Cluster expansion: → weird behavior at low temperature → is it real?
→ what is happening?

Mean-field Theory

$$\frac{1}{2}\int d\vec{q}\, \rho(\vec{q}) \int d\vec{q}\,'\rho(\vec{q}\,')\, v(\vec{q}-\vec{q}\,') \simeq \frac{1}{2}\int d\vec{q}\,\rho(\vec{q})\,\rho_0 \underbrace{\int_d 4\pi r^2 dr\, v(r)}_{-u}$$

$$\simeq -\frac{\rho_0^2 V u}{2}$$

$$Z = \frac{1}{N!\Lambda^{3N}} \int d\vec{q}_1 \dots d\vec{q}_N\; e^{-\frac{\beta}{2}\int d\vec{q}\,d\vec{q}\,'\rho(\vec{q})\rho(\vec{q}\,')v(\vec{q}-\vec{q}\,')} \simeq \frac{e^{\frac{\beta N^2 u}{V}}}{N!\Lambda^{3N}} \cdot V.(V-\Omega)\cdot\ldots\cdot(V-(N-1)\Omega)$$

All in all $$Z = \underbrace{\frac{1}{N!\,\Lambda^{3N}}}_{\text{ideal gas}}\; \underbrace{e^{\beta\frac{N^2 u}{2V}}}_{\text{attraction}}\; \underbrace{\left(V-\frac{N\Omega}{2}\right)^N}_{\text{exclusion}}$$ Nice physics!

Back to pressure

In a homogeneous phase, we thus have

$$\beta P_H = \frac{\partial \ln Z}{\partial V} = \frac{N}{V-\frac{N\Omega}{2}} - \beta\frac{N^2 u}{2V^2} \Rightarrow \boxed{P_H = \frac{NkT}{V-\frac{N\Omega}{2}} - \frac{u}{2}\left(\frac{N}{V}\right)^2}$$

This is the celebrated van der Walls' equation

Comment: cluster expansion: $\beta P = n + n^2\frac{\Omega}{2}(1-\beta u_0)$

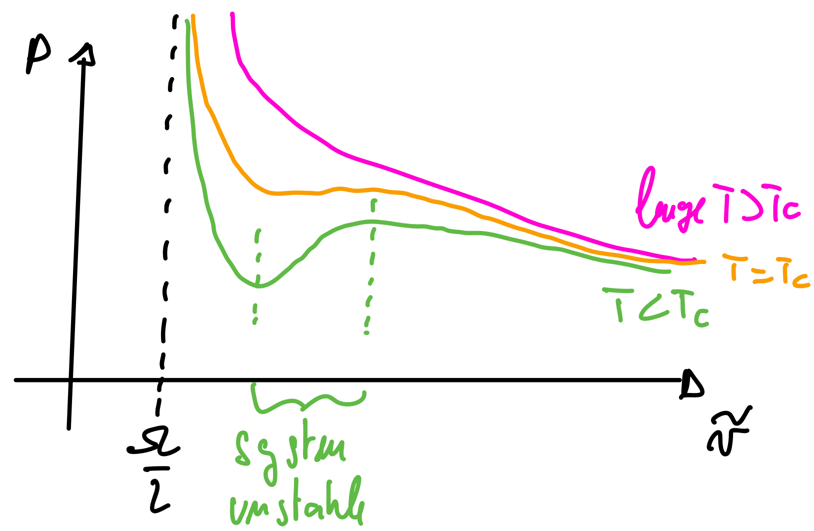
$$\Leftrightarrow \beta\left(P + u_0\frac{n^2\Omega}{2}\right) = n\left(1+n\frac{\Omega}{2}\right) \simeq \frac{n}{1-n\frac{\Omega}{2}} + O(n^2\Omega^2)$$

$$\Leftrightarrow P = \frac{NkT}{V-\frac{\Omega}{2}N} - \frac{u_0\Omega}{2}\left(\frac{N}{V}\right)^2$$

The cluster expansion is compatible with MF & VDW equation for the pressure up to the second Virial coefficient (i.e. $O(n\Omega)$).

