Lecture 8: Interacting classical fluids

Recap Generic classical Hamiltonian (no internal degrees of freedom)

$$H(\vec{r}^N,\vec{p}^N)=\sum_{i=1}^{N}\frac{\vec{p}_i^{\,2}}{2m}+\underbrace{\Phi(\vec{r}^N)}_{\sum_{i=1}^{N}V_{ext}(\vec{r}_i)+\sum_{i<j}v(|\vec{r}_i-\vec{r}_j|)+\ldots\ldots}$$

The canonical partition function in the classical limit is

$$Z(N,V,T)=\frac{1}{h^{3N}N!}\int d\vec{p}^N\int d\vec{r}^N\,e^{-\beta H(\vec{r}^N,\vec{p}^N)}$$

$$=\frac{Q(N,V,T)}{N!\,\Lambda^{3N}}$$

momentum integrations are Gaussian

with $Q(N,V,T)=\int d\vec{r}^N\,e^{-\beta\Phi(\vec{r}^N)}$

configurational integral

Here, $\Lambda=\dfrac{h}{\sqrt{2\pi m k_B T}}$

(Notice we cannot use statistical field theory methods generally speaking since the functional inverse of v does not necessarily exist!)

$\rightsquigarrow$ Problem boils down to computing $Q(N,V,T)$.

For now, let us consider the case where $V_{ext}=0$ (homogeneous/bulk systems).

Furthermore, we neglect three-body interactions.

Then

$$Z(N,V,T)=\frac{1}{N!\Lambda^{3N}}\int d\vec{r}^N\,\underbrace{\exp\Big[-\beta\sum_{i<j}v(r_{ij})\Big]}_{\prod_{i<j}\big(\underbrace{e^{-\beta v(r_{ij})}-1}_{:=f_M(r_{ij})}+1\big)}$$

$\vec{r}_{ij}=\vec{r}_i-\vec{r}_j$

$r_{ij}=|\vec{r}_{ij}|$.

Mayer function.

$$=\prod_{i<j}(1+f_M(r_{ij}))=1+\sum_{i<j}f_M(r_{ij})+\ldots\ldots$$

identical particles and there are $\frac{N(N-1)}{2}$ pairs.

$\vec{R} = (\vec{r}_1 + \vec{r}_2)/2 \; ; \; \vec{r} = \vec{r}_1 - \vec{r}_2 .$

② $Z(N,V,T) =$

$$\frac{V^N}{N!\Lambda^{3N}} + \frac{V^{N-2}}{N!\Lambda^{3N}} \frac{N(N-1)}{2} \int d\vec{r}_1 \underbrace{\int d\vec{r}_2 \, f_M(r_{12})}_{= V \int d\vec{r} \, f_M(r)}$$

$$= \frac{V^N}{N!\Lambda^{3N}} \left[1 - \frac{N(N-1)}{V} B_2 + \ldots\ldots \right]$$

where we have defined the second virial coefficient

$$B_2 = -\frac{1}{2} \int d\vec{r} \, f_M(r) \qquad \text{Note that } B_2 = B_2(T)$$

