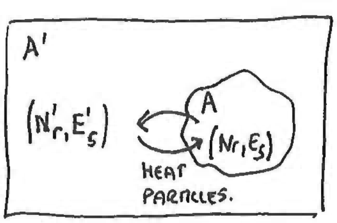
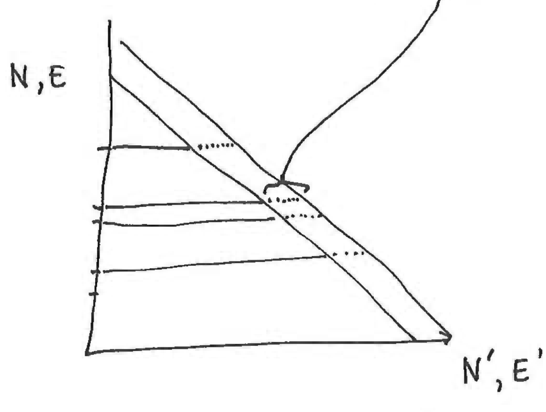
4. GRAND CANONICAL ENSEMBLE

We made the transition from the micro-canonical, to the canonical ensemble by considering a system in equilibrium with a heat bath. It proves very useful to extend the concept of a canonical ensemble to also incorporate a "particle bath", with which particles are exchanged in equilibrium. Just as the canonical ensemble introduced a Lagrange multiplier conjugate to energy $\left(\beta = \frac{1}{k_B T}\right)$, in the Grand Canonical ensemble, there is an additional Lagrange multiplier, the <u>chemical potential</u> μ, associated with particle number exchange.



$P_r \propto \Omega(N^0 - N_r, E^0 - E_s)$



$$N_r + N_r' = N^0$$
$$E_s + E_s' = E^0$$

$$P_r \propto \exp\left[\ln \Omega(N^0 - N_r, E^0 - E_s)\right]$$

$$\left.\begin{aligned} \hat{H}\,|r,s\rangle &= E_r\,|r,s\rangle \\ \hat{N}\,|r,s\rangle &= N_s\,|r,s\rangle \end{aligned}\right\}$$

$$\ln \Omega(N^0 - N_r, E^0 - E_s) = \ln \Omega'(N^0, E^0) - N_r\left(\frac{\partial \ln \Omega'}{\partial N'}\right) - E_s\left(\frac{\partial \ln \Omega'}{\partial E'}\right) + \ldots$$

$$\simeq \ln \Omega'(N^0, E^0) - \alpha N_r - \beta E_s$$

$$dE = TdS + \mu dN - PdV$$

$$dS = \frac{dE}{T} - \frac{\mu}{T} dN + \frac{P dV}{T}$$

$$\frac{dS}{k_B} = d\ln\Omega = \frac{dE}{k_BT} - \frac{\mu dN}{k_BT} + \frac{P}{k_BT} dV$$

$$\Rightarrow \quad \alpha = \frac{\partial \ln \Omega}{\partial N} = \frac{-\mu}{k_BT} = -\beta\mu; \quad \beta = \frac{\partial \ln\Omega}{\partial E} = \frac{1}{k_BT} \equiv \beta.$$

$$p_r \propto e^{-\alpha N_r - \beta E_s} \equiv e^{-\beta(E_r - \mu N_s)}$$

Normalizing

$$\boxed{p_r = \frac{e^{-\beta(E_r - \mu N_s)}}{\sum_{r,s} e^{-\beta(E_r - \mu N_s)}}}$$

$$Z = \sum e^{-\beta(E_r - \mu N_r)} \quad \text{"GRAND PARTITION FN"}$$

$$F = -k_BT \ln Z \quad \text{"GRAND POTENTIAL"}$$

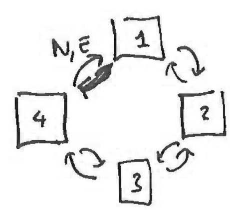
- Now the summation is over the many particle Hilbert space involving states with $N_r = 0, 1, 2 \ldots 10^{23}\ldots$ particles. (Fock space)

