Chapter 4: Interacting systems

So far: dilute systems

Beautiful theory on relatively simple systems.

The world around us is rich because more is different

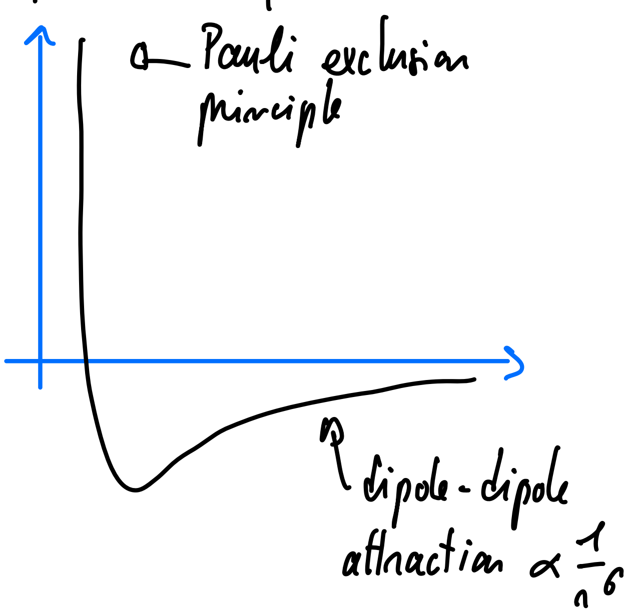
Let's show that interplay between fluctuations & interactions lead to complex forms of matter.

① The liquid gas transition ② the ferromagnetic transition

4.1) Interacting fluids: liquid-gas phase separation

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \sum_{i<j} U(\vec{q}_i - \vec{q}_j) \quad : \; u(\vec{r}) \text{ pair interaction potential}$$

Simple atomic fluids



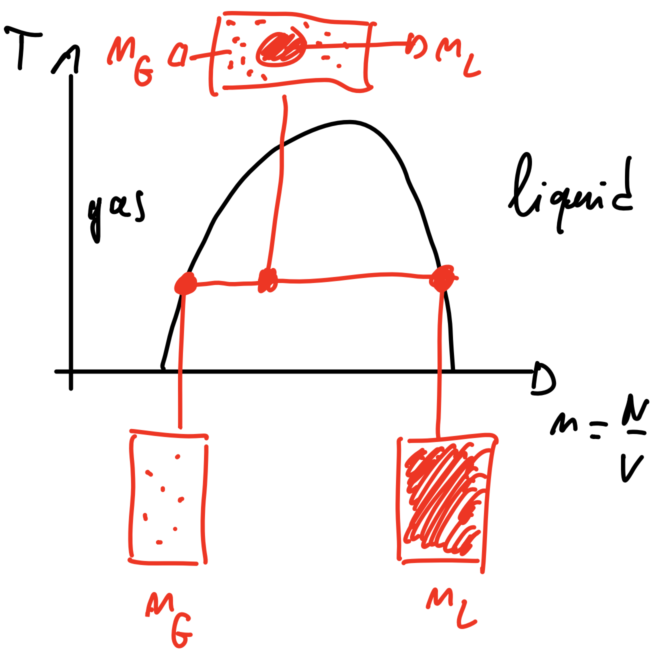
Model: Lennard Jones Potential

$$u(\vec{r}) = \frac{\varepsilon}{4}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Phenomenology: (i) lowering T at fixed $n = \frac{N}{V}$ $\Rightarrow$ liquid-gas phase separation

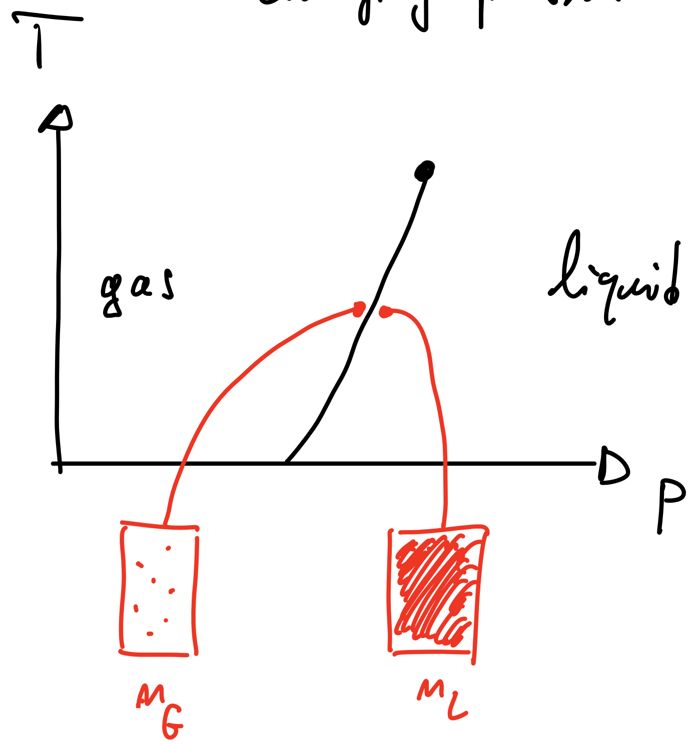
(ii) Increasing p at fixed T leads to a discontinuous liquid-gas transition