Define $F_{ex}(N,V,T) = F(N,V,T) - F_{id}(N,V,T)$

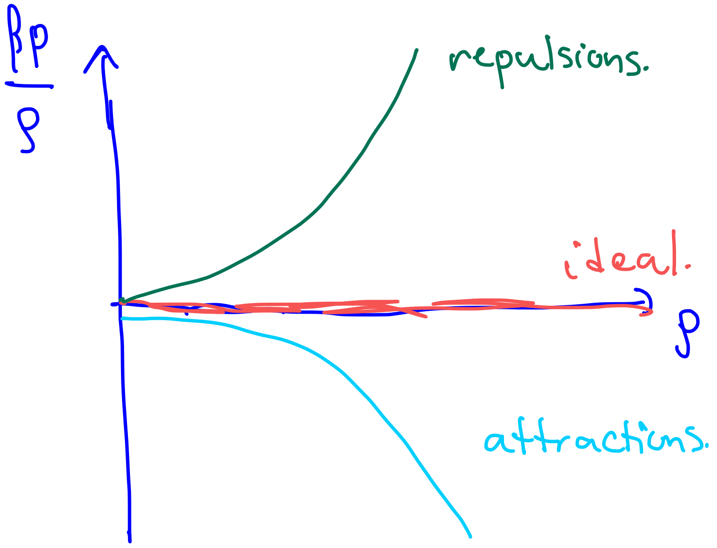
$$f = \frac{F}{V}$$

$$\Rightarrow f_{ex} = \frac{\beta F_{ex}(N,V,T)}{V} = \frac{N(N-1)}{V^2} B_2 \overset{N\gg 1}{=} \rho^2 B_2(T).$$

We can obtain the pressure as $\beta p = -f + \rho \left(\frac{\partial f}{\partial \rho}\right)_T$ and find

$$\Rightarrow \beta p = \rho + B_2(T)\rho^2 + \ldots\ldots \quad \begin{cases} B_2 > 0 & \text{repulsions} \\ B_2 < 0 & \text{attractions} \end{cases}$$

$\Downarrow$ corresponds to whether B_2 is dominated by attractions or repulsions!



How to obtain higher order corrections?

$$Z(N,V,T) = \frac{1}{N!\Lambda^{3N}} \int d\vec{r}^N \left[1 + \sum_{i<j} 1 + \sum_{i<j} \sum_{k<l} f_M(r_{ij}) f_M(r_{kl}) + \ldots\ldots \right]$$

In principle, we could continue with this computation. However, the fixed particle constraint is tedious to handle ...

Solution: Let's go to the grand-canonical ensemble!

Define: $Q_N(V,T) = Q(N,V,T)$; $z = \frac{e^{\beta\mu}}{\Lambda^3}$ (fugacity).

Then: $\Xi(\mu,V,T) = \sum_{N=0}^{\infty} \frac{z^N}{N!} Q_N(V,T)$

Furthermore, $\beta\Omega = -\ln \Xi$ and define $\beta\Omega = -V \sum_{n=1}^{\infty} b_n z^n$ $\Bigg\} \Rightarrow$

$$b_1 = \frac{Q_1}{V}, \quad b_2 = \frac{Q_2 - Q_1^2}{2!\,V}, \quad b_3 = \frac{Q_3 - 3Q_2Q_1 + 2Q_1^3}{3!\,V}, \quad \dots$$

where we used $\ln(1+x) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{x^n}{n}$.

We conclude that: • $\Omega(\mu,V,T) = -p(\mu,T)V \Rightarrow \beta p(z,T) = \sum_{n=1}^{\infty} b_n z^n$.

• $\langle N \rangle = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{V,T} = -z\left(\frac{\partial\Omega}{\partial z}\right)_{V,T} \Rightarrow \rho(z,T) = \sum_{n=1}^{\infty} n\, b_n z^n$

However, we want to express z in terms of ρ. So we write $z = \sum_{n=1}^{\infty} a_n \rho^n$ $\Bigg\} \Rightarrow$

We find (see Tutorials): $a_1 = 1$; $a_2 = -b_2$; $a_3 = -3b_3 + 8b_2^2$.

Let us compute pressure. $\beta p(\rho,T) = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots$

We find:

$$B_2(T) = -\frac{1}{2V}\int d\vec{r}_1 \int d\vec{r}_2\, f_M(r_{12}) = -\frac{1}{2}\int d\vec{r}\, f_M(r).$$

and $$B_3(T) = \frac{1}{3V}\int d\vec{r}_1 \int d\vec{r}_2 \int d\vec{r}_3\, f_M(r_{12}) f_M(r_{13}) f_M(r_{23})$$

Remark: $B_2(T_B) = 0 \Leftrightarrow T_B$: Boyle temperature

(signifies transition between repulsion / attraction dominated at sufficiently low density).

