RECITATION 8

Thermodynamics

We distinguished between two types of thermodynamic variables:

1) Extensive variables → they grow with the system size
   N, V, E
2) Intensive variables → they are independent of the system size μ, P, T

A system is in thermodynamic equilibrium if it is in thermal, mechanical and material equilibrium.
(E, T) (P, V) (N, μ)

To describe uniquely a system in equilibrium that it is open (it can exchange matter), we need therefore 3 variables: the choice of which variables to pick as independent variables defines the ensemble

All the other variables can be expressed as state function of the independent ones.

Thermodynamic potential	Natural ensemble	Differential
		fundamental thermodyn. relation
$S(E, N, V)$	μ-canonical (entropy)	$\boxed{dE = TdS - pdV + \mu dN}$ (*)
$F(T, N, V)$	Canonical (Helmholtz free energy)	$dF = -SdT - pdV + \mu dN$
$G(T, V, \mu)$	Grand canonical (grand potential)	$dG = -SdT - pdV - Nd\mu$
$G(T, P, N)$	Isobaric, isothermal (Gibbs free energy)	$dG = -SdT + Vdp + \mu dN$

(*) this is the fundamental thermodynamic relation. It relates all the extensive variables. It tells that they are not independent.

- μ-canonical ensemble

$S_m(E) = k_B \ln \Omega(E)$ ⟶ the system at equilibrium maximizes the entropy (II law)

- canonical ensemble

$F(N, T, V) = E^* - TS(E^*)$ ⟶ this holds in the $N \to \infty$ limit where

Helmholtz free energy.

$\left.\frac{\partial S}{\partial E}\right|_{E^*} = \frac{1}{T}$ fixes the value of E in order to minimize F.

For systems of finite size, $F = E - TS(E)$ is called Landau free energy and depends on E.

NB In the microcanonical ensemble E was an independent variable, now it is a function of (T, N, V) through the saddle point relation!

$$F(N, T, V) = E(T, N, V) - T\, S(E(T, N, \underline{V}), N, \underline{V})$$

ex.
$$\left.\frac{\partial F}{\partial V}\right|_{N,T} = \left.\frac{\partial E}{\partial V}\right|_{N,T} - T\left[\left.\frac{\partial S}{\partial V}\right|_{E,N} + \underbrace{\left.\frac{\partial S}{\partial E}\right|_{N,V}}_{\frac{1}{T}} \left.\frac{\partial E}{\partial V}\right|_{T,N}\right]$$

Using the standard chain rule

$$= \cancel{\left.\frac{\partial E}{\partial V}\right|_{N,T}} - T\left.\frac{\partial S}{\partial V}\right|_{E,N} - \cancel{\left.\frac{\partial E}{\partial V}\right|_{T,N}}$$

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

$$\boxed{p = T\left(\frac{\partial S}{\partial V}\right)_{E,N}}$$

Using the "wrong chain rule":

$$\left(\frac{\partial E}{\partial V}\right)_{S,N}\left(\frac{\partial V}{\partial S}\right)_{E,N}\left(\frac{\partial S}{\partial E}\right)_{V,N} = -1$$

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

definition of pressure that we saw in the micro canonical

$$\boxed{p = -\left.\frac{\partial E}{\partial V}\right|_{S,N}}$$

So the "wrong chain rule" is useful when you want to shuffle the position of three variables.

- In the Grand canonical ensemble

$$G(\mu, T, V) = E - \mu N - TS$$

the system in equilibrium maximizes this potential through the saddle point relations:

$$\left.\frac{\partial S(E,N,V)}{\partial E}\right|_{E^*,N^*} = \frac{1}{T}$$

$$\left.\frac{\partial S(E,N,V)}{\partial N}\right|_{E^*,N^*} = -\frac{\mu}{T}$$

} In the μ-canonical N, E were independent variables. Now they become functions of V, T, μ through these relations

$$G(\mu,T,V) = E(T,\mu,V) - \mu N(T,\mu,V) - TS(E(T,\mu,V), N(T,\mu,V), V)$$

Useful mathematical properties to remember:

