Lecture 11: Applications of DFT

Classical density functional theory recap.

$$\mathcal{F}[\rho] = \langle K_N + \Phi_N + k_B T \ln f_N \rangle$$

f_N : grand-canonical phase-space probability density.

$\mathcal{F}[\rho]$ is a unique functional of the equilibrium density $\rho(\vec{r})$.

Variational principle: $\Omega_V[\tilde{\rho}] = \mathcal{F}[\tilde{\rho}] - \int d\vec{r}\, u(\vec{r})\tilde{\rho}(\vec{r})$.

← some density profile.

$$\left.\frac{\delta \Omega_V[\tilde{\rho}]}{\delta \tilde{\rho}(\vec{r})}\right|_{\tilde{\rho}=\rho} = 0 \quad ; \quad \Omega_V[\rho] = \Omega.$$

$$\Rightarrow \quad \mu = V_{ext}(\vec{r}) + \frac{\delta \mathcal{F}[\rho]}{\delta \rho(\vec{r})}$$

(constancy of chemical potential).

Two hierarchies of correlation functions

Direct correlation functions: $c^{(n)}(\vec{r}_1, \ldots \vec{r}_n) = -\dfrac{\delta^n \beta \mathcal{F}_{ex}[\rho]}{\delta\rho(\vec{r}_1) \ldots \delta\rho(\vec{r}_n)}$

Density-density correlation functions:

$$G^{(n)}(\vec{r}_1, \ldots, \vec{r}_n) = -\frac{\delta^n \beta \Omega[u]}{\delta \beta u(\vec{r}_1) \ldots \delta \beta u(\vec{r}_n)}$$

with: $G^{(n)}(\vec{r}_1, \ldots, \vec{r}_n) = \begin{cases} \rho(\vec{r}_1) & n=1 \\ \langle \delta\hat{\rho}(\vec{r}_1) \ldots \delta\hat{\rho}(\vec{r}_n) \rangle & n \geq 2. \end{cases}$

Two generating functionals:

$\mathcal{F}_{ex}[\rho]$ and $\Omega[u]$ related by Legendre transform $\Rightarrow$ OZ equation.

What is $\mathcal{F}_{ex}[\rho]$? Do certain thermodynamic relations follow from DFT?

Integration wrt particle density.

Define parameter $\rho_\alpha(\vec{r}) = \rho(\vec{r};\alpha) = \begin{cases} \rho_{ref}(\vec{r}), & \alpha = 0 \\ \rho(\vec{r}) & , \alpha = 1. \end{cases}$

Idea: $\mathcal{F}_{ex}[\rho] = \mathcal{F}_{ex}[\rho_{ref}] + \int_0^1 d\alpha \, \frac{\partial \mathcal{F}_{ex}[\rho_\alpha]}{\partial \alpha}$

$$= \mathcal{F}_{ex}[\rho_{ref}] + \int_0^1 d\alpha \int d\vec{r} \, \underbrace{\frac{\delta \mathcal{F}_{ex}[\rho_\alpha]}{\delta \rho(\vec{r};\alpha)}}_{-\beta^{-1} c^{(1)}([\rho_\alpha];\vec{r})} \frac{\partial \rho(\vec{r};\alpha)}{\partial \alpha}$$

$\mathcal{F}_{ex}[\rho]$ unique funct.

can be shown it is path independent in single-phase region.

$\Rightarrow$ So use: $\rho(\vec{r};\alpha) = \rho_{ref}(\vec{r}) + \alpha[\rho(\vec{r}) - \rho_{ref}(\vec{r})]$.

$$\Rightarrow \beta \mathcal{F}_{ex}[\rho] = \beta \mathcal{F}_{ex}[\rho_{ref}] - \int_0^1 d\alpha \int d\vec{r} \, c^{(1)}([\rho_\alpha];\vec{r})[\rho(\vec{r}) - \rho_{ref}(\vec{r})].$$

Do this procedure twice (convince yourself!)

