Lecture 6: Construction of the density functional.

Results for homogeneous fluids ($V_{ext}(\vec{r}) = 0$)

Partition function for interacting particles → Virial expansions

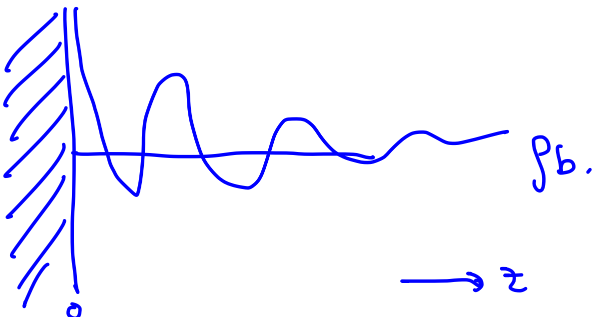
→ Determination of $g(r)$ → "Three routes to thermodynamics"

using approximative closure (e.g., RPA, MSA, PY, ...) via the Ornstein-Zernike relation.

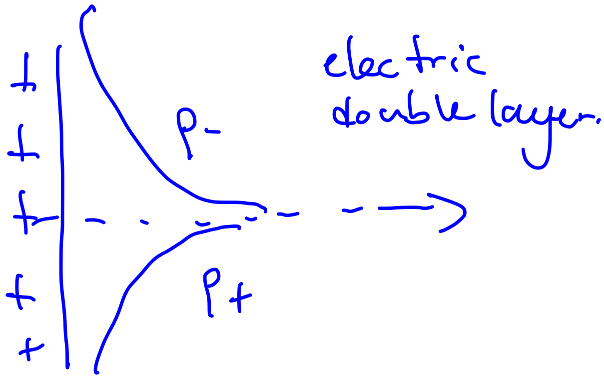
OZ: $h(r) = c(r) + \rho \int d\vec{r}\,' \, c(|\vec{r} - \vec{r}\,'|)\, h(r')$. $\quad (h(r) = g(r) - 1)$.

$h(r)$ quantifies pure correlations, whereas $g(r)$ is more related to counting particles around center particle.

What happens when $V_{ext}(\vec{r}) \neq 0$?



$V_{ext}(\vec{r}) = \infty$ for $z < 0$
$\qquad\quad = 0$ for $z > 0$



We need the language of density functional theory (DFT). (known for quantum systems, but also used for classical systems!)

Framework for.

Thermodynamic properties → Phase behaviour → Experiment

Correlation functions. → Microscopic structure. → Experiment

Key idea: There is a unique functional $\mathcal{F}[\rho]$ of the one-body density $\rho(\vec{r})$. The form of $\mathcal{F}[\rho]$ does not depend on $V_{ext}(\vec{r})$.

i.e. Single form of $\mathcal{F}[\rho]$ valid for e.g.,
- fluids in gravitational field
- Confined fluids in pores,
- Adsorbed fluids on walls

⋮

Advantages:
- Via functional differentiation easier to obtain exact results that follow from the partition function.
- For given $\Phi(\vec{r}^N)$ easy to devise approximations for all types of inhomogeneities.

Disadvantages:
- Different types of fluids require different approximate functionals. (Contrast to quantum DFT that only involves the Coulomb potential.)
- Skill and intuition are required to construct $\mathcal{F}[\rho]$. Not a lot of systematic approaches.
- Often approximate functionals omit fluctuation effects.

Caveat: $\mathcal{F}[\rho]$ does not define a model fluid. One should always keep the underlying microscopic Hamiltonian in mind. (Unless the functional is known exactly, e.g. one-dimensional hard-rod fluids).

Construction of the density functional.

Grand-canonical ensemble: $u(\vec{r}) = \mu - V_{ext}(\vec{r})$ (intrinsic chemical potential)

We can view $\Omega := \Omega[u]$;

$$e^{-\beta\Omega[u]} = \sum_{N=0}^{\infty} \frac{1}{N!\Lambda^{3N}} \int d\vec{r}^N \, e^{-\beta\left[\Phi(\vec{r}^N) - \int d\vec{r}\, u(\vec{r})\hat{\rho}(\vec{r})\right]} = \Xi[u].$$

Note that $\rho(\vec{r}) = \langle \hat{\rho}(\vec{r}) \rangle = -\dfrac{\delta \Omega[u]}{\delta u(\vec{r})}$ (functional derivative)

Mathematical intermezzo: Functionals (pragmatic view)

Function: e.g. $f: \mathbb{R} \to \mathbb{R}$ given by $x \mapsto f(x)$. $x \in \mathbb{R}$, $f(x) \in \mathbb{R}$.