It is useful sometimes to define excess quantities, e.g. $F_{ex} := F - F_{id}$ (so the contribution over the ideal case)

Similarly, $\beta f_{ex} = \frac{F-F_{id}}{V k_B T} = \sum_{n=2}^{\infty} C_n(T)\rho^n$.

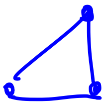
$$\left.\begin{aligned}&\beta f_{ex} = \frac{F-F_{id}}{V k_B T} = \sum_{n=2}^{\infty} C_n(T)\rho^n \\ &\beta p = -\left(\frac{\partial \beta F}{\partial V}\right)_{N,T} = -\beta f + \rho\left(\frac{\partial \beta f}{\partial \rho}\right)_T\end{aligned}\right\} \Rightarrow \quad C_n = \frac{B_n}{n-1}$$

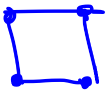
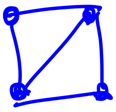
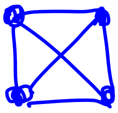
We conclude that:

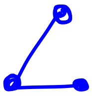
$$\beta f = \frac{\beta F}{V} = \rho\left[\log(\rho\Lambda^3)-1\right] + B_2(T)\rho^2 + \frac{B_3(T)}{2}\rho^3 + \ldots\ldots$$

The virial coefficients can be represented graphically as:

$B_2(T) = -\frac{1}{2V}\int d\vec{r}_1 \int d\vec{r}_2$ 

$B_3(T) = -\frac{1}{3V}\int d\vec{r}_1 \int d\vec{r}_2 \int d\vec{r}_3$ 

$B_4(T) = -\frac{1}{8V}\int d\vec{r}_1 \int d\vec{r}_2 \int d\vec{r}_3 \int d\vec{r}_4 \Big($ 3  + 6  +  $\Big)$

Note that diagrams like  drop out. Only irreducible clusters, i.e only connected graphs. (cutting one line doesn't make the graph to disconnect in two pieces)

Examples of virial expansions

Very important model system is the hard-sphere system:

(i)

$$v_{HS}(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma. \end{cases}$$

From now on: only 3d systems!

We find:

$$B_2 = \frac{2}{3}\pi\sigma^3$$

Note that $B_n \neq f(T)$!

$$B_3 = \frac{5\pi^2}{18}\sigma^6$$

$$B_4 = \left[-\frac{89}{280} + \frac{219\sqrt{2}}{2240\pi} + \frac{4131}{2240\pi}\arccos\left(\frac{1}{\sqrt{3}}\right)\right]B_2^3$$

It is convenient to define the volume fraction: $\eta = \frac{\text{volume occupied by particles}}{\text{total volume}}$

For hard spheres: $\eta = \frac{\pi}{6}\sigma^3\rho$.

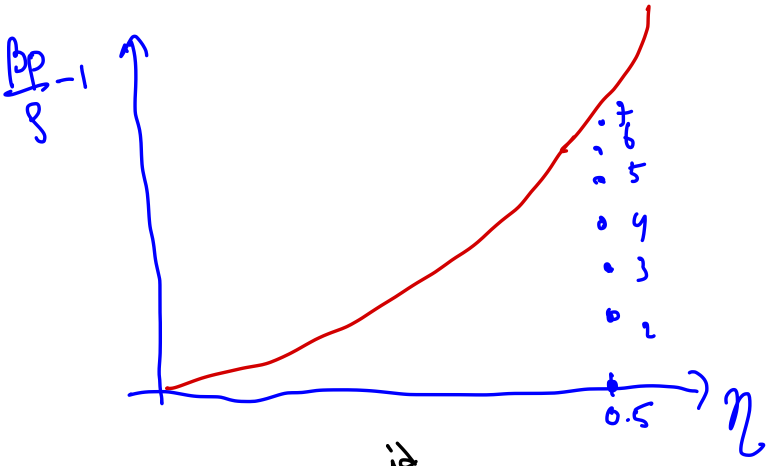
We find:

$$\frac{\beta p}{\rho} = \underbrace{1+4\eta+10\eta^2+18.365\eta^3+28.225\eta^4+39.74\eta^5+53.5\eta^6+70.8\eta^7+\dots}_{\approx \sum_{n=1}^{\infty}(n^2+3n)\eta^n}$$

This series can be summed.

$$\Rightarrow \frac{\beta p}{\rho} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}$$

Carnahan-Starling equation of state. | max 1% deviation in entire fluid range!



