Variational approach in statistical mechanics

≈ (Mean field treatment).

Thermodynamics: Recall "thermodynamic variational principle": for fixed T, V, the free energy F attains its minimal value.

In the statmech, we are simply calculating F

$$F = -k_B T \ln Z, \qquad Z = \mathrm{Tr}\, e^{-\beta H}$$

⇒ unique fnctn of T, V; there is no sense to speak about different F-s at given T, V, since we are summing over all states (all accessible configurations). Ultimately, we just want to know $F(T, V)$ as accurately as possible.

Variational approach allows us to strictly bound the exact $F(T, V)$ from above. If we try to come up with as stringent bound as possible, we can hope to capture the important properties of the system.

Interacting system – $Z = \mathrm{Tr}\, e^{-\beta H}$ is very difficult to calculate. $F = -k_B T \ln Z$

Suppose we have H_0 defined on the same degrees of freedom (on the same $\{p_i, q_i\}$ in classical statmech or the same Hilbert space in quantum statmech), and suppose we can easily calculate with H_0

$$Z_0 = \mathrm{Tr} \underbrace{e^{-\beta H_0}}_{\rho_{trial}}; \quad F_0 = -k_B T \ln Z_0.$$

Then we can provide an upper bound:

$$\boxed{F \le F_0 + \langle H \rangle_0 - \langle H_0 \rangle_0}$$

$$\langle H \rangle_0 = \mathrm{Tr}\left(H \frac{e^{-\beta H_0}}{Z_0}\right), \quad \langle H_0 \rangle_0 = \mathrm{Tr}\left(H_0 \frac{e^{-\beta H_0}}{Z_0}\right)$$

Proof: Classical statmech (so as not to worry about commutators)

$$Z = \mathrm{Tr}\, e^{-\beta H} = \mathrm{Tr}\left(e^{-\beta(H-H_0)} e^{-\beta H_0}\right) = Z_0 \mathrm{Tr}\left(e^{-\beta(H-H_0)} \frac{e^{-\beta H_0}}{Z_0}\right)$$

$$\ln Z = \ln Z_0 + \ln\left(\sum_{\text{states } S} e^{-\beta(H(S)-H_0(S))} p_S^{(0)}\right)$$

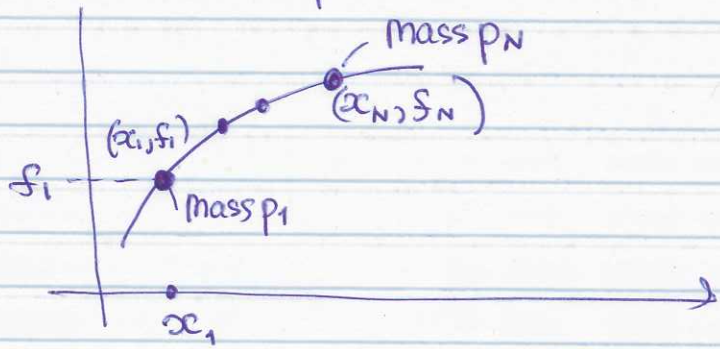
Use the following inequality: $\ln(\langle x \rangle) \ge \langle \ln x \rangle$

$$\boxed{\ln\left(\sum_i x_i p_i\right) \ge \sum_i p_i \ln x_i} \qquad \sum_i p_i = 1$$

(actually, "ln" can be replaced with any concave fnctn f:

$$\boxed{f\left(\sum_i x_i p_i\right) \ge \sum_i f_i p_i},$$

with geometric proof:



p_i – "mass" s.t. total mass = 1
Center of mass is at $\sum_i p_i (x_i, f_i)$
must lie below the curve
$\Rightarrow f(x_{CM}) \ge f_{CM} = \sum_i f_i p_i$)

$$\ln Z \ge \ln Z_0 + \sum_S p_S^{(0)} \cdot (-\beta)\left(H(S) - H_0(S)\right)$$

$$F = -\frac{1}{\beta} \ln Z \le F_0 + \langle H \rangle_0 - \langle H_0 \rangle_0 = F_{\text{trial}}$$

