THERMAL AND STATISTICAL PHYSICS

(I) Thermodynamics.

Concerns the flow of energy from (i) macroscopic ⇔ microscopic length scales (ii) one kind of microscopic degree of freedom to another.

1) Thermodynamic variables

- macroscopic observables
- Don't average to zero when averaging over large #'s of events.

└ Functions of State. i.e depend only on system contents + environment. NOT past system.

Two types. **EXTRINSIC** - scales with system size. V, N, U, S

INTRINSIC - independent of system size. P, T, μ

2) First law of Thermodynamics

"Energy is conserved if heat is taken into account"

Define $U = U(S,V,N)$ as internal energy, (of a system) — prog later

$\text{đ}W$ = change in U due to work done on the system

$\text{đ}Q$ = heat transferred to system. ($\not\Rightarrow$ no functional form of W, Q) — system only contains energy, not work or heat

$\therefore$ 1st law $\Rightarrow$ $dU = \text{đ}W + \text{đ}Q$. Now $\text{đ}Q_{rev} = TdS + \mu dN$ (a) definition of S, μ

$\text{đ}W = -pdV$ for REVERSIBLE processes.

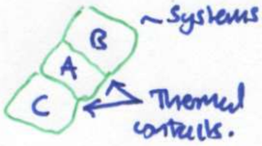
$$dU = TdS - pdV + \mu dN \quad (1)$$

T	Absolute temperature	$/K$
S	Entropy	$/JK^{-1}$
μ	chemical potential	$/J$
N	Particle #	
p	Pressure of system.	$/Jm^{-3}$
V	volume of system.	$/m^3$

Now dS, dV, dN are differential functions of state so providing we refer to a change between two EQUILIBRIUM STATES (1) is quite general, even if the processes connecting the eq. states are IRREVERSIBLE. (Since we can always get the same result by choosing a reversible path).

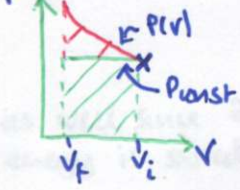
3) The other laws of thermodynamics

$\boxed{0}$ - If A is in thermal e.q with B and A " " " " " C $\Rightarrow$ B is in thermal e.q with C.



$\boxed{2}$ - $\dfrac{dS_{universe}}{dt} \geqslant 0$ $\boxed{3}$ - Entropy changes $\to 0$ as $T \to 0$.

Proof of $\boxed{2}$: CLAUSIUS' INEQUALITY states $\text{đ}Q^{sys}_{rev} > \text{đ}Q^{sys}_{irrev}$ for any heat change of a system. $\to$ consider isothermal compression of a system. $W_{rev} = -\int_{V_i}^{V_f} p(V)dV$. $W_{irrev} = -\int_{V_i}^{V_f} P_{const}\, dV$. Now P_{system} increases as V_{sys} decreases. $\therefore$ Reversible path (where $p = P_{sys}$) must have $\partial p/\partial(-V) \geqslant 0 \Rightarrow \dfrac{\partial p}{\partial V} < 0$. Hence using graph $-W_{rev} = \int_{V_f}^{V_i} p(V)dV \geqslant -W_{irrev} \Rightarrow W_{irrev} \geqslant W_{rev}$. Now for isothermal process no energy is stored $\Rightarrow dU = 0$. $\therefore \text{đ}Q = -\text{đ}W$. Now clearly since $\partial p(V)/\partial V \leq 0\ \forall V$ $\Rightarrow \text{đ}W_{irrev} \geqslant \text{đ}W_{rev} \Rightarrow \text{đ}Q_{rev} \geqslant \text{đ}Q_{irrev}$. (This is in fact quite a general result).



Now if $dN = 0$ $\text{đ}Q_{rev} = TdS$ so $dS_{universe} = dS_{sys} + dS_{surr} = \dfrac{\text{đ}Q^{sys}_{rev}}{T} + \dfrac{\text{đ}Q^{surr}_{rev}}{T}$

Now assume surroundings represent an infinite heat reservoir $\Rightarrow \text{đ}Q^{surr}$ is always reversible. [Note REVERSIBLE process is one which can be reversed by an infinitessimal modification of a thermodynamic variable]. $\therefore \text{đ}Q^{surr}_{rev} = \text{đ}Q^{surr} = -\text{đ}Q^{sys}_{irrev}$

$\therefore TdS_{universe} = \text{đ}Q^{sys}_{rev} - \text{đ}Q^{sys}_{irrev}$ which is $\geqslant 0$ by Clausius' inequality.

So $dS_{universe} \geqslant 0$ for any change taking place in time dt. i.e $\dfrac{dS_{universe}}{dt} \geqslant 0$ QED.

4) Manipulations with U and Euler relations.

Assume $U = U(T,S,P,V,\mu,N)$

Now U, S, V, N are all extensive variables (extrinsic!) $\Rightarrow U(T,\lambda S, p, \lambda V, \mu, \lambda N) = \lambda U \equiv U_\lambda$. {$\lambda$ is a scaling factor}

$\therefore \partial U_\lambda/\partial\lambda = U$. Now

$$\frac{\partial U_\lambda}{\partial \lambda} = \left(\frac{\partial U_\lambda}{\partial \lambda S}\right)_{\lambda V, \lambda N}\left(\frac{\partial \lambda S}{\partial \lambda}\right)_{\lambda V,\lambda N} + \left(\frac{\partial U_\lambda}{\partial \lambda V}\right)_{\lambda S, \lambda N}\left(\frac{\partial \lambda V}{\partial \lambda}\right)_{\lambda S,\lambda N} + \left(\frac{\partial U_\lambda}{\partial \lambda N}\right)_{\lambda S, \lambda V}\left(\frac{\partial \lambda N}{\partial \lambda}\right)_{\lambda S,\lambda V}$$

since T, P, μ effectively behave as constants w.r.t U_λ and $\lambda S, \lambda V, \lambda N$ variables - hence chain rule above.

$$\Rightarrow \partial U_\lambda/\partial\lambda = \left(\frac{\partial U_\lambda}{\partial \lambda S}\right)_{\lambda V,\lambda N} S + \left(\frac{\partial U_\lambda}{\partial \lambda V}\right)_{\lambda S,\lambda N} V + \left(\frac{\partial U_\lambda}{\partial \lambda N}\right)_{\lambda S,\lambda V} N$$

let $\lambda = 1 \Rightarrow U_\lambda = U$

$$\Rightarrow U = \left(\frac{\partial U}{\partial S}\right)_{V,N} S + \left(\frac{\partial U}{\partial V}\right)_{S,N} V + \left(\frac{\partial U}{\partial N}\right)_{S,V} N$$

so $U = U(S,V,N)$ (QED. proof above).

Now using $dU = TdS - pdV + \mu dN$ and fact that since $U = U(S,V,N)$ we can write $dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$

$$\Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \quad p = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

$\therefore$ $U = TS - PV + \mu N$ (Euler #1). $\therefore$ $dU = TdS + SdT - pdV - Vdp + \mu dN + Nd\mu$ $= TdS - pdV + \mu dN$ from 1st law. $\Rightarrow$ $SdT - Vdp + Nd\mu = 0$ $\Rightarrow$ $d\mu = \frac{V}{N}dp - \frac{S}{N}dT$

GIBBS-DUHEIM RELATION. Now if $U = U(S,V,N)$ $\Rightarrow$ $S = S(U,V,N)$

$\Rightarrow$ $dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$. Now from 1st law

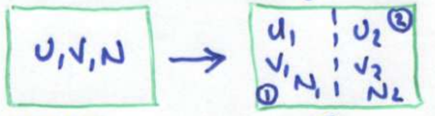
$$dS = \frac{dU}{T} + \frac{pdV}{T} - \frac{\mu dN}{T} \Rightarrow \frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} ; \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} ; \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{U,V}$$

Better definition of μ.

one last manipulation of Euler #1 gives $S = \frac{U}{T} + \frac{PV}{T} - \frac{\mu N}{T}$ (Euler #2) which $\Rightarrow$ dS can be integrated easily like dU w.r.t the other extensive variables.

extrinsic

5) Equilibrium of closed systems - By doing thought experiments using internal constraints $\rightarrow$ derive e.q. conditions for closed systems. Use principle of maximum entropy to determine e.q. point. i.e $\partial S / \partial x = 0$ where x is some thermodynamic variable that classifies a particular eq.



CLOSED SYSTEM

$dU = dV$
$= dN = 0$

imaginary partition {Energy and particles can flow through it.

$U_1 + U_2 = U$
$V_1 + V_2 = V$
$N_1 + N_2 = N$ $\rightarrow$ $dU_1 = -dU_2$, $dV_1 = -dV_2$, $dN_1 = -dN_2$

Now $dS_{sys} = dS_1 + dS_2 = \frac{dU_1 + P_1 dV_1 - \mu_1 dN_1}{T_1} + \frac{dU_2 + P_2 dV_2 - \mu_2 dN_2}{T_2}$

so $dS_{sys} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1$

Now since $dS_{surr} = 0$ $\Rightarrow$ $dS_{sys} \geq 0$ by 2nd law.

3 special cases: ① $dV_1 = dN_1 = 0$ $\Rightarrow$ $\left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 \geq 0$ $\begin{cases} T_1 > T_2 \Rightarrow dU_1 < 0 \\ T_1 < T_2 \Rightarrow dU_1 > 0 \end{cases}$ $\Big|$ $\frac{\partial S_{sys}}{\partial U_1} = \frac{1}{T_1} - \frac{1}{T_2} = 0$ when $T_1 = T_2$

- Approach to e.q : "Heat flows from hot to cold"

② $dN_1 = 0$, $T_1 = T_2$ $\Rightarrow$ $(P_1 - P_2) dV_1 \geq 0$ $\begin{cases} P_1 > P_2 \Rightarrow dV_1 > 0 \\ P_1 < P_2 \Rightarrow dV_1 < 0 \end{cases}$ $\Big|$ $\frac{\partial S_{sys}}{\partial V_1} = P_1 - P_2 = 0$ when $P_1 = P_2$

- "Higher pressure subsystem expands".

