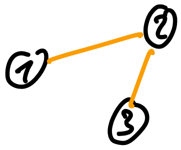
Recap:

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

Q: How can we account for the emerging physics as $n = \frac{N}{V}$ increases?

$f_{ij} = \left(e^{-\beta v(\vec{q}_i - \vec{q}_j)} - 1\right)$ & diagrammatic expansion;  $= \int d\vec{q}_1 d\vec{q}_2 d\vec{q}_3 \, f_{12} f_{23}$

Grand canonical ensemble

$$Q = \sum_N e^{\beta\mu N} Z_N = \prod_{\ell=1}^{\infty} \exp\left[\frac{b_\ell}{\ell!} z^\ell\right]$$

where b_ℓ = total contribution of diagrams with ℓ particles

$$G = -PV = -kT \sum_{\ell=1}^{\infty} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^\ell \frac{b_\ell}{\ell!} \Rightarrow P(\mu) = kT \sum_{\ell=1}^{\infty} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^\ell \frac{\bar{b}_\ell}{\ell!}$$

where $\bar{b}_\ell = \frac{b_\ell}{V}$.

Go from $P(\mu)$ to $P(n) \Rightarrow$ need $\mu(n)$ or $z(n)$

$$N_{GC} = -\frac{\partial G}{\partial \mu}\Big|_T = V \frac{\partial P}{\partial \mu}\Big|_T \Rightarrow n = \frac{N_{GC}}{V} = kT \sum_{\ell=1}^{\infty} \ell \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^{\ell-1} \frac{e^{\beta\mu}}{\lambda^3} \beta \frac{\bar{b}_\ell}{\ell!}$$

$$n = \sum_{\ell=1}^{\infty} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^\ell \frac{\bar{b}_\ell}{(\ell-1)!} = z + \bar{b}_2 z^2 + \frac{\bar{b}_3}{2} z^3 + \dots$$ $\Rightarrow$ but we need $z(n)$!

$\Rightarrow$ Invert: $z = \sum_{k=1}^{\infty} c_k n^k$ & inject in $\uparrow$ + solve order by order

$$\Rightarrow z = n - \bar{b}_2 n^2 + \left(2\bar{b}_2 - \frac{\bar{b}_3}{2}\right) n^3 + O(n^4)$$

$$n = \sum_{k=1}^{\infty} c_k n^k + \bar{b}_2 \left[\sum_k c_k n^k\right]^2 + \frac{\bar{b}_3}{2} \left[\sum_k c_k n^k\right]^3 + \dots$$

$\mathcal{O}(n)$: $n = c_1 n \Rightarrow c_1 = 1$

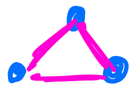
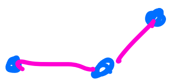
$\mathcal{O}(n^2)$: $0 = c_2 n^2 + b_2 c_1^2 n^2 \Rightarrow c_2 = -b_2$

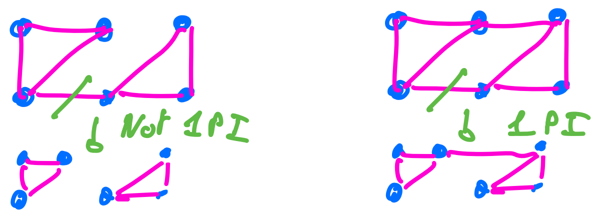
$\mathcal{O}(n^3)$: $0 = c_3 n^3 + 2 b_2 c_1 c_2 n^3 + \frac{b_3}{2} c_1 n^3 \Rightarrow c_3 = 2 b_2^2 - \frac{b_3}{2}$

Back to P:

$$\beta P = \sum_{k=1}^{\infty} z^k \frac{b_k}{k!} = n - b_2 n^2 + \left(2 b_2 - \frac{b_3}{2}\right) n^3 + \frac{b_2}{2}\left(n^2 - 2 b_2 n^3\right) + \frac{b_3}{6} n^3$$

$$\boxed{\beta P = n - \frac{b_2}{2} n^2 + \left[b_2^2 - \frac{b_3}{3} \right] n^3 + \mathcal{O}(n^4)}$$

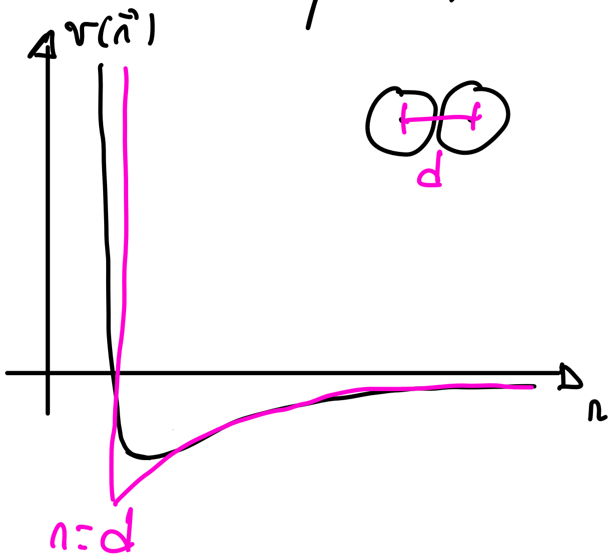
Comment: $b_2^2 - \frac{b_3}{3} = -\frac{1}{3}$  . Expected since diagrams like  scale as n^2. Only the so-called "1 particle irreducible (1PI) diagrams" matter. These are diagrams that cannot be split into two by removing 1 bond.