Summary of the derivation of variational mf

$$Z = \mathrm{Tr}\, e^{-\beta H} = \mathrm{Tr}\left(e^{-\beta(H+\frac{1}{\beta}\ln\rho_0)}\, \rho_0 \right)$$

$$\ln Z = \ln \left\langle e^{-\beta(H+\frac{1}{\beta}\ln\rho_0)} \right\rangle_0 \geq \left\langle -\beta(H+\tfrac{1}{\beta}\ln\rho_0) \right\rangle_0$$

$$\boxed{F = -\frac{1}{\beta}\ln Z \leq \langle H\rangle_0 + \frac{1}{\beta}\langle \ln\rho_0\rangle_0 \equiv F_{trial}}$$

$$\boxed{F_{trial} = \langle H\rangle_0 - T\cdot \underbrace{\left[-k_B\, \mathrm{Tr}(\rho_0 \ln\rho_0)\right]}_{\text{entropy of mixing}}}$$

(Recall "entropy of mixing":
example: binary degree of freedom which can be in state $\begin{cases} A \text{ with prob } p_A \\ B \text{ with prob } p_B \end{cases}$
$\rightarrow$ entropy $= -p_A \ln p_A - p_B \ln p_B$)

Choice of ρ_0 is often guided by trial or mean field H_0

$$\rho_0 = \frac{e^{-\beta H_0}}{Z_0} \Rightarrow \langle \ln\rho_0\rangle = -\beta\langle H_0\rangle_0 - \ln Z_0$$

$$\boxed{F_{trial} = \langle H\rangle_0 - \langle H_0\rangle_0 + F_0}$$

Remarks: ⊛ In the $T \to 0$ limit, $F = U - TS \to U$, and this reduces to $\boxed{E_{exact} \leq \langle H \rangle_0}$ – familiar variational principle in quantum mechanics

⊛ Choice of $H_0 \leftrightarrow$ choice of $\rho_0 = \frac{e^{-\beta H_0}}{Z_0}$ – reflects our idea about the phase of the system. H_0 may have ~~variational~~ parameters, which we can vary to minimize $F_{trial} = F_0 + \langle H \rangle_0 - \langle H_0 \rangle_0$, in the hope that a tighter bound corresponds to a more accurate description.

⊛ Naively, if $H = H_0 + U$ ← interactions,

$F_{trial} = F_0 + \langle U \rangle_0$ – similar to the first term in the cummulant expansion. However, in the perturbative treatment we must use $\langle \dots \rangle_0$ wrt noninteracting gas, while in the variational (mean field) treatment we can choose nontrivial $\langle \dots \rangle_0$ inspired by the expected physics — e.g. phase-separated state as in the discussion of vdW gas below.

"non-perturbative" treatment

⊛ $\rho_0 = \frac{e^{-\beta H_0}}{Z_0} \to H_0 = -\frac{1}{\beta} \ln(Z_0 \rho_0)$

$\Rightarrow F_0 - \langle H_0 \rangle_0 = -\frac{1}{\beta} \ln Z_0 - \mathrm{Tr}\, \rho_0 \cdot \left[-\frac{1}{\beta} \times (\ln Z_0 + \ln \rho_0) \right] =$

$= \frac{+1}{\beta} \mathrm{Tr}\, \rho_0 \ln \rho_0 = +T \cdot k_B \mathrm{Tr}\, \rho_0 \ln \rho_0 = +k_B T \langle \ln \rho_0 \rangle_0$

Can work directly with trial ρ_0 without specifying H_0

$\boxed{F_{trial} = \langle H \rangle_0 + T k_B \mathrm{Tr}\, \rho_0 \ln \rho_0}$ $\Leftarrow$ $\boxed{(-k_B \mathrm{Tr}(\rho_0 \ln \rho_0)) \text{ is "entropy of mixing"}}$

Mean field description of the liquid – gas transition

Work in the canonical ensemble to parallel our discussion of the free energy of the van der Waals gas.

$$H = H_{kin} + \underset{\text{repulsion}}{\text{hard-core}} + \underset{\text{attraction}}{\text{(weak) long-range}}$$

(we need attraction to cause transition to more dense liquid phase and repulsion to prevent collapse)

Consider uniform density "trial states"

$$H_0 = H_{kin} + \text{hard-core repulsion}$$

(there are no variational parameters here – these will appear shortly when we take phase-separated states).