$$\beta \mathcal{F}_{ex}[\rho] = \beta \mathcal{F}_{ex}[\rho_{ref}] - \int d\vec{r} \, c^{(1)}([\rho_{ref}];\vec{r})[\rho(\vec{r}) - \rho_{ref}(\vec{r})]$$

$$- \int_0^1 d\alpha \int d\vec{r} \, [\rho(\vec{r}) - \rho_{ref}(\vec{r})] \int_0^\alpha d\alpha' \int d\vec{r}' \, c^{(2)}([\rho_{\alpha'}];\vec{r},\vec{r}')[\rho(\vec{r}') - \rho_{ref}(\vec{r}')] \qquad (*)$$

Still need prescription for $c^{(2)}$.

For $V_{ext}(\vec{r}) = 0$; ρ constant and taking $\rho_{ref}(\vec{r}) = 0$

$$c^{(1)}(\rho) = \int_0^\rho d\rho' \int d\vec{r}' \, c^{(2)}(\rho';\vec{r},\vec{r}')$$

Furthermore: $\beta\mu(\rho) = \beta\mu_{id} - c^{(1)}(\rho)$

$\Rightarrow \beta\rho \left(\frac{\partial \mu}{\partial \rho}\right)_T = 1 - \rho \int d\vec{r} \, c^{(2)}(\rho, r)$

Compressibility sum rule!

(*) can be starting point for approximations.

Choose $\rho_{ref}(\vec{r}) = \rho_b$. ; $c^{(2)}([\rho_\alpha];\vec{r},\vec{r}') = c^{(2)}(\rho_b;|\vec{r}-\vec{r}'|)$.

Then we find:

$$\Omega_v[\rho] = \beta\Omega[\rho_b] + \int d\vec{r}\, \beta V_{ext}(\vec{r})\rho(\vec{r}) + \int d\vec{r} \left[\rho(\vec{r}) \ln \frac{\rho(\vec{r})}{\rho_b} - \rho(\vec{r}) + \rho_b\right]$$

$$- \frac{1}{2}\int d\vec{r} \int d\vec{r}\,' c^{(2)}(\rho_b; |\vec{r}-\vec{r}\,'|)[\rho(\vec{r})-\rho_b][\rho(\vec{r}\,')-\rho_b].$$

Above relation can also be obtained from functional Taylor expansion of $\Omega_v[\rho]$ around ρ_b.

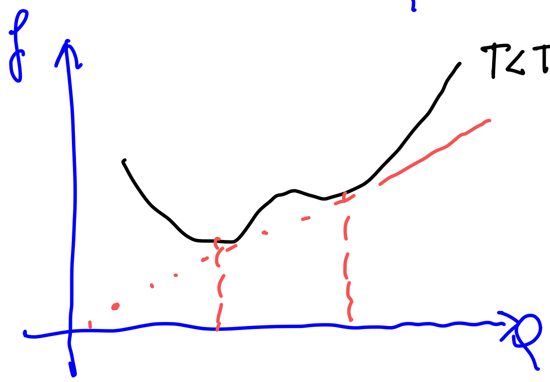
DFT also useful to derive approximate closure relations (Percus test particle, see LN).

Gas-liquid interface   Recall from previous lecture:

$$\beta f(\rho) = \rho \log\left(\frac{\rho\Lambda^3}{1-b\rho}\right) - \beta a \rho^2$$

Different from HS we have a "vdW loop"

Diffrent prescription for cut off e.g. give ϕ and T dependent a,b! Thermodyn. pert. theory.



$$\frac{\partial^2 f}{\partial \rho^2} < 0 \Rightarrow \text{Thermodynamic instability}$$

$$\left(\frac{\partial^2 f}{\partial \rho^2}\right)_T\Bigg|_{\rho=\rho_s} = 0 \quad (\text{spinodal; limit of stability}) \quad \rho_s(T)$$

Common tangent construction: $\left(\frac{\partial f}{\partial \rho}\right)_T\Big|_{\rho=\rho_g} = \left(\frac{\partial f}{\partial \rho}\right)_T\Big|_{\rho=\rho_l} = \mu_{co}$. equal chemical potential