Functional: $\mathcal{F}: X \to \mathbb{R}$. given by $f \mapsto \mathcal{F}[f]$ $f \in X$. $\mathcal{F}[f] \in \mathbb{R}$.

X: function space.

Functional depends on a function $f(x)$ $a < x < b$.

It can be regarded as a continuous version of a function of several variables, ie $F(y_1, y_2, \ldots, y_N)$ with $y_1 = f(x_1)$ etc.

Examples:

(i): $F(y_1, y_2, \ldots y_N) = \sum_{i=1}^{N} a_i y_i \longrightarrow F[y] = \int dx\, a(x) f(x)$

(ii) $G(y_1, y_2, \ldots, y_N) = \sum_{i,j} h_{ij} y_i y_j \to G[y] = \int dx \int dx'\, h(x,x') f(x) f(x')$

Differentiation: Take $f(\vec{y})$ with f function of N variables $\vec{y} = (y_1, \ldots, y_N)$.

Then total differential: $df = \sum_{i=1}^{N} \dfrac{\partial f}{\partial y_i} dy_i = \sum_{i=1}^{N} A_i(\vec{y})\, dy_i$

df can be interpreted as: $df = f(y + dy) - f(y)$.

Similarly, for functional $\mathcal{F}[u]$:

$$\delta \mathcal{F}[u] = \mathcal{F}[u + \delta u] - \mathcal{F}[u] = \int dx\, A[u; x]\, \delta u(x).$$

functional derivative.

$$=: \int dx\, \frac{\delta \mathcal{F}[u]}{\delta u(x)}\, \delta u(x).$$

Note integration boundaries appropriate to particular problem.

Let ϕ be a test function. Then we can also define the functional derivative as

$$\lim_{\epsilon \to 0} \frac{d}{d\epsilon} \mathcal{F}[u+\epsilon\phi] = \int dx \, \frac{\delta \mathcal{F}[u]}{\delta u(x)} \phi(x).$$

We can by above construction also define higher order functional derivatives: We find:

$$\frac{\delta^2 \mathcal{F}[u]}{\delta u(x)\delta u(x')} = \frac{\delta^2 \mathcal{F}[u]}{\delta u(x')\delta u(x)} \quad \text{etc.} \quad \left(\text{compare } \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}\right)$$

Functional Taylor expansion.

Suppose we expand around a given function $u_0(x)$:

$$\mathcal{F}[u] = \mathcal{F}[u_0] + \int dx \left.\frac{\delta \mathcal{F}}{\delta u(x)}\right|_{u=u_0} [u(x) - u_0(x)]$$

$$+ \frac{1}{2} \int dx \int dx' \underbrace{\left.\frac{\delta^2 \mathcal{F}}{\delta u(x)\delta u(x')}\right|_{u=u_0}}_{\text{just functions of } x \text{ and } x' \ldots} [u(x)-u_0(x)][u(x')-u_0(x')] + \ldots\ldots$$

<u>Chain rule</u>: $\mathcal{F}$ functional of u, depends solely on v, which is also functional of u.

$$\frac{\delta \mathcal{F}}{\delta u(x)} = \int dx' \frac{\delta \mathcal{F}}{\delta v(x')} \frac{\delta v(x')}{\delta u(x)}. \qquad \text{(End of intermezzo).}$$

So we ended with $\Omega[u]$. We can make a functional Legendre transform:

$$\mathcal{F}[\rho] = \Omega[u] - \int d\vec{r}\, u(\vec{r}) \frac{\delta \Omega[u]}{\delta u(\vec{r})} = \Omega[u] + \int d\vec{r}\, \rho(\vec{r})[\mu - V_{ext}(\vec{r})]$$

Note alternatively: $\mathrm{Tr}_{cl}^{(\dots)} = \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} \int d\vec{p}^{\,N} \int d\vec{r}^{\,N} (\dots)$; $f_N = \frac{1}{\Xi} e^{-\beta(H-\mu N)}$

$\langle \dots \rangle = \mathrm{Tr}_{cl}[f_N (\dots)]$

$$\mathcal{F}[\rho] = \langle K_N + \Phi_N + k_B T \ln f_N \rangle = \mathrm{Tr}_{cl}\left[f_N \left(K_N + \Phi_N + k_B T \ln f_N \right) \right]$$

kinetic   potential (without external potential). (see P3.1).