For simplicity, assume that $F_0(T,V) = F^{gas}_{ideal}(T, V-Nb)$

$$F_0(T,V) = F^{gas}_{ideal}(T, V-Nb) = -Nk_BT \ln(V-Nb) + Nk_BT\{\ln N + \ln \lambda^3(T) - 1\}$$

$$F_{trial}(T,V) = F_0(T,V) + \left\langle \text{long-range attraction} \right\rangle_0 .$$

$$\left\langle U(\{q_i\}) \right\rangle_0 = \sum_{i<j} \left\langle v(q_i - q_j) \right\rangle_0 \overset{\text{uniform dens.}}{=} \frac{N\cdot(N-1)}{2} \int \frac{d^3q_1}{V} \frac{d^3q_2}{V} v(q_1 - q_2) =$$

$$= \frac{N\cdot(N-1)}{2V} \int d^3q\, v(q) \equiv \text{[shaded]} - \frac{N^2}{V} a$$

↑ attractive

$$F_{trial} = -\frac{N^2}{V}a - NK_BT \ln(V-Nb) + NK_BT\{\ln N + \ln\lambda_{(T)}^3 - 1\}$$

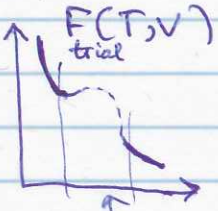
- this is precisely the free energy of van der Waals gas that we obtained by integrating van der Waals equation of state. Alternatively, we can derive equation of state from F_{trial}:

$$p = -\frac{\partial F_{trial}}{\partial V} = \frac{NK_BT}{V-Nb} - \frac{N^2}{V^2}a \quad \left.\right\} \leftarrow \text{vdW equation!}$$

We can now interpret what we did after deriving F_{vdW} as follows.

- For $T > T_c$, the above trial state gives sensible results, with $\frac{\partial^2 F_{trial}}{\partial V^2} > 0$ everywhere

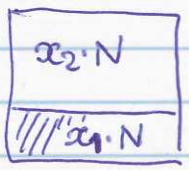
- For $T < T_c$, upon seeing



we realize that we can actually do better in this region by taking phase-separated trial state.

Calculations (of the F_{trial}) with such phase-separated states are precisely like the calculations we did with F_{vdW}:

Trial state $x_1 \cdot N$ particles in (V_1, F_1) state



$x_2\, N = (1-x_1)N$ particles in (V_2, F_2) state

constraint

$$x_1 V_1 + x_2 V_2 = V = x_1 V_1 + (1-x_1)V_2$$

e.g.

- variational parameters are [redacted] V_1 and V_2

(which states to phase-separate to)

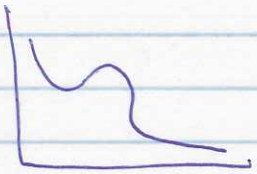
assuming N fixed, $V_i \Leftrightarrow \frac{V_i}{N} = v_i$ - vol per particle, etc.

$\Rightarrow$

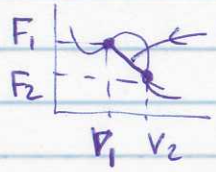
$$x_1 = \frac{V - V_2}{V_1 - V_2} \text{ - unique} \; ; \quad x_2 = 1 - x_1$$

$$\left.\begin{aligned} F_{trial} &= x_1 F_1 + x_2 F_2 = x_1 F_1 + (1-x_1) F_2 \\ V &= x_1 V_1 + x_2 V_2 = x_1 V_1 + (1-x_1) V_2 \end{aligned}\right\} \text{ - straight line connecting } (V_1, F_1), (V_2, F_2).$$