1) Chain rule:

$$f(u(x,t),t)$$

$$\frac{\partial}{\partial x} f\Big|_t = \frac{\partial f}{\partial u}\Big|_t \frac{\partial u}{\partial x}\Big|_t$$

$$\frac{\partial}{\partial t} f\Big|_x = \frac{\partial f}{\partial t}\Big|_u + \frac{\partial f}{\partial u}\Big|_t \frac{\partial u}{\partial t}\Big|_x$$

2) "Wrong chain rule", also known as triple product rule
if you have three variables which are interdependent

$$f(x,y,z) = 0 \quad \Rightarrow \quad z = z(x,y)$$
$$y = y(x,z)$$
$$x = x(y,z)$$

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1}$$

3) Schwartz's identity:

$$\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x = \frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y \qquad \text{(Maxwell's relations)}$$

Recap interacting classical particles:

Canonical partition function

$$Z = \frac{1}{N!\,\Lambda^{3N}} \int \prod_{i=1}^{N} d^3\vec{q}_i \underbrace{\prod_{i<j}}_{\frac{N(N-1)}{2}\text{ terms}} e^{-\beta v(|\vec{q}_i - \vec{q}_j|)} \qquad \text{with} \quad \Lambda = \sqrt{\frac{h^2}{2\pi m k_B T}}$$

(v: pairwise potential)

- Idea: perturbation theory from the ideal gas
- Cluster expansion:

$f(r_{ij}) \equiv e^{-\beta v(|\vec{r}_i - \vec{r}_j|)} - 1$ → it has the nice property that

$f(r_{ij}) \longrightarrow 0$ as $|r_{ij}| \to \infty$ and

$f(r_{ij}) \longrightarrow -1$ as $|r_{ij}| \to 0$.

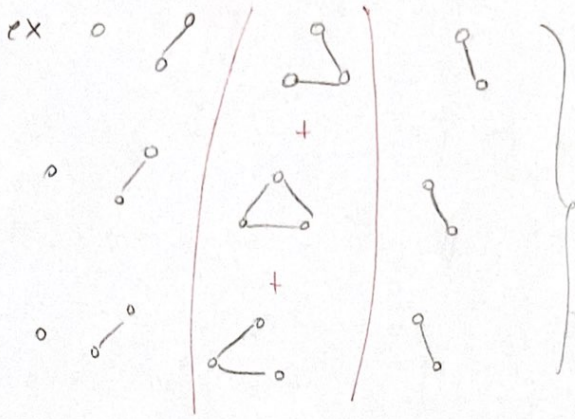
So we expand in this quantity.

$$\int \prod_i d^3\vec{q}_i \underbrace{(1+f_{12})(1+f_{23})(1+f_{34}) \cdots (1+f_{1N}) \cdots}_{\text{this is a sum of } 2^{N(N-1)/2} \text{ terms}}$$

You can also think of this graphically. You can consider your N particles as N nodes. Then, $\frac{N(N-1)}{2}$ is the number of edges in the fully connected graph.

You have $2^{\frac{N(N-1)}{2}}$ different diagrams obtained by either

Keeping or not each of the edges. Every diagram contributes as a product of its connected clusters.

ex 

$N = 8$ $\int d\vec{q}_1 \int d\vec{q}_2 d\vec{q}_3 f_{23} \int d\vec{q}_4 d\vec{q}_5 d_{56} f_{45} f_{56}$ $\int d\vec{q}_7 \int d\vec{q}_8 f_{78}$

three different diagrams, but they are factorizable

you do it for all the clusters of three nodes and this is b_3

Conceptually, you have many many diagrams but in all these diagrams many parts will be factorizable (every time two or more diagrams have the same connected clusters).