③ $T_1 = T_2$, $dV_1 = 0$ $\Rightarrow$ $(\mu_2 - \mu_1) dN_1 \geq 0$ $\begin{cases} \mu_1 > \mu_2 \Rightarrow dN_1 < 0 \\ \mu_1 < \mu_2 \Rightarrow dN_1 > 0 \end{cases}$ $\Big|$ $\frac{\partial S_{sys}}{\partial N_1} = \mu_2 - \mu_1 = 0$ when $\mu_1 = \mu_2$

- "particles flow from high to low chemical potential"

6) Equilibrium in open systems. Same approach to above except the two subsystems are the system in question and the surroundings - (an infinite reservoir where intrinsic variables P, T, μ do not vary). label "system" 1 and "surroundings" 0. (Together form a closed system) Second law $\Rightarrow$ $dS_1 + dS_0 \geq 0$ using 1st law

$dU_1 = -dU_2$ etc....

$$dS_0 = \frac{dU_0 + P_0 dV_0 - \mu_0 dN_0}{T_0} = \frac{-dU_1 - P_0 dV_1 + \mu_0 dN_1}{T_0}$$

$\therefore$ 2nd law $\Rightarrow$ $\frac{1}{T_0}\left(T_0 dS_1 - dU_1 - P_0 dV_1 + \mu_0 dN_1\right) \geq 0$

$\Rightarrow$ $-\frac{1}{T_0} d\left(U_1 + P_0 V_1 - T_0 S_1 - \mu_0 N_1\right)$ since $dP_0 = dT_0 = d\mu_0 = 0$. Define AVALIABILITY A_1 as

$A_1 = U_1 + P_0 V_1 - T_0 S_1 - \mu_0 N_1$ $\Rightarrow$ $-\frac{1}{T_0} dA_1 \geq 0$ ✓ $\therefore$ $dA_1 / T_0 \leq 0$ So 2nd law becomes this and eq condition for open systems is MINIMISATION of Availability. Note using Euler #1 we can write

$A_1 = (T_1 - T_0) S_1 - (P_1 - P_0) V_1 + (\mu_1 - \mu_0) N_1$ - we will drop the 1 suffix from now on..... well when clear!

4 special cases: ① constant T, V, N i.e $T_1 = T_0$ $dV_1 = 0$, $dN_1 = 0$ $\Rightarrow$ $dA_1 = d(U - T_1 S_1)$

Define HELMHOLTZ FREE ENERGY $F = U - TS$. At eq F is minimised.

② P, S, N constant i.e $P_1 = P_0$ $dS_1 = 0$, $dN_1 = 0$ $\Rightarrow$ $dA_1 = d(U + P_1 V_1)$. Define ENTHALPY $H = U + PV$ @ eq H is minimised. ③ constant T, P, N $\Rightarrow$ $T_1 = T_0$, $P_1 = P_0$, $dN_1 = 0$ $\Rightarrow$ $dA_1 = d(U_1 + P_1 V_1 - T_1 S_1)$ $= d(\mu_1 N_1)$ using Euler #1. Define GIBBS FREE ENERGY $G = \mu N$. @ eq G is minimised.

Note $dG = \mu dN + Nd\mu = -SdT + Vdp + \mu dN$ using Gibbs-Duheim relation.

④ constant $T, V, \mu \Rightarrow T = T_0,\ dV_1 = 0,\ \mu_1 = \mu_0 \Rightarrow dA_1 = d(U_1 - T_1 S_1 - \mu_1 N_1)$ Define GRAND POTENTIAL $\Phi = U - TS - \mu N = F - \mu N = -pV$ (from Euler #1).
$d\Phi = -SdT - pdV - Nd\mu$ (using 1st law).

7) Analytic Methods and Applications * Techniques with partial derivatives

chain rule $\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial u}\right)_z \left(\frac{\partial u}{\partial y}\right)_z$ for $x(y)$ - all other variables represented by z held constant.

and if $\phi = \phi(x, y, z \ldots)$ $d\phi = \left(\frac{\partial \phi}{\partial x}\right)_{y,z\ldots} dx + \left(\frac{\partial \phi}{\partial y}\right)_{x,z\ldots} dy + \ldots\ldots$

Reciprocity theorem if $\phi = \phi(x, y)$
$d\phi = \left(\frac{\partial \phi}{\partial x}\right)_y dx + \left(\frac{\partial \phi}{\partial y}\right)_x dy$ let $d\phi = 0$

$$\Rightarrow \left(\frac{\partial \phi}{\partial x}\right)_y = -\left(\frac{\partial \phi}{\partial y}\right)_x \frac{dy}{dx} = -\left(\frac{\partial \phi}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_\phi$$

* Maxwell relations

- use differential forms of Potentials F, H, G, Φ defined above. (Actually U is used instead of Φ). i.e $dG = -SdT + Vdp + \mu dN$. Now since $G = G(U, P, V, T, S)$ by chain rule
$dG = \frac{\partial G}{\partial U} dU + \frac{\partial G}{\partial p} dp + \frac{\partial G}{\partial V} dV + \frac{\partial G}{\partial T} dT + \frac{\partial G}{\partial S} dS$. compare with dG above:

$\Rightarrow \frac{\partial G}{\partial T} = -S \quad \frac{\partial G}{\partial p} = V$ and all others are zero. (let's assume $dN = 0$) Now since $\frac{\partial^2 G}{\partial p \partial T} = \frac{\partial^2 G}{\partial T \partial p}$

$\Rightarrow -\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$. Repeat process...., ($dN = 0$ always)

POTENTIAL	MAXWELL RELATION
$dU = TdS - pdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
$dF = -SdT - pdV$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$
$dH = TdS + Vdp$	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
$dG = -SdT + Vdp$	$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

CRUCIAL STATEMENT !!!!!

* Applications

- since all thermodynamic variables are functions of state the path between successive eq does not affect either eq. Also, we are free to assign the thermodynamic variable dependent of each state. - usually done in pairs. This of course very much depends of the system in question.

Example 1: Entropy of a perfect gas. System described by EQUATION OF STATE of form $f(P, V, T, N) = 0$ Quantities U, S, μ can be derived from the equation of state. In the case of an ideal/perfect gas $pV = Nk_BT$. Let's assume N constant so $S = S(p, T)$ or $S(V, T)$ or $S = (p, V)$ since we have two equations ($dN = 0$ and $f = 0$) which relate p, V, N, T and $\therefore$ reduce the # of independent variables to 2. It doesn't actually matter which pair we use → Maxwell relations will help. So, let's use $S = S(T, p)$.

$\therefore dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp \xrightarrow[\text{via MAXWELL EQ}]{\text{removes dependence}} dS = -\left(\frac{\partial V}{\partial T}\right)_p dp + \left(\frac{\partial S}{\partial T}\right)_p dT$

Now C_p is defined $C_p = \left(\frac{\partial Q}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$ so $dS = -\left(\frac{\partial V}{\partial T}\right)_p dp + \frac{C_p}{T} dT$

Now $\left(\frac{\partial V}{\partial T}\right)_p = \frac{Nk_B}{p}$ from Equation of State $\Rightarrow dS = -\frac{Nk_B}{p} dp + \frac{C_p}{T} dT$

$\therefore S(p, T) = NS_0 - Nk_B \ln p + C_p \ln T$ with NS_0 the integration constant.

E.g 2 : Relate C_p and C_V use $S = S(T, V)$ since $C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$

i.e $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \Rightarrow \frac{dS}{dT} = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \frac{dV}{dT}$ Now since p = constant would allow the total derivatives to be evaluated

$\Rightarrow \left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$ Now $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$ (MAXWELL RELATION)

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

{C_p easy to measure, C_V not so use this relation to calculate C_V}

$$\Rightarrow C_p = C_V + T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$$

For an ideal gas $\left(\frac{\partial p}{\partial T}\right)_V = \frac{TNk_B}{V} \Rightarrow C_p = C_V + Nk_B$
$\left(\frac{\partial V}{\partial T}\right)_p = Nk_B/p$

E.G.3 Derivation (1) of the Sackur-Tetrode Equation for the Entropy of an ideal gas i.e $S=S(U,V,N)$

Already proved for an ideal gas of constant N $S = NS_0 - Nk_B\ln p + C_p\ln T$ Now from 1st law $dU = TdS - pdV$ if $dN=0$ if $dV=0$ $\frac{dU}{dT} = T\frac{dS}{dT} \Rightarrow \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$ Now for a monatomic ideal gas with 3 D.O.F → Equipartition theorem $\Rightarrow U = \frac{3}{2}Nk_BT$. $\therefore T\left(\frac{\partial S}{\partial T}\right)_V \equiv C_V = \frac{3}{2}Nk_B$ ∴ using $C_p = C_V + Nk_B$

$\Rightarrow C_p = \frac{5}{2}Nk_B$. $\therefore S = NS_0 - Nk_B\ln\left(\frac{Nk_BT}{V}\right) + \frac{5}{2}Nk_B\ln T$. Now $T = \frac{2}{3}\frac{U}{Nk_B}$

~~$\Rightarrow S = NS_0 - Nk_B\ln\left(\frac{2}{3}\frac{U}{V}\right) + \frac{5}{2}Nk_B\ln\left(\frac{2}{3}\frac{U}{Nk_B}\right) = NS_0$ ……….~~ oops missed out a step - collect T terms first!

$\hookrightarrow S = NS_0 + \frac{3}{2}Nk_B\ln T - Nk_B\ln(Nk_B/V)$

$= NS_0 + \frac{3}{2}Nk_B\ln\left(\frac{2}{3}\frac{U}{Nk_B}\right) - Nk_B\ln(Nk_B/V) = NS_0 + \frac{3}{2}Nk_B\left\{\ln\left(\frac{2}{3}\frac{U}{Nk_B}\right) - \frac{2}{3}\ln\left(\frac{Nk_B}{V}\right)\right\}$

$$\Rightarrow S(U,V,N) = NS_0 + \frac{3}{2}Nk_B\ln\left\{\frac{2}{3}\frac{U}{Nk_B}\left(\frac{V}{Nk_B}\right)^{2/3}\right\}$$

E.G.4 Joule Expansion

No change in U
$\therefore U(T,P,V,N) = 0$ (1)
$N =$ constant (2)
$f(T,P,V,N) = 0$ (3)
← state equation.

Equations (1) → (3) ⇒ only one independent thermodynamic variable. out of T, P, V. Want to know $T_2(V_2)$

so consider $T = T(V) \Rightarrow dT = \left(\frac{\partial T}{\partial V}\right)_U dV$ Now $T = (V,U)$ ⇒ reciprocity: $\left(\frac{\partial T}{\partial V}\right)_U = -\left(\frac{\partial T}{\partial U}\right)_V\left(\frac{\partial U}{\partial V}\right)_T$

Now from 1st law $dU = TdS - pdV$ if $dN=0$

$\therefore \frac{dU}{dV} = T\frac{dS}{dV} - p \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p$ (MAXWELL RELATION)

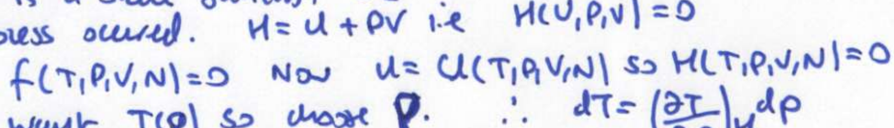
Now $\left(\frac{\partial T}{\partial U}\right)_V = \frac{1}{\left(\partial U/\partial T\right)_V} = \frac{1}{\left(\partial Q/\partial T\right)_V}$ using $dU = đQ - pdV$ $= \frac{1}{C_V}$

$\therefore \left(\frac{\partial T}{\partial V}\right)_U = \frac{-1}{C_V}\left(T\left(\partial p/\partial T\right)_V - p\right)$ JOULE COEFFICIANT. $\Rightarrow T_2 = T_1 + \int_{V_1}^{V_2} -\frac{1}{C_V}\left(T(\partial p/\partial T)_V - p\right)dV$

For ideal gas $T_2 = T_1$ but for V.D.W gas $p = \frac{Nk_BT}{V-Nb} - \frac{N^2a}{V^2}$; $\left(\frac{\partial T}{\partial V}\right)_U = \frac{-1}{C_V}a\frac{N^2}{V^2}$

so $T_2 < T_1$.

