Lecture 10: Classical density functional theory.

Last lecture: $g(r)$
- conditional probability
- potential of mean force
- access to thermodynamics (caloric, virial, compress.)
- scattering (static structure factor)

To compute $g(r)$, we defined the indirect correlation function $h(r)=g(r)-1$

$h(r) = c(r) + \rho \int d\vec{r}'\, c(|\vec{r}-\vec{r}'|)\, h(r')$ This equation defines the direct correlation function $c(r)$.

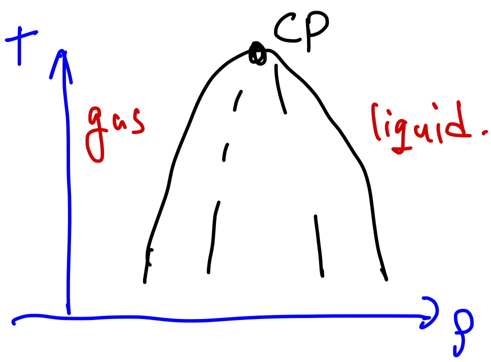
Ornstein-Zernike (OZ) equation.

To compute $c(r)$ in practical situations, we have to provide a closure relation

The OZ equation was first written down to describe critical opalescence (without derivation): strong scattering at small $\vec{k}$ when a fluid is close to the critical point. (small angle neutron scattering, x-rays)

Critical opalescence

Recall:



Reasoning: • Order parameter correlation function near the CP has form $\tilde{G}(k) = \frac{\tilde{G}(0)}{1+\xi^2 k^2}$ (recall Landau theory)

Here $\tilde{G}(0)$ and ξ^2 diverge at the critical point.

- However $S(k) = \frac{\tilde{G}(k)}{\rho}$ and compressibility sum rule says:

$$\lim_{k\to 0} S(k) = \rho \kappa_T k_B T \sim \langle N^2\rangle - \langle N\rangle^2.$$

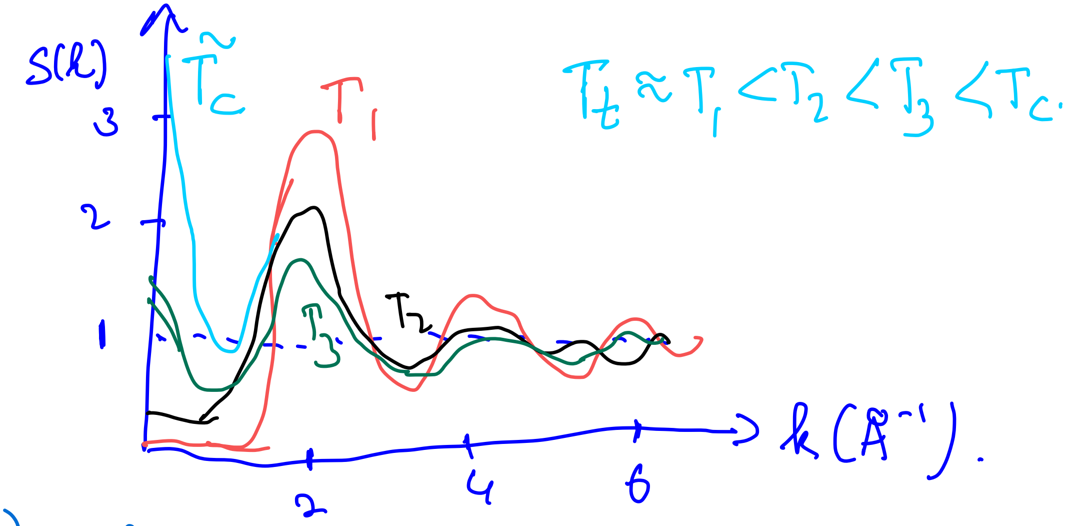
$$\Rightarrow S(0) \sim \kappa_T \sim |T-T_c|^{-\gamma}$$ γ: critical exponent.

Suppose incident wavelength $\lambda \sim 500$ Å ⇒ density fluctuations with $k < 2\pi/\lambda$ will scatter the light ⇒ Close to CP $I(\theta)$ or $S(k)$ grows large!

⇒ Strong scattering gives rise to milky appearance

We shall show that this occurs when $\xi \sim \lambda$

Experimentally:



$$I(\theta) \sim S(k) \approx \frac{S(0)}{1+\xi^2 k^2} \quad (\text{small } k) \quad (\text{OZ-behaviour})$$

ξ OZ correlation length.