Virial expansion converges slowly.

What happens for $\eta \gtrsim 0.5$?

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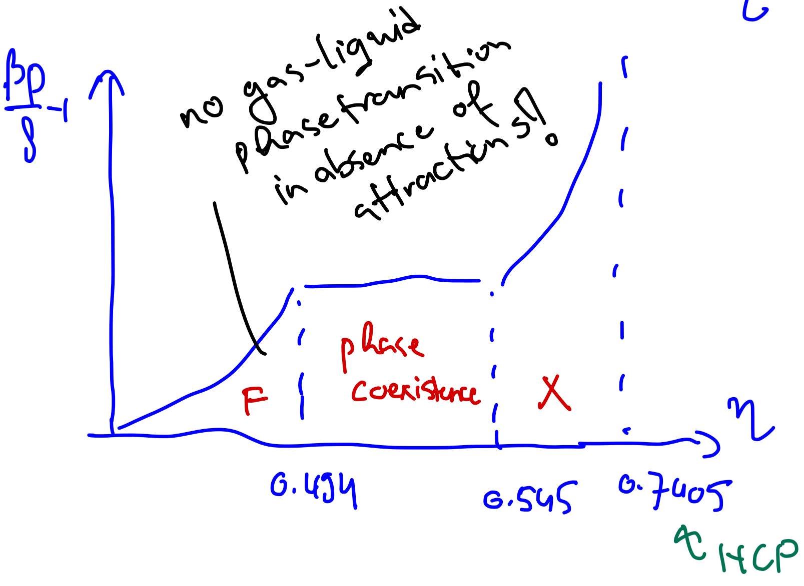


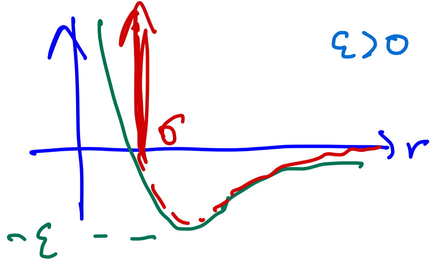
Reason crystallization:

Entropy!

Free volume at high η is higher when particles are ordered on a crystal lattice.

(ii) A model which contains attractions is the Lennard-Jones potential

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



We approximate: $v_{LJ}(r) = \begin{cases} v_{HS}(r) & r<\sigma \\ -4\varepsilon\left(\frac{\sigma}{r}\right)^6 & r>\sigma \end{cases}$ (σ can be free parameter) WCA theory.

The free energy density can be written as

$$f(\rho,T) = f_{HS}(\rho) - \frac{\rho^2}{2} k_B T \int d\vec{r}\, \left[e^{-\beta v_{att}(r)} - 1\right]$$

$$\approx f_{HS}(\rho) - \frac{\rho^2}{2}\int d\vec{r}\, 4\varepsilon\left(\frac{\sigma}{r}\right)^6 =: f_{HS} - a\rho^2.$$

with $a = 16\varepsilon v_0$

$v_0 = \frac{\pi}{6}\sigma^3$

$\downarrow$ could be approximated by Carnahan-Starling. However, alternative approximation:

The T is silent :)

$$Q_{HS}(N,V,T) = \int d\vec{r}\, \exp\left[-\beta \sum_{i<j} v_{HS}(r_{ij})\right] = V(V-8v_0)(V-2\cdot 8v_0)\cdots(V-(N-1)8v_0)$$

$$\approx V^N\left(1 - \frac{N^2}{2}\frac{8v_0}{V} + \dots\right)$$

binomial expansion

$$\approx \left(V - \frac{N}{2}8v_0\right)^N =: (V-Nb)^N \qquad (8v_0 \ll V)$$

We thus find: $\beta f(\rho) = \rho\left[\log\left(\frac{\rho\Lambda^3}{1-b\rho}\right) - 1\right] - \beta a\rho^2$ Precisely the VdW approximation.