E.G. 5 : Joule-Kelvin Expansion



$\to đW = -pdV$

Since process is rapid ⇒ pressures P_1, P_2 are ≈ constant. $\therefore U_2 = U_1 + P_1V_1 - P_2V_2$ or $U_1 + P_1V_1 = U_2 + P_2V_2$

∴ work done $= P_1V_1 - P_2V_2 = U_2 - U_1$ i.e $H_1 = H_2$. → want to calculate $T_2(V_2)$ i.e V_1, T_1 known

Now J.K is irreversible but since T is a state function we can pretend a reversible constant H process occured. $H = U + PV$ i.e $H(U,P,V) = 0$

Now $N =$ constant and e.o.state $\Rightarrow f(T,P,V,N) = 0$ Now $U = U(T,P,V,N)$ so $H(T,P,V,N) = 0$

Again - only 1 independent variable. want $T(p)$ so choose P. $\therefore dT = \left(\frac{\partial T}{\partial p}\right)_H dp$

Now using reciprocity: $\left(\frac{\partial T}{\partial p}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_p\left(\frac{\partial H}{\partial p}\right)_T$ using $dH = TdS + Vdp$

$\Rightarrow \frac{dH}{dp} = T\frac{dS}{dp} + V$ $\therefore \left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V = -T\left(\partial V/\partial T\right)_p + V$ using Maxwell relation.

Now $\left(\frac{\partial T}{\partial H}\right)_p = \frac{1}{\left(\partial H/\partial T\right)_p}$ Now $dH = dU + Vdp + PdV$ if $dp = 0$ $\frac{dH}{dT} = \frac{dU + pdV}{dT} = \frac{đQ}{dT}$

$\Rightarrow \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial Q}{\partial T}\right)_p = C_p$

$\therefore \left(\frac{\partial T}{\partial p}\right)_H = \frac{-1}{C_p}\left(-T\left(\partial V/\partial T\right)_p + V\right)$ JOULE-KELVIN COEFFICIANT $\Rightarrow T_2 = T_1 + \int_{P_1}^{P_2} -\frac{1}{C_p}\left(-T\left(\partial V/\partial T\right)_p + V\right)dp$

Quick proof that for an Adiabatic process via and ideal gas $PV^\gamma =$ const.

Adiabatic: $dU = -pdV$ $(\partial Q = 0)$ if N = const $dU = \frac{\alpha}{2}Nk_BdT$

$PV = Nk_BT$ $U = \frac{\alpha}{2}Nk_BT$ (α = D.O.F) so $\frac{\alpha}{2}\frac{dT}{T} = -\frac{dV}{V} \Rightarrow \ln T = -\frac{2}{\alpha}\ln V + \text{const}$

$\to T = \text{const}\,V^{-2/\alpha}$

$\therefore PV^{1+2/\alpha} = \text{const}$

$1 + \frac{2}{\alpha} = \frac{C_p}{C_V} = \gamma$ ✓

using $C_p = C_V + Nk_B$ and $C_V = \frac{\partial U}{\partial T}\Big|_V$

TASP

8) Phase Equilibria. For P, T, N fixed, minimisation of $G = \mu N$ characterises an equilibrium point. Consider eq of two phases that compose the system. i.e $N = N_1 + N_2$, $G = G_1 + G_2$ for phases 1,2

Now at eq $dG = 0 \Rightarrow dG_1 = -dG_2$. Now $dG = -SdT + Vdp + \mu dN$

$\Rightarrow -\mu_2 dN_2 = \mu_1 dN_1$ @ e.q since $T_1 = T_2$ and $P_1 = P_2$ and are fixed. Now $dN = 0$ $\Rightarrow dN_1 = -dN_2$ so @ e.q $\mu_1 = \mu_2$. (consistent with result proved for eq of closed systems).

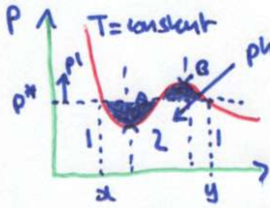
Now $\mu = \mu(T, P, V, N)$, $N =$ constant, $f(T, P, V, N) = 0$ for a particular system obeying state equation $f = 0$. $\therefore$ one independent variable. choose p. $\therefore$ $d\mu = \left(\frac{\partial \mu}{\partial p}\right)_T dp$ if $T =$ constant.

$\Rightarrow$ $\mu_2 = \mu_1 + \int_{p_1}^{p_2} \left(\frac{\partial \mu}{\partial p}\right)_T dp$ where P_1, P_2 correspond to pressures either side of a phase transition along a constant T line in P,V space. Now using Gibbs-Duheim $Nd\mu = -SdT + Vdp \Rightarrow d\mu = \frac{V}{N} dp$ since $dT = 0$. So $\left(\frac{\partial \mu}{\partial p}\right)_T = \frac{V}{N}$

$\Rightarrow$ $\mu_2 = \mu_1 + \int_1^2 \frac{V}{N} dp$. Now at e.q $\mu_2 = \mu_1 \Rightarrow \int_1^2 \frac{V}{N} dp = 0$ @ e.q.

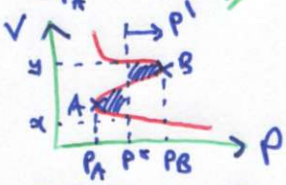
*Application – "equal areas rule for calculating eq pressure for a VAN DER WAALS isotherm"

Along $P = p^*$ line $\int_x^y p' dV = \int_{p_A}^{p_B} V dp = 0$



phase transition since $dP/dV < 0$ to avoid inverse compressibility

(Easier seen like this:)
Clearly $\int_{p_A}^{p_B} V dp = \int_x^y p' dV$



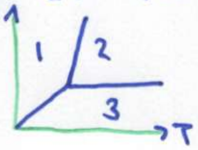
* Clausius-Clapeyron Equation defines e.q between phases 1,2.

Proved above that for fixed P, T, N; $\mu_1 = \mu_2$. Consider a coexistence curve on a P,T diagram for a system of N particles. At all points along the curve $\mu_1 = \mu_2$. $\Rightarrow d\mu_1 = d\mu_2$ for differentially small deviations of μ_1 along the curve. Using Gibbs Duheim $\Rightarrow (V_1 dp - S_1 dT) N_2 = (V_2 dp - S_2 dT) N_1$ (P,T same for 1,2 along the line). $\therefore$

$$\frac{dP}{dT} = \frac{S_1 N_2 - S_2 N_1}{N_2 V_1 - N_1 V_2} = \frac{S_1/N_1 - S_2/N_2}{V_1/N_1 - V_2/N_2} = \frac{L}{T\left(\frac{V_1}{N_1} - \frac{V_2}{N_2}\right)}$$

where L is the LATENT HEAT.

Note coexistence curves are straight lines.



calculate dp/dT by finding $L(P, T, N)$ and $V_1 - V_2$

-> ASSUME $N_1 = N_2$ reasonable?

-> if phases pure either side of line OK.

-> assumes discontinuous phase transition in P,T space.

* Landau Theory of phase transitions

- Identify "order parameter" that characterises an equilibrium state at particular temperature. e.g. Magnetisation of a solid M. - Parameterise Free Energy which applies to the problem (T,V,N for solids $\Rightarrow$ F) in terms of order parameter.

assume $F(M, T = \text{const})$ symmetry so only even powers.

i.e $F(T, M) = F_0 + a(T) M^2 + b(T) M^4 + c(T) M^6 \ldots\ldots$

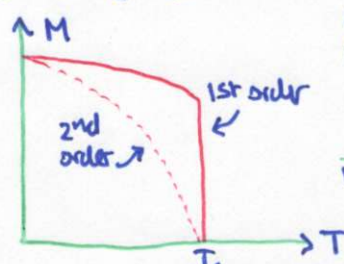
- At critical point $a(T)$ changes sign so minimum value of F (which characterises equilibrium) moves from $M = 0$ to $M \neq 0$. $\therefore$ Write $a(T) = \alpha(T - T_c)$. Near transition $a(T)$ dominates physics and $\therefore$ can approximate $b, c \ldots\ldots$ to be independent of T:

So write $F(T, M) = F_0 + \alpha(T - T_c) M^2 + \beta M^4 + \gamma M^6$ as an approximate model.

-> consider case $\alpha = a/2$ $\beta = b/4$ $\gamma M^5 = -H$ ↓ look at $H = 0$ @ eq.

TWO CASES: ① if β +ve 2ND order transition at $T = T_c$ i.e M changes continuously from zero to a finite value as T decreases

② if β -ve and γ +ve 1ST order transition at $T = T_c$ i.e M changes discontinuously from zero to a finite value as T decreases.



M(T) often power law behaviour i.e $M \propto (T - T_c)^k$ for $T < T_c$. Landau case $k = \frac{1}{2}$. Real magnets, liq/vap transitions, binary fluid phase separations have $k \sim 0.33$

-> NEED TO CONSIDER FLUCTUATIONS

9) Ideal gas mixtures - consider ith gas to be ideal.

Dalton's law: $P = \sum_i p_i$ (P = total gas pressure)

Entropy: $S = \sum_i (N_i s_{0,i} + {}^ic_p \ln T - N_i k_B \ln p_i)$

Now for pure gas $S_{pure} = NS_0 + C_p \ln T - Nk_B \ln p$. Now $\sum_i N_i S_{0i} = NS_0$, $\sum_i {}^i C_p \ln T = C_p \ln T$ since all gases are ideal and $\therefore$ have ${}^i C_p = \frac{5}{2} N_i k_B T$. (or $\frac{7}{2} N k_B T$ if you allow vibration → assume low T limit particle model)

Define Entropy of Mixing as $\Delta S_{mix} = S - S_{pure}$

$$\Rightarrow \Delta S_{mix} = -k_B\left(\sum_i N_i \ln p_i - N \ln p\right) = -k_B\left(\sum_i N_i \ln p_i - \ln p \sum_i N_i\right) = -k_B \sum_i N_i \ln \frac{p_i}{p}$$

Now $p_i = N_i k_B T/V$, $p = N k_B T/V$ i.e. T, V fixed so $\frac{p_i}{p} = \frac{N_i}{N} \equiv c_i$

Now $G = G(\mu, N) = G(T, p, V, N)$; $N =$ const ; $f = f(T, p, V, N) = 0$ so if T constant ⇒ one independent variable - choose p. $\therefore dG = \left(\frac{\partial G}{\partial p}\right)_T dp$ Now let $N_i =$ constant as well

$$\Rightarrow dG_i = \left(\frac{\partial G_i}{\partial p_i}\right)_{T, N_i} dp_i \Rightarrow G_i(p_i, T) = G_i(p, T) + \int_p^{p_i} \left(\frac{\partial G_i}{\partial p_i}\right)_{T, N_i} dp_i'$$

dummy variable

Now since $dG_i = -S_i dT + V_i dp_i + \mu_i dN_i$ ($G_i = \mu_i N_i$ and Gibbs Duhem) and if $dT = dN_i = 0$

$\Rightarrow dG_i = V_i dp_i$ so $\left(\frac{\partial G_i}{\partial p_i}\right)_{T, N_i} = V_i$. Now since we can't really talk about partitioned volumes of gases since they are all mixed → let $V_i = V$. (reasonable since each gas occupies as much space as another).