DFT: Focus on functionals of $\rho(\vec{r})$ rather than $u(\vec{r})$.

<u>Not so obvious result:</u> Given Φ_N, fixed $\mu, T \Rightarrow \exists!\, V_{ext}(\vec{r})$ that gives rise to specific $\rho(\vec{r})$.

f_N is a functional of $V_{ext}(\vec{r}) \rightsquigarrow \rho(\vec{r})$.

$\Rightarrow$ Any quantity for given Φ_N, μ, T fully determined by f_N is necessarily a functional of $\rho(\vec{r})$. There is no functional dependence on $V_{ext}(\vec{r})$.

$\Rightarrow \mathcal{F}[\rho]$ is a <u>unique</u> functional of $\rho(\vec{r})$ and has the same form for <u>every</u> external potential

Let us formalize the above.

<u>Lemma:</u> Let f be a phase space probability function with $\mathrm{Tr}_{cl} f = 1$.

Let $\Omega[f] = \mathrm{Tr}_{cl}[f(H_N - \mu N + k_B T \ln f]$. Then $\Omega[f] \geq \Omega[f_N]$

<u>Proof:</u> Recall that $f_N = \frac{e^{-\beta(H_N - \mu N)}}{\Xi} \Rightarrow \Omega[f_N] = -k_B T \ln \Xi =: \Omega$.

Note furthermore: $H_N - \mu N = -k_B T \ln [f_N \Xi]$

So we find:

$$\Omega[f] = \mathrm{Tr}_{cl}\left\{ f\left[-k_B T \ln(f_N \Xi) + k_B T \ln f \right] \right\}$$

$$= k_B T\, \mathrm{Tr}_{cl}\left[f \ln f - f \ln f_N - f \ln \Xi \right].$$

$$k_B T\, \mathrm{Tr}_{cl}(f \ln f - f \ln f_N) - k_B T \ln \Xi \underbrace{\mathrm{Tr}_{cl} f}_{=1}$$

$$= k_B T\, \mathrm{Tr}_{cl}(f \ln f - f \ln f_N) + \Omega[f_N].$$

$$\Rightarrow \Omega[f] - \Omega[f_N] = k_B T\, \mathrm{Tr}_{cl} f_N \left(\frac{f}{f_N} \ln \frac{f}{f_N} \right)$$

Recall: $\mathrm{Tr}_{cl} f = \mathrm{Tr}_{cl} f_N$

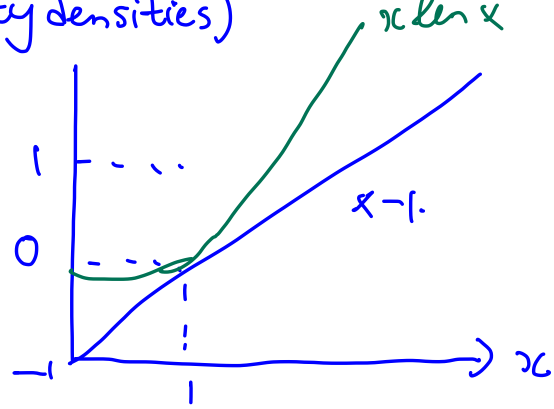
$$\Rightarrow \Omega[f] - \Omega[f_N] = k_B T \, \mathrm{Tr}_{cl}\left[f_N\left(\frac{f}{f_N}\ln\frac{f}{f_N} - \frac{f}{f_N} + 1\right)\right]$$

Note that $f, f_N > 0$ (probability densities)

Using that $x \ln x \geq x - 1$

$\Rightarrow \Omega[f] \geq \Omega[f_N]$

$\square$



Theorem 1 For given Φ_N, T, μ, the quantity $\mathcal{F}[\rho]$ is a unique functional of the equilibrium density $\rho(\vec{r})$.

Proof Assume there is an external potential $V'_{ext}(\vec{r}) \neq V_{ext}(\vec{r})$ that gives rise to the same $\rho(\vec{r})$. Define $V_N = \sum_{i=1}^{N} V_{ext}(\vec{r}_i)$ and $V_N' = \sum_{i=1}^{N} V'_{ext}(\vec{r}_i)$

