Density Functional Theory

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1 Fundamentals

- Basic approach is to treat equilibrium systems as a special case of non-uniform systems, where cause of non-uniformity is an external single particle potential $\phi(\mathbf{r})$.
- We write the grand canonical partition function in presence of external potential:

  $$\begin{aligned} \Xi = e^{\beta PV} &= e^{\Omega} = \sum_N e^{\beta\mu N} Q_N \qquad Q_N = \frac{1}{N!\lambda^{3N}} \int d\mathbf{r}^{(N)} e^{-\beta U(\mathbf{r}^{(N)})} \\ U(\mathbf{r}^{(N)}) &= \frac{1}{2}\sum_{i\neq j} u(\mathbf{r}_{ij}) + \sum_i \phi(\mathbf{r}_i). \end{aligned}$$

  with $\lambda = h/\sqrt{2\pi mkT}$.
- We can rewrite the external potential contribution to the potential energy as:

  $$\sum_i \phi(\mathbf{r}_i) = \sum_i \int d\mathbf{r}\ \phi(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}_i) = \int d\mathbf{r}\ \phi(\mathbf{r})N(\mathbf{r}).$$

- We define the chemical potential field

  $$\psi(\mathbf{r}) = \beta\mu - \beta\phi(\mathbf{r})$$

  and since $\int d\mathbf{r}\ \beta\mu N(\mathbf{r}) = \beta\mu N$, $\int d\mathbf{r}\ \psi(\mathbf{r}) = \beta\mu N - \beta\sum_i \phi(\mathbf{r}_i)$ and

  $$e^{\Omega} = \sum_N \frac{1}{N!\lambda^{3N}} \int d\mathbf{r}^{(N)}\ e^{-\frac{\beta}{2}\sum_{i\neq j} u(\mathbf{r}_{ij})} e^{\int d\mathbf{r}\ \psi(\mathbf{r})N(\mathbf{r})}.$$

- Clearly $\Omega[\psi(\mathbf{r})]$ is a *functional* of the chemical potential field $\psi(\mathbf{r})$ since changing the functional form of $\psi(\mathbf{r})$ through the external potential changes Ω.
- Just as N is *conjugate* to $\beta\mu$ in a uniform system, we see that $N(\mathbf{r})$ is conjugate to the chemical potential field $\psi(\mathbf{r})$. Thus, noting that

  $$\frac{\delta e^{\int d\mathbf{r}'\ \psi(\mathbf{r}')N(\mathbf{r}')}}{\delta\psi(\mathbf{r})} = N(\mathbf{r})\, e^{\int d\mathbf{r}'\ \psi(\mathbf{r}')N(\mathbf{r}')},$$

we see that

$$\begin{aligned}
\frac{\delta \ln \Xi}{\delta \psi(\mathbf{r})} &= \frac{\delta \Omega[\psi(\mathbf{r})]}{\delta \psi(\mathbf{r})} = \frac{1}{\Xi}\frac{\delta \Xi}{\delta \psi(\mathbf{r})} \\
&= \frac{1}{\Xi}\sum_N \frac{1}{N!\lambda^{3N}} \int d\mathbf{r}^{(N)}\; N(\mathbf{r}) e^{-\frac{\beta}{2}\sum_{i\neq j} u(\mathbf{r}_{ij})} e^{\int d\mathbf{r}'\;\psi(\mathbf{r}')N(\mathbf{r}')} \\
&= \langle N(\mathbf{r})\rangle = \rho^{(1)}(\mathbf{r}) = \rho(\mathbf{r}).
\end{aligned}$$

- Similarly,

$$\begin{aligned}
\frac{\delta^2 \Omega}{\delta \psi(\mathbf{r})\delta \psi(\mathbf{r}')} &= \frac{\delta \langle N(\mathbf{r})\rangle}{\delta \psi(\mathbf{r}')} = \langle N(\mathbf{r})N(\mathbf{r}')\rangle - \rho(\mathbf{r})\rho(\mathbf{r}') \equiv \chi(\mathbf{r},\mathbf{r}') \\
&= \rho^{(2)}(\mathbf{r},\mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}') + \delta(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}).
\end{aligned}$$