Intensive form: $\boxed{P = \frac{kT}{\tilde{v} - \frac{\Omega}{2}} - \frac{\mu_0 \Omega}{2\tilde{v}^2}}$; $\tilde{v} = \frac{V}{N}$ free volume per particle

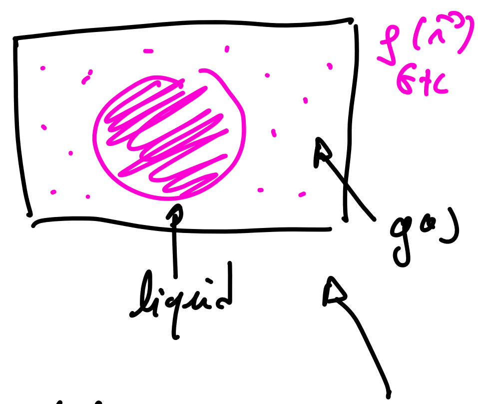
Onset of phase separation: Plot the so-called Isothermal lines



$$P_H = \underbrace{\frac{kT}{\tilde{v} - \frac{\Omega}{2}}}_{\substack{\text{leading contribution} \\ \text{at large } T \,\&\, V \\ \&\text{ as } V \to \frac{\Omega}{2} N}} - \underbrace{\frac{\mu_0 \Omega}{2\tilde{v}^2}}_{\substack{\text{Important at} \\ \text{small } T \,\&\, V}}$$

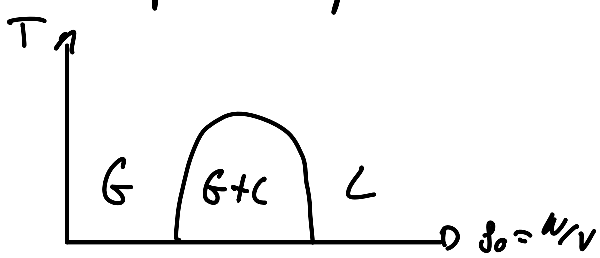
From the MF picture, we can understand what goes wrong: the system cannot remain homogeneous $\Rightarrow$

How to describe phase-separated states?

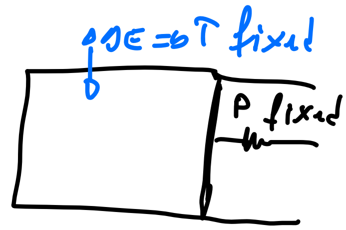


Consider macrostate defined by $\rho(\vec{r})$ and build $P(\rho(\vec{r}))$. Compare probability between $\rho(\vec{r}) = \rho_{G+L}(\vec{r})$ & $\rho(\vec{r}) = \rho_0$. If $P(\rho_{G+L}) > P(\rho_0) \Rightarrow$ phase separation

$\Rightarrow$ Pset 7, problem 1.



Alternative: Isobaric Gibbs ensemble



$$P(\varphi) = \frac{1}{Z_c} \exp[-\beta E(\varphi) - \beta P V(\varphi)]$$

$$Z_I(P,T,N) = \int_0^\infty dV\, e^{-\beta P V} Z_c(V,T,N) = \int_0^\infty dV\, e^{-\beta[PV+F]}$$

At large N, $F(V,T,N) = N f(\tilde v, T) \Rightarrow Z_I = \int_0^\infty dV\, e^{-\beta N[p\tilde v + f(\tilde v,T)]}$

$$\Rightarrow Z_I \sim e^{-\beta N^*[p\tilde v^* + f(\tilde v^*,T)]} = e^{-\beta[PV^*+F(V^*)]}$$

where $\tilde v^* = \underset{\tilde v}{\mathrm{argmin}} \, [p\tilde v + f(\tilde v,T)]$