Virial coefficients

$$\boxed{B_2 = -\frac{1}{2V} \int dq_1 d\vec{q}\, f(\vec{q}) = -\frac{1}{2} \int d\vec{q} \left(e^{-\beta v(\vec{q})} - 1 \right)}$$

Can also compute B_3, etc.



Let's evaluate B_2 for an atomic fluid.

Approximation

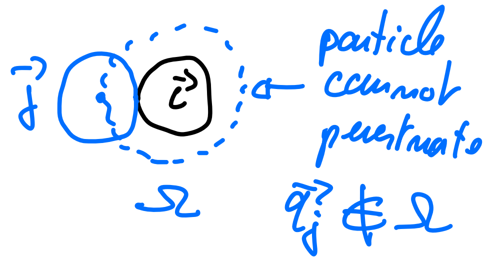
$$v(r) = \begin{cases} 0 & \text{if } r < r_0 \\ -v_0 \left(\frac{d}{r}\right)^6 & \text{if } r > r_0 \end{cases}$$

$$B_2 = -\frac{1}{2}\int d^3\vec{r}\,\left(e^{-\beta v}-1\right) = -\frac{1}{2}\left[-\frac{4}{3}\pi d^3 + \int_d^\infty 4\pi r^2 dr\left[e^{\beta v_0\left(\frac{d}{r}\right)^6}-1\right]\right]$$

High temperature expansion $\beta v_0 << 1$

$$e^{\beta v_0\left(\frac{d^6}{r^6}\right)}-1 \simeq \beta v_0 \frac{d^6}{r^6} \Rightarrow \int_d^\infty 4\pi r^2 dr\left(e^{\beta v_0\left(\frac{d}{r}\right)^6}-1\right) = 4\pi\beta v_0 d^6\left[-\frac{r^{-3}}{3}\right]_d^\infty = \frac{4\pi d^3}{3}\,\frac{v_0}{kT}$$

$$B_2 = \frac{\Omega}{2}\left[1-\frac{v_0}{kT}\right] \text{ with } \underbrace{\Omega = \frac{4\pi d^3}{3}}_{\text{excluded volume due to interactions}}$$



$$\Rightarrow \boxed{P = nkT\left[1+\frac{n}{2}\Omega\left(1-\frac{v_0}{kT}\right)\right]} \quad (*)$$

Nature of the Virial expansion

* The expansion in n is actually an expansion in $n\Omega$ which is the average number of particles that would be in Ω if there was not a particle

* $\Omega^{-1} \sim$ density of the liquid phase $\Rightarrow n\Omega \simeq \frac{n}{n_{liq}}$

  $n\Omega << 1$ only at density $<< n_{liquid}$

$\Rightarrow$ for $n \simeq n_{liquid} \Rightarrow$ need other methods/expansions
See Hansen & McDonald

* To expand $e^{-\beta u} \simeq 1-\beta u$, we need $\beta u_0 \ll 1$

$\Rightarrow$ only valid at high temperature.

$\Rightarrow$ How bad is it at low temperature?

$$P = \frac{NkT}{V} + \frac{N^2 kT}{2V^2}\,\Omega\left[1-\frac{u_0}{kT}\right] = \frac{a}{V} + \frac{b}{V^2}$$

$$\Rightarrow \frac{\partial P}{\partial V} = -\frac{a}{V} - \frac{2b}{V^2} > 0 \text{ if } b < -\frac{aV}{2}$$

$$\Leftrightarrow \frac{N^2 kT\Omega}{2}\left(1-\frac{u_0}{kT}\right) < -\frac{NkTV}{2}$$

$$\Leftrightarrow 1-\frac{u_0}{kT} < -\frac{V}{N\Omega} = -\frac{1}{n\Omega}$$

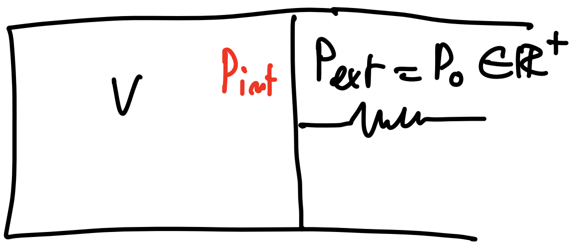
$$\frac{u_0}{kT} > \frac{V-N\Omega}{N\Omega}$$

$$\frac{\partial P}{\partial V} > 0 \text{ if } \boxed{kT < u_0\frac{N\Omega}{V-N\Omega}}$$

Large T, small n $\Rightarrow$ never but small T / large n $\Rightarrow$ $\frac{\partial P}{\partial V} > 0$ $\Rightarrow$ problem!