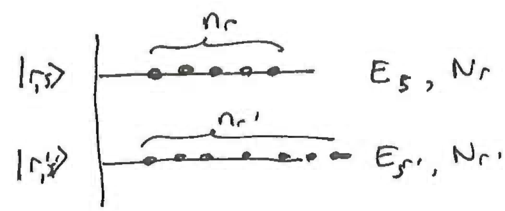
Alternative derivation: Ensemble of $\mathcal{N}$ identical systems

$\sum_{r,s} n_{rs} = \mathcal{N}$ # of systems in ensemble

$\sum N_r n_r = \bar{N}\mathcal{N}$ $\bar{N}$ = avge # of particles in each system

$\sum E_s n_s = \bar{E}\mathcal{N}$ $\bar{E}$ = avge energy of each system





$$W[\{n\}] = \frac{\mathcal{N}!}{\prod_r n_r!} \qquad \ln W = N \ln \frac{N}{e} - \sum_r n_r \ln \frac{n_r}{e}$$

Method of Lagrange multipliers

$$\ln W + \alpha \sum n_r N_r + \beta \sum n_r E_r + \gamma \sum n_r = \mathcal{L}$$

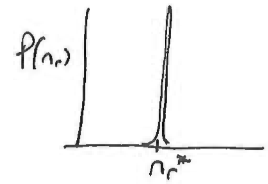
$$\delta \mathcal{L} = \sum \delta n_r \left\{ - \ln n_r + \alpha N_r + \beta E_r + \gamma \right\} = 0$$

$$\Rightarrow \boxed{n_r^* = e^{-\gamma - \alpha N_r - \beta E_r}}$$

$$p_r = \frac{n_r^*}{\mathcal{N}} \propto e^{-\beta E_r - \alpha N_r} \qquad p_{rs} = \frac{e^{-\beta E_s - \alpha N_r}}{Z}$$

$$Z = \sum_{r,s} e^{-\beta E_s - \alpha N_r}.$$

In the limit $N \to \infty$ $\quad \dfrac{\overline{\delta n_r^2}}{\overline{n_r}^2} \sim O\left(\dfrac{1}{N}\right)$



$$\frac{\langle n_{rs} \rangle}{N} = p_r = \frac{e^{-\beta(E_s) - \alpha N_r}}{Z}.$$

—

<u>Interpretation of α, β & partition function</u>

$$\frac{\mathcal{S}}{N} = S = \sum -k_B\, p_{rs} \ln p_{rs}$$

$$= -k_B \sum p_{rs}\left(-\beta E_s - \alpha N_r - \ln Z\right)$$

$$= k_B \beta \sum p_{rs} E_s + \alpha k_B \sum p_{rs} N_r + k_B \ln Z$$

$$= k_B \beta\, E + \alpha k_B N + k_B \ln Z$$

But from thermodynamics

$$F = E - TS - \mu N \iff S = \frac{E}{T} - \frac{\mu}{T} N - \frac{F}{T}$$

Comparing

$$\boxed{\begin{aligned} k_B\beta &= \frac{1}{T} \quad \Rightarrow \quad \beta = \frac{1}{k_B T} \\ k_B\alpha &= -\frac{\mu}{T} \quad \Rightarrow \quad \alpha = -\mu\beta \\ F &= -k_B T \ln Z \end{aligned}}$$

$$\bar{N} = \sum p_{rs} N_r = -\frac{\partial}{\partial \alpha} \ln \mathcal{Z}$$

$$\bar{E} = \sum p_{rs} E_s = -\frac{\partial}{\partial \beta} \ln \mathcal{Z} .$$

Also, since
$$dF = d(E - TS - \mu N)$$
$$= -S dT - N d\mu - P dV .$$

$$-\frac{\partial F}{\partial T} = -\frac{\partial}{\partial T}\left(-k_B T \ln \mathcal{Z}\right) = +S$$

$$-\frac{\partial F}{\partial \mu} = N$$

Also $\quad F = F(T, \mu, V)$

Since F is extensive in V $\quad F = V f(T, \mu)$

$$P = -\frac{\partial F}{\partial V} = -f(T, \mu) \Rightarrow f = -P$$

$$\boxed{F = -PV} \qquad P = -F/V .$$

4.4. CLASSICAL GAS IN THE G.C.E

$$\left.\begin{aligned} Q_N &= \frac{1}{N!}\left[Q_1(V,T)\right]^N \quad \text{in the G.E} \\ Q_1 &= V f(T) \end{aligned}\right\}$$