As usual $P(\tilde v) \underset{N\to\infty}{\sim} \delta(\tilde v - \tilde v^*)$ when $\tilde v^*$ is such that

(1) $p + \frac{\partial f}{\partial \tilde v} = 0 \iff p = -\frac{\partial F}{\partial V}$

(2) $\tilde v^*$ minimizes $\hat\mu_L(\tilde v) \equiv p\tilde v + f(\tilde v, T)$

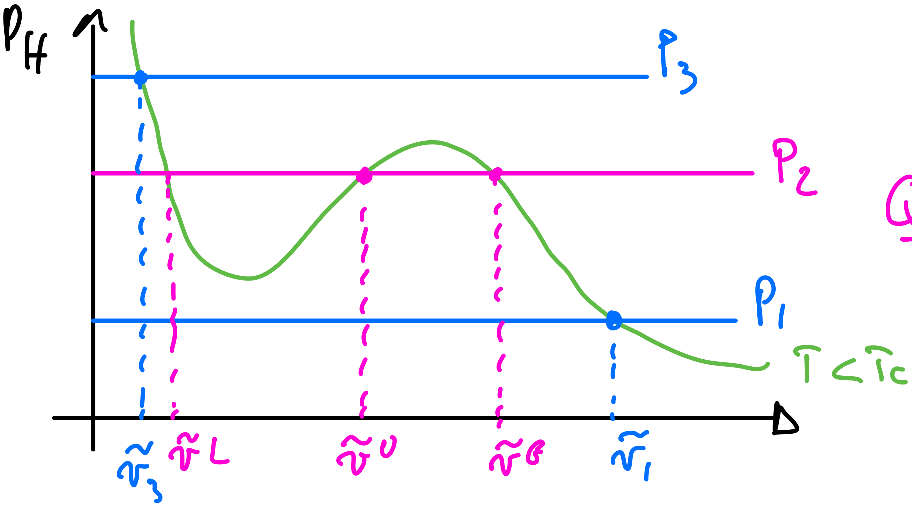
For large systems, $PV + F = F - \mathcal{G} = F - (F - \mu N) = \mu N$

$\Rightarrow \hat\mu_L$ is the chemical potential of a system with free volume $\tilde v$.

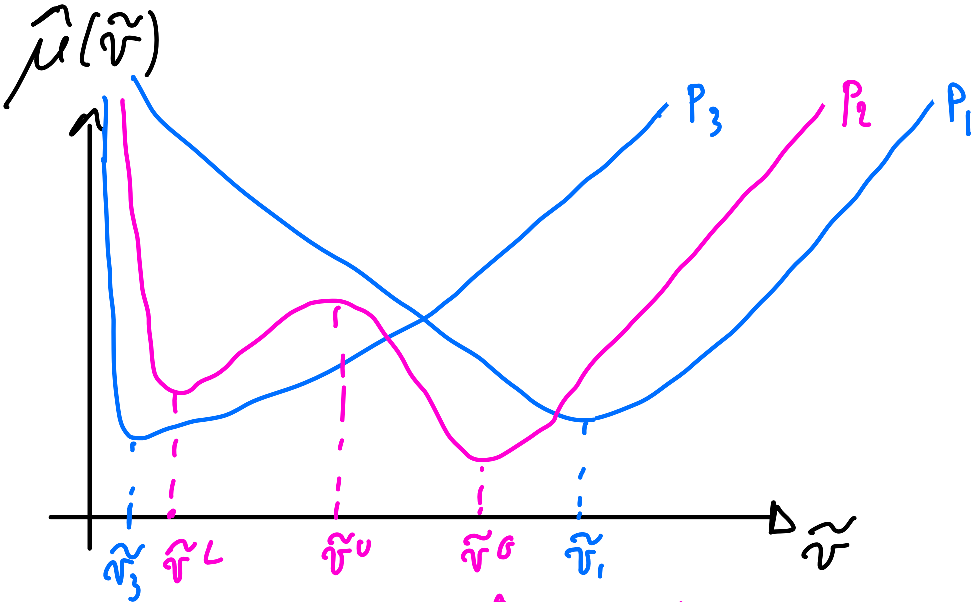
⚠ $\hat\mu_L(V) \equiv PV + F(V)$ is only the chemical potential at $N\to\infty$, when $V = V^*$.
This is like the $F_L(E) = E - TS(E)$ being a free energy in the canonical ensemble. $F_L(E) \neq F(\beta)$ except when $V\to\infty$ & $F(\beta) = F(E^*)$ ("L" stands for Landau). Here $\hat\mu_L(V^*) = \mu$ ...

