Lecture 7: 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: $\Omega_V[\tilde{\rho}] = \mathcal{F}[\tilde{\rho}] - \int d\vec{r}\, u(\vec{r})\tilde{\rho}(\vec{r})$.

$\tilde{\rho}$ ← some density profile.

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

$$\Rightarrow \mu = V_{ext}(\vec{r}) + \frac{\delta \mathcal{F}[\rho]}{\delta \rho(\vec{r})} \quad \text{(constancy of chemical potential).}$$

Two hierarchies of correlation functions

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

Density-density correlation functions:

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

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

Two generating functionals:

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

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!)

$$\beta \mathcal{F}_{ex}[\rho] = \beta \mathcal{F}_{ex}[\rho_{ref}] - \int d\vec{r} \, c^{(1)}([\rho_{ref}];\vec{r})[\rho(\vec{r}) - \rho_{ref}(\vec{r})]$$
$$- \int_0^1 d\alpha \int d\vec{r} \, [\rho(\vec{r}) - \rho_{ref}(\vec{r})] \int_0^\alpha d\alpha' \int d\vec{r}\,' \, c^{(2)}([\rho_{\alpha'}];\vec{r},\vec{r}\,')[\rho(\vec{r}\,') - \rho_{ref}(\vec{r}\,')] \quad (*)$$

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.

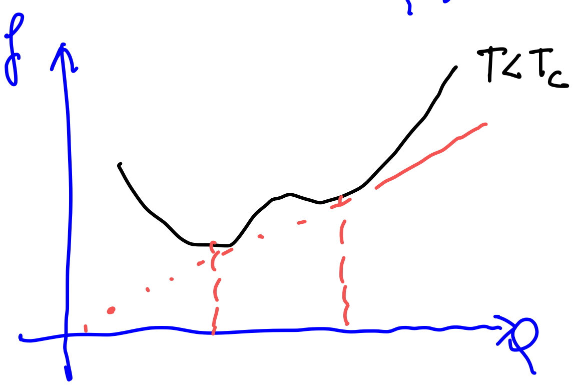
DFT also useful to derive approximate closure relations (Percus test particle, see LN).

__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"

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



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

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

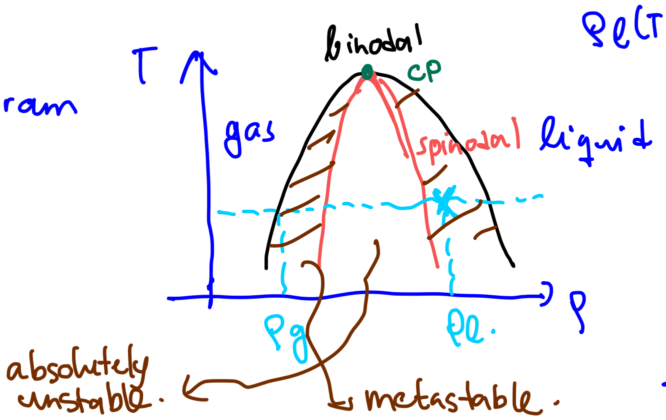
Common tangent construction: $\left(\frac{\partial f}{\partial\rho}\right)_T\Big|_{\rho=\rho_g} = \left(\frac{\partial f}{\partial\rho}\right)_T\Big|_{\rho=\rho_l} = \mu_{co}$. equal chemical potential

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

equal pressure.

Phase diagram

$\Rightarrow$



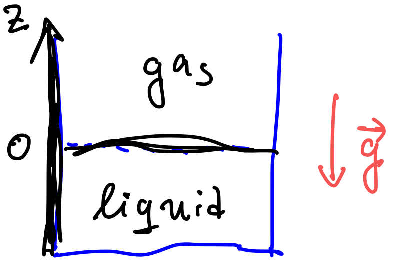
V fixed canonical:

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

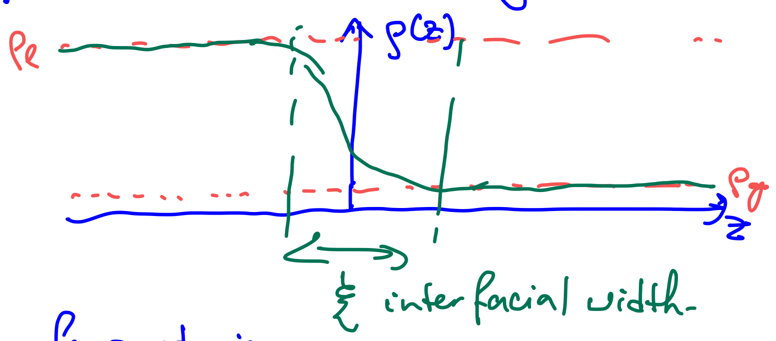
$$\Rightarrow N_g = \rho_g V_g \;;\; N_l = \rho_l V_l.$$

(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 $r_0 \to \infty$.