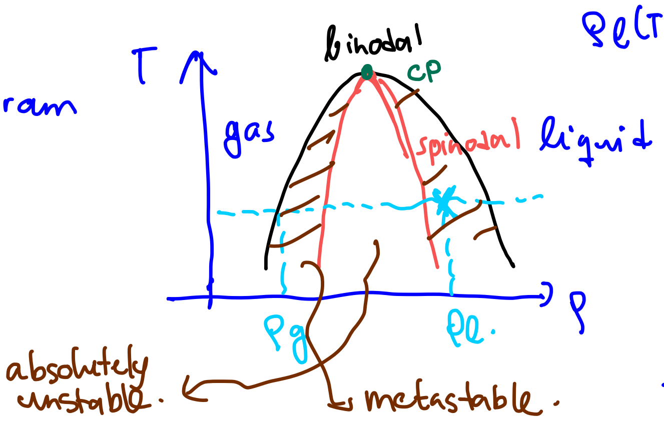
$$\mu_{co} = \frac{f(\rho_l(T)) - f(\rho_g(T))}{\rho_l(T) - \rho_g(T)}$$

equal pressure.

⇓

Phase diagram

⇒



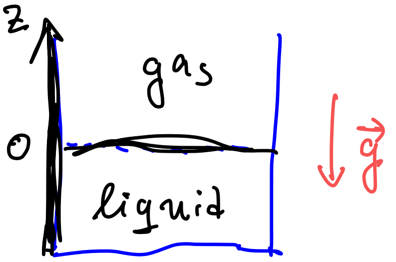
V fixed canonical:

$$\frac{V_l}{V} = \frac{\rho - \rho_g}{\rho_l - \rho_g} \qquad V_g = V - V_l.$$

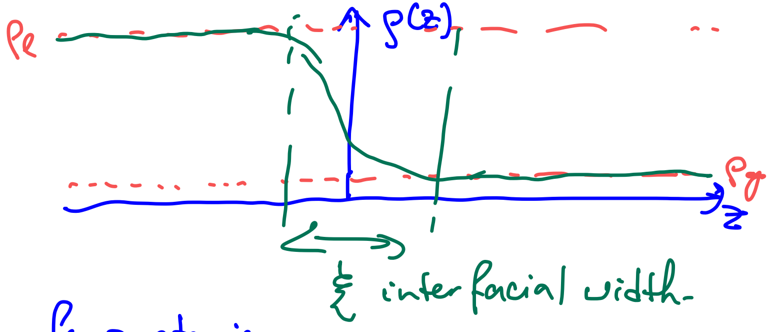
$$\Rightarrow N_g = \rho_g V_g \; ; \; N_l = \rho_l V_l.$$

(lever rule).

Focus on liquid-gas interface. Consider a (vanishing) external potential $V_{ext}(z) = mgz$ that localizes the interface near $z=0$. We let $g \to 0$



So we expect:



For T sufficiently below T_c, ξ is a few atomic diameters.

$\rightsquigarrow$ LDA will not work. We will perform a gradient expansion: $\rho(\vec{r}) = \psi\left(\frac{\vec{r}}{r_0}\right)$ where $r_0 \to \infty$.

$$\mathcal{F}[\rho] = \int d\vec{r} \left\{ f_0(\rho(\vec{r})) + \sum_{i=1}^{3} f_i(\rho(\vec{r}))\overset{\partial_i \rho(\vec{r})}{\vee} + \sum_{i,j} \left[f^{(1)}_{i,j}(\rho(\vec{r}))\, \partial_i \rho(\vec{r})\, \partial_j \rho(\vec{r}) + f^{(2)}_{i,j}(\rho(\vec{r}))\, \partial_i \partial_j \rho(\vec{r}) \right] + \dots \right\}$$

" Expansion in r_0^{-1}

$\mathcal{F}[\rho]$ is unique functional of $\rho(\vec{r})$ independent of $V_{ext}(\vec{r})$