(3) To proceed, assume $-\frac{\partial F}{\partial V} = P_H(\tilde v)$

For given P, find V such that (1) holds.



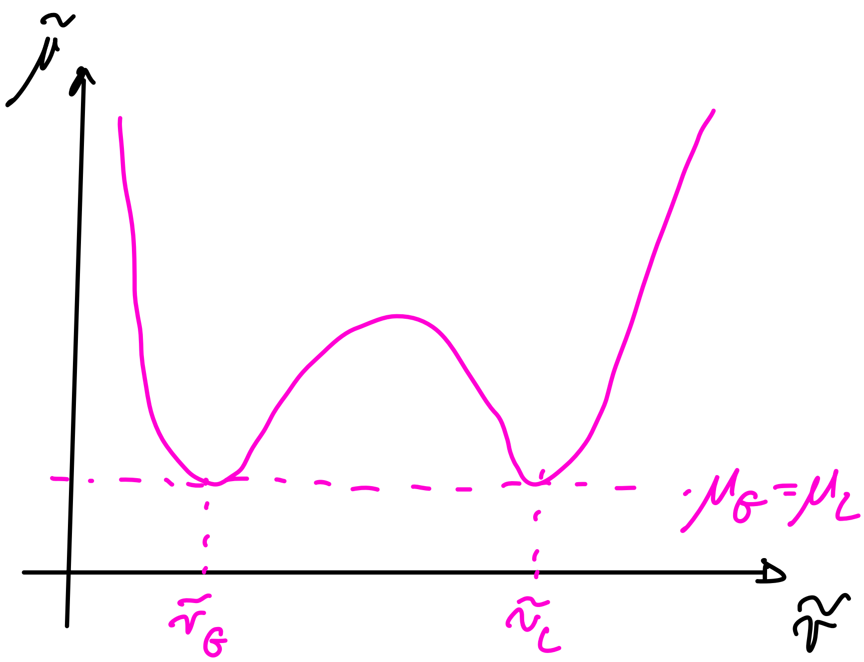
Q: which v_2^i dominates?

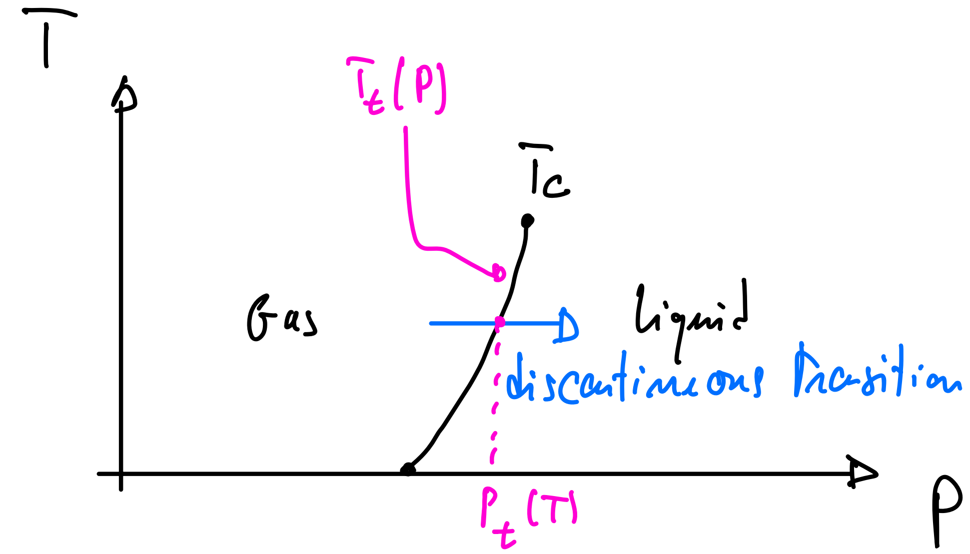


this dominates

As P varies, either V_2^1 or V_2^3 dominates.

