Chapter 4: Interacting particle systems

So far: How to describe dilute systems

Beautiful self consistent theory on relatively simple systems. World around us is rich & complex because more is different. The interplay between fluctuations & interactions are what allows matter to take complex forms.

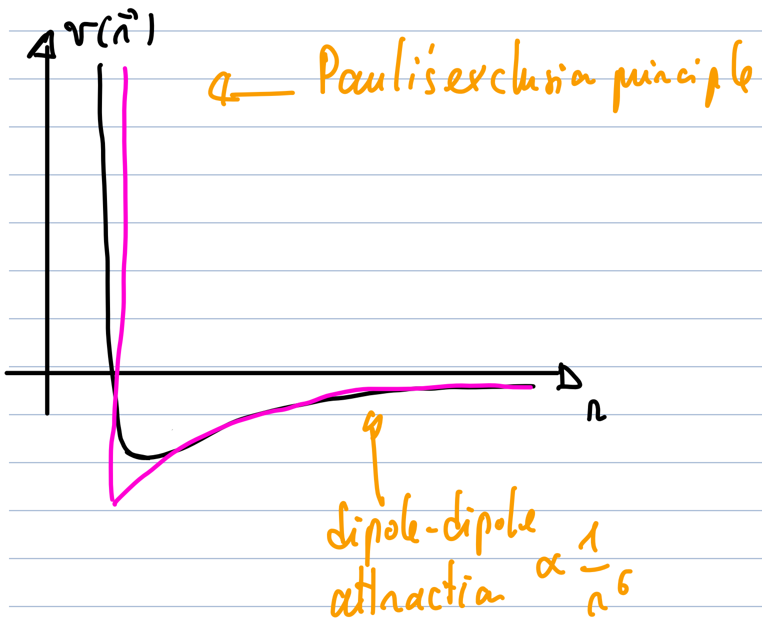
Q1: How do we account for the role of interactions?

Q2: What new phenomena does this leads to?

1. The liquid-gas transition
2. The ferromagnetic transition

4.1) Interacting fluids: liquid-gas phase separation

$$H=\sum_{i=1}^{N}\frac{\vec{p}_i^{\,2}}{2m}+\sum_{i<j}v(\vec{q}_i-\vec{q}_j)$$ ← pair potential

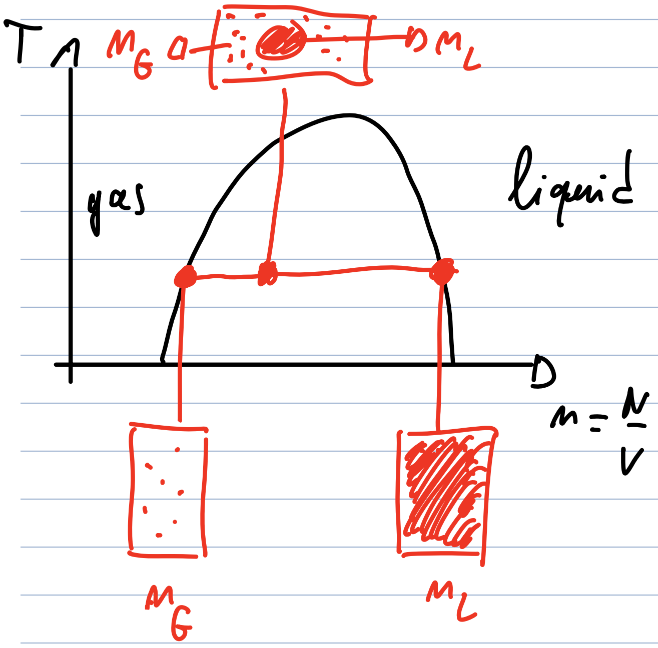


Model: Lennard Jones potential

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

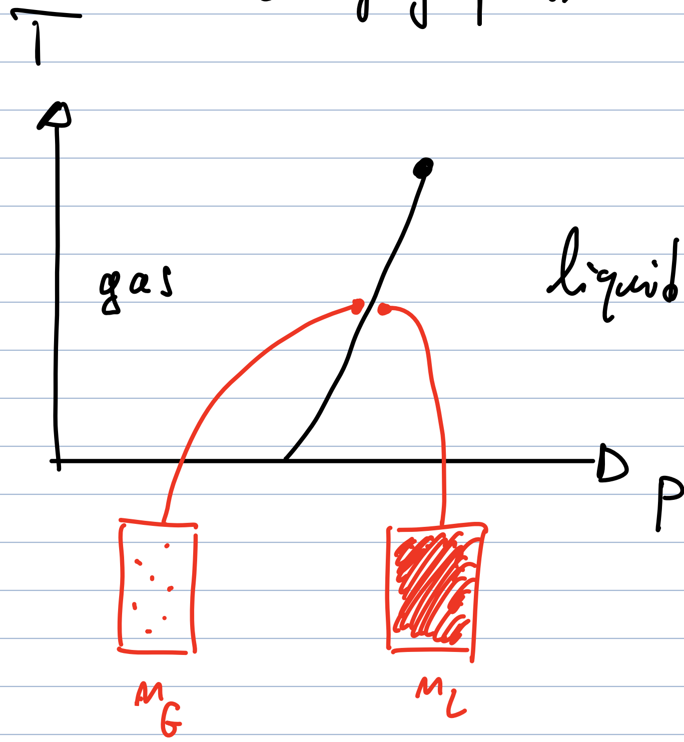
At low temperature, as $n=\frac{N}{V}$ increases, gas is replaced by liquid gas coexistence.