That's why it is convenient to group clusters of same size! (b_ℓ)

Then you basically just care about the cluster decomposition

$$Z = \frac{1}{N\Lambda^{3N}} \sum_{\substack{\{n_\ell\} \\ \text{such that} \\ \sum_\ell n_\ell \ell = N}} \prod_{\ell=1}^{N} (b_\ell)^{n_\ell} \times \frac{N!}{\prod_\ell (\ell!)^{n_\ell} n_\ell!}$$

in the previous case
$n_1 = 1$
$n_2 = 2$
$n_3 = 1$

Sum over all the possible different decomposition of a graph with N nodes into connected clusters

ex $N = 8$

$h_1 = 2$
$h_2 = 0$
$h_3 = 2$

$h_1 = 2$
$h_2 = 0$
$h_3 = 2$

after a lot of math...

$$\Rightarrow \boxed{P = nk_BT\left(1 + \frac{n\Omega}{2}\left(1 - \frac{v_0}{k_BT}\right)\right)}$$ Virial expansion

where $n = \frac{N}{V}$ = density

$\Omega = \frac{4\pi d^3}{3}$ excluded volume

v_0 = typical attractive potential

- Mean-field theory

Under the hypothesis of homogeneous density ρ_0

$$\boxed{P_H = \frac{Nk_BT}{V - N\Omega/2} - \frac{a}{2}\frac{N^2}{V^2}}$$

$$= \frac{k_BT}{\tilde{v} - \Omega/2} - \frac{a}{2\tilde{v}^2}$$

Van der Waals equation

→ originally postulated by Van der Waals at the end of the 19th century from experimental observations

So the virial expansion and the Van der Waals equation are compatible with each other ($a = \Omega v_0$) but they both predict a negative compressibility for low temperature...

PROBLEM!

Reminder: we saw in the Grand canonical ensemble that

$$\langle N \rangle = \frac{\partial}{\partial(\beta\mu)} \ln \Xi = -\frac{\partial}{\partial \mu} G\Big|_{T,V} \overset{G=-PV}{=} +V \frac{\partial P}{\partial \mu}\Big|_{T,V}$$

- $\frac{\partial}{\partial(\beta\mu)} \ln \Xi$: cumulant-generating function
- $-\frac{\partial}{\partial \mu} G\Big|_{T,V}$: def of grand potential
- $V \frac{\partial P}{\partial \mu}\Big|_{T,V}$: thermodynamic relations in the large N limit (N no longer fluctuates)

$$\langle N^2 \rangle_c = \frac{\partial^2}{\partial(\beta\mu)^2} \ln \Xi = k_B T \frac{\partial}{\partial \mu} \langle N \rangle\Big|_{T,V}$$

Using the modified chain rule...

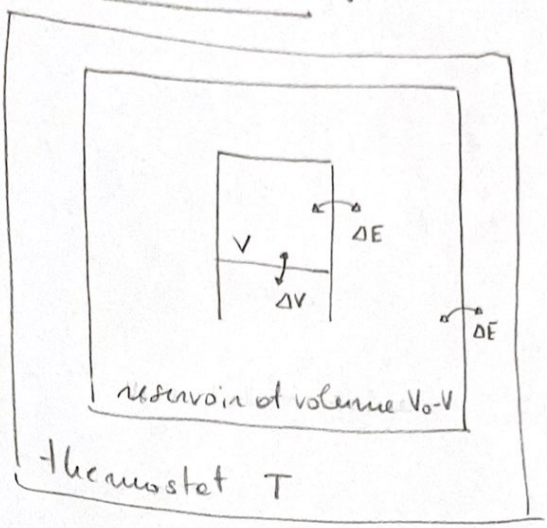
$$\Rightarrow \boxed{\frac{\langle N^2 \rangle_c}{\langle N \rangle} = k_B T \rho_0 K_T} \quad \text{where} \quad \boxed{K_T = -\frac{1}{V} \frac{\partial V}{\partial P}\Big|_{T,N}}$$

K_T: isothermal compressibility

$K_T < 0$ thermodynamic instability!

Indeed, what breaks down is the hypothesis of homogeneity.