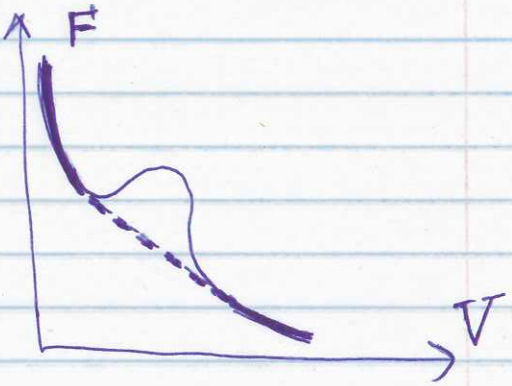
$\Rightarrow$ Given $F_{trial}(V)$ curve constructed using only uniform trial states,



we can construct more trial energies using phase-separated states



Minimizing over all possible such constructions $\rightarrow$ "enveloping curve"



Once we have such F_{trial} satisfying $\frac{\partial F}{\partial V^2} \geq 0$

we cannot do any better with any other attempt at phase separation [redacted] $x_i N$ @ [redacted] $v_i = \frac{V_i}{N}$

$V = \sum_i x_i N \cdot v_i = \sum_i x_i V_i$, $\sum x_i = 1$

$F_{ps} = \sum_i x_i N \cdot f_i = \sum_i x_i F_i \geq F(V)$ by convexity.

Kardar's text

Variational approach in the grand canonical ensemble

$$\text{"}H\text{"} = H_{kin} + \underset{\text{repulsion}}{(\text{hard-core})} + \underset{\text{attraction}}{(\text{long-distance})} - \mu N$$

$$\text{"}Tr_{(\cdots)}\text{"} = \sum_N \int \frac{d^{3N}q\, d^{3N}p}{h^{3N}} \frac{1}{N!}(\cdots) \; ; \quad \mathcal{Z} = Tr\, e^{-\beta H}$$

$$\Omega(T,V,\mu) = -k_B T \ln \mathcal{Z}$$

Variational approach: $\Omega \leq \Omega_0 + \langle H - H_0 \rangle_0$

$$\text{"}H_0\text{"} = H_{kin} + \underset{\text{repulsion}}{(\text{hard-core})} - \mu_{var} N$$

μ_{var} ↑ variational parameter.

Recall calculations for the ideal gas in the absence of hard core interactions

$$\Omega_{\text{ideal gas}} = -k_B T \frac{V e^{\beta \mu_{\text{ideal gas}}}}{\lambda^3}$$

$$\langle N \rangle_{\text{ideal gas}} = \frac{e^{\beta \mu_{\text{ideal gas}}}}{\lambda^3} V$$

$$\Omega_{\text{ideal gas}} = -\langle N \rangle k_B T$$

Treat the hard-core repulsion approximately by

$$V \to V - \langle N \rangle b$$

$$\Rightarrow \langle N \rangle = \frac{e^{\beta \mu_{var}}}{\lambda^3} (V - \langle N \rangle b)$$

$$\underbrace{n = \frac{e^{\beta \mu_{var}}}{\lambda^3}}_{x} (1 - nb) \Rightarrow n = \frac{x}{1 + xb}$$

$n = n(\mu_{var}) \leftrightarrow \mu_{var} = \mu_{var}(n)$ — can view either μ_{var} or n as variational param.

monotonic fnctn

$$\Omega_0 = -\langle N\rangle k_B T = -nVk_BT$$

long-range attraction

$$\Omega_{trial} = \Omega_0 + \langle H - H_0\rangle_0 = \Omega_0 + \langle \mathcal{U}\rangle_0 - (\mu - \mu_{var})\langle N\rangle$$

$$= -nVk_BT - \frac{\langle N\rangle^2}{V}a - (\mu - \mu_{var})\langle N\rangle,$$

$$\frac{\Omega_{trial}}{V} = -nk_BT - an^2 - \left(\mu - \frac{1}{\beta}\ln\frac{n\lambda^3}{1-nb}\right)n =$$