$\Rightarrow$ Rotational invariant (so no odd gradients)

$$\mathcal{F}[\rho] = \int d\vec{r} \left\{ f_0(\rho(\vec{r})) + f_2^{(a)}(\rho(\vec{r}))\nabla^2 \rho(\vec{r}) + f_2^{(b)}(\rho(\vec{r}))\, |\nabla\rho(\vec{r})|^2 + \dots \mathcal{O}(\nabla_i^4) \right\}$$

Hence, we find:
$$\mathcal{F}[\rho] = \int dr \left\{ \underbrace{f_0(\rho(\vec{r})) + f_2(\rho(\vec{r}))\, |\nabla\rho(\vec{r})|^2}_{\text{square-gradient approximation.}} + \dots \right\}.$$

Evidently, for $\rho(\vec{r}) = \rho_b \Rightarrow f_0(\rho_b)$ Helmholtz free energy density of uniform fluid with bulk density ρ_b.

We can actually also get microscopic expression for $f_2(\rho_b)$!.

We find: $\beta f_2(\rho_b) = \frac{1}{12} \int d\vec{r}\, r^2 c^{(2)}(\rho_b; r)$. (Higher order coefficients depend on $c^{(n)}$ $n>2$)

$\Rightarrow$ VdW theory for the gas-liquid interface. (See tutorials for details)

General for now:
$$\Omega_V[\rho] = \int d\vec{r} \left[f(\rho(\vec{r})) + f_2(\rho(\vec{r}))\, |\nabla\rho(\vec{r})|^2 \right] - \int d\vec{r}\, u(\vec{r})\rho(\vec{r}).$$

with $u(\vec{r}) = u(z) = \mu - mgz$. $\Rightarrow \rho(r) = \rho(z)$.

Euler-Lagrange equation: $\mu - m\cancel{gz} = f'(\rho(z)) - f_2'(\rho(z))\left(\frac{d\rho}{dz}\right)^2 - 2f_2(\rho(z))\frac{d^2\rho}{dz^2}$

$g \to 0$

Define: $w(\rho(z)) = f(\rho(z)) - \mu\rho(z)$ Grand potential density.

$\Rightarrow$ $\left.\begin{array}{l} w(\rho_\ell) = -p_\ell \\ w(\rho_g) = -p_g \end{array}\right]$ at coexistence are equal: $p_\ell = p_g \equiv p_{co}$.

$f_2(\rho) = \text{constant}$ (vdW model).

$\Rightarrow$ EL becomes by multiplying with $\frac{d\rho}{dz}$ and integrating:

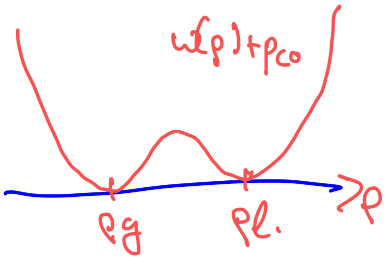
$$f(\rho(z)) - \mu(\rho(z)) - f_2\left(\frac{d\rho}{dz}\right)^2 = \text{const} = -p_{co}.$$

$$\Rightarrow f_2\left(\frac{d\rho}{dz}\right)^2 = w(\rho(z)) + p_{co}.$$

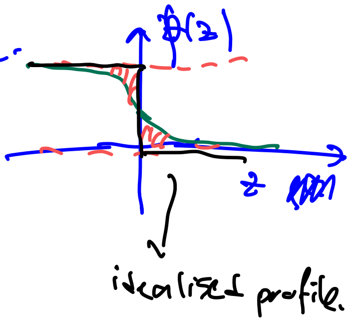
or $z = -f_2^{1/2}\int_{\rho_0}^{\rho} d\rho' \left(w(\rho') + p_{co}\right)^{-1/2}$ $\rho_0 = \rho(z=0)$

↓

for example Gibbs dividing plane.



(Note $\rho(z)$ monotonic in this theory).