changing density.



phase coexistence

changing pressure



discontinuous transition

Q: Can we understand this?

4.2) Mean-field theory & van der Waals equation

Canonical ensemble: $$Z = \frac{1}{N!\,\Lambda^{3N}} \int \prod_i d\vec{q}_i \; e^{-\beta \sum_{i<j} \mathcal{U}(\vec{q}_i - \vec{q}_j)}$$

Density field $\rho(\vec{q}) \equiv \sum_{i=1}^{N} \delta(\vec{q} - \vec{q}_i)$ (fluctuating quantity $\neq$ average density n)

$$U_{tot} = \frac{1}{2} \sum_{i \neq j} \mathcal{U}(\vec{q}_i - \vec{q}_j) = \frac{1}{2} \int d\vec{q}\, d\vec{q}\,' \, \mathcal{U}(\vec{q} - \vec{q}\,')\, \rho(\vec{q})\, \rho(\vec{q}\,') \quad , \text{ setting } \mathcal{U}(0) = 0$$

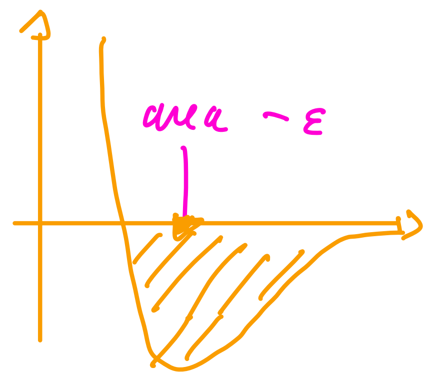
Mean-field approximation: Assume the system is homogeneous & uncorrelated,

$\rho(\vec{r}) \simeq \rho_0$, while enforcing excluded volume

← volume $\Omega = \frac{4}{3}\pi d^3$ out of which particle j is excluded

Total energy

$$\mathcal{U}_{tot} \simeq \frac{1}{2} \underbrace{\int d\vec{q}\, \rho(\vec{q})}_{\rho_0 V} \underbrace{\int_{|\vec{q} - \vec{q}\,'| > d} d\vec{q}\,' \, \mathcal{U}(\vec{q} - \vec{q}\,')\, \underbrace{\rho(\vec{q}\,')}_{\simeq \rho_0}}_{-\rho_0 \varepsilon}$$



$\mathcal{U}_{tot} \simeq -\frac{V}{2} \rho_0^2 \varepsilon$ for admissible configurations

$= +\infty$ if particles overlap

⚠ dimension of ε is NRG × volume

Boltzmann weight: $e^{-\beta \mathcal{U}_{tot}} = 0$ if particles overlap

$= e^{\beta \frac{V \rho_0^2}{2} \varepsilon} = e^{\beta \frac{N^2 \varepsilon}{2V}}$ otherwise

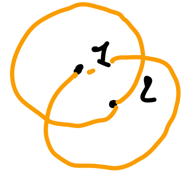
Partition function: $Z = \frac{1}{N! \Lambda^{3N}} \int_{\substack{\text{Non-overlapping} \\ \text{config.}}} \prod_i d\vec{q}_i \; e^{\beta \frac{N^2 \varepsilon}{2V}}$

$$\Rightarrow Z = \frac{e^{\beta \frac{N^2 \varepsilon}{2V}}}{N! \Lambda^{3N}} \underbrace{V}_{\vec{q}_1} \cdot \underbrace{(V - \Omega)}_{\vec{q}_2} \cdot \underbrace{(V - 2\Omega)}_{\vec{q}_3} \cdot \ldots \cdot (V - (N-1)\Omega)$$

vol accessible $= V - 2\Omega$

the integral over $\vec{q}_3$ assume particles 1 & 2 far away

$\Rightarrow$ should break down at high density



excluded vol $< 2\Omega$.

