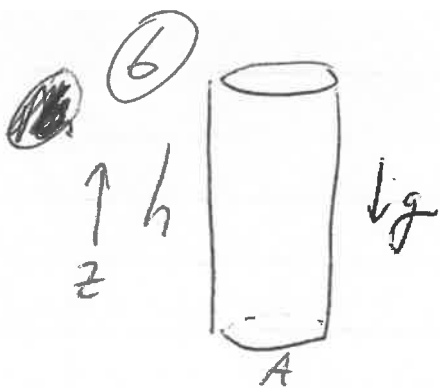
$$\Rightarrow C_V = 3N \left(\frac{h\nu_E}{k} \right)^2 \cdot \frac{k}{T^2} \cdot \frac{e^{h\nu_E/kT}}{(e^{h\nu_E/kT} - 1)^2} \quad \frac{h\nu_E}{k} = \epsilon_E$$

$$= 3Nk \left(\frac{\epsilon_E}{T} \right)^2 \cdot \frac{e^{\epsilon_E/T}}{(e^{\epsilon_E/T} - 1)^2}$$

Note: McQuarrie: $C_V = 3Nk \left(\frac{\epsilon_E}{T} \right)^2 \frac{e^{-\epsilon_E/T}}{(1 - e^{-\epsilon_E/T})^2}$

$$= 3Nk \left(\frac{\epsilon_E}{T} \right)^2 \cdot \frac{e^{-\epsilon_E/T}}{(1 - e^{-\epsilon_E/T})^2} \cdot \left(\frac{e^{\epsilon_E/T}}{e^{\epsilon_E/T}} \right)^2 =$$

$$= 3Nk \left(\frac{\epsilon_E}{T} \right)^2 \frac{e^{\epsilon_E/T}}{(e^{\epsilon_E/T} - 1)^2}$$



$$a) \quad \rho_{\text{class}} = \frac{1}{h^3} \int \int e^{-\beta H(p, z)} dp dz$$

→ extra potential energy term: $U_g = mgh \rightarrow mgz$

$$H(p, z) = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + mgz$$

$$\rho_{\text{class}} = \frac{1}{h^3} \int \int e^{-\beta \left[\frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + mgz \right]} dp dz$$

~~$$= \frac{1}{h^3} \int \int \int e^{-\beta \left[\frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + mgz \right]} dp_x dp_y dp_z dz$$~~

$$= \frac{1}{h^3} \underbrace{\int e^{-\beta \frac{p_x^2}{2m}} dp_x}_{\text{all the same!}} \underbrace{\int e^{-\beta \frac{p_y^2}{2m}} dp_y}_{\text{all the same!}} \underbrace{\int e^{-\beta \frac{p_z^2}{2m}} dp_z}_{\text{all the same!}} \underbrace{\int dx \int dy}_{A} \int e^{-\beta mgz} dz =$$

$$= \frac{1}{h^3} \left[\int_{-\infty}^{\infty} e^{-\beta \frac{p^2}{2m}} dp \right]^3 A \int_0^h e^{-\beta mgz} dz$$

Gaussian Integral: $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \quad a = \frac{\beta}{2m}$

$$\rho_{\text{class}} = \frac{1}{h^3} \left[\sqrt{\frac{\pi}{\frac{\beta}{2m}}} \right]^3 A \left[-\frac{1}{\beta mg} e^{-\beta mgz} \right]_0^h =$$

$$= \frac{1}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} \cdot A \left[\frac{-1}{\beta mg} e^{-\beta mgh} - \frac{-1}{\beta mg} \right] =$$

$$= \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} \cdot \frac{A}{\beta mg} \left[1 - \exp(-\beta mgh) \right]$$

$$q_{\text{class}} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{A k_B T}{mg} \left[1 - \exp\left(-\frac{mgh}{k_B T}\right) \right]$$

b). In the limit of no gravity $\rightarrow g \downarrow 0$

$$\hookrightarrow \therefore \exp\left(-\frac{mgh}{k_B T}\right) = \exp(-x) \underset{\substack{\uparrow \\ \text{Taylor}}}{\approx} 1 - x + \dots$$

$$\begin{aligned} \therefore q_{\text{class}} &= \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{A k_B T}{mg} \left[1 - \left(1 - \frac{mgh}{k_B T} \right) \right] = \\ &= \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{A k_B T}{mg} \cdot \frac{mgh}{k_B T} \end{aligned}$$

$$\text{as } A \cdot h = V \rightarrow q_{\text{class}} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \cdot V$$

c). X_e : h at which this breaks down = h^* : $mgh^* = k_B T$

$$h^* = \frac{k_B T}{mg}$$

$$M_{Xe} = 131 \times 1.661 \cdot 10^{-27} \text{ kg}$$

$$h^* = \frac{1.38 \cdot 10^{-23} \cdot 293}{131 \cdot 1.66 \cdot 10^{-27} \cdot 9.81} = 10.94 \text{ m} = \underline{\underline{1.1 \text{ km}}}$$

↓
so pretty high!