$$f(T) = \int \frac{d^3p}{h^3}\, e^{-\beta\epsilon(p)} = \begin{cases} \dfrac{1}{\lambda_T^3} = \left(\dfrac{2\pi m k_B T}{h^2}\right)^{3/2} & \text{Non relativistic} \\[2ex] \dfrac{1}{\lambda_a^3} = \left(\dfrac{(8\pi)}{(\beta c h)^3}\right) & \text{Relativistic} \end{cases}$$

$$\mathcal{Z} = \sum z^N Q_N \qquad z = e^{\beta\mu} = e^{-\alpha}$$

$$= \sum \frac{1}{N!}(Vzf)^N = \exp\left[Vzf\right]$$

$$F = -k_B T \ln \mathcal{Z} = -Vz(k_B T) f(T)$$

$$F = V\Phi(\mu,T) \qquad -\partial F/\partial V = P \Rightarrow \quad F = -PV$$

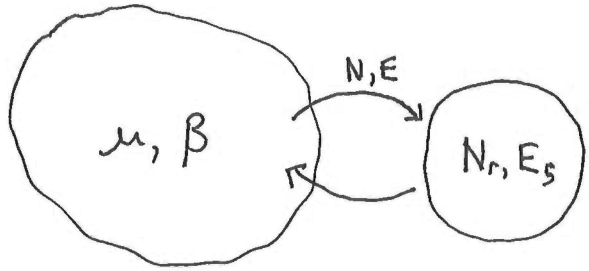
$$P = z k_B T f(T)$$

$$N = \frac{-\partial F}{\partial \mu} = Vz f(T)$$

$$U = -\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_\alpha = -\frac{\partial}{\partial \beta}\left(zVf\right)_z = z k_B T^2 \frac{\partial}{\partial T}(Vf) = zV k_B T^2 f'(T)$$

$$S = \frac{1}{T}\left(U - F + \mu N\right) = -N k_B \ln z + z k_B V\left[f + Tf'\right]$$

4.5 DENSITY AND ENERGY FLUCTUATIONS



FLUCTUATIONS IN ENERGY + PARTICLE NUMBER.

$$\begin{cases} \langle \delta E^2 \rangle = k_B T^2 C_{V,\alpha} \\ \langle \delta N^2 \rangle = k_B T \left(\frac{dN}{d\mu} \right) \end{cases}$$

$$\boxed{p_{rs} = \frac{e^{-(\alpha N_r + \beta E_s)}}{\sum_{r,s} e^{-(\alpha N_r + \beta E_s)}}}$$

$$\bar{E} = \sum E_s p_{rs}$$

Before
$$-\frac{\partial \bar{E}}{\partial \beta}\bigg)_{\alpha, V} = \sum p_{rs} E_s^2 - \left(\sum E_s p_{rs} \right)^2 = \langle \delta E^2 \rangle$$

$$= k_B T^2 \frac{\overset{C_{V,\alpha}}{\partial \bar{E}}}{\partial T} = C_{V,\alpha} k_B T^2$$

$$\Rightarrow \boxed{\langle \delta E^2 \rangle = C_{V,\alpha} k_B T^2}$$

Now
$$-\frac{\partial \bar{N}}{\partial \alpha}\bigg)_{T,V} = \langle \delta N^2 \rangle = k_B T \frac{\overset{\chi_N}{\partial \bar{N}}}{\partial \mu}\bigg)_{T,V}.$$

$\alpha = -\beta\mu \quad d\alpha = -d\mu / k_B T$

$$\Rightarrow \boxed{\langle \delta N^2 \rangle = k_B T \chi_N} \qquad O(N)$$

$$\boxed{\frac{\langle \delta N^2 \rangle}{\langle N \rangle^2} = \frac{k_B T}{\langle N \rangle^2} \chi_N} \; ; \quad \chi_N = \frac{\partial N}{\partial \mu} = \frac{\langle \delta N^2 \rangle}{k_B T},$$