Then the compressibility of the fluid $\kappa = -\frac{1}{V}\frac{\partial V}{\partial P} < 0$

$\Rightarrow$ the system is unstable.



$t=0$; $P_{int} = P_{ext}$

fluctuation $V \to V-\delta V \Rightarrow \delta P < 0$

$\Rightarrow P_{int} < P_{ext} \Rightarrow \delta V$ increases

$\Rightarrow$ the piston compresses the gas even further.

$\Rightarrow$ the system is unstable

$\Rightarrow$ Something has to happen as we lower T.

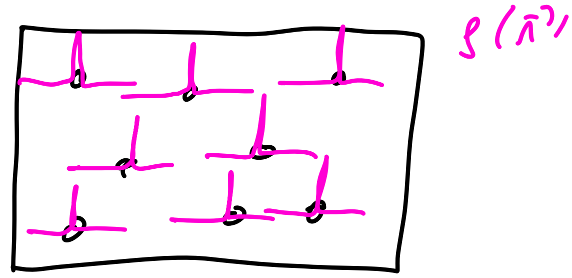
$\Rightarrow$ Cluster expansion hard to use & not very intuitive

$\Rightarrow$ Mean-field theory instead

4.3) Mean-field theory & van der Waals equation

Canonical ensemble

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



Density field $\varrho(\vec{q}\,) = \sum_{i=1}^{N} \delta(\vec{q} - \vec{q}_i)$

$\varrho(\vec{r}\,)$ to distinguish from $n = \frac{N}{V}$

$\Rightarrow$ same as $n(\vec{r}\,)$ in chapter 2.

$$U = \frac{1}{2}\sum_{i \neq j} v(\vec{q}_i - \vec{q}_j) = \frac{1}{2}\int d\vec{q}\, d\vec{q}\,'\, v(\vec{q} - \vec{q}\,')\, \varrho(\vec{q}\,)\, \varrho(\vec{q}\,')$$

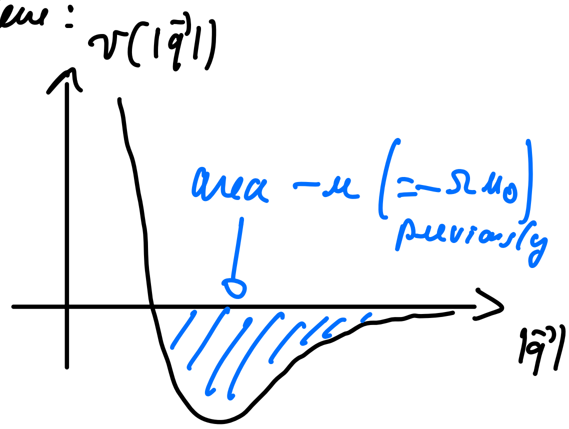
(setting $v(0)=0$)

Mean-field approximation

Assume the system homogeneous & the particles uncorrelated:

$\varrho(\vec{r}\,) \simeq \varrho_0$, while enforcing excluded volume:

$$U = \frac{1}{2}\underbrace{\int d\vec{q}\, \varrho(\vec{q}\,)}_{\varrho_0 V} \underbrace{\int_{|\vec{q}-\vec{q}\,'|>d} d\vec{q}\,'\, v(\vec{q}-\vec{q}\,')\, \underbrace{\varrho(\vec{q}\,')}_{\simeq \varrho_0}}_{-\varrho_0 u}$$



$\Rightarrow U = -\frac{V}{2}\varrho_0^2 u$

$\Rightarrow$ Boltzmann weight $e^{-\beta U} = e^{\beta \frac{V \varrho_0^2 u}{2}} = e^{\beta \frac{N^2 u}{2V}}$

$\Rightarrow$ Partition function $Z = \frac{1}{N!\,\Lambda^{3N}} \int d\vec{q}_1 \dots d\vec{q}_N\; e^{\beta \frac{N^2 u}{2V}}$

$$= \frac{e^{\frac{\beta N^2 u}{2V}}}{N!\,\Lambda^{3N}}\; \underbrace{V}_{\text{volume accessible to } \vec{q}_1} \times \underbrace{(V - \Omega)}_{\dots\text{ to } \vec{q}_2} \times \underbrace{(V - 2\Omega)}_{\dots\text{ to } \vec{q}_3} \times \dots \times \underbrace{(V - (N-1)\Omega)}_{\text{to } \vec{q}_N}$$

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

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 Waals' equation

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

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

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

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

Intensive form: $\boxed{P = \frac{kT}{\tilde{v} - \frac{\Omega}{2}} - \frac{u_0 \Omega}{2\tilde{v}^2}}$; $\tilde{v} = \frac{V}{N}$ free volume per particle