- In case where $\phi(\mathbf{r})$ arises from the presence of a particle fixed at the origin, $\sum_i \phi(\mathbf{r}_i) = \sum_{i=1}^{N} u(\mathbf{r}_i)$.
  - Source of non-uniformity is the fixed particle, and

$$\rho^{(1)}(\mathbf{r}) = \langle N(\mathbf{r})\rangle = \rho g(\mathbf{r}).$$

- We can create a functional of the density profile $\rho(\mathbf{r})$ by *Legendre transform* using the fact that $\rho(\mathbf{r})$ and $\psi(\mathbf{r})$ are conjugate fields,

$$\begin{aligned}
-F &= \Omega - \int d\mathbf{r}\; \rho(\mathbf{r})\psi(\mathbf{r}) = \beta PV - \int d\mathbf{r}\; \langle N(\mathbf{r})\rangle \left(\beta\mu - \beta\phi(\mathbf{r})\right) \\
&= \beta PV - \beta\mu\langle N\rangle + \beta \int d\mathbf{r}\; \rho(\mathbf{r})\phi(\mathbf{r}) = -\beta A + \beta\langle\phi\rangle = -\beta\left(A - \langle\phi\rangle\right)
\end{aligned}$$

since $G = \mu\langle N\rangle = A + PV$

- F is a functional of $\rho(\mathbf{r})$ since

$$\begin{aligned}
\delta F &= -\delta\Omega + \int d\mathbf{r}\; \left(\delta\rho(\mathbf{r})\right)\psi(\mathbf{r}) + \int d\mathbf{r}\,\rho(\mathbf{r})\delta\psi(\mathbf{r}) \qquad \text{but since} \\
\delta\Omega &= \int d\mathbf{r}\,\rho(\mathbf{r})\delta\psi(\mathbf{r}) \qquad \text{we get} \qquad \delta F = \int d\mathbf{r}\,\psi(\mathbf{r})\delta\rho(\mathbf{r})
\end{aligned}$$

and our fundamental equation is

$$\boxed{\frac{\delta F[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})} = \psi(\mathbf{r}) = \psi[\mathbf{r};\rho(\mathbf{r})].}$$

- What is the functional $\psi[\mathbf{r};\rho(\mathbf{r})]$ of the density field? Consider and gas in an external potential with no interactions between particles:

$$\begin{aligned}
\rho_0(\mathbf{r}) = \langle N(\mathbf{r})\rangle_0 &= \frac{\delta}{\delta\psi_0(\mathbf{r})} \ln\left(\sum_N \frac{1}{N!\lambda^{3N}} \int d\mathbf{r}^{(N)}\; e^{-\beta\sum_i \phi(\mathbf{r}_i)} e^{\beta\mu}\right) \\
&= \frac{\delta}{\delta\psi_0(\mathbf{r})} \ln\left(\sum_N \frac{1}{N!\lambda^{3N}} \int d\mathbf{r}^{(N)} \prod_i e^{\psi_0(\mathbf{r}_i)}\right) \qquad \text{but} \\
\int d\mathbf{r}^{(N)} \prod_i e^{\psi_0(\mathbf{r}_i)} &= \left(\int d\mathbf{r}\, e^{\psi_0(\mathbf{r})}\right)^N \qquad \text{so} \qquad \sum_N \frac{1}{N!}\left(\frac{1}{\lambda^3}\int d\mathbf{r}\, e^{\psi_0(\mathbf{r})}\right)^N = e^{1/\lambda^3 \int d\mathbf{r}\; \exp\{\psi_0(\mathbf{r})\}}
\end{aligned}$$

Thus

$$\begin{aligned}\rho_0(\mathbf{r}) &= \frac{\delta}{\delta\psi_0(\mathbf{r})}\ln\left(e^{1/\lambda^3\int d\mathbf{r}\,\exp\{\psi