Also if $\bar{v} = V/N \iff \bar{N} = V/\bar{v}$

$$\frac{\overline{\Delta N^2}}{\bar{N}^2} = \frac{k_B T \bar{v}^2}{V^2}\left(\frac{dV/\bar{v}}{\partial \mu}\right)_T = -\frac{k_B T}{V}\left(\frac{\partial v}{\partial \mu}\right)_T \sim o\left(\frac{1}{V}\right).$$

- Note that energy fluctuations at constant μ induce a change in particle number, so that $\delta U = \frac{\partial U}{\partial N}\delta N$

$$\overline{\Delta E^2}_{G.C} = \overline{\Delta E^2}_{CAN} + \left(\frac{\partial N}{\partial N}\right)^2 \langle \Delta N^2 \rangle_{G.C.}$$

Proof.

$$\langle \Delta E^2 \rangle = k_B T^2 \left(\frac{\partial U}{\partial T}\right)_{V,\alpha}$$

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

$$U(N(z,V,T),V,T)$$

Also $N = -\partial \ln Z/\partial\alpha$, $U = -\partial \ln Z/\partial\beta$

Maxwell reln $\left.\frac{\partial N}{\partial \beta}\right)_\alpha = \frac{-\partial^2 \ln Z}{\partial\alpha\partial\beta} = \left.\frac{\partial U}{\partial\alpha}\right)_\beta$

$$-k_B T^2 \frac{\partial N}{\partial T} = -k_B T \frac{\partial U}{\partial \mu} \implies \left.\frac{\partial N}{\partial T}\right|_{V,z} = \frac{1}{T}\left.\frac{\partial U}{\partial\mu}\right|_{V,T} = \frac{1}{T}\left.\frac{\partial U}{\partial N}\right|_{V,T}\left.\frac{\partial N}{\partial \mu}\right|_{V,T}$$

$$U(\mu(N,V,T),V,T) = U(N(\mu,V,T),V,T)$$

$$\left(\frac{\partial u}{\partial T}\right)_{z,V} = \left(\frac{\partial u}{\partial T}\right)_{N,V} + \frac{1}{T}\left(\frac{\partial u}{\partial N}\right)^2_{V,T}\left(\frac{\partial N}{\partial \mu}\right)_{V,T} \qquad (*)$$

$$\begin{array}{cc} \parallel & \parallel \\ C_{z,N} & C_{N,V} \end{array}$$

$$\overline{\Delta E^2}_{G.C} = k_B^2\, T\, C_{z,N}$$

$$\overline{\Delta E^2}_{CAN} = k_B^2\, T\, C_{N,V}$$

$$\overline{\Delta N^2}_{G.V} = k_B T \left(\frac{\partial N}{\partial \mu}\right)_{N,T}$$

$(*) \times k_B^2 T$

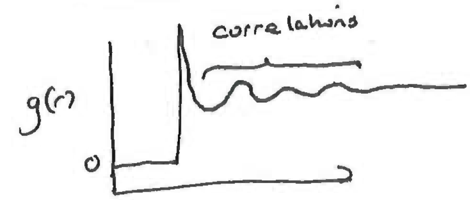
$$\Rightarrow \overline{\Delta E^2}_{G.C} = \overline{\Delta E^2}_{CAN} + \left(\frac{\partial u}{\partial N}\right)^2 \overline{\Delta N^2}_{G.C.}$$

4.6 PHASE DIAGRAMS.

T

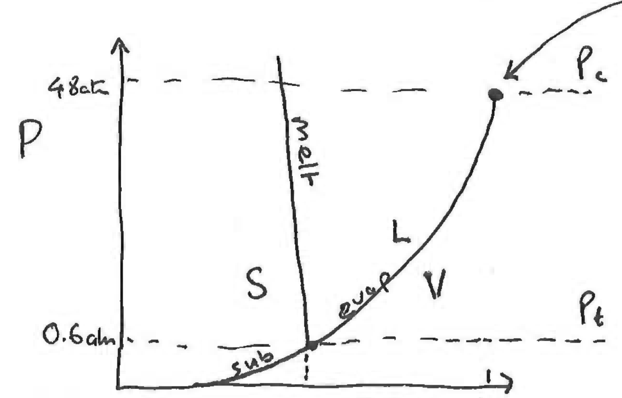
GAS —— $P = nk_BT$ + corrections described by VIRIAL EXPANSION