At $P = P_t$, we have a transition from $\tilde{v}_G$ to $\tilde{v}_L$:



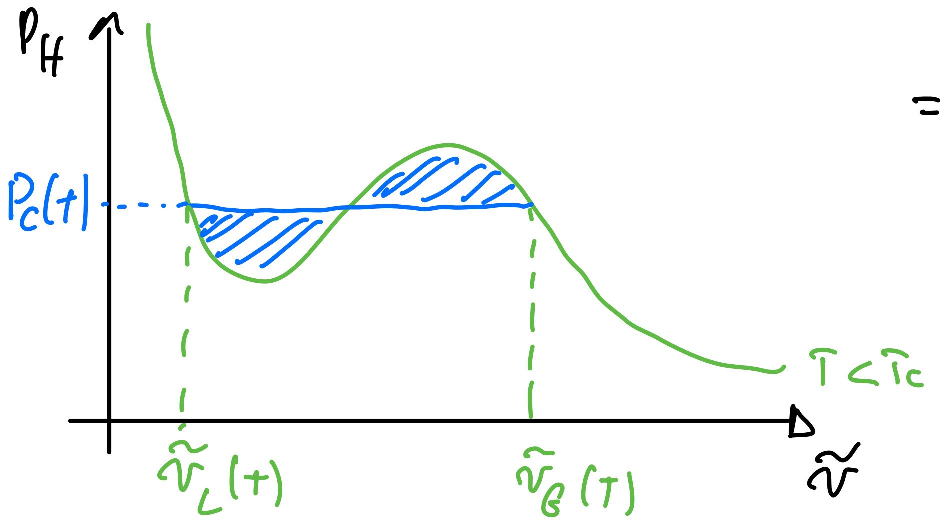


Q: How do we find P_t?

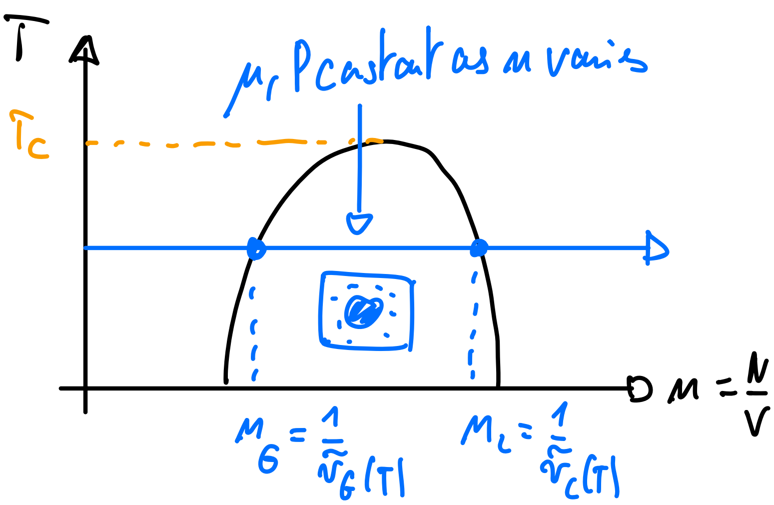
$$\hat{\mu}(\tilde{v}_G) = \hat{\mu}(\tilde{v}_L) \Rightarrow \hat{\mu}(\tilde{v}_G) - \hat{\mu}(\tilde{v}_L) = \int_{\tilde{v}_L}^{\tilde{v}_G} d\tilde{v} \, \frac{d\mu}{d\tilde{v}} = 0$$

$$= \int_{\tilde{v}_L}^{\tilde{v}_G} d\tilde{v} \, \left(P_t - P_H(\tilde{v})\right) = 0$$