We define surface tension as:

$\gamma = \frac{\Omega_{ex}}{A}$: surface excess grand potential per unit area.

$$= \int_{-\infty}^{\infty} dz \left[\underbrace{f(\rho(z)) + f_2\left(\frac{d\rho}{dz}\right)^2 - \mu\rho(z)}_{\text{inhomogeneous}} + \underbrace{p_{co}}_{\text{bulk}}\right]$$

$\Rightarrow$ Straightforward to generalise to $f_2(\rho) \neq$ constant.

↳ when you have $c^{(2)}(r;\rho)$: microscopic description of interface.

$\Rightarrow$ We find $\rho(z) - \rho_g \sim e^{-z/\xi_b}$ $(z \to \infty)$

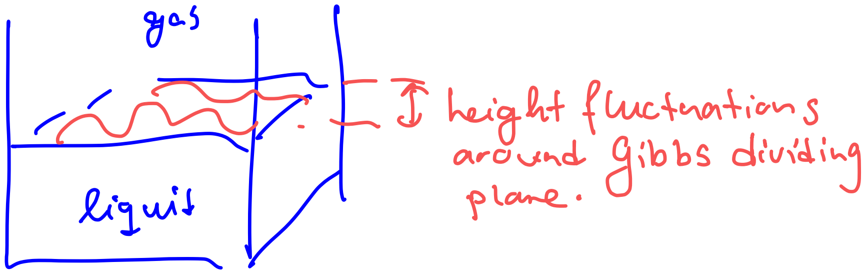
↳ bulk correlation length.

Near critical point: $\gamma \sim (T_c - T)^{3/2}$ $T \to T_c$. (mean-field critical exponent).

$\gamma \to 0$ $(T \to T_c)$ $\Rightarrow$ interface disappears at critical point.

Reality: $\gamma \sim (T_c - T)^{\tilde{\mu}}$ with exponent $\tilde{\mu} = 2\nu = 1.26$.

Furthermore, beyond mean-field causes capillary waves!



Typical length scale:

$$\ell = \sqrt{\frac{\gamma}{mg(\rho_l - \rho_g)}}$$

E.g. Ar close to triple point $\ell \sim O(mm)$.

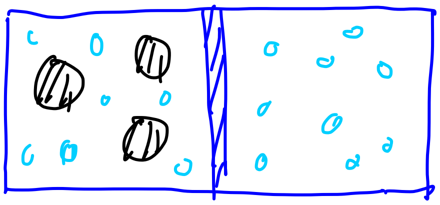
$\xi \ll \ell \ll L$: $\langle \overline{h^2} \rangle \sim \frac{k_B T}{2\pi \gamma} \ln \frac{\ell}{\xi}$

Medium-induced interactions

Consider a multicomponent system

What happens if we integrate out all degrees of freedom of another component?

For example, colloidal particles in a solvent.



semipermeable membrane: only solvent particles can pass.

N interacting "interesting" particles $\{\vec{R}^N\}$

N_s "uninteresting" particles.

E.g. solvent. $\{\vec{r}^{N_s}\}$.

Idea: treat interesting particles canonical, whereas uninteresting particles grand-canonical.

Thermodynamic potential: $\Omega(N, V, T, \mu_s) = F(N, N_s, V, T) - \mu_s N_s$.

$$d\Omega = -p\,dV + \mu\,dN - S\,dT - \langle N_s \rangle d\mu_s.$$

Osmotic ensemble

$$\left.\begin{aligned} e^{-\beta\Omega} &= \sum_{N_s=0}^{\infty} e^{\beta\mu_s N_s}\, Z(N,N_s,V,T) \\ Z(N,N_s,V,T) &= \frac{1}{N!\,\Lambda_1^{3N}}\,\frac{1}{N_s!\,\Lambda_s^{3N_s}} \int d\vec{R}^N \int d\vec{r}^{N_s}\, e^{-\beta\Phi(\vec{R}^N,\vec{r}^{N_s})} \end{aligned}\right\} \Rightarrow$$