$\therefore G_i(p_i, T) = G_i(p, T) + \int_p^{p_i} V dp_i'$ Now for ideal gas $V = Nk_BT/p$ and since $dp_i' = \frac{N_i}{N} dp'$

$$\Rightarrow G_i(p_i, T) = G_i(p, T) + \int_p^{p_i} \frac{dp'}{p'} \cdot N_i k_B T \Rightarrow G_i(p_i, T) = G_i(p, T) + N_i k_B T \ln c_i$$

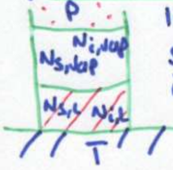
Now since $G_i = \mu_i N_i$ $\Rightarrow$ $\mu_i(p_i, T) = \mu_i(p, T) + k_B T \ln c_i$

$dG = -SdT + Vdp + \sum_i \mu_i dN_i$

* Maxwell relation for mixtures

$\therefore \mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T, p, N_{j \neq i}}$ Now since $\frac{\partial^2 G}{\partial N_i \partial N_j} = \frac{\partial^2 G}{\partial N_j \partial N_i} \Rightarrow \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T, p, N_{i \neq j}} = \left(\frac{\partial \mu_j}{\partial N_i}\right)_{T, p, N_{j \neq i}}$

10) Membrane Equilibrium and osmotic pressure



liquid vapour e.g.
S = solvent
i = solute
vap ≡ v = vapour
l = liquid

→ Assume $N_{s,l} \gg N_{i,l}$. Now at constant T, p

TWO mutual equilibriums occur

$\Rightarrow \mu_{i,l} = \mu_{i,v}$ and $\mu_{s,v} = \mu_{s,l}$ @ e.q.

Since $N_i \ll N_s$ can assume HENRY'S LAW $\Rightarrow \frac{p_i}{p} = \frac{N_{i,l}}{N_l} \Rightarrow c_{i,v} = c_{i,l}$

Want $\Delta\mu_{s,l} = \mu_{s,l}(N_{i,l}) - \mu_{s,l}(0)$ Clearly $\Delta \mu_{s,l} = \int_0^{N_i} \left(\frac{\partial \mu_{s,l}}{\partial N_{i,l}}\right)_{T, p, N_{s,l}} dN_{i,l}$ since $N_{i,l}$ independent variable.

Now using Maxwell relation above:

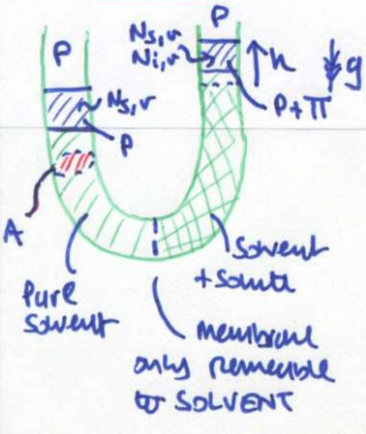
$$\left(\frac{\partial \mu_{s,l}}{\partial N_{i,l}}\right)_{T, p, N_{s,l}} = \left(\frac{\partial \mu_{i,l}}{\partial N_{s,l}}\right)_{T, p, N, N_{i,l}} = \frac{\partial}{\partial N_{s,l}}\Big[\underset{\uparrow \text{ eq condition}}{\mu_{i,v}}\Big] = \frac{\partial}{\partial N_{s,l}}\Big(\underset{\uparrow}{\mu_{i,v}(p,T)} + k_B T \ln \underset{\nwarrow\, c_{i,l} = c_{i,v}}{c_{i,l}}\Big)$$

proved above

$$= k_B T \frac{\partial}{\partial N_{s,l}} \ln\left(\frac{N_{i,l}}{N_{i,l} + N_{s,l}}\right) = \frac{-k_B T}{N_{i,l} + N_{s,l}} \quad \therefore \Delta\mu_{s,l} = -k_B T \ln\left(\frac{N_{s,l} + N_{i,l}}{N_{s,l}}\right) = k_B T \ln c_{s,l}$$

Now $c_{i,l} = 1 - c_{s,l}$ and $\ln(1 - c_{i,l}) \simeq -c_{i,l}$ since $c_{i,l} \ll 1$ (Taylor expand)

$\therefore \Delta\mu_{s,l} \simeq -k_B T c_{i,l}$ //



Now place this dilute solution next to a pure solvent separated by a solvent only permeable membrane.

→ Get extra "osmotic pressure" as a result of solvent diffusion across membrane. i.e. $\pi = \bar{\rho} g h A$. $\rho_{solvent} \simeq \rho_{dil\ solution}$.

→ At eq at the membrane: $\mu_{s,l}(T, p+\pi, c_{i,l}) = \mu_{s,l}(p, 0)$ Above ↓

Now $\mu_{s,l}(T, p+\pi, c_{i,l}) = \mu_{s,l}(T, p+\pi, 0) + \Delta\mu_{s,l} = \mu_{s,l}(T, p+\pi, 0) - k_B T c_{i,l}$

Now $\mu_{s,l}(T, p+\pi, 0) = \mu_{s,l}(T, p, 0) + \int_p^{p+\pi} \left(\frac{\partial \mu_s}{\partial p}\right)_T dp$ Now Gibbs Duhem at constant T $\Rightarrow \left(\frac{\partial \mu_s}{\partial p}\right)_T = \frac{V_{s,l}}{N_{s,l}}$

Now $V_{s,l} \simeq$ constant (well not p dependent)

$\Rightarrow \mu_{s,l}(T, p+\pi, 0) \simeq \mu_{s,l}(T, p, 0) + \frac{V_{s,l}}{N_{s,l}} \pi$ → cont....

$$\therefore \mu_{s,l}(T,P+\Pi, c_{i,l}) = \mu_{s,l}(T,P,0) + \frac{v_{s,l}\Pi}{N_{s,l}} - k_BT\left(\frac{N_{i,l}}{N_{i,l}+N_{s,l}}\right) = \mu_{s,l}(T,P,P)$$

$\Rightarrow$ $V_{s,l}\Pi \approx k_BTN_{i,l}$ $(N_{s,l} \gg N_{i,l})$

Question: Does it matter how much purse solvent we have? - In principle NO but in order to achieve hydrostatic e.q in the 1st place in the U tube we need the correct amount g solvent... (In reality this depends where the e.q point is....) → Best way is to use same volumes g solvent, solute to start with.

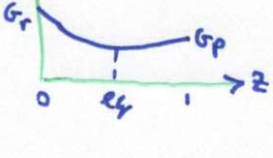
II) Chemical equilibrium g ideal gases in reactions

Consider general reaction $\sum_r v_r r \rightarrow \sum_p v_p p$ ← v = # particles

r = reactants.

p = products. At constant T, P, (N ← though not so clearly defined since many different species react though no particles leave), $dG=0$ defines e.q.

Define reaction parameter z (varying from 0-1) which yields proportion g products present and characterises the 'extent g reaction'.



$(G_r = \mu_r N_r \ldots\ldots)$

e.q when $\frac{dG}{dz} = 0$ or simply $dG=0$

Now $dG = -SdT + VdP + \sum_i \mu_i dN_i$

So at constant T, P $dG = \sum_i \mu_i dN_i$.

(Mathematically nicer if we retain dz and use $\frac{dG}{dz}=0$ @ e.q)

Now $dN_i = -v_r dz$ for $i=r$

and $dN_p = v_p dz$ $\therefore$ @ e.q $\sum_p v_p\mu_p - \sum_r v_r\mu_r = 0$

Now use $\mu_i = \mu_i(P_i,T) = \mu_i(P,T) + k_BT\ln c_i$ $\Rightarrow 0 = \sum_p v_p(\mu_p(P,T) + k_BT\ln c_p) - \sum_r v_r(\mu_r(P,T) + k_BT\ln c_r)$

$$\Rightarrow -\frac{1}{k_BT}\left(\sum_p v_p\mu_p(P,T) - \sum_r v_r\mu_r(P,T)\right) = \sum_p \ln c_p^{v_p} - \sum_r \ln c_r^{v_r}$$

$$= \ln\prod_p c_p^{v_p} - \ln\prod_r c_r^{v_r}$$. Define $K_c = \prod_p c_p^{v_p} \Big/ \prod_r c_r^{v_r}$ "Equilibrium constant"

Now $G_p = \sum_p v_p\mu_p(P,T)$, $G_r = \sum_r v_r\mu_r(P,T)$ so define $\Delta G = G_p - G_r$ $\therefore -\frac{1}{k_BT}\Delta G = \ln K_c$

Now use K_c to determine progress g reaction. Note $c_p = \frac{z v_p}{v_p} = z$ and $c_r = (1-z)\frac{v_r}{v_r}$

so $K_c = \prod_p z^{v_p} \Big/ \prod_r (1-z)^{v_r}$ (could in principle find $z(K_c)$ ...)

(II) Statistical Mechanics

1) Boltzmann Definition g Entropy.

Consider a system characterised by thermodynamic variables P, V, T, U, N, μ, S to consist g a finite # g possible energy states given energy U put into system. i.e for one MACROSTATE characterised by energy U we will have many microscopic configurations g energy arrangements i.e MICROSTATES. ⇒ U comes in discrete quanta

Consider system g n elements sharing m quanta g energy U. Divide n into SUBSYSTEM $n_s \ll n$ and RESERVOIR $n_r \sim n$. $n_r + n_s = n$.