Only valid for $k \ll k_{max} \approx \frac{2\pi}{\sigma}$ ← typical hard-core size. SLIDES

Rewriting the OZ behaviour criterion:

$$\frac{1}{S(k)} = \frac{1}{S(0)} + R^2 k^2 + \mathcal{O}(k^4) \qquad R^2 S(0) = \xi^2.$$

Experimentally we find $R \sim$ const (only small variation for $T \downarrow T_c$)

$R \sim$ few Å (short range correlation length).

With $R \sim$ cst. ⇒ $\xi \sim |T-T_c|^{-\nu}$ close to CP. ⇒ $\gamma = 2\nu$.

The contribution of OZ is to give a microscopic theory for $S(k) \approx \frac{S(0)}{1+\xi^2 k^2}$ and $\xi^2 = R^2 S(0)$ with R finite at $T \downarrow T_c$.

For this consider the direct correlation function $c(r)$. Let's assume that its Fourier transform exists.

Now: $\tilde{c}(k) = \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\, c(r) = 4\pi \int_0^\infty dr\, r^2 \, \frac{\sin(kr)}{kr}\, c(r)$

$$= 4\pi \int_0^\infty dr\, r^2 \left(1 - \frac{(kr)^2}{3!} + \dots\right) c(r) = \tilde{c}(0) + \alpha k^2 + \dots$$

assume low k expansion.

So we conclude that: $\tilde{c}(0) = 4\pi \int_0^\infty dr\, r^2 c(r)$

$\alpha = -\frac{4\pi}{3!} \int dr\, r^4 c(r)$.

⇒ Assume that both quantities exist.

Hence: $S(k) = \frac{1}{1-\rho\tilde{c}(k)} = \frac{1}{1-\rho[\tilde{c}(0)+\alpha k^2+\dots]}$

$S(0) = \frac{1}{1-\rho\tilde{c}(0)}$

$\Rightarrow S(k) = \frac{S(0)}{1-\rho\alpha S(0) k^2 + \dots}$

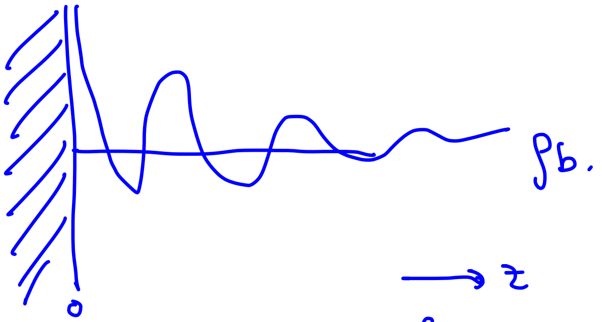
and we find $R^2 = -\rho\alpha$. $\Rightarrow R^2 = \frac{4\pi\rho}{3!} \int_0^\infty dr\, r^4 c(r) > 0$ ← for fluid with gas-liquid coexistence.

Recall that $g(r) - 1 \sim \frac{1}{r^{d-2+\eta}}$ So beyond OZ theory:

$\gamma = 2\nu \rightarrow \gamma = (2-\eta)\nu$ ($\eta \approx 0.03$ for 3D Ising universality class)

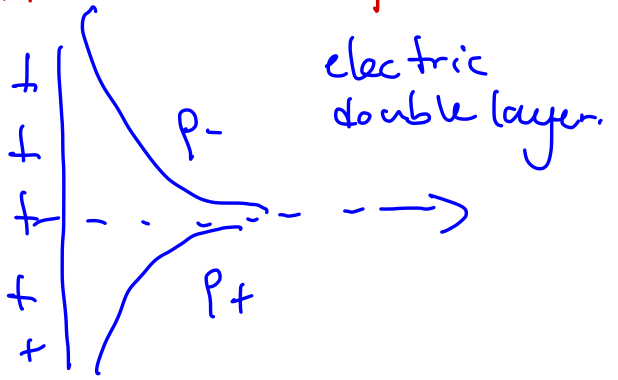
Up until now the OZ equation was stated without derivation. It turns out we can derive it if we consider the physics of inhomogeneous fluids.

We are interested now in cases when $V_{ext}(\vec{r}) \neq 0$. Examples:



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

$= 0$ 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

Correlation functions ↓ Microscopic structure.