$$e^{-\beta\Omega} = \frac{1}{N!\,\Lambda_1^{3N}} \int d\vec{R}^N \underbrace{\sum_{N_s=0}^{\infty} \frac{e^{\beta\mu_s N_s}}{N_s!\,\Lambda_s^{3N_s}} \int d\vec{r}^{N_s}\, e^{-\beta\Phi(\vec{R}^N,\vec{r}^{N_s})}}_{:=\, e^{-\beta\Phi_{eff}(\vec{R}^N;\,\mu_s,T)}}$$

$$\Rightarrow \boxed{e^{-\beta\Omega} = \frac{1}{N!\,\Lambda_1^{3N}} \int d\vec{R}^N\, e^{-\beta\Phi_{eff}(\vec{R}^N;\,\mu_s,T)}.}$$

Φ_{eff}: effective interaction potential between "interesting" particles.

Let's make decomposition:

$$\Phi(\vec{R}^N,\vec{r}^{N_s}) = \underset{\substack{\text{"bare" interactions}\\ \text{(also present in}\\ \text{vacuum)}}}{\Phi_{11}(\vec{R}^N)} + \underset{\substack{\text{particle-}\\ \text{medium}\\ \text{interactions.}}}{\Phi_{1s}(\vec{R}^N;\vec{r}^{N_s})} + \underset{\substack{\text{solvent-}\\ \text{solvent}\\ \text{interactions}}}{\Phi_{ss}(\vec{r}^{N_s})}$$

This is generally true (no approximation).

$$\Rightarrow e^{-\beta\Phi_{eff}(\vec{R}^N;\,\mu_s,T)} = e^{-\beta\Phi_{11}(\vec{R}^N)} \sum_{N_s=0}^{\infty} \frac{e^{\beta\mu_s N_s}}{N_s!\,\Lambda_s^{3N_s}} \int d\vec{r}^{N_s}\, e^{-\beta\Phi_{1s}(\vec{R}^N,\vec{r}^{N_s}) - \beta\Phi_{ss}(\vec{r}^{N_s})}$$

$$:= e^{-\beta\Phi_{11}(\vec{R}^N)}\, e^{-\beta W(\vec{R}^N;\,\mu_s,V,T)}$$

Clearly: tremendous task to compute Φ_{eff}.

W is the grand potential of the inhomogeneous solvent in the external field caused by the fixed configuration of particles $\{\vec{R}^N\}$!

Solution strategy:

$N=0$: Pure solvent, one-component system:

$$\Rightarrow W = -p_0(\mu_s,T)V. \quad \text{(pressure of solvent reservoir)}$$

$N=1$: Pure solvent + one particle.

$$\Rightarrow W = -p_0(\mu_s,T)V + \omega_1(\mu_s,T)$$

↑ excess grand potential of solvent due to presence of particle.

ω_1 includes entropic effects due to restructuring of solvent close to particle surface, but also energetic effects with particle.

Note translational invariance ⇒ no dependence on $\vec{R}_1$!

$N=2$: Two particles: $\{\vec{R}_1, \vec{R}_2\}$

$$\Rightarrow W = -p_0(\mu_s,T)V + 2\omega_1(\mu_s,T) + \omega_2(|\vec{R}_1-\vec{R}_2|;\mu_s,T)$$

↑ solvent-induced pair interaction.

Note that $\omega_2(r) \to 0$ $(r \to \infty)$ by construction.