$\Rightarrow$ low density approximation, $n\Omega \ll 1$.

$$Z = \frac{e^{\beta \frac{N^2 \varepsilon}{2V}}}{N!\,\Lambda^{3N}} V^N \Big[\underbrace{1 - \frac{\Omega}{V}\big(\overbrace{1 + 2 + \dots + N-1}^{\frac{N(N-1)}{2} \sim \frac{N^2}{2}}\big) + \mathcal{O}\left(\frac{\Omega^2}{V^2}\right)}_{\simeq\, 1 - \frac{n\Omega}{2}N \,\simeq\, \left(1 - \frac{n\Omega}{2}\right)^N} \Big]$$

All in all

$$\boxed{Z = \underbrace{\frac{1}{N!\,\Lambda^{3N}}}_{\text{ideal gas}} \; \underbrace{e^{\beta \frac{N^2 \varepsilon}{2V}}}_{\text{attraction}} \; \underbrace{\left(V - \frac{N\Omega}{2}\right)^N}_{\text{excluded volume}}}$$

Pressure The canonical pressure is

$$\boxed{P_c = -\frac{\partial F}{\partial V} = kT \frac{\partial \ln Z}{\partial V} = \frac{N kT}{V - \frac{N\Omega}{2}} - \frac{\varepsilon}{2}\left(\frac{N}{V}\right)^2}$$

$$\Leftrightarrow \left[P_c + \frac{\varepsilon}{2}\left(\frac{N}{V}\right)^2\right]\left(V - \frac{N\Omega}{2}\right) = NkT$$

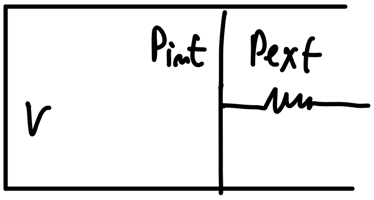
van der Waals equation for weakly interacting gas.

$$\Leftrightarrow \boxed{P_c = \frac{kT}{v - \frac{\Omega}{2}} - \frac{\varepsilon}{2v^2}}$$

where $v = \frac{V}{N} = \frac{1}{n}$ is the free volume per particle

Mechanical stability For a system to be mechanically stable, one needs its compressibility $\kappa = -\frac{1}{v}\frac{\partial v}{\partial p}$ to be positive & $\frac{\partial v}{\partial p} < 0$.

Intuition:



$t=0 \quad P_{int} = P_{ext}$

Fluctuation $V \to V + \delta V$

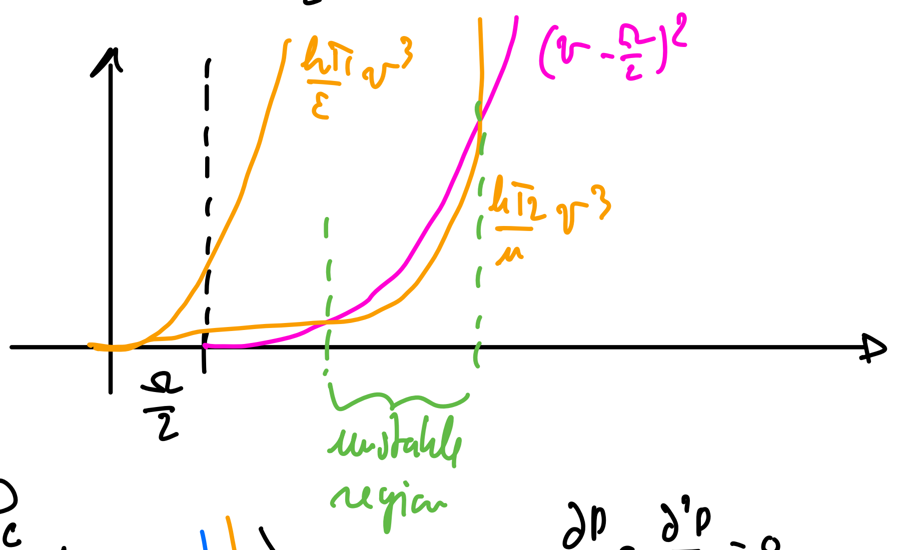
$$\Rightarrow P_{int} \to P_{int} + \frac{\partial P_{int}}{\partial V}\,\delta V$$

if $\frac{\partial P_{int}}{\partial V} > 0$, $\delta V > 0 \Rightarrow \delta P_{int} > 0$ & the volume keeps expanding