→ Experiment ←

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

Construction of the density functional ($V_{ext} \neq 0$)

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

We can view: $\Omega := \Omega[u]$, since

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

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

We can do a functional Legendre transform:

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

We use the following notation (as before)

$$\mathrm{Tr}_{cl}(\dots) = \sum_{N=0}^{\infty} \frac{1}{h^{3N}N!} \int d\vec{p}^N \int d\vec{r}^N (\dots)$$

$$f_N = \frac{1}{\Xi} e^{-\beta(H-\mu N)}$$

$$\langle\dots\rangle = \mathrm{Tr}_{cl}\left(f_N(\dots)\right)$$

Note alternatively:

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

kinetic ↗ ↖ potential

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

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

Not so obvious result: 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 $V_{ext}(\vec{r}) \longrightarrow \rho(\vec{r})$.

$\Rightarrow$ 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 unique functional of $\rho(\vec{r})$ and has the same form for every external potential

Let us formalize the above.

Lemma: 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 $\Omega[f] \geq \Omega[f_N]$

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

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

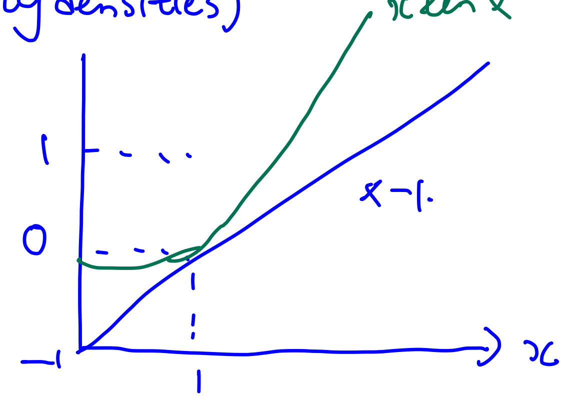
$$\Rightarrow \Omega[f]-\Omega[f_N] = k_BT\,\mathrm{Tr}_{cl}\left[f_N\left(\frac{f}{f_N}\ln\frac{f}{f_N}-\frac{f}{f_N}+1\right)\right]$$

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

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

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

□



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:

$$\Omega' := \Omega[f_N'] = \mathrm{Tr}_{cl}\left[f_N'(H_N'-\mu N + k_BT\ln f_N')\right]$$

$$\overset{\text{(Lemma)}}{<} \mathrm{Tr}_{cl}\left[f_N(H_N'-\mu N + k_BT\ln f_N)\right]$$

$H_N' = H_N + V_N' - V_N$

$$= \mathrm{Tr}_{cl}\left[f_N\left(H_N - \mu N + k_BT\ln f_N + V_N' - V_N\right)\right] \qquad (*)$$

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

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

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

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:

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

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

$$= \mathrm{Tr}_{cl}[f_N(H_N - \mu N + \mu N - V_N + k_B T \ln f_N)].$$

$$\hookrightarrow K_N + \Phi_N + V_N$$

$$= \mathrm{Tr}_{cl}[f_N(K_N + \Phi_N + k_B T \ln f_N)].$$

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

□.

Theorem 2 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: $\Omega_V[\rho] = \Omega$ $\quad \left.\dfrac{\delta \Omega_V[\tilde{\rho}]}{\delta \tilde{\rho}(\vec{r})}\right|_{\tilde{\rho}=\rho} = 0$

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

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

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

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.

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

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

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! $\mathcal{F}_{id}[\rho] = \int d\vec{r}\, f_{id}(\rho(\vec{r}))$.

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

$\leftarrow$ some density profile.

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

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

(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:

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

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

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

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

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

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:

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

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

From (*):

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

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

$$\left.\begin{aligned}
&\int d\vec{r}''\, G(\vec{r},\vec{r}'')\, c^{(2)}(\vec{r}'',\vec{r}') = \frac{G(\vec{r},\vec{r}')}{\rho(\vec{r}')} - \delta(\vec{r}-\vec{r}') .\\
&G(\vec{r},\vec{r}') = \rho^{(2)}(\vec{r},\vec{r}') - \rho(\vec{r})\rho(\vec{r}') + \rho(\vec{r})\,\delta(\vec{r}-\vec{r}') . \qquad \rho^{(2)}(\vec{r},\vec{r}') = \rho(\vec{r})\rho(\vec{r}')\,[h(\vec{r},\vec{r}')+1]\\
&\quad = \rho(\vec{r})\rho(\vec{r}')\,h(\vec{r},\vec{r}') + \cancel{\rho(\vec{r})\rho(\vec{r}')} - \cancel{\rho(\vec{r})\rho(\vec{r}')} + \rho(\vec{r})\,\delta(\vec{r}-\vec{r}') .
\end{aligned}\right\} \Rightarrow$$

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

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

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

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 $\underline{\underline{\text{two}}}$ 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:

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

<u>Determination of $\mathcal{F}_{ex}[\rho]$</u>

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.