Arbitrary number of particles:

$$W(\vec{R}^N;\mu_s,T) = -p_0(\mu_s,T)V + N\omega_1(\mu_s,T) + \sum_{i<j}^{N} \omega_2(R_{ij};\mu_s,T)$$
$$+ \sum_{i<j<k}^{N} \omega_3(R_{ijk};\mu_s,T) + \dots$$

We did not explicitly calculate anything! Just bookkeeping.

$$\Rightarrow \Phi_{eff}(\vec{R}^N) = \Phi_{11}(\vec{R}^N) + W(\vec{R}^N;\mu_s,T)$$

$$= -p_0(\mu_s,T)V + N\omega_1(\mu_s,T) + \overbrace{\Phi_{11}(\vec{R}^N) + \sum_{i<j} \omega_2(R_{ij};\mu_s,T) + \dots}^{:= H_{eff}(\vec{R}^N;\mu_s,T).}$$

Hence, $\Omega(N,\mu_s,V,T) = -p_0(\mu_s,T)V + N\omega_1(\mu_s,T) + A(N,V,T;\mu_s)$

where: $e^{-\beta A} = \frac{1}{N!\Lambda^{3N}} \int d\vec{R}^N \, e^{-\beta H_{eff}(\vec{R}^N;\mu_s,T)}$

Interpretation: A: Helmoltz free energy of the N "interesting" dressed particles

⇒ Note that we did no approximations!

Thermodynamics: $p = -\left(\frac{\partial \Omega}{\partial V}\right)_{N,T,\mu_s}$.

$\Rightarrow \quad p = p_0(\mu_s,T) + \Pi(\rho,\mu_s,T) \quad ; \Pi = -\left(\frac{\partial A}{\partial V}\right)_{N,\mu_s,T}$.

↑ osmotic pressure (pressure of dressed colloid system)

$\mu = \left(\frac{\partial \Omega}{\partial N}\right)_{V,T,\mu_s}$

$= \omega_1(\mu_s,T) + \mu'(\rho,\mu_s,T) \quad ; \mu' = \left(\frac{\partial A}{\partial N}\right)_{V,\mu_s,T}$

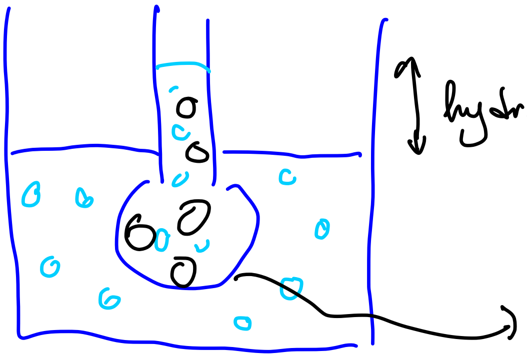
Often we are interested what happens as function of $\rho = \frac{N}{V}$,

↳ not interested in constant offsets p_0, μ'.

Example, where three-body terms are neglected:

Two charges: $\frac{q_1 q_2}{4\pi\epsilon_0 r} \rightsquigarrow \frac{q_1 q_2}{4\pi\epsilon_0\epsilon_r r}$.