changing density.



phase coexistence

changing pressure



discontinuous transition

Q: Can we understand this?

$$Z = \frac{1}{N!}\int \prod_{i=1}^{N} \frac{d^3\vec{q}_i\, d^3\vec{p}_i}{h^3}\, e^{-\beta \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}}\, e^{-\beta \sum_{i<j} v(\vec{q}_i - \vec{q}_j)}$$

$$= \frac{1}{N!\,\Lambda^{3N}} \underbrace{\int \prod_{k=1}^{N} d^3\vec{q}_k \prod_{i<j} e^{-\beta v(\vec{q}_i - \vec{q}_j)}}_{\neq Z_1^N \Rightarrow \text{hard to analyze}} \qquad \Lambda = \sqrt{\frac{h^2}{2\pi m k_B T}}$$

Very dilute gas: $v(\vec{q}_i - \vec{q}_j) = 0 \Rightarrow e^{-\beta v} = 1 \Rightarrow$ easy

Perturbation theory: $e^{-\beta v(\vec{q}_i - \vec{q}_j)} = 1 + \underbrace{\left(e^{-\beta v(\vec{q}_i - \vec{q}_j)} - 1\right)}_{\equiv f(\vec{q}_i - \vec{q}_j) \equiv f_{ij}} = (1 + f_{ij})$

in $n = \frac{N}{V}$

small when $n = \frac{N}{V}$ is small

4.2) The Virial expansion

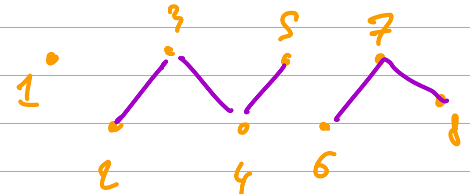
Idea: $P = n kT\left[1 + B_2 n + B_3 n^2 + \dots\right] \Rightarrow$ Virial expansion

B_n : Virial coefficient.

$$Z = \frac{1}{N!\,\Lambda^{3N}} \int \prod_i d\vec{q}_i \left[1 + \sum_{i<j} f_{ij} + \sum_{\substack{i<j \\ k<l}} f_{ij} f_{kl} + \dots \right] \Rightarrow$$ all possible combinations of products

Diagrammatic expansion

$$\int d\vec{q}_1\, 1 \times \int d\vec{q}_2\, d\vec{q}_3\, d\vec{q}_4\, d\vec{q}_5\, f_{23} f_{34} f_{45} \times \int d\vec{q}_6\, d\vec{q}_7\, d\vec{q}_8\, f_{67} f_{78} \Rightarrow$$ product of cluster contributions



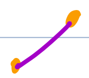
$\Rightarrow$ sum all possible diagrams

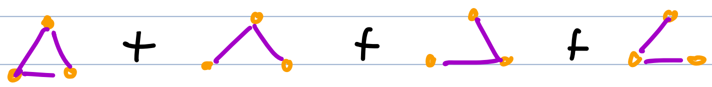
All particles are identical $\Rightarrow$ only the diagram matters.

Define b_ℓ = Sum of contributions of linked clusters

$b_1 = \bullet = \int d\vec{q}_1 = V$

$\rightarrow$ given the potential $v(\vec{q})$, this is a number that can be computed

$b_2 =$  $= \int \underbrace{d\vec{q}_1\, d\vec{q}_2}_{d\vec{q}\,'\, d\vec{q}_2} f(\overbrace{\vec{q}_1 - \vec{q}_2}^{\vec{q}}) = V \int d\vec{q}\, f(\vec{q})$

$b_3 =$ 

etc.