LIQUID —— Strong interactions Between atoms

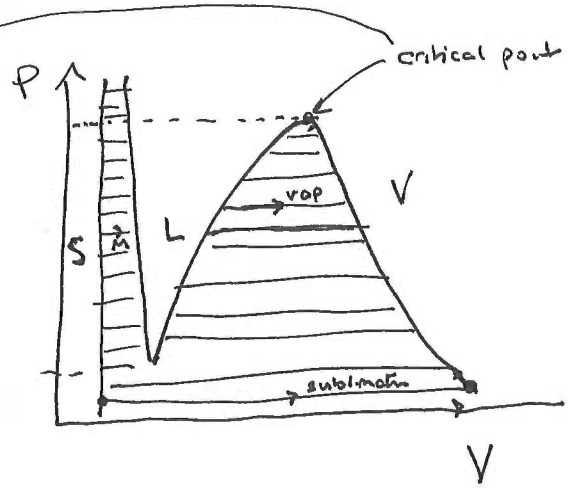


SOLID —— Crystal. L.R.O. Bragg Peaks. in S(q)

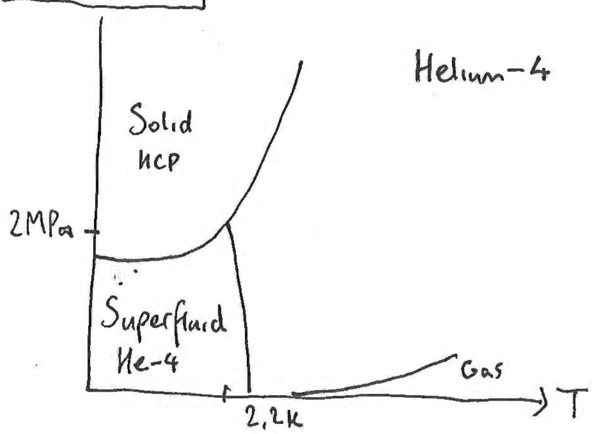
All of this is described by equilibrium Statistical Mechanics



$\boxed{1atm = 0.1 MPa}$



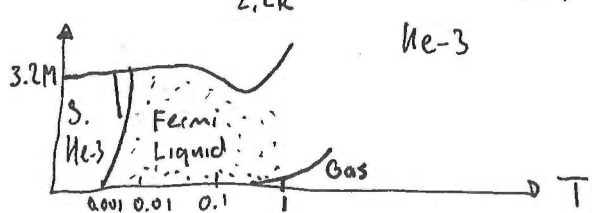
ARGON



$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}}$$

When $\lambda_T \ll a$ CLASSICAL

$\lambda_T \gg a$ QUANTUM



He-4 $T_\lambda = 2.18K$ ~ BEC

He-3 $T_F \sim 1K$ $T_c \sim 1mK$ B.C.S.