$$= -k_BT\left\{n + \beta a n^2 + \beta\mu n - n\ln\frac{\lambda^3}{\frac{1}{n}-b}\right\}$$

same as Kardar's (5.77) with $a = \frac{1}{2}\mathcal{A}$, $b = \frac{\Omega}{2}$

$$\frac{\Omega_{trial}(T,V,\mu)}{V} = \min_n\left(-k_BT\{\dots\}\right)$$

Equation for n:

$$1 + \beta a\cdot 2n + \beta\mu - \ln\left(\frac{\lambda^3}{\frac{1}{n}-b}\right) + n\frac{1}{\frac{1}{n}-b}\cdot\frac{-1}{n^2} = 0.$$

$$1 + \beta\mu + 2\beta a\cdot n - \ln\frac{\lambda^3 n}{1-nb} - \frac{1}{1-nb} = 0$$

$\leftarrow n = n(\mu)$

$$\mu = -2an + k_BT\left(\ln\frac{\lambda^3 n}{1-nb} + \frac{1}{1-nb} - 1\right)$$

$\rightarrow$ math. equivalent to earlier treatment in the canonical ensemble!

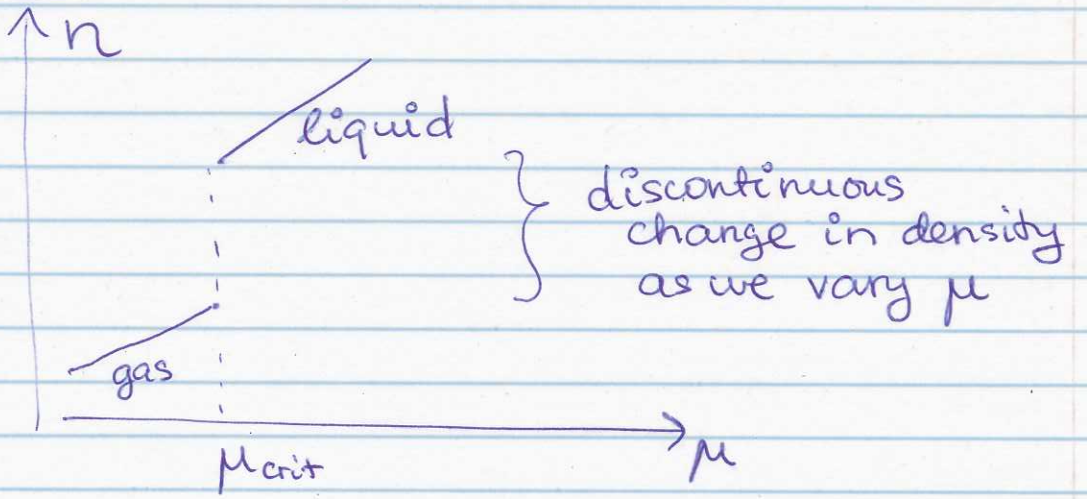
Indeed,
Compare with earlier treatment when discussing Maxwell construction

$$G_{vdW} = F_{vdW} + pV = -\frac{N^2}{V}a - Nk_BT\ln(V-Nb) +$$

$$+ Nk_BT\{\ln N + \ln\lambda^3 - 1\} + \left(\frac{Nk_BT}{V-Nb} - \frac{N^2}{V^2}a\right)\cdot V$$

$$= -2\frac{N^2}{V}a + Nk_BT\left\{\ln\frac{N\lambda^3}{V-Nb} - 1\right\} + \frac{Nk_BT}{V-Nb}V$$

$$\boxed{\mu = \frac{G}{N} = -2an + k_BT\left\{\ln\frac{n\lambda^3}{1-nb} - 1\right\} + \frac{k_BT}{1-nb}}$$



$\mu < \mu_{crit}$ $\quad n = n_{gas}(\mu)$ – all gas

$\mu > \mu_{crit}$ $\quad n = n_{liq.}(\mu)$ – all liquid

$\mu = \mu_{crit}$ – ~~critical point~~
1st-order transition