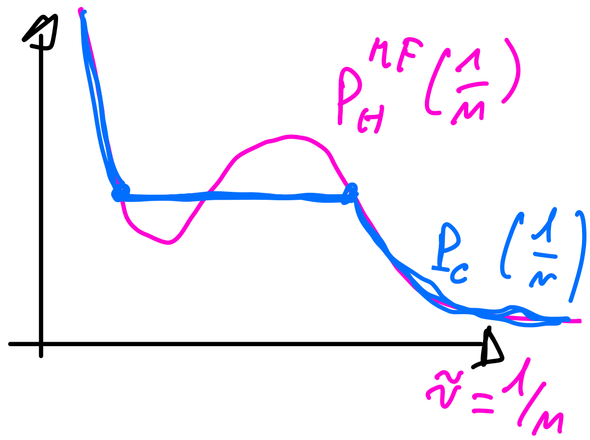
Maxwell construction

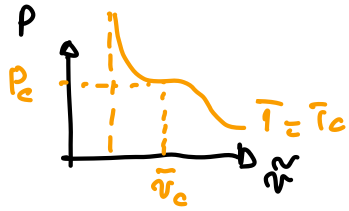


Comment: In the canonical ensemble, the system phase separates between the gas and liquid phases that have equal pressures & chemical potential.



⇒ the "real" P is thus constant in the phase separated state





Universality

Let us look at the behaviour of the system close to P_c, T_c, μ_c.

$$P(\tilde{v}) = P(\tilde{v}_c) + \left.\frac{\partial P}{\partial \tilde{v}}\right|_{T_c} (\tilde{v} - \tilde{v}_c) + \frac{1}{2}\frac{\partial^2 P}{\partial \tilde{v}^2}(\tilde{v} - \tilde{v}_c)^2 + \frac{1}{6}\frac{\partial^3 P}{\partial \tilde{v}^3}(\tilde{v} - \tilde{v}_c)^3 + \dots \quad (1)$$

At T_c, V_c, $\frac{\partial P}{\partial \tilde{v}} = \frac{\partial^2 P}{\partial \tilde{v}^2} = 0$ Mean-field: $P = \frac{kT}{\tilde{v} - \frac{\Omega}{2}} - \frac{u}{2\tilde{v}^2}$

$$P'(\tilde{v}) = 0 \Leftrightarrow -\frac{kT_c}{(\tilde{v} - \frac{\Omega}{2})^2} + \frac{u}{\tilde{v}^3} = 0 \Leftrightarrow \frac{\tilde{v}^3}{u} = \frac{(\tilde{v} - \frac{\Omega}{2})^2}{kT_c} \qquad (*)$$

$$P''(\tilde{v}) = 0 \Leftrightarrow \frac{2kT_c}{(\tilde{v} - \frac{\Omega}{2})^3} - \frac{3u}{\tilde{v}^4} \Leftrightarrow \frac{\tilde{v}^4}{3u} = \frac{(\tilde{v} - \frac{\Omega}{2})^3}{2kT_c} \qquad (**)$$

$$\frac{(**)}{(*)} \Rightarrow \frac{\tilde{v}_c}{3} = \frac{(\tilde{v}_c - \frac{\Omega}{2})}{2} \Rightarrow \tilde{v}_c = \frac{3\Omega}{2}$$

$$(*) \Rightarrow kT_c = u \cdot \frac{(\tilde{v}_c - \frac{\Omega}{2})^2}{\tilde{v}_c^3} = u \cdot \frac{\Omega^2 8}{27\Omega^3} = \frac{8u}{27\Omega}$$

$$P_c = \frac{2u}{27\Omega^2}$$