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

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

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 $c^{(n)}$ $n>2$)

How to get this? $\Rightarrow$ Tutorial

$\Rightarrow$ 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: $\mu - \cancel{mgz} = f'(\rho(z)) - f_2'(\rho(z))\left(\frac{d\rho}{dz}\right)^2 - 2f_2(\rho(z))\frac{d^2\rho}{dz^2}$

$g \to 0$

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

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

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

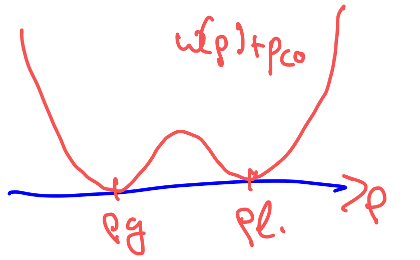
$\Rightarrow$ EL becomes by multiplying with $\frac{d\rho}{dz}$ and integrating:

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

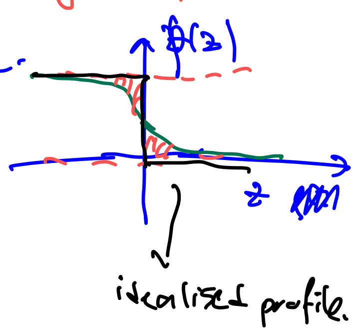
$$\Rightarrow \quad f_2\left(\frac{d\rho}{dz}\right)^2 = w(\rho(z)) + p_{co}.$$

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

$\downarrow$ 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 $f_2(\rho) \neq \text{constant}$.

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

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

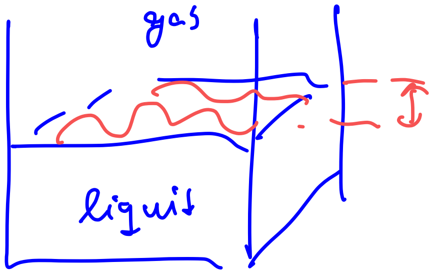
↳ bulk correlation length.

Near critical point: $\gamma \sim (T_c - T)^{3/2}$ $T \to T_c$. (mean-field critical exponent). ⑥

$\gamma \to 0$ $(T \to T_c)$ $\Rightarrow$ 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!



height fluctuations around gibbs dividing plane.

Typical length scale:

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

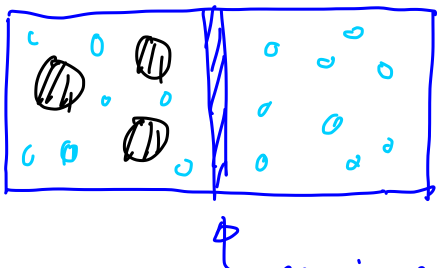
E.g. Ar close to triple point $\ell \sim O(\text{mm})$.

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

Medium-induced interactions

Up until now we focused what happens when we integrate out "internal degrees of freedom". However, what happens if we integrate out "all" degrees of freedom of another component.

For example, colloidal particles in a solvent.



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

N_s "uninteresting" particles.

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

semipermeable membrane: only solvent particles can pass.

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: $\Phi(\vec{R}^N,\vec{r}^{N_s}) = \Phi_{11}(\vec{R}^N) + \Phi_{1s}(\vec{R}^N;\vec{r}^{N_s}) + \Phi_{ss}(\vec{r}^{N_s})$

"bare" interactions (also present in vacuum) — particle-medium interactions. — solvent-solvent interactions

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 $\Rightarrow$ 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 $\omega_2(r) \to 0 \quad (r \to \infty)$ by construction.

Arbitrary number of particles:

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

We did not explicitly calculate anything! Just bookkeeping.

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

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

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

$\Rightarrow$ Note that we did no approximations!

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

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

osmotic pressure (pressure of dressed colloid system)

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

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

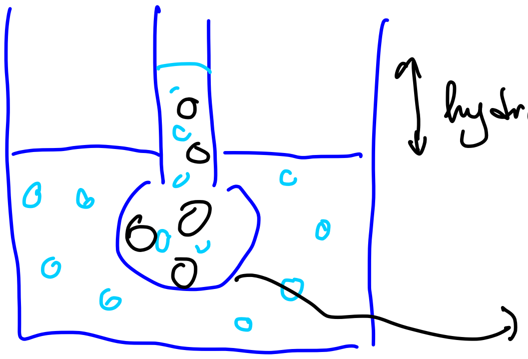
Often we are interested what happens as function of $\rho = \frac{N}{V}$,

$\hookrightarrow$ not interested in constant offsets p_0, μ'.

Example, where three-body terms are neglected:

Two charges : $\frac{q_1 q_2}{4\pi\varepsilon_0 r} \rightsquigarrow \frac{q_1 q_2}{4\pi\varepsilon_0\varepsilon_r r}$.