4.7 PHASE EQUILIBRIUM

$$U = U(V,S,N)$$

$$\downarrow A = U - TS$$

$$A = A(V,T,N) \xrightarrow{G = U - TS + PV} G(P,T,N) = \mu N$$

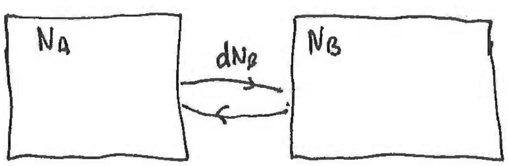
$$\downarrow F = U - TS - \mu N$$

$$F = F(V,T,\mu) = -VP(T,\mu)$$

$$dG = -SdT + \mu dN + VdP .$$

$$\boxed{N\mu(P,T) = G(N,P,T)}$$

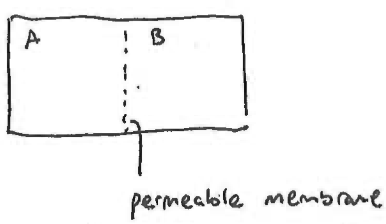
$$\boxed{d\mu = -sdT + vdP}$$



$$G = G_A + G_B .$$

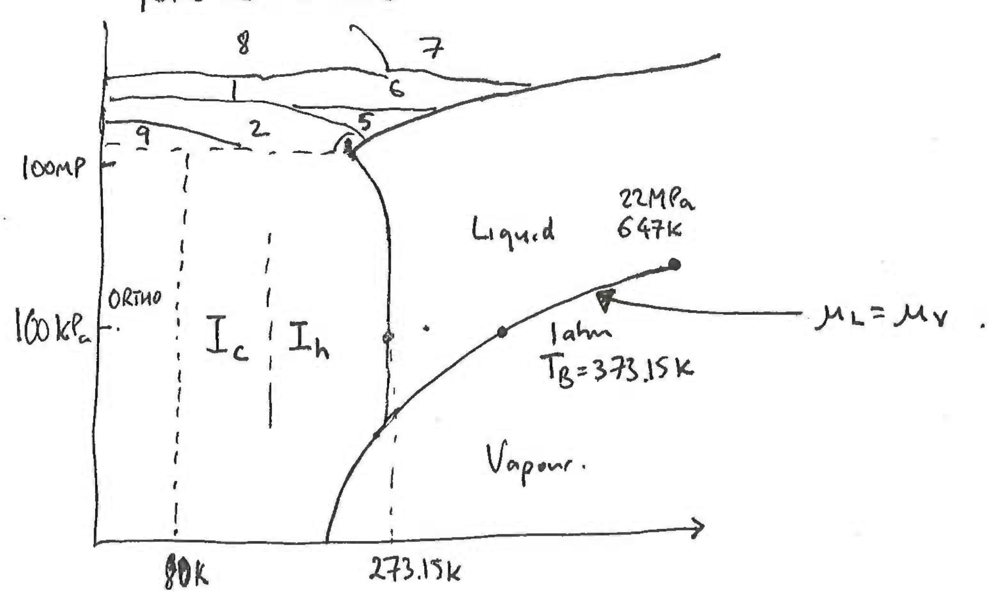
$$dG = \mu_A dN_A + \mu_B dN_B$$

$$= (\mu_A - \mu_B) dN_A$$



$\mu_A = \mu_B$ THERMAL EQN @ CONS PRESSURE.

Water



$$\mu_A(P_\sigma(T), T) = \mu_B(P_\sigma(T), T)$$

$$\left.\frac{\partial \mu_A}{\partial T}\right)_P + \left.\frac{\partial \mu_A}{\partial P}\right)_T \frac{\partial P_\sigma}{dT} = \left.\frac{\partial \mu_B}{\partial T}\right)_P + \left.\frac{\partial \mu_B}{\partial P}\right)_T \frac{dP_\sigma}{dT}$$

$$-\frac{\partial G}{\partial T} = S = -N\frac{\partial \mu}{\partial T} \Rightarrow -\frac{\partial \mu}{\partial T} = s = \frac{S}{N}.$$

$$\left.\frac{dG}{dP}\right)_{T,N} = V \qquad \left.\frac{d\mu}{\partial P}\right)_T = v = \frac{V}{N}.$$

$$\boxed{d\mu = -s\,dT + v\,dP}.$$

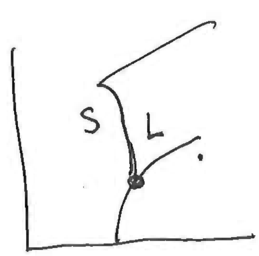
$$-s_A + v_A\frac{dP}{dT} = -s_B + v_B\frac{dP}{dT}$$

$$\Rightarrow \frac{dP}{dT} = \frac{s_B - s_A}{v_B - v_A}$$

CLAUSIUS-CLAPEYRON

$L = \Delta s\, T$ = Latent heat of $\left\{ \begin{array}{l} \text{vaporization} \\ \text{melting ... etc.} \end{array} \right.$

$$\frac{dP}{dT} = \frac{L}{T(v_B - v_A)}$$



Ice-water $\frac{dP}{dT} < 0$

$V_L < V_S$

TRIPLE POINT $\mu_A = \mu_B = \mu_C$.