Define Hamiltonians: $H_N = K_N + \Phi_N + V_N$; $H_N' = K_N + \Phi_N + V_N'$

with $f_N \neq f_N'$ given by: $f_N = \dfrac{e^{-\beta(H_N - \mu N)}}{\Xi}$

$$f_N' = \frac{e^{-\beta(H_N' - \mu N)}}{\Xi'}$$

Then:

$$\Omega' := \Omega[f_N'] = \mathrm{Tr}_{cl}\left[f_N'\left(H_N' - \mu N + k_B T \ln f_N'\right)\right]$$

$$\overset{\text{(Lemma)}}{<} \mathrm{Tr}_{cl}\left[f_N\left(H_N' - \mu N + k_B T \ln f_N\right)\right]$$

$H_N' = H_N + V_N' - V_N$

$$= \mathrm{Tr}_{cl}\left[f_N\left(H_N - \mu N + k_B T \ln f_N + V_N' - V_N\right)\right] \qquad (*)$$

$$= \Omega[f_N] + \mathrm{Tr}_{cl}\left[f_N\left(V_N' - V_N\right)\right] = \Omega + \int d\vec{r}\, \rho(\vec{r})\left[V'_{ext}(r) - V_{ext}(\vec{r})\right]$$

Here, we used: $Tr_{cl}(f_N V_N) = \int d\vec{r}\, V_{ext}(\vec{r})\, Tr_{cl}[\hat{\rho}(\vec{r}) f_N]$

$$= \int d\vec{r}\, \rho(\vec{r})\, V_{ext}(\vec{r})$$

Similarly, $\Omega < \Omega' + \int d\vec{r}\, \rho(\vec{r})\, [V_{ext}(\vec{r}) - V'_{ext}(\vec{r})]$. (**)

(*) + (**) $\Rightarrow$ $\Omega + \Omega' < \Omega' + \Omega$. ↯ $\Rightarrow$ $V_{ext}(\vec{r}) = V'_{ext}(\vec{r})$.

In other words, $\exists!$ $V_{ext}(\vec{r})$ that determines $\rho(\vec{r})$, which fixes f_N.

Furthermore:

$$\mathcal{F}[\rho] = \Omega[\mu] + \int d\vec{r}\, \rho(\vec{r})\, [\mu - V_{ext}(\vec{r})]$$

$$= Tr_{cl}\left[f_N\left(H_N - \mu N + k_B T \ln f_N\right)\right] + Tr_{cl}\left[f_N\left(\mu N - f_N V_N\right)\right].$$

$$= Tr_{cl}\left[f_N\left(H_N - \mu N + \mu N - V_N + k_B T \ln f_N\right)\right].$$

$\hookrightarrow K_N + \Phi_N + V_N$

$$= Tr_{cl}\left[f_N\left(K_N + \Phi_N + k_B T \ln f_N\right)\right].$$

This depends only on f_N, and hence depends only on $\rho(\vec{r})$. $\square$.

<u>Theorem 2</u> Consider the functional

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

$\tilde{\rho}(\vec{r})$ some density profile (not necessarily equilibrium one).

Then: $\Omega_V[\rho] = \Omega$ $\qquad \left.\dfrac{\delta \Omega_V[\tilde{\rho}]}{\delta \tilde{\rho}(\vec{r})}\right|_{\tilde{\rho}=\rho} = 0$

(When $\tilde{\rho}(\vec{r}) = \rho(\vec{r})$ the eq. density profile, then Ω_V reduces to Ω. Ω is minimum of Ω_V)

Proof: When $\tilde{\rho} = \rho$ then:

$$\Omega_V[\rho] = \mathcal{F}[\rho] - \int d\vec{r}\, u(\vec{r})\rho(\vec{r}) = \mathrm{Tr}_{cl}\left[f_N\left(H_N - V_N + k_B T \ln f_N - \mu N + V_N\right)\right]$$
$$= \Omega[f_N] = \Omega \cdot \text{(i)}$$

Assume now $\exists \rho'(\vec{r})$ for a given $V_{ext}(\vec{r})$ and H_N different from $\rho(\vec{r})$. Associated probability density is $f'[\rho'(\vec{r})]$ with $\mathrm{Tr}_{cl} f' = 1$.

Here, we assumed that $\exists V'_{ext}(\vec{r})$ that would give rise to the eq. density profile $\rho'(\vec{r})$ in order that f' exists. Then the existence of $\mathcal{F}[\rho']$ is guaranteed.

$$\Rightarrow \Omega[f'] = \mathrm{Tr}_{cl}\left[f'\left(H_N - \mu N + k_B T \ln f'\right)\right] = \mathcal{F}[\rho'] - \int d\vec{r}\, u(\vec{r})\rho'(\vec{r})$$
$$=: \Omega_V(\rho').\text{(ii)}$$

From the lemma: $\Omega[f'] > \Omega[f_N] \underset{\text{(ii)}}{\overset{\text{(i)}}{\Longrightarrow}} \Omega_V[\rho] < \Omega_V[\rho']$ $\square$.