$\delta V < 0 \Rightarrow \delta P_{int} < 0$ & ——— shrinking

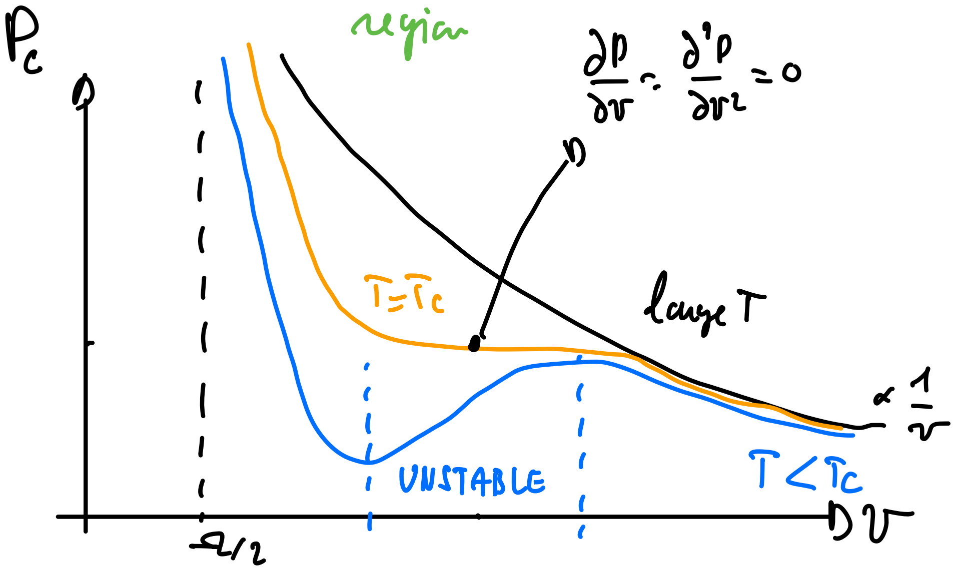
$\Rightarrow$ stability requires $\frac{\partial P}{\partial V} < 0$ so that variations in P restore the fluctuations of V back to $\delta V = 0$.

$$\frac{\partial P_c}{\partial v} = -\frac{NkT}{\left(V - \frac{N\Omega}{2}\right)^2} + \frac{\varepsilon N^2}{V^3} < 0 \iff \frac{kT v^3}{\varepsilon} > \left(v - \frac{\Omega}{2}\right)^2$$



$T_2 < T_1$

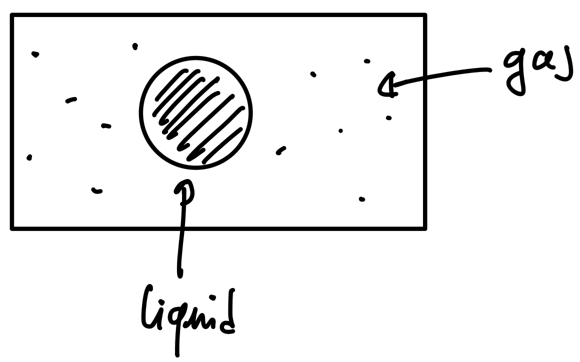
For $\frac{kT}{\varepsilon}$ low enough, the system becomes unstable!



$$P = \underbrace{\frac{kT}{v - \frac{\Omega}{2}}}_{\text{leading order as } v \to \frac{\Omega}{2} \text{ \& } T \text{ large}} - \underbrace{\frac{\varepsilon}{2v^2}}_{\text{important at small } T \text{ \& } v}$$

⇒ What happens? Depends on the ensemble.

Canonical ensemble: the system does not remain homogeneous & mean-field breaks down. Instead, one observes phase separation

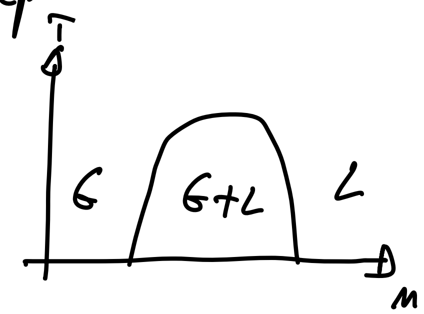


Consider a macrostate defined by the density field $\rho(\vec{r})$. Build & maximize $P[\rho(\vec{r})]$.

Compare $\rho(\vec{r}) = \rho_{\substack{\text{phase}\\\text{separated}}}(\vec{r})$ & $\rho(\vec{r}) = n = \frac{N}{V}$

If $P(\rho_{\substack{\text{phase}\\\text{separated}}}) > P(\rho = n)$ ⇒ phase separation

⇒ leads to



See Pset 7, problem 1