Recall this was already written down when people were still disputing the existence of molecules & atoms!

Remarks on the virial expansion:

- Virial coefficients become progressively harder to calculate for large n and more general model potentials (see Tutorials)
- For long-ranged interaction potentials $B_n(T)$ is ill-defined.
  E.g.: Point Coulomb interactions, dipole-dipole interactions.
- Slowly converging series $\Rightarrow$ problem for dense fluids!

Furthermore, as before we are interested in correlation functions!

Density-density correlation functions

We define the classical dencity operator as: $\hat{\rho}(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i)$

Observe that $\rho(\vec{r}) := \langle \hat{\rho}(\vec{r}) \rangle$ is the local density of the system.

E.g. in canonical ensemble with $\Phi(\vec{r}_1, \ldots, \vec{r}_N)$ completely symmetric (identical particles)

$$\langle \hat{\rho}(\vec{r}) \rangle = \frac{1}{Q(N,V,T)} \int d\vec{r}^{N} \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i)\, e^{-\beta \Phi(\vec{r}^{N})}$$

$$= \frac{N}{Q(N,V,T)} \int d\vec{r}_2 \ldots \int d\vec{r}_N\, e^{-\beta \Phi(\vec{r}, \vec{r}_2, \ldots, \vec{r}_N)}$$

Now: $\int d\vec{r}\, \rho(\vec{r}) = \int d\vec{r} \langle \hat{\rho}(\vec{r}) \rangle = \frac{N}{Q(N,V,T)} \underbrace{\int d\vec{r} \int d\vec{r}_2 \ldots \int d\vec{r}_N\, e^{-\beta \Phi(\vec{r}, \vec{r}_2, \ldots \vec{r}_N)}}_{= Q(N,V,T)}$

$\Rightarrow \int d\vec{r}\, \rho(\vec{r}) = N$ $\Rightarrow$ $\rho(\vec{r})$ is indeed the local density.

Interpretation: Probability to find a particle at position $\vec{r}$, irrespective of what the other particles' positions & momenta are.

Note that for homogeneous (i.e. bulk) fluid: $V_{ext}(\vec{r}) = 0$

$\Rightarrow \rho(\vec{r}) = \rho = cst.$ (Prove this!)

What about 2-body correlations?

We introduce the two-body density operator:

$\hat{\rho}^{(2)}(\vec{r}, \vec{r}\,') = \sum_{i \neq j} \sum_{j=1}^{N} \delta(\vec{r}-\vec{r}_i)\, \delta(\vec{r}\,'-\vec{r}_j)$. and define: $\rho^{(2)}(\vec{r}, \vec{r}\,') = \langle \hat{\rho}^{(2)}(\vec{r}, \vec{r}\,') \rangle$

Note the normalisation: $\int d\vec{r} \int d\vec{r}\,' \rho^{(2)}(\vec{r}, \vec{r}\,') = N(N-1)$

Interpretation: $\rho^{(2)}(\vec{r},\vec{r}')$ is the probability to find a particle at $\vec{r}$ and one at $\vec{r}'$; irrespective of what we know about the position and momenta of the other particles

For suitable Φ: $\rho^{(2)}(\vec{r},\vec{r}') \longrightarrow \rho(\vec{r})\rho(\vec{r}')$ $\quad (|\vec{r}-\vec{r}'| \to \infty)$.