Intrinsic Helmholtz free energy functional

We find for the Helmholtz free energy:

$$F(N,V,T) = \Omega(\mu,V,T) + \mu \int d\vec{r}\, \rho(\vec{r}) = \mathcal{F}[\rho] + \int d\vec{r}\, \rho(\vec{r}) V_{ext}(\vec{r}).$$

$\Rightarrow \mathcal{F}[\rho]$ contribution to $F(N,V,T)$ that does not explicitly depend on the external potential!

From theorem 2: $\mu = V_{ext}(\vec{r}) + \dfrac{\delta \mathcal{F}[\rho]}{\delta \rho(\vec{r})}$. (constancy of chemical potential).

$\dfrac{\delta \mathcal{F}[\rho]}{\delta \rho(\vec{r})}$ can be viewed as an intrinsic chemical potential. (In general not a local function of $\rho(\vec{r})$).

Exception: $\Phi_N = 0$ (ideal gas): $\beta \mathcal{F}_{id}[\rho] = \int d\vec{r}\, \rho(\vec{r}) \{ \ln[\rho(\vec{r})\Lambda^3] - 1 \}$.

$\mathcal{F}_{id}[\rho]$ is of the local form! $\mathcal{F}_{id}[\rho] = \int d\vec{r}\, f_{id}(\rho(\vec{r}))$. P2.8+3.1

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.

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

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

Hierarchies of correlation functions.

Recall that Ω can be viewed as $\Omega[u]$ and we have seen in P.3.1

$$\rho(\vec{r}) = -\frac{\delta \beta \Omega[u]}{\delta \beta u(\vec{r})} \qquad G(\vec{r},\vec{r}\,') = -\frac{\delta^2 \beta \Omega[u]}{\delta \beta u(\vec{r})\, \delta \beta u(\vec{r}\,')}$$

and for $n \geq 2$: $G^{(n)}(\vec{r}_1, \dots, \vec{r}_N) = \langle \delta\hat{\rho}(\vec{r}_1) \dots \delta\hat{\rho}(\vec{r}_N) \rangle$

$$= -\frac{\delta^{(n)} \beta \Omega[u]}{\delta \beta u(\vec{r}_1) \dots \delta \beta u(\vec{r}_N)}$$ (Density-density correlation function hierarchy).

$G^{(2)}(\vec{r},\vec{r}\,') = G(\vec{r},\vec{r}\,')$.

$\Omega[u]$ is a generating functional for density-density correlation functions.

We can obtain a second hierarchy of correlation functions from $\mathcal{F}[\rho]$: Define: $\mathcal{F}_{ex}[\rho] = \mathcal{F}[\rho] - \mathcal{F}_{id}[\rho]$.

We define direct correlation functions as:

$$c^{(1)}(\vec{r}) = -\frac{\delta \beta F_{ex}[\rho]}{\delta\rho(\vec{r})}, \quad c^{(2)}(\vec{r},\vec{r}\,') = -\frac{\delta^2 \beta F_{ex}[\rho]}{\delta\rho(\vec{r})\,\delta\rho(\vec{r}\,')} = c^{(2)}(\vec{r}\,',\vec{r}).$$

$$c^{(n)}(\vec{r}_1,\dots,\vec{r}_n) = -\frac{\delta^n \beta F_{ex}[\rho]}{\delta\rho(\vec{r}_1)\dots\delta\rho(\vec{r}_n)}$$

From: $\mu = \dfrac{\delta F[\rho]}{\delta\rho(\vec{r})} + V_{ext}(\vec{r})$

$$\Rightarrow \mu = \underbrace{\frac{\delta F_{ex}[\rho]}{\delta\rho(\vec{r})}}_{=-\beta^{-1}c^{(1)}(\vec{r})} + \underbrace{\frac{\delta F_{id}[\rho]}{\delta\rho(\vec{r})}}_{\beta^{-1}\ln[\rho(\vec{r})\Lambda^3]} + V_{ext}(\vec{r}).$$

$$\Rightarrow c^{(1)}(\vec{r}) = \ln[\rho(\vec{r})\Lambda^3] - \beta u(\vec{r}). \Rightarrow \rho(\vec{r})\Lambda^3 = \exp\left[\beta u(\vec{r}) + c^{(1)}(\vec{r})\right].$$

We see that $-k_B T c^{(1)}(\vec{r})$ acts as an effective one-body potential that determines $\rho(\vec{r})$.