Isobaric ensemble :



system + reservoir: canonical ensemble at temperature T

Microstate : $P(\epsilon_s, \epsilon_R) = \frac{1}{Z_{R+S}(T, N, V_0)} e^{-\beta\left[E(\epsilon_s)+E(\epsilon_R)\right]}$

Macrostate: $P(\epsilon_s)$ $E_S + E_R$ can fluctuate but $V_S + V_R = V_0$ is fixed

$$P(\epsilon_s) = \sum_{\epsilon_R \mid V_S+V_R=V_0} \frac{e^{-\beta\left[E(\epsilon_s)+E(\epsilon_R)\right]}}{Z_{R+S}} = \frac{e^{-\beta E(\epsilon_s)}}{Z_{R+S}} \underbrace{\sum_{\epsilon_R \mid V_R+V_S=V_0} e^{-\beta E(\epsilon_R)}}_{Z_c(T, N, V_0-V_S)}$$

$$= \frac{e^{-\beta E(\epsilon_s)}}{Z_{R+S}} \underbrace{e^{-\beta F_R(T, N, V_0-V_S)}}$$

we want to express it in terms of properties of the system : $V_S \ll V_0$

$$F_R(T, N, V_0-V_S) \simeq \underbrace{F_R(T, N, V_0)}_{-k_BT \ln Z_R(T, V_0, N)} - V_S \underbrace{\left.\frac{\partial F_R}{\partial V}\right|_{T,N}}_{-P_R(V_0)}$$

P_R: pressure of the reservoir!

$$\Rightarrow P(e_s) = \underbrace{\frac{Z_R(T,N,V_0)}{Z_{R+S}(T,N,V_0)}}_{\frac{1}{Z_I}} e^{-\beta E(e_s) - \beta P_R V(e_s)}$$

Isobaric ensemble: $P(e_s) = \frac{1}{Z_I} e^{-\beta E(e_s) - \beta P_R V(e_s)}$

$$Z_I = \sum_{e_s} e^{-\beta E(e_s) - \beta P_R V(e_s)}$$

$$= \sum_{E, V_s} \Omega(E, V_s, N)\, e^{-\beta E - \beta P_R V_s}$$

$$= \sum_{E, V_s} e^{-\beta(E + P_R V_s - T S_m)} = \sum_{V_s} e^{-\beta P_R V_s} \underbrace{\sum_{E} e^{-\beta(E - T S_m)}}_{\text{canonical partition } Z_c(T, V_s, N)}$$

continuous limit

$$Z_I = \int_0^\infty dV\, e^{-\beta P_R V} Z_c = \int_0^\infty dV\, e^{-\beta[P_R V + F(T, V_s, N)]} = \int dV\, e^{-\beta N[P_R \tilde{v} + A]}$$

Saddle point in the limit $N \to \infty$ } the integral is dominated by $\tilde{v}$ such that

$$P_R + \frac{\partial A}{\partial \tilde{v}} = 0 \Rightarrow \boxed{P_R = -\left.\frac{\partial F}{\partial V}\right|_{N,T}}$$

So in the large N limit $\tilde{v} \to \tilde{v}^*$ which is the volume per particle fixed by the pressure via the saddle point.

If you remember $P_R = -\left.\frac{\partial F_R}{\partial V}\right|_{T,N}$

So what the saddle point relation is saying is that the volume of the system in the large N limit will go to a value $\tilde{v}^*$ such that the internal pressure of the system is equal to the pressure of the reservoir.