What is probability g MACROSTATE m_s quanta in the subsystem? Well, # ways g arranging m quanta in n 'containers' $= g_n(m) = \binom{n+m-1}{m} = \frac{(m+n-1)!}{m!(n-1)!}$

Proof: $|| \times | \times\times | \times | \ldots. ||$ $g_n(m)$ = # ways g arranging | and ×.

wall ↑quanta ↑container wall

m ×'s and n-1 |'s ⇒ Binomial distribution yields $\binom{N}{R} = \frac{N!}{R!(N-R)!}$ = # ways g ~~[illegible]~~ arranging R and N-R objects g different type i.e ×, |. Hence $g_n(m) = \binom{n+m-1}{m}$ QED.

microstates for m_s quanta in subsystem $= g_{n_s}(m_s)g_{n_r}(m-m_s)$ {For every subsystem microstate there are $g_{n_r}(m-m_s)$ reservoir microstates}

$$\therefore P(m_s, n_s) = \frac{g_{n_s}(m_s)g_{n_r}(m-m_s)}{g_n(m)}$$

So consider closed system with energy U and U_s in subsystem. Since $g_n(m)$ is a macrostate → $P(U_s, U-U_s) = \frac{g_s(U_s)g_r(U-U_s)}{g(U)}$

↑ probability g U_s energy in subsystem, $U-U_s$ in reservoir

↖ slight change in notation for clarity

This of course assumes all microstates are equally likely. → Principle of Equal Equilibrium Probability (PEEP). So given U, we expect at e.g. $P(U_s, U-U_s)$ to be maximised. i.e since U_s is the only independent variable $\frac{dP}{dU_s} = 0$

$$\therefore 0 = \frac{1}{g(U)}\left[g_s(U_s)\frac{dg_r(U-U_s)}{dU_s} + g_r(U-U_s)\frac{dg_s(U_s)}{dU_s}\right] \text{ @ e.g.}$$

Now $dU_s = -d(U-U_s)$ since $dU = 0$

$$\Rightarrow \quad g_s(U_s)\frac{dg_r(U-U_s)}{d(U-U_s)} = g_r(U-U_s)\frac{dg_s(U_s)}{dU_s} \Rightarrow \frac{1}{g_r(U-U_s)}\frac{dg_r(U-U_s)}{d(U-U_s)} = \frac{1}{g_s(U_s)}\frac{dg_s(U_s)}{dU_s}$$

$$\Rightarrow \quad \frac{d\ln g_s(U_s)}{dU_s} = \frac{d\ln g_r(U-U_s)}{d(U-U_s)} \text{ @ e.g.}$$

Now at e.g $S_{total} = S_s + S_r$ is maximised. If $dV_s = dN_s = 0$ $dS_{tot} = \left(\frac{1}{T_s} - \frac{1}{T_r}\right)dU_s$ i.e, at e.g $T_s = T_r$. Now $\frac{1}{T_i} = \frac{\partial S_i}{\partial U_i}$ for any closed system i.

So if we define $S_i = k_B \ln g_i(U_i)$ (k_B just a constant to get dimensions correct) above shows at e.g $\frac{\partial S_s}{\partial U_s} = \frac{\partial S_r}{\partial U_r} \Rightarrow \frac{1}{T_s} = \frac{1}{T_r}$ i.e agrees with our thermodynamic condition.

Hence $S = k_B \ln g$ is a good definition of entropy. $g = g(U) = g_n(m\varepsilon) = \frac{(m+n-1)!}{m!(n-1)!}$ ε = energy of 1 quantum

Now if we had two systems with g_1, g_2 total entropy $= k_B \ln g_1 g_2 = k_B \ln g_1 + k_B \ln g_2$ $= S_1 + S_2$. So S is additive as we might have hoped from thermodynamics!

But what happens if PEEP is not true i.e each microstate has a particular probability due to a distribution which is not uniform? ⇒ GIBBS ENTROPY. Start with a system where $S_B = k_B \ln g$ is true. $P_i = \frac{1}{g}$ (P_i = probability of ith microstate) and $\sum P_i = 1$. $\therefore$ $S_B = -k_B \ln \frac{1}{g} = -k_B \times 1 \times \ln P_i = -k_B \sum_i P_i \ln P_i \equiv S_G$ (last step works because all $\ln P_i$'s are the same for this system) – but result is more general. i.e when P_i's not all $\frac{1}{g}$.

2) Ensembles, Boltzmann and Gibbs distributions. (i) In a MICROCANONICAL ENSEMBLE $P_i = \frac{1}{g}$ i.e, all states have same energy → Not much bearing on reality.

(ii) In a CANONICAL ENSEMBLE, ith subsystem has energy E_i out of total system energy U. Assume only one possible subsystem configuration $\therefore P_i(E_i) \propto g_r(U-E_i)$ ← reservoir or "rest of system"

$= e^{\ln g_r(U-E_i)} = \exp\left[\ln g_r(U) - E_i\frac{\partial \ln g_r(U)}{\partial U} + \ldots\right] \approx \exp\left[\ln g_r(U) - E_i/k_BT\right]$ using $S_r = k_B \ln g_r$ and $\frac{\partial S_r}{\partial U} = \frac{1}{T_r}$ $(= 1/T)$. $\therefore P_i(E_i) \propto e^{-E_i/k_BT}$ ↖ $g_r(U)$ is a constant

$$\Rightarrow \quad P_i(E_i) = \frac{e^{-E_i/k_BT}}{Z}$$

Boltzmann Distribution where PARTITION FUNCTION $Z = \sum_i e^{-E_i/k_BT}$

(iii) In a GRAND CANONICAL ENSEMBLE subsystem i has energy E_i shared amongst movable PARTICLES of # N_i which unlike the fixed "volumes" above can be transferred to the reservoir and vice versa. Let total energy be U, total # particles N.

$\therefore P(E_i, N_i) \propto e^{\ln g_r(U-E_i, N-N_i)}$ assuming degeneracy of state of subsystem $|E_i, N_i\rangle = 1$.

Now $\ln g_r(U-E_i, N-N_i) \approx \ln g_r(U,N) - E_i\left(\frac{\partial \ln g_r(U,N)}{\partial U}\right)_N - N_i\left(\frac{\partial \ln g_r(U,N)}{\partial N}\right)_U$ (Two variable Taylor expansion).

Now $S_r = k_B \ln g_r$ and use thermodynamic results $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N$ $\mu = -T\left(\frac{\partial S}{\partial N}\right)_U$

(V, constant here) $\Rightarrow \left(\frac{\partial \ln g_r(U,N)}{\partial U}\right)_N = \frac{1}{k_BT}$

$\left(\frac{\partial \ln g_r(U,N)}{\partial N}\right)_U = -\frac{\mu}{k_BT}$ $\therefore$ $P(E_i, N_i) \propto e^{-\frac{1}{k_BT}(E_i - \mu N_i)}$

⇒ GIBBS DISTRIBUTION $P(E_i, N_i) = \frac{e^{-\frac{1}{k_BT}(E_i - \mu N_i)}}{\Xi}$

→ $\Xi = \sum_N \sum_i e^{-\frac{1}{k_BT}(E_i - \mu N)}$ GRAND PARTITION FUNCTION

N, E_i independent so drop i suffix off N and Σ over.

start from Gibbs Entropy $S_G = -k_B \sum_i P_i \ln P_i$

Substitute $P_i = \frac{e^{-E_i/k_BT}}{Z}$ $\Rightarrow$ $S_G = -k_B \sum_i P_i \left(-\frac{E_i}{k_BT} - \ln Z \right)$ Now $\sum_i P_i E_i = U$ and $\sum_i P_i = 1$ $\Rightarrow$ $S_G = \frac{U}{T} + k_B \ln Z$ Now FREE ENERGY $F = U - TS$

$\Rightarrow$ $F = -k_BT \ln Z$ So if one can calculate Z one can calculate all other thermodynamic variables since $S = -(\partial F/\partial T)_V$ and $p = -(\partial F/\partial V)_T$ (So requires $Z = Z(T,V)$ in general). $\therefore$ $U = F + TS$, $\mu = \frac{U - TS + pV}{N_{i=1}}$, $G = \mu N$, $H = U + pV$

↑ N constant as well → (i.e we can use B.D)

……. Note F is free energy / particle → multiply EXTRINSIC variables by N. particle energy E_i

So if know $Z(T,V,N)$ can calculate anything!

e.g. Paramagnetic salt in uniform $\underline{B}$ field. $E_\uparrow (\parallel \underline{B}) = -mB$ $E_\downarrow = mB$. m = magnetic moment.

If N atoms with spin $\frac{1}{2}$, magnetic moment m : $N_\uparrow = \frac{Ne^{-E_\uparrow/k_BT}}{Z}$ $N_\downarrow = \frac{Ne^{-E_\downarrow/k_BT}}{Z}$

$Z = e^{mB/kT} + e^{-mB/kT} = 2\cosh\left(\frac{mB}{kT}\right)$. $\therefore$ $F = -k_BT \ln\left(2\cosh\left(\frac{mB}{kT}\right)\right)$

$\therefore$ $S = -(\partial F/\partial T)_V = k_B \ln\left(2\cosh\left(\frac{mB}{kT}\right)\right) + \frac{k_BT}{2\cosh\left(\frac{mB}{k_BT}\right)} \cdot 2\sinh\left(\frac{mB}{k_BT}\right) \cdot \left(\frac{-mB}{k_BT^2}\right)$

$\therefore$ $U = F + TS = -mB \tanh\left(\frac{mB}{k_BT}\right)$ → This is AVERAGE energy / atom.

$\Rightarrow$ $\langle m \rangle = -U/B = m \tanh\left(\frac{mB}{k_BT}\right)$ * Microscopic meaning of heat and work

$dS_G = -k_B \sum_i (dP_i \ln P_i + dP_i)$ – substitute for $P_i = \frac{e^{-E_i/k_BT}}{Z}$ and note if $\sum_i P_i = 1$ $\sum_i dP_i = 0$.

$\Rightarrow$ $dS_G = -k_B \sum_i dP_i \left(-\frac{E_i}{k_BT} - \ln Z\right) = k_B \sum_i dP_i \frac{E_i}{k_BT}$

$\therefore$ $T dS_G = \sum_i dP_i E_i$ Now if $dN = 0$ and $U = \sum_i E_i P_i \Rightarrow dU = \sum_i E_i dP_i + P_i dE_i$

$= TdS + đW$ $\therefore$ $đW = \sum_i P_i dE_i$ So.... Heat $\Rightarrow$ change in probability distribution with energy levels unchanged

Work $\Rightarrow$ shift in energy levels with probability distribution unchanged.

+) Applications of Gibbs Distribution

lart from Gibbs ~~distribution~~ Entropy $S_G = -k_B \sum_{N,i} P_{N,i} \ln P_{N,i}$. Substitute P_i for Gibbs distribution

$S_G = -k_B \sum_{N,i} P_{N,i} \left(-\frac{(E_i - \mu N)}{k_BT} - \ln \Xi \right)$ using $\sum_{N,i} P_{N,i} = 1$ and $\sum_{N,i} P_{N,i}(E_i - \mu N) = U - \mu\langle N \rangle$

$\Rightarrow$ $TS = U - \mu\langle N \rangle + k_BT \ln \Xi$. Now $\Phi = U - TS - \mu \langle N \rangle$ GRAND POTENTIAL

$\Rightarrow$ $\Phi = -k_BT \ln \Xi$ So if know $\Xi(T,V,\mu)$ can calculate anything!

N not fixed as with Z). $S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu}$ $P = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu}$ $\langle N \rangle = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}$

te here U is the average energy of $\langle N \rangle$ particles. Scale extrinsic variables by $\frac{N'}{\langle N \rangle}$ here N' is total # particles in the system. $\langle N \rangle$ is average # particles with energy l.