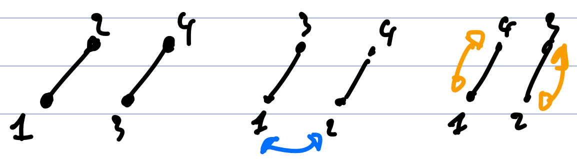
# of ways to split N particles in $m_1, \dots, m_N$ clusters with $1, \dots, N$ part.

$$Z = \frac{1}{N!\,\Lambda^{3N}} \sum_{\{m_\ell \text{ s.t. } N = \sum_\ell m_\ell \ell\}} \prod_\ell b_\ell^{m_\ell} \times \frac{N!}{\prod_\ell (\ell!)^{m_\ell}\, (m_\ell)!}$$

$N!$ ← all possible permutations

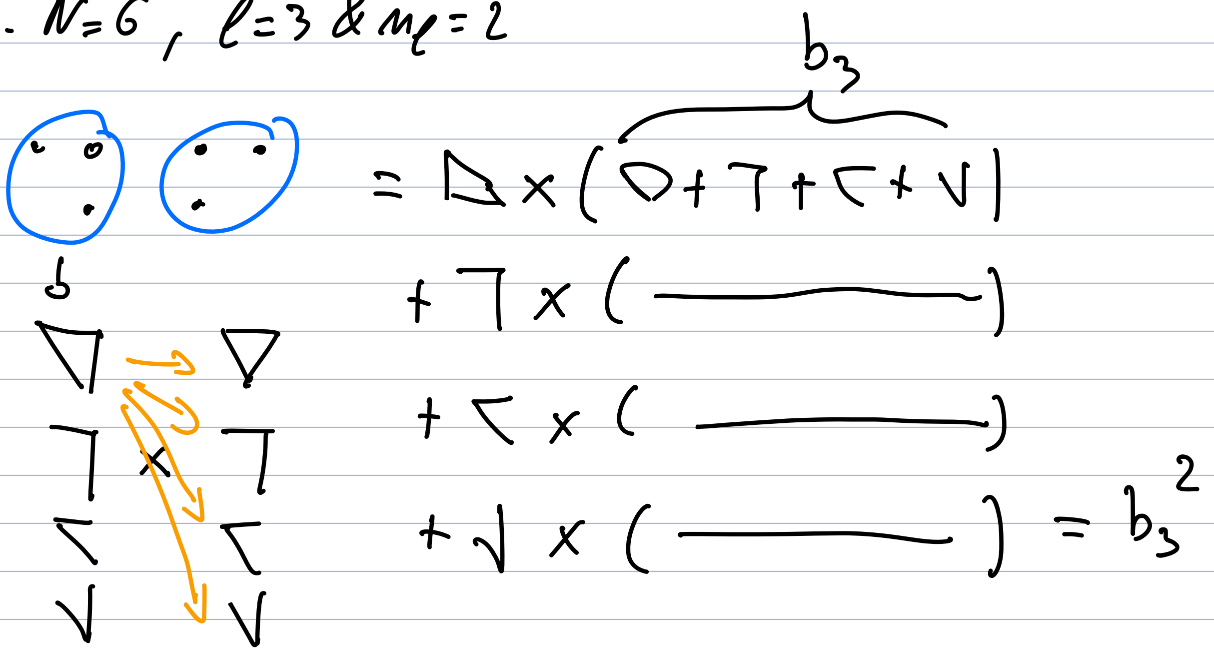
$(\ell!)^{m_\ell}$: permutations within a cluster do not create a new cluster

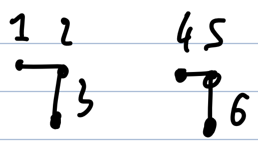
$(m_\ell)!$: permutations of clusters do not create a new term

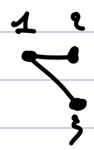


$$3 = \frac{4!}{(2!)^2\,(2!)}$$

E.g. $N=6$, $l=3$ & $m_l=2$



Take 

Swap 1 & 2 $\Rightarrow$  already in b_3 $\rightarrow \frac{1}{(l!)}$

Swap 1,2,3 & 4,5,6 $\Rightarrow$ already in b_3^2 $\rightarrow \frac{1}{m_l!}$

$$\sum_{\{m_l \mid \sum_l m_l l = N\}} \Rightarrow \text{horrible combinatorial pb}$$

Grand canonical ensemble

$$Q = \sum_N e^{\beta\mu N} Z_N$$

$$= \sum_{\{m_l\}} \cancel{\frac{1}{N!}} \prod_{l=1}^{\infty} (b_l)^{m_l} \Big(\underbrace{\frac{e^{\beta\mu}}{\Lambda^3}}_{z}\Big)^{N=\sum_l m_l l} \frac{\cancel{N!}}{\prod_l (l!)^{m_l}(m_l)!}$$

$$= \prod_{l=1}^{\infty} \sum_{m_l} \left[b_l \frac{z^l}{l!} \right]^{m_l} \times \frac{1}{(m_l)!} = \prod_{l=1}^{\infty} \exp\left[\frac{b_l}{l!} z^l \right]$$

$$\Rightarrow G = -PV = -kT \sum_{l=1}^{\infty} \left(\frac{e^{\beta\mu}}{\Lambda^3} \right)^l \frac{b_l}{l!} \Rightarrow P(\mu) = kT \sum_{l=1}^{\infty} \left(\frac{e^{\beta\mu}}{\Lambda^3} \right)^l \frac{\bar{b}_l}{l!}$$

where $\bar{b}_l = \frac{b_l}{V}$.