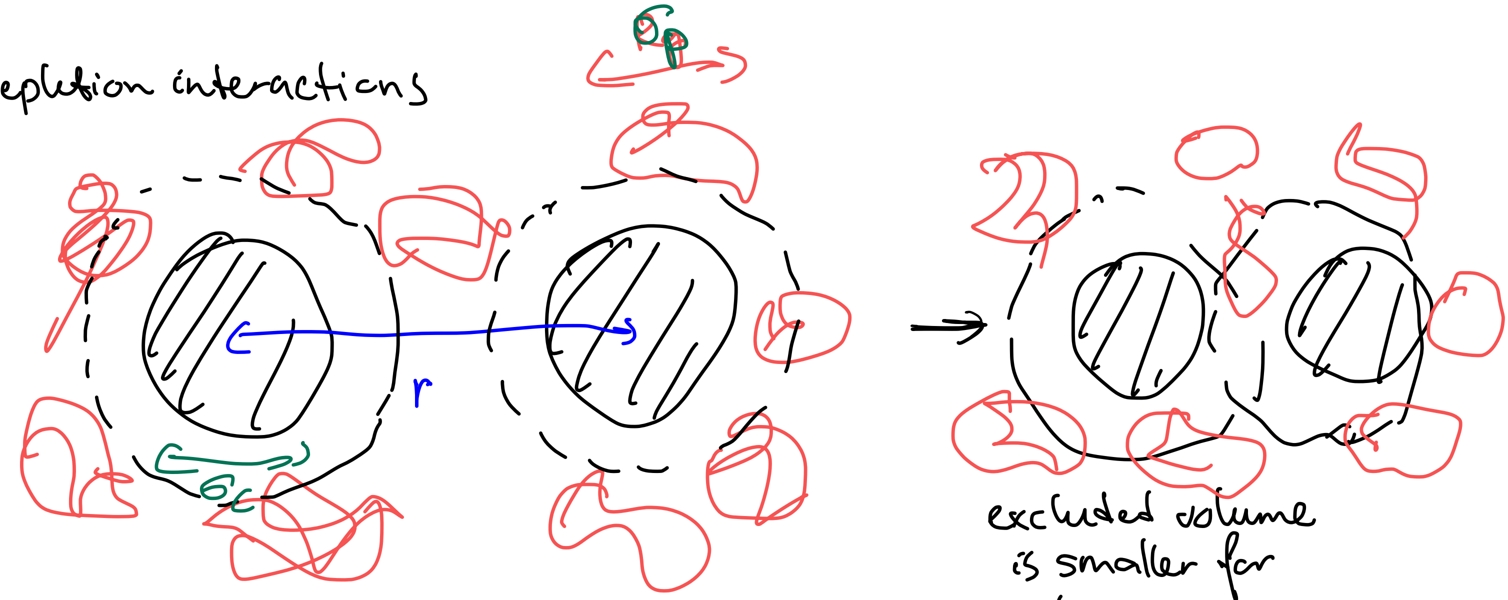
$\epsilon_r = \epsilon_r(\mu_s,T)$!



hydrostatic pressure is osmotic pressure.

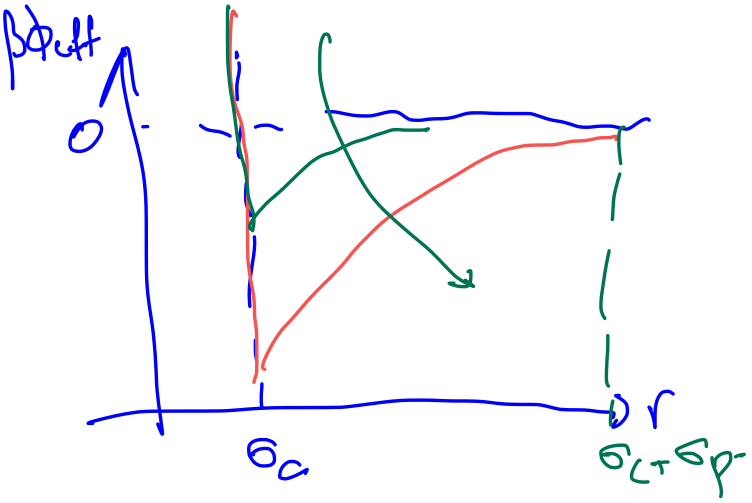
semi-permeable membrane.

Depletion interactions



excluded volume is smaller for polymers.

higher entropy ⇒ attraction



$$\Phi_{IS}(\vec R^{N}, \vec r^{N_s}) = \sum_{i=1}^{N}\sum_{j=1}^{N_s}\phi_{IS}(|\vec R_i - \vec r_j|)$$

$$= \sum_{j=1}^{N_s} V_{ext}(\vec r_j; \vec R^{N})$$

Finally note that:

$$e^{-\beta W(\vec R^{N};\mu_s,T)} = \underbrace{\sum_{N_s=0}^{\infty}\frac{e^{\beta\mu_s N_s}}{\Lambda_2^3 N_2!}\int d\vec r^{N_s}\, e^{-\beta\Phi_{SS}(\vec r^{N_s}) - \beta\sum_{j=1}^{N_s} V_{ext}(\vec r_j;\vec R^{N})}}_{\text{inhomogeneous solvent in external field caused by fixed configuration of particles ! } \Rightarrow \text{ DFT!}}$$