The system at equilibrium is minimizing $\underbrace{PV + F}$

which in the large N limit (using thermodynamic relations)

is $PV + F = F - G = \mathcal{F} - (F - \mu N) = \mu N$

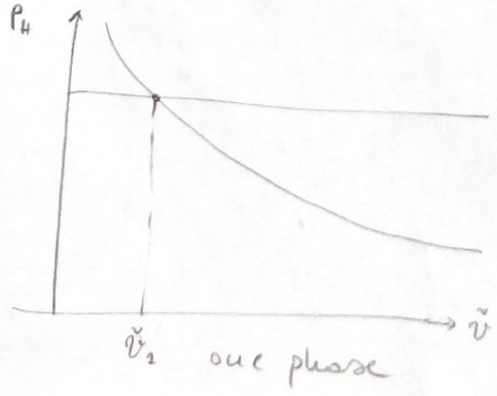
$\Rightarrow$ $\tilde{v} + \mathcal{A} = \hat{\mu}(\tilde{v})$ the corresponding intensive quantity

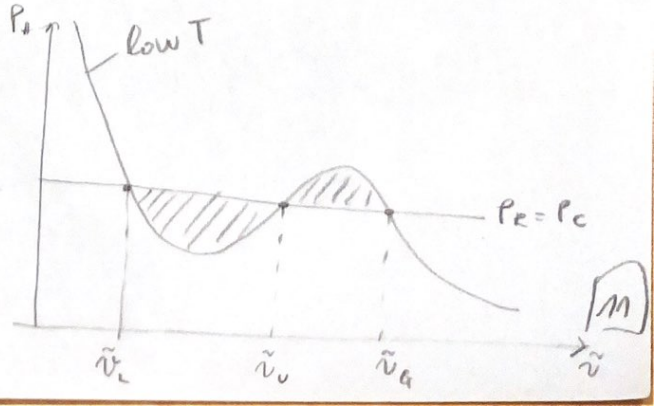
that the system is minimizing is the chemical potential in the large system size. So we call it a "Landau chemical potential"

Combining with the previous result: $\boxed{P_R = -\left.\frac{\partial F}{\partial V}\right|_{N,T} = P_H(\tilde{v})}$ (pressure obtained for a homogeneous system in the mean-field approximation)

If there are several values for $\tilde{v}$ that satisfies this condition (i.e. for which $P_H = P_R$)

it tells that $\hat{\mu}(\tilde{v})$ is not a convex function!





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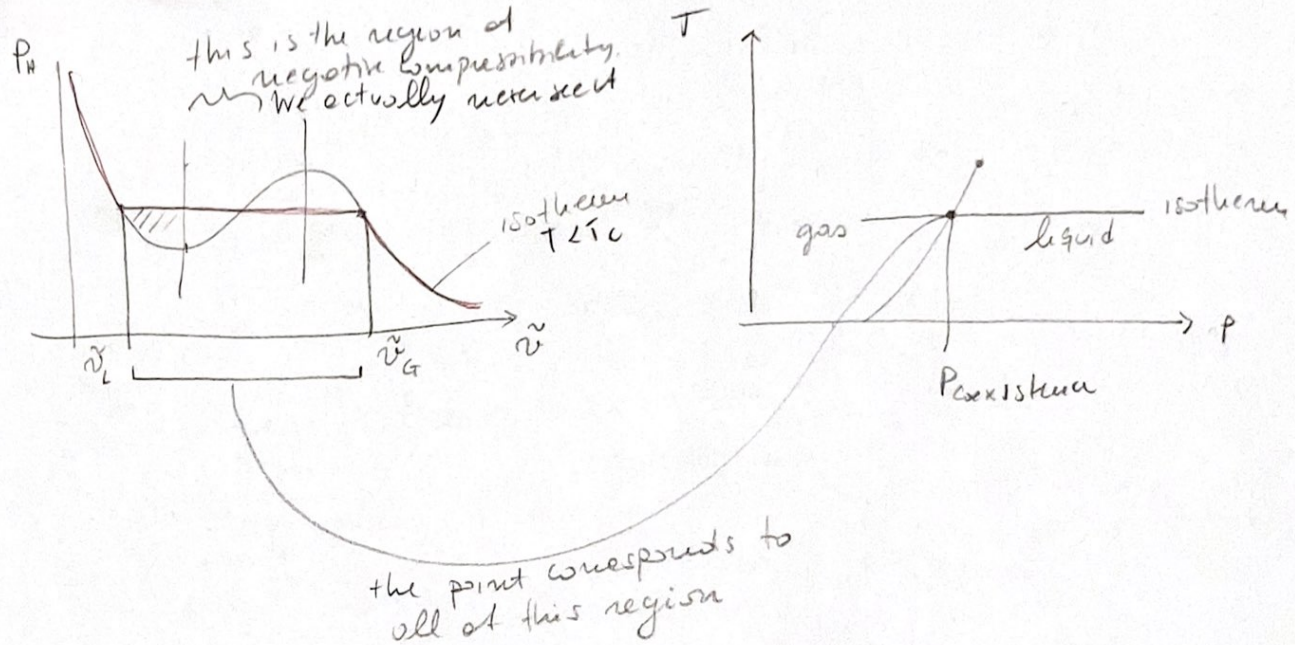
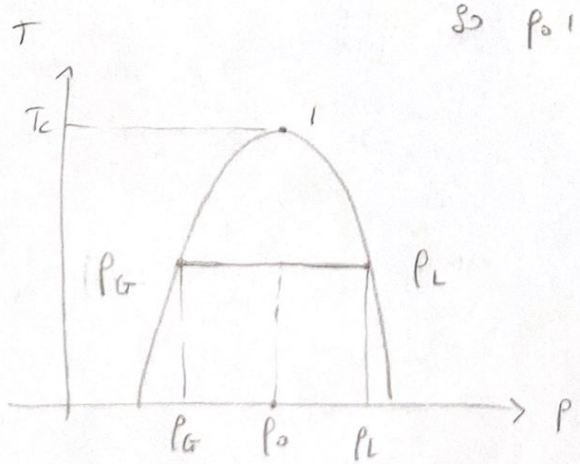