One more functional differentiation:

$$c^{(2)}(\vec{r},\vec{r}\,') = \frac{\delta(\vec{r}-\vec{r}\,')}{\rho(\vec{r})} - \beta\frac{\delta u(\vec{r})}{\delta\rho(\vec{r}\,')} = \frac{\delta(\vec{r}-\vec{r}\,')}{\rho(\vec{r})} - G^{-1}(\vec{r},\vec{r}\,'). \quad (*)$$

with inverse defined as:

$$\int d\vec{r}\,'' \, G(\vec{r},\vec{r}\,'')\, G^{-1}(\vec{r}\,'',\vec{r}\,') = \delta(\vec{r}-\vec{r}\,'). \quad (i)$$

(Compare with: $\underline{A}$ matrix. $A_{ik}A^{-1}_{kj} = \delta_{ij}$).

From $(*)$:

$$G(\vec{r},\vec{r}\,'')c^{(2)}(\vec{r}\,'',\vec{r}\,') = \frac{\delta(\vec{r}\,''-\vec{r}\,')}{\rho(\vec{r}\,'')}G(\vec{r}\,'',\vec{r}) - G(\vec{r},\vec{r}\,'')G^{-1}(\vec{r}\,'',\vec{r}\,')$$

and integrate over $\vec{r}\,''$.

$$\int d\vec{r}\,'' G(\vec{r},\vec{r}\,'')c^{(2)}(\vec{r}\,'',\vec{r}\,') = \frac{G(\vec{r},\vec{r}\,')}{\rho(\vec{r}\,')} - \delta(\vec{r}-\vec{r}\,').$$

$$G(\vec{r},\vec{r}\,') = \rho^{(2)}(\vec{r},\vec{r}\,') - \rho(\vec{r})\rho(\vec{r}\,') + \rho(\vec{r})\delta(\vec{r}-\vec{r}\,').$$

$$\rho^{(2)}(\vec{r},\vec{r}\,') = \rho(\vec{r})\rho(\vec{r}\,')[h(\vec{r},\vec{r}\,')+1]$$

$$= \rho(\vec{r})\rho(\vec{r}\,')h(\vec{r},\vec{r}\,') + \cancel{\rho(\vec{r})\rho(\vec{r}\,')} - \cancel{\rho(\vec{r})\rho(\vec{r}\,')} + \rho(\vec{r})\delta(\vec{r}-\vec{r}\,').$$

$\Rightarrow$

$$\cancel{\rho(\vec{r})}h(\vec{r},\vec{r}\,') = \int d\vec{r}\,'' \cancel{\rho(\vec{r})}\rho(\vec{r}\,'')h(\vec{r},\vec{r}\,'')c^{(2)}(\vec{r}\,'',\vec{r}\,').$$

$$+ \int d\vec{r}\,'' \cancel{\rho(\vec{r})}\delta(\vec{r}-\vec{r}\,'')c^{(2)}(\vec{r}\,'',\vec{r}\,').$$

$$\boxed{\Rightarrow h(\vec{r},\vec{r}\,') = c^{(2)}(\vec{r},\vec{r}\,') + \int d\vec{r}\,'' h(\vec{r},\vec{r}\,'')\rho(\vec{r}\,'')c^{(2)}(\vec{r}\,'',\vec{r}\,').}$$

Inhomogeneous OZ equation! For $V_{ext}(\vec{r}) \to 0$ reduces to bulk OZ eqn.

We conclude that the OZ equation is a natural consequence of having two generating functionals $\Omega[u]$ and $\mathcal{F}[\rho]$ that are linked via Legendre transform: $\mathcal{F}[\rho] = \Omega[u] + \int d\vec{r}\, u(\vec{r})\rho(\vec{r})$

Condition (i) is equivalent to:

$$\int d\vec{r}\,'' \frac{\delta^2 \mathcal{F}[\rho]}{\delta\rho(\vec{r})\,\delta\rho(\vec{r}\,'')} \frac{\delta^2 \Omega[u]}{\delta u(\vec{r}\,'')\,\delta u(\vec{r}\,')} = -\delta(\vec{r}-\vec{r}\,').$$

Determination of $\mathcal{F}_{ex}[\rho]$

Formally, we can obtain formal expressions for $\mathcal{F}_{ex}[\rho]$ that forms a basis for approximations.

(·) Integration wrt particle density.

(·) Integration wrt interaction potential.