Fluctuations The mean square fluctuation (or variance) " $\langle \Delta x^2 \rangle$ of a thermodynamic quantity X often instructive to calculate. often this is small but can sometimes diverge at critical ts / phase transitions and $\therefore$ dominate the physics describing the situation. Define $\langle \Delta x^2 \rangle$ as:

$\Delta x^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2$. Can often use Boltzmann or Gibbs distribution to find $\langle \Delta x^2 \rangle$

with paramagnetic salt want $\langle \Delta M^2 \rangle$ where $\langle M \rangle = N\langle m \rangle$. $= Nm\tanh\left(\frac{mB}{k_BT}\right)$

$M \rangle = \frac{1}{Z} \sum_i M_i e^{M_iB/kT} = \frac{kT}{Z}\left(\frac{\partial Z}{\partial B}\right)_T$ $\langle M^2 \rangle = \frac{1}{Z} \sum_i M_i^2 e^{M_iB/k_BT} = \frac{(k_BT)^2}{Z}\left(\frac{\partial^2 Z}{\partial B^2}\right)_T$

(which is probably a quicker method of finding ⟨M⟩ than using $F=-k_BT\ln Z$).

Now $\left(\frac{\partial\langle M\rangle}{\partial B}\right)_T = \frac{-k_BT}{Z^2}\left(\frac{\partial Z}{\partial B}\right)_T^2 + \frac{k_BT}{Z}\left(\frac{\partial^2 Z}{\partial B^2}\right)_T = -\frac{\langle M\rangle^2}{k_BT} + \frac{\langle M^2\rangle}{k_BT}$ So $\langle M^2\rangle - \langle M\rangle^2 = k_BT\left(\frac{\partial\langle M\rangle}{\partial B}\right)_T = \langle\Delta M^2\rangle$

very common step!

$\therefore\ \langle\Delta M^2\rangle = \frac{Nm^2}{\cosh^2(mB/k_BT)}$ and R.M.S fluctuation $\frac{\langle\Delta M^2\rangle^{\frac12}}{\langle M\rangle} = \frac{1}{\sqrt N}\left[\sinh\left(\frac{mB}{kT}\right)\right]^{-1}$

* Availability Method consider a system within an infinite reservoir. As shown above, probability of system being characterised by macrostate x (x is a thermodynamic variable) $P(x) = N g_s(x) g_r(x)$ (In above case $x = U_s$ and $g_r(U_s) = g_r(U-U_s)$ - abbreviate to $g_r(U_s)$ and then apply constraint of constant total U)

↑ Normalisation

$= Ne^{\ln g_s(x) + \ln g_r(x)} = N\exp\left[\frac{S_s}{k_B} + \frac{S_r}{k_B}\right]$ using $S = k_B\ln g$. $\Rightarrow P(x) = Ne^{S_{tot}/k_B}$

Now $S_{tot} = S_{tot}(\langle x\rangle) + \Delta S_{tot}$ Now use result $dS_{tot} = -dA/T_r$ AVAILABILITY only concerns system variables

So $\Delta S_{tot} = -\Delta A/T_r = -\frac{1}{T_r}\left(A(x) - A(\langle x\rangle)\right)$ $\therefore\ S_{tot} = \text{const.} - A(x)/T_r$ const = $S_{tot}(\langle x\rangle) + A(\langle x\rangle)/T_r$

$\Rightarrow P(x) = N'e^{-A(x)/T_rk_B}$ (N' is modified normalisation)

Now $A(x) = A(\langle x\rangle) + \Delta x\frac{\partial A}{\partial x}\Big|_{\langle x\rangle} + \frac{\Delta x^2}{2}\frac{\partial^2 A}{\partial x^2}\Big|_{\langle x\rangle} + \ldots\ldots$ Now @ eq $\frac{\partial A}{\partial x} = 0$ i.e, at $x = \langle x\rangle$

So $A(x) \cong \langle A\rangle + \frac{\Delta x^2}{2}\frac{\partial^2 A}{\partial x^2}\Big|_{\langle x\rangle}$. Now $e^{-\langle A\rangle/k_BT_r} \simeq 1$

So $P(x) = P(\Delta x) \propto \frac{1}{\sqrt{2\pi k_BT_r\left[\left(\frac{\partial^2 A}{\partial x^2}\right)_{\langle x\rangle}\right]^{-1}}}\, e^{-\frac{\Delta x^2}{2k_BT_r}\frac{\partial^2 A}{\partial x^2}\big|_{\langle x\rangle}}$

i.e. Gaussian of general form $P(x) = \frac{1}{\sigma\sqrt{2\pi}}e^{-\Delta x^2/2\sigma^2}$ Variance $= \sigma^2 \equiv \langle\Delta x^2\rangle$

$x - \langle x\rangle = \Delta x$

$\therefore\ \langle\Delta x^2\rangle = k_BT_r\Big/\frac{\partial^2 A}{\partial x^2}\Big|_{\langle x\rangle}$ So since $A = U - T_rS + P_rV - \mu_rN$ $\Rightarrow dA = dU - T_rdS + P_rdV - \mu_rdN$ one can calculate $\langle\Delta x^2\rangle$ taking care what is fixed and what is not.

e.g. $\langle\Delta U^2\rangle_{T,V} = k_BT^2C_V$ R.M.S fluctuation $= \frac{\langle\Delta U^2\rangle^{\frac12}_{T,V}}{\langle U\rangle} = \frac{T\sqrt{k_BC_V}}{\frac32Nk_BT}$ $C_V = \frac32Nk_B$

So $\frac{\langle\Delta U^2\rangle^{\frac12}}{\langle U\rangle} = \frac{1}{\sqrt{3/2}\sqrt N}$ IDEAL GAS.

N ~ 10^{23} for 1 moles

So fluctuations v. small.

5) Fluctuation-Dissipation Theorem. Consider system described by equation in variable x $m\ddot x + \Gamma\dot x + kx = f(t)$ i.e. if x is displacement - damped, driven S.H.O. Consider an ensemble of N such systems. Now define $\alpha(\omega) = \langle x_\omega/f_\omega\rangle$ where $x_\omega = x(t)/e^{i\omega t}$ steady state resp

$\Rightarrow$ if $f(t) = f_\omega e^{i\omega t}$, $\alpha(\omega) = \frac{m(\omega_0^2-\omega^2) - i\Gamma\omega}{m^2(\omega_0^2-\omega^2)^2 + \Gamma^2\omega^2}$ $\omega = \sqrt{\frac{k}{m}}$

Now any fluctuating system can be represented as a damped S.H.O with a random force f(t). So consider fluctuating system to be an N member ensemble of such SHO's.

jth member has $\langle x^2\rangle_j = \frac{1}{\theta}\int_{-\theta/2}^{\theta/2}dt\,x_j^2(t)$ ~ observation time - long. using F.T of $x(t)$, $x(\omega_n)$ can show , and $x(t) = \frac{1}{\theta}\sum_{-\infty}^{\infty}x(\omega_n)e^{i\omega_nt}$ $\omega_n = \frac{2\pi n}{\theta}$

$\langle x^2\rangle_j = \frac{1}{\theta^2}\sum_n|x_j(\omega_n)|^2 \Rightarrow \langle x^2\rangle = \frac{1}{\theta^2}\sum_n\langle|x(\omega_n)|^2\rangle$ averaging over ensemble. Since $\langle|x(\omega_n)|^2\rangle$ varies slowly on the scale of $\Delta\omega = 2\pi/\theta$ $\Rightarrow \langle x^2\rangle = \frac{1}{\theta}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\langle|x(\omega)|^2\rangle$ Now $\langle|x(\omega)|^2\rangle = |\alpha(\omega)|^2\langle|f_n(\omega)|^2\rangle$

So using $\alpha(\omega)$ can show $\langle x^2\rangle = \frac{\langle|f_n(\omega_0)|^2\rangle}{\theta}\frac{1}{2\Gamma k}$

Now by equipartition $\frac{1}{2}k\langle x^2\rangle = \frac{1}{2}k_BT$ $\therefore$ $\frac{2}{\Theta}\langle|f_n(\omega_0)|^2\rangle = 4\Gamma k_BT$

$\approx \frac{2}{\Theta}\langle|f_n(\omega)|^2\rangle$ { $f_n(\omega_0)$ was used instead of $f_n(\omega)$ to bring it out of an integral where it was deemed not to vary much }

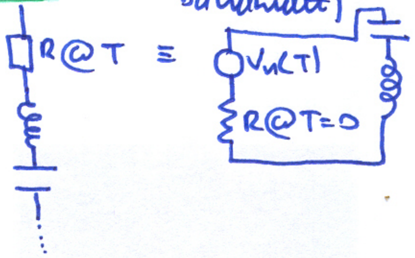
$\therefore \frac{2}{\Theta}\langle|x(\omega)|^2\rangle = 4\Gamma k_BT\,|\alpha(\omega)|^2$ = Power spectrum of x $C_x(\omega)$.

$$\therefore \langle x^2\rangle = \int_0^\infty d\omega\, 4\Gamma k_BT|\alpha(\omega)|^2$$ (or over a finite interval if limited bandwidth)

i.e. for noise voltage in circuits (LRC)

$\Gamma|\alpha(\omega)|^2 = R$

So $C_V(\omega) = 4k_BTR$



"Johnson Noise"

6) Classical and not so classical gases – Statistical Mechanics of continuous systems

The Quantum states of an ideal gas are the 'particle in a 3D box' solutions to Schrödinger's equation. If the box has dimensions L_x, L_y, L_z (i.e. rectangular)

$\psi = \psi_0\sin(k_xx)\sin(k_yy)\sin(k_zz)$ where since $\psi=0$ at $x=y=z=0$ and at walls

$k_x = \frac{\pi n}{L_x}$ etc.... Allowed values of k form a lattice in k space with volume / point $= \frac{\pi^3}{L_xL_yL_z} = \frac{\pi^3}{V}$. Hence # states / unit volume of k space is $\frac{V}{\pi^3}$

$\uparrow$ integer

– we must also multiply by any spin degeneracy $\sigma = 2s+1$ where s = spin of gas particle.

Hence any sums over states of the particle can be written as a k space integral

i.e. $\sum_{k,\text{spin}} D f(\varepsilon_k) \longrightarrow \frac{\sigma V}{8\pi^3}\int_0^\infty f(\varepsilon_k)\,k^2\,dk.4\pi$ i.e. $D(k) = \frac{\sigma V}{2\pi^2}k^2dk$

degeneracy of state k

energy of state k

volume of k space shell

$\uparrow$ +ve octant only

More useful to use energy as variable. use $\varepsilon_k = \frac{\hbar^2k^2}{2m}$ for particle of mass m.