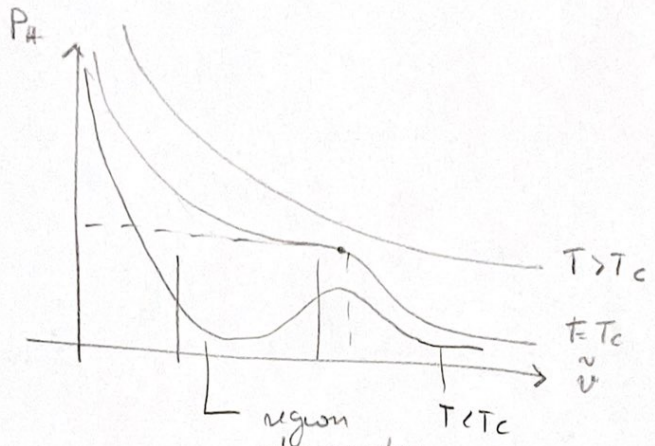
NB the volume is not constrained in the isobaric ensemble!
At the coexistence point it jumps btw $\tilde{v}_L$ and $\tilde{v}_G$.

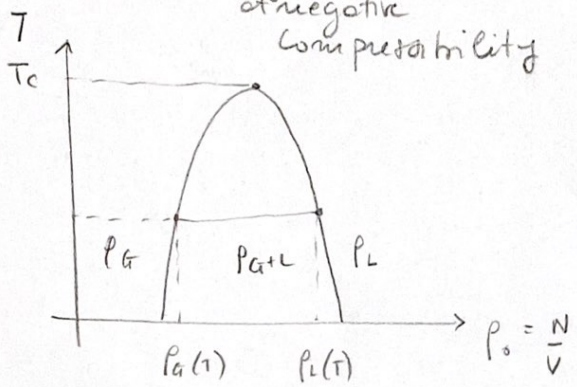
Different phenomenology in the canonical ensemble where we control T, N, V.
So ρ_0 is fixed!



$\rho_0 = \alpha \rho_G + (1-\alpha)\rho_L$

fixing ρ_0 fixes α!





Inflection point

$$\frac{\partial P}{\partial V} = 0$$

$$\frac{\partial^2 P}{\partial^2 V} = 0$$

} compressibility diverges...