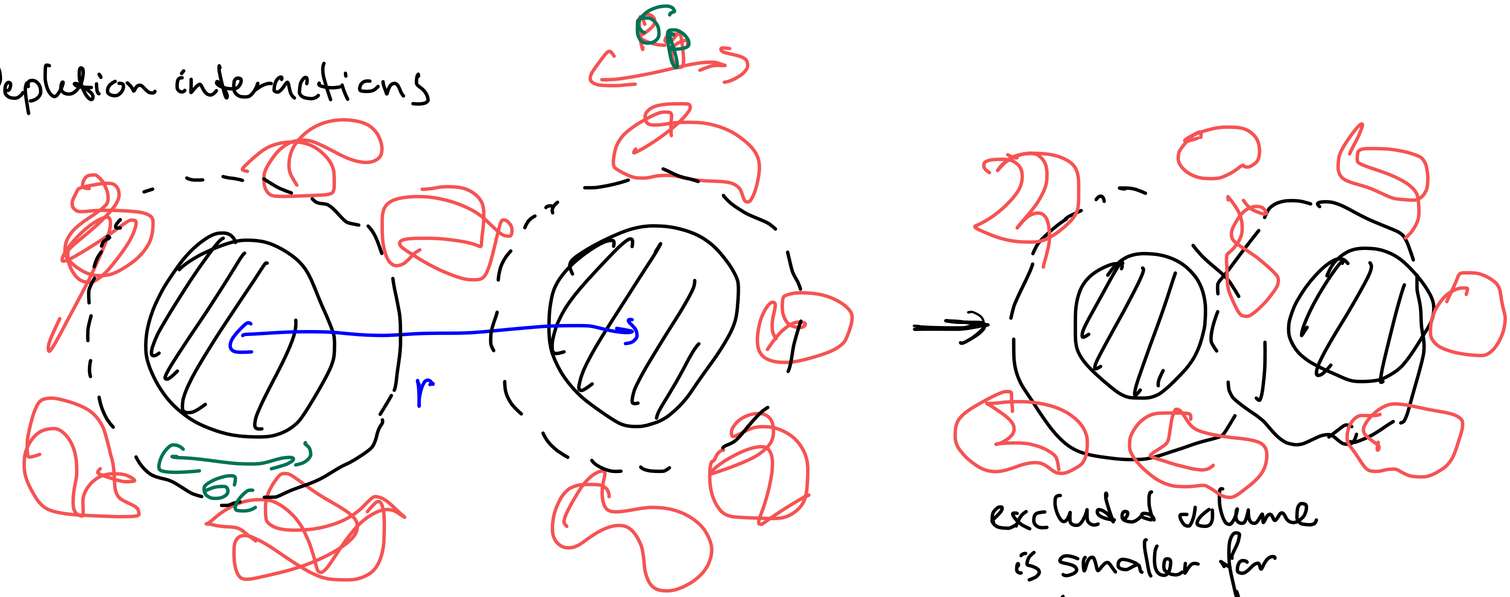
$\varepsilon_r = \varepsilon_r(\mu_s,T)$!



hydrostatic pressure is osmotic pressure.

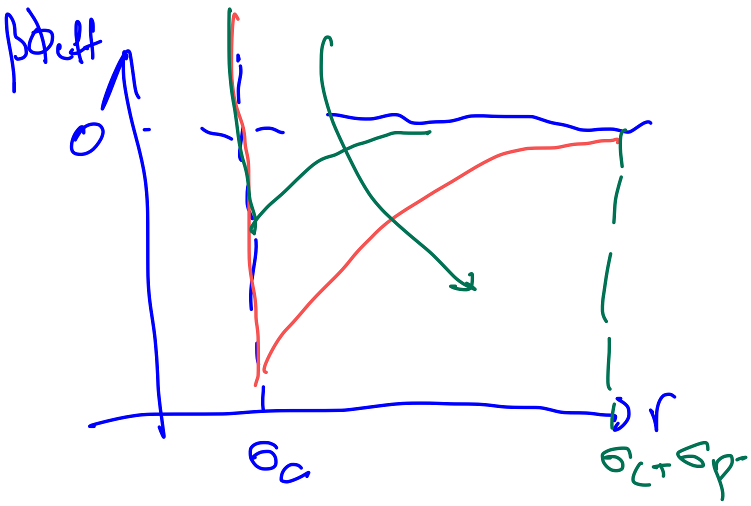
semi-permeable membrane.

Depletion interactions



excluded volume is smaller for polymers.

higher entropy $\Rightarrow$ attraction



$$\Phi_{1s}(\vec{R}^N, \vec{r}^{N_s}) = \sum_{i=1}^{N} \sum_{j=1}^{N_s} \phi_{1s}(|\vec{R}_i - \vec{r}_j|)$$

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

Finally note that:

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