$\Rightarrow \int_0^\infty f(\varepsilon)D(\varepsilon)d\varepsilon = \frac{\sigma V}{4\pi^2}\left(\frac{2\pi}{\hbar}\right)^{3/2}\int_0^\infty f(\varepsilon)\sqrt{\varepsilon}\,d\varepsilon$ so $D(\varepsilon) = \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar}\right)^{3/2}\sqrt{\varepsilon}$

Note
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Now for 1 ideal gas particle can use partition function to find u, S

$Z = \sum_{k,\text{spin}} D(\varepsilon_k)f(\varepsilon_k)$ where $f(\varepsilon_k) = e^{-\varepsilon_k/k_BT}$ $\Rightarrow Z = \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty e^{-\varepsilon/kT}\sqrt{\varepsilon}\,d\varepsilon$

using $\varepsilon/kT = x^2$ substitution $Z = \sigma V\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} = \sigma V n_Q(T)$ ⇐ QUANTUM CONCENTRATI

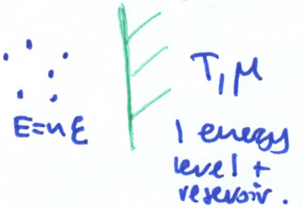
Now $u = \sum_k \frac{\varepsilon_k e^{-\varepsilon_k/kT}}{Z} = -\frac{\partial Z}{\partial(1/k_BT)}\cdot\frac{1}{Z} = \frac{3}{2}\left(\frac{1}{k_BT}\right)^{-5/2}\left(\frac{1}{k_BT}\right)^{3/2} = \frac{3}{2}k_BT$ as expected

and $S = -\left(\frac{\partial F}{\partial T}\right)_V = -\frac{\partial}{\partial T}(-k_BT\ln Z) = k_B\ln Z + \frac{k_BT}{Z}\cdot\frac{3}{2}\sigma V\left(\frac{mk_B}{2\pi\hbar^2}\right)^{3/2}T^{\frac{1}{2}}$

$= k_B\ln Z + \frac{3}{2}k_B = k_B\ln Z + k_B\ln e^{3/2} \Rightarrow S = k_B\ln\left\{\exp(3/2)\,\sigma V\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}\right\}$

This DOES NOT scale up to N particles. Need to consider what states are distinct – quantum symmetry etc.... → consider occupation # of each energy level of the ENTIRE gas $f(\varepsilon)$ to be n particles and energy $E = n\varepsilon$.

Since n, E can vary use Ξ, Φ to describe system.



$\Xi = \sum_{n=0}^{\infty}\left(e^{-(\varepsilon-\mu)/kT}\right)^n$ Now for BOSONS $n = 0,1,2,\ldots\infty$ and for FERMIONS $n = 0,1$

So $\Xi_B = \sum_{n=0}^{\infty}\left(e^{-(\varepsilon-\mu)/kT}\right)^n = \frac{1}{1-e^{-(\varepsilon-\mu)/kT}}$ $\Xi_F = 1 + e^{-(\varepsilon-\mu)/kT}$

$\uparrow$ geometric progression.

∴ BOSE – EINSTEIN distribution is $P_B(n) = \frac{e^{-\frac{1}{kT}(n\varepsilon - n\mu)}}{\Xi_B}$ $n = 0, 1, \ldots \infty$

and FERMI – DIRAC distribution is

$P_F(n) = \frac{e^{-\frac{1}{kT}(n\varepsilon - n\mu)}}{\Xi_F}$ $n = 0, 1.$ Average occupancy is $\sum_n nP(n) = \begin{cases} \text{B.E} & \frac{1}{e^{\frac{1}{kT}(\varepsilon-\mu)}-1} \\ \text{F.D} & \frac{1}{e^{\frac{1}{kT}(\varepsilon-\mu)}+1} \end{cases}$

(Trick: for B.E $\sum_n nP(n) = \frac{1}{\Xi} k_BT \frac{\partial \Xi}{\partial \mu}$)

Now in classical regime probability of double occupancy becomes v. rare – in fact one would expect $\langle n \rangle \ll 1$. In this case B.E and F.D yield the same result of $\langle n \rangle_{classical} \propto e^{-\frac{1}{kT}(\varepsilon-\mu)}$. For this to be correct $\mu_{classical}$ must be large and -ve. Now since $n>1$ terms yield tiny contributions to $\Xi_{classical}$ ⇒ $\Xi_{classical} = 1 + e^{-\frac{1}{kT}(\varepsilon-\mu)}$

↖ small term. i.e F.D Ξ.

∴ $\Phi(\varepsilon) = -k_BT \ln \Xi_c \cong -k_BT e^{-\frac{1}{kT}(\varepsilon-\mu)}$

∴ overall grand potential of gas is $\Phi_g = \int_0^\infty \Phi(\varepsilon) D(\varepsilon) d\varepsilon = -k_BT \sigma V n_Q(T) e^{\frac{1}{kT}\mu}$

v. handy. $N = -\left(\partial \Phi_g / \partial \mu\right)_{T,V} = \sigma V n_Q(T) e^{\mu/kT}$ ⇒ $\mu = k_BT \ln\left(\frac{N}{\sigma V n_Q(T)}\right)$

* Substitute μ into $n(\varepsilon)D(\varepsilon)d\varepsilon$ get Maxwell Boltzmann distribution

$\langle n \rangle_{classical}$

* Sub. into Φ_g get $\Phi_g = -Nk_BT.$ * Sub into $p = -\left(\partial \Phi_g / \partial V\right)_{T,\mu}$ ⇒ $p = \frac{Nk_BT}{V}$

* ⇒ $\Phi = -pV$ (GENERAL RESULT) * $S = -\left(\partial \Phi / \partial T\right)_{\mu,V} = k_BN \ln\left\{\exp\left(\frac{5}{2}\right) \frac{\sigma V}{N} n_Q(T)\right\}$

i.e Sackur – Tetrode Equation.

* The expression for μ has other uses. 1 particle partition function $Z_1 = \sigma V n_Q(T)$ for ideal gas. ∴ since $\mu = k_BT \ln(N \div \sigma V n_Q(T)) = k_BT(\ln N - \ln \sigma V n_Q(T))$

⇒ $\mu = k_BT(\ln N - \ln Z_1)$ This in fact is a general result when ε_k has rotational, gravitational and other terms. Now equilibrium constant $k_c = \frac{\prod_p (N_p/N)^{\nu_p}}{\prod_r (N_r/N)^{\nu_r}}$

Define $k_N = \frac{\prod_p N_p^{\nu_p}}{\prod_r N_r^{\nu_r}}$ $\left(k_c = \frac{\prod_p N^{-\nu_p}}{\prod_r N^{-\nu_r}} k_N \right)$ At eq $\sum_p \nu_p \mu_p - \sum_r \nu_r \mu_r = 0$

→ substitute for μ_p, μ_r ⇒ $N_p = Z_{1,p}$ @ eq. ∴ $k_N = \frac{\prod_p Z_p^{\nu_p}}{\prod_r Z_r^{\nu_r}}$ — Work out Z_1 for each species → k_N.

7) Classical ⇔ Quantum crossover

In classical limit particle energy $\varepsilon \sim k_BT$. Now $\varepsilon = \hbar^2 k^2 / 2m$ so max k at T is $k_{max} \sim \sqrt{\frac{2mk_BT}{\hbar^2}}$ ∴ minimum wave packet size to make particle $\sim \frac{2\pi}{k_{max}} \sim \sqrt{\frac{h^2}{2mk_BT}} = \lambda_{thermal}$ (Thermal De Broglie wavelength) wave packets overlap if $V < N\lambda^3_{thermal}$ ↖

i.e $\frac{N}{V} > \lambda^{-3}_{thermal} = \left(\frac{2mk_BT}{h^2}\right)^{3/2} = \left(\frac{mk_BT}{2\pi \frac{h^2}{4\pi^2} \pi}\right)^{3/2} = \pi^{-\frac{3}{2}} n_Q \sim n_Q$. So QUANTUM if $\frac{N}{V} > n_Q$

8) Ideal Bose-Einstein Gases

* Black Body radiation – Photons. Photons are non self interacting so achieve eq in a Black Body cavity by being absorbed and re-radiated by the walls. ⇒ N not constant. However, @ eq $\left(\frac{\partial F}{\partial N}\right)_{T,V} = 0$ Now $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$ so $\mu = 0$ for Black body radiation. (Hmm.... dF=0 @ eq when T, V, N fixed.....)

∴ $n(\varepsilon) = \frac{1}{e^{\varepsilon/kT}-1}$ Now $\varepsilon = \hbar\omega$, $\omega = ck$, $\sigma = 2$ (2 polarisations) for photons so $D(\omega) = \frac{\sigma V}{8\pi^3} 4\pi k^2 dk = \frac{V}{\pi^2 c^3} \omega^2 d\omega$

∴ energy density $u(\omega) = \hbar\omega n(\omega) D(\omega) = \frac{V}{\pi^2 c^3} \frac{\hbar\omega^3}{e^{\hbar\omega/kT}-1} d\omega$

↑ energy / angular frequency

PLANCK RADIATION LAW

Number density $= \frac{u(\omega)}{\hbar\omega}$ varies strongly with T → Predicts $\int_0^\infty \frac{u(\omega)}{\hbar\omega} =$ @ T=0 ... ok for photons but N is fixed for atoms ≠

* Bose Einstein condensation For a gas of B.E atoms $N = \int_0^\infty n(\varepsilon) D(\varepsilon) = \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\sqrt{\varepsilon}}{e^{\frac{\varepsilon-\mu}{kT}}-1} d\varepsilon$

N is a fixed quantity, hence problem at $T=0$.

Rectify this by asserting below a certain temperature T_0, atoms start to fill up in ground state s.t at $T=0^+$ $\langle n\rangle \equiv n(\varepsilon) = n(0) = \frac{1}{e^{\frac{\varepsilon-\mu}{kT}}-1} = N \Rightarrow N = \frac{1}{e^{-\mu/kT}-1}$ ↙ No need for integral DISCRETE distribut

Now μ/kT small so that $e^{-\mu/kT} \sim 1$ to get N to be macroscopically large $(\sim 10^{23})$

$e^{-\mu/kT} = 1 - \mu/kT + \frac{1}{2}(\mu/kT)^2 + \ldots$ Hence since $\frac{\mu}{kT}$ small $e^{-\mu/kT} - 1 \simeq -\mu/kT$

$\therefore N \simeq -k_BT/\mu$ in this limit $\Rightarrow \mu \simeq -k_BT/N$

So: At $T < T_0$ $N - N'$ atoms in $\varepsilon = 0$ state " Bose Einstein condensate " and N' in excited states with B.E occupation #. These excited atoms have $\mu \simeq -k_BT/N$. (Purpose of retaining T in analysis above. Assume $T_0 \sim 0$ K). i.e since N is large and k_B small and T small $\mu = 0$ to v. good approximation.

$\therefore N' = \frac{\sigma V}{4\pi^2}\left(\frac{2mk_BT}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\sqrt{x}}{e^x-1}dx$ [set $\frac{\varepsilon}{kT} = x$] $\equiv N\left(\frac{T}{T_0}\right)^{3/2}$ use this to DEFINE T_0

i.e at $T = T_0$ $N' = 0$ and condensate dissapears, $T=0$ $N'=0$.

$T_0 = \frac{2\pi\hbar^2}{mk_B}\left(\frac{N}{2{\cdot}612\,\sigma V}\right)^{2/3}$ (~3K for ^{4}He at liq. He densities).

Below T_0 (i.e $\mu = 0$) we can calculate $U = \int_0^\infty \varepsilon\, n(\varepsilon) D(\varepsilon) d\varepsilon = \text{const.}\, T^{5/2}$

$\Rightarrow$ specific heat $C_V(T) = \left(\frac{\partial U}{\partial T}\right)_V \propto T^{3/2}$

9) Ideal Fermi Gas At $T=0$ $n(\varepsilon) = 1$ $\forall\, \varepsilon$ upto a particular value limited by N.

i.e $1 = \frac{1}{e^{\frac{\varepsilon-\mu}{kT}}+1}$ when $T=0$ For $\varepsilon > \mu(T=0)$ $n(\varepsilon) = 0$ since $\varepsilon - \mu$ becomes +ve.

Clearly μ is +ve since ε=μ yields $n(\varepsilon) = 1$ and $\varepsilon > 0$.

So if $n(\varepsilon) = \begin{cases} 1 & \varepsilon < \mu(0) \\ 0 & \varepsilon > \mu(0) \end{cases}$ ↙ FERMI ENERGY

↙ k_F corresponds to $\varepsilon_F = \mu(0) = \frac{\hbar^2 k_F^2}{2m}$ //

$\Rightarrow N = \frac{\sigma V}{8\pi^3}\int_0^\infty 4\pi k^2 n(\varepsilon) dk = \frac{\sigma V}{2\pi^2}\int_0^{k_F} k^2 dk = \frac{\sigma V}{6\pi^2} k_F^3$ $k_F = \left(\frac{6\pi^2 N}{\sigma V}\right)^{\frac{1}{3}}$ FERMI WAVEVECTOR

characteristic temperature is $T_F = \varepsilon_F/k_B$ ~ 50,000 K for metals.

Fermi gas $(T \ll T_F)$ has thermodynamic properties calculable from $\Phi(\varepsilon) = -k_BT \ln \Xi_{FD}$

$\Rightarrow \Phi_g = \int_0^\infty -k_BT\ln\left(1 + e^{-\frac{1}{kT}(\varepsilon-\mu)}\right) D(\varepsilon) d\varepsilon$ Turns out in the limit $T \ll T_F$ integrals of form

$\int_0^\infty \frac{f(\varepsilon)d\varepsilon}{e^{\beta(\varepsilon-\mu)}+1} \simeq \int_0^{\varepsilon_F} f(\varepsilon)d\varepsilon + \frac{\pi^2}{6}k_B^2T^2 f'(\varepsilon_F)$ $\Phi_g = -\frac{2}{3}\frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{3/2}}{e^{\frac{1}{kT}(\varepsilon-\mu)}+1} d\varepsilon$

$\beta = \frac{1}{kT}$

So $\Phi_g = -\frac{2}{3}\frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(\frac{5}{2}\varepsilon_F^{5/2} + \frac{\pi^2}{6}k_B^2T^2 \cdot \frac{3}{2}\varepsilon_F^{\frac{1}{2}}\right)$

$\therefore S = -\left(\partial \Phi_g/\partial T\right)_{\mu,V} = \frac{\pi^2}{3} D(\varepsilon_F) k_B^2 T$ (electrons $\sigma = 2$)

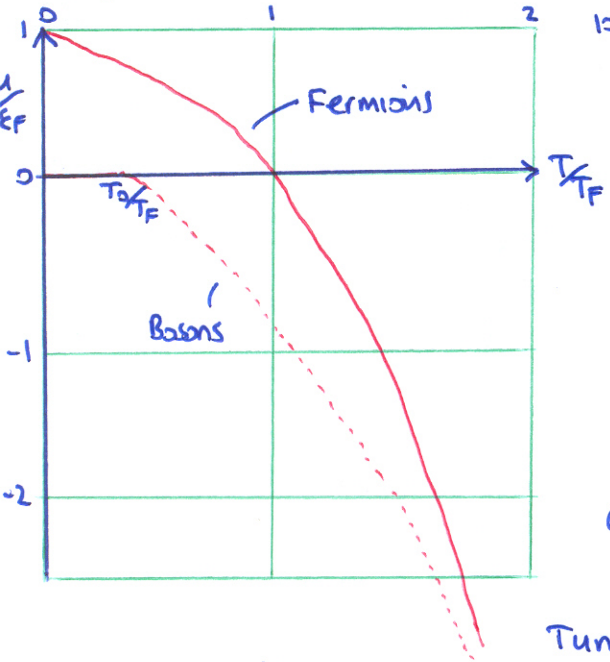
and $C_V = T\left(\partial S/\partial T\right)_V = \frac{\pi^2}{3} D(\varepsilon_F) k_B^2 T$ So $C_V \propto T$ $D(\varepsilon_F) = \frac{\sigma V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon_F}$

*Entropy of a Fermi Gas is $S = -k_B \sum_n P_n \ln P_n$ for energy level k.

Now level is either occupied with probability $\langle n_k\rangle$ or empty with probability $\frac{1-\langle n_k\rangle}{1}$

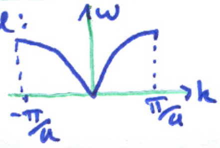
$\Rightarrow S = -k_B \sum_k \left\{\langle n_k\rangle \ln\langle n_k\rangle + (1-\langle n_k\rangle)\ln(1-\langle n_k\rangle)\right\}$

An informative plot that summarises much of the above is μ/E_F vs T/T_F



10) Interacting Many particle systems

If a system has NORMAL MODES can treat as non interacting system with energy states of energy $\hbar\omega$. i.e. an ideal gas of PHONONS. At low temperature phonons have similar dispersion relation to photons i.e. $\omega = c_{sound} k$. Actual dispersion relation is more like:



a = lattice parameter of solid producing normal modes.

* Debye Theory – treat as $\omega = ck$ but truncate integral over states to ω_D where $3N = \int_0^{\omega_D} n(\omega) D(\omega) d\omega$ Defines ω_D.

(N = # atoms – 3 D.O.F).

$\therefore U = \int_0^{\omega_D} \hbar\omega\, n(\omega) D(\omega) d\omega$ $n(\omega)$ is B.E distribution with $\mu = 0$

(can $\approx$ integral to ∞ since integrand dies away with ω rapidly)

Turns out at low T phonons behave like photons i.e. have $U \propto T^4$ and $C_V \propto T^3$.

* Quantum systems ($N/V \sim n_Q$) sometimes benefit from this normal mode approach but often not. i.e. high temp superconductors etc....

* Classical liquids (i.e. classical gases with strong interactions) No normal modes so need different approach.

Define VIRIAL $\mathcal{V} = -\frac{1}{2}\sum_i \underline{f}_i \cdot \underline{r}_i$ i corresponds to ith particle in the liquid.

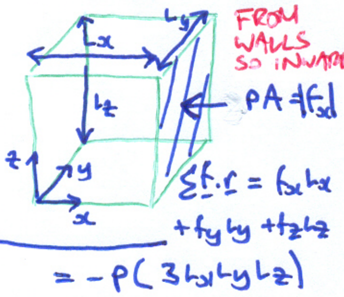
Now $\sum_i \underline{f}_i \cdot \underline{r}_i = \sum_i m \frac{d\underline{v}_i}{dt} \cdot \underline{r}_i = \sum_i m \frac{d}{dt}(\underline{v}_i \cdot \underline{r}_i) - \sum_i m v_i^2$ $\Leftarrow \frac{d\underline{r}_i}{dt} \cdot \underline{v}_i = \underline{v}_i \cdot \underline{v}_i = v_i^2$

So $\langle \mathcal{V} \rangle = -\frac{1}{2} m \langle \sum_i \underbrace{\frac{d}{dt}(\underline{v}_i \cdot \underline{r}_i)}_{=0} \rangle + \frac{1}{2}\sum_i m\langle v_i^2 \rangle = \frac{1}{2}\sum_i m \langle v_i^2 \rangle = \frac{3}{2} N k_B T$ using equipartition.

Now can also write $\langle \mathcal{V} \rangle = \langle \mathcal{V}_{int} \rangle + \langle \mathcal{V}_{ext} \rangle$ – collisions with walls containing liquid

– due to inter-particle interactions

$\langle \mathcal{V}_{ext} \rangle = -\frac{1}{2}\langle \sum \underline{f} \cdot \underline{r} \rangle_{walls} = \frac{3}{2} pV$ $\therefore \langle \sum \underline{f} \cdot \underline{r} \rangle_{walls} = -3pV$



$\sum \underline{f} \cdot \underline{r} = f_x L_x + f_y L_y + f_z L_z = -p(3 L_x L_y L_z)$

Now if inter particle potential is ϕ $\mathcal{V}_{12} = -\frac{1}{2}\underline{f}_{12} \cdot \Delta\underline{r} = \frac{1}{2}\frac{d\phi}{dr} r$ if $\underline{r}_1 = 0$, $\underline{r}_2 = \underline{r}$

$\Rightarrow \langle \mathcal{V}_{int} \rangle$ = Sum of virials due to interaction of 1 with all the other particles. Note # of particles at a distance r from the origin is $4\pi r^2 dr\, n\, g(r)$ (n is density). $g(r)$ is Radial Distribution Function – probability that two particles are separated by distance r.

↓ multiply by N particles in liquid – each interacts with all the others.

$$\Rightarrow \langle \mathcal{V}_{int} \rangle = \frac{N}{2}\int_0^\infty \frac{d\phi}{dr} r^3 . 4\pi n g(r) dr$$

$$\therefore \langle \mathcal{V} \rangle = \frac{3}{2} pV + 2Nn \int_0^\infty r^3 \pi \frac{d\phi}{dr} g(r) dr$$

$$\Rightarrow p = nk_B T - \frac{n^2}{6}\int_0^\infty 4\pi r^3 \frac{d\phi}{dr} g(r) dr$$

GENERAL EQUATION OF STATE

⇐ use $\langle \mathcal{V} \rangle = \frac{3}{2} N k_B T$, $n = N/V$

Now in low density limit $g(r) \cong e^{-\phi/k_B T}$ (This is correctly normalised)

can write p in terms of a VIRIAL EXPANSION $\frac{p}{k_B T} = n + B_2(T) n^2 + B_3(T) n^3 + \ldots\ldots$ Virial expansion in terms of density

for $g(r) = e^{-\phi/kT}$ integration by parts $\Rightarrow$ $B_2(T) = \int_0^\infty 2\pi r^2 (1 - e^{-\phi/kT}) dr$

$B_3(T)$ (and higher) $= 0$. So generate equation of state by using a model like the 6-12 potential $\phi(r) = 4\varepsilon\left(\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right)$. Now if we define P_0, n_0, T_0 as characteristic pressures, densities and temperatures for each material (i.e. boiling point etc) and define dimensionless variables by (e.g) $p' p_0 = p$ $\Rightarrow$ eq. of state remains unchanged but related to the dimensionless variables i.e. is universal. → so solve for p' etc and find $p = p_0 p'$ | know two boiling points and density characteristics → can find critical pressures

LAW OF CORRESPONDING STATES