This motivates us to define: $g(\vec{r},\vec{r}') = \dfrac{\rho^{(2)}(\vec{r},\vec{r}')}{\rho(\vec{r})\rho(\vec{r}')}$

with property $g(\vec{r},\vec{r}') \to 1$ for $|\vec{r}-\vec{r}'| \to \infty$.

For bulk ($V_{ext}=0$) we have translational invariance + isotropy.

$\Rightarrow g(\vec{r},\vec{r}') = g(|\vec{r}-\vec{r}'|)$ This is called the radial distribution function or pair correlation function.

Interpretation: Reminder on probability theory.

Let X and Y be continuous stochastic variables with joint probability density $p(x,y)$. Then the so-called marginal distributions are:

$$p_X(x) = \int dy\, p(x,y)$$

$$p_Y(y) = \int dx\, p(x,y)$$

$\uparrow$ "integrating out dofs" in physics language

Then the conditional probability density of Y given that $X=x$ is $\quad p(y|x) = \dfrac{p(x,y)}{p_x(x)}$

Apply this terminology to the density-density correlation functions:

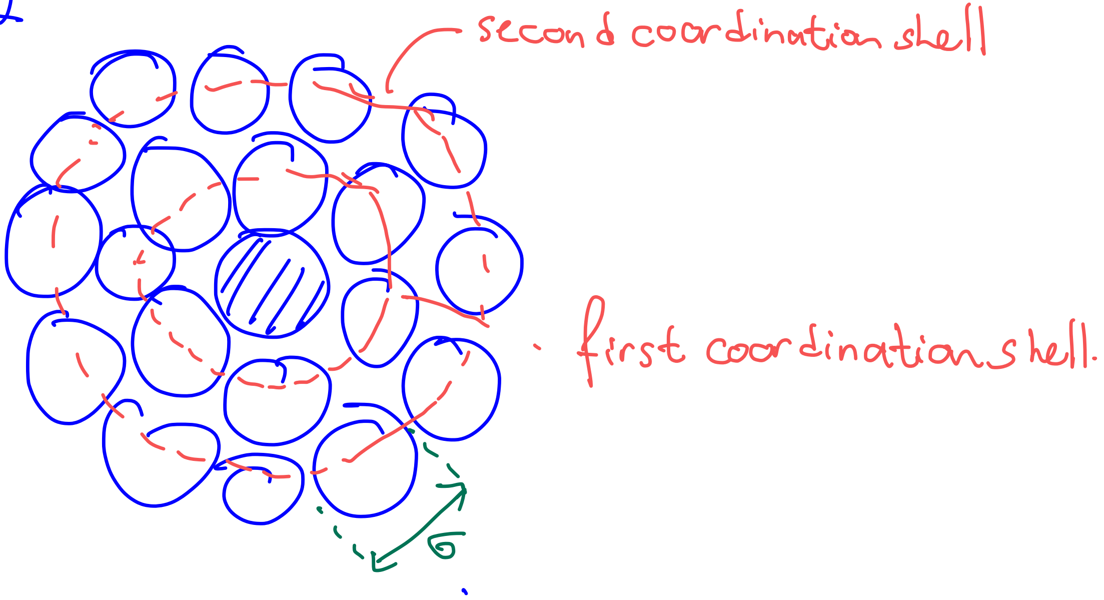
$\frac{\rho^{(2)}(\vec{r},\vec{r}')}{N(N-1)}$: probability to find one particle at $\vec{r}$ and one at $\vec{r}'$

$\frac{\rho(\vec{r})}{N}$: probability to find one particle at $\vec{r}$.

$\Rightarrow$ $\frac{\rho(\vec{r})\,g(\vec{r},\vec{r}')}{N-1}$: probability to find particle at $\vec{r}$ knowing there is a particle at $\vec{r}'$.

$\Rightarrow$ $4\pi r^2 \rho\, g(r)\, dr$: given a particle in the origin, it says what is the number of particles between r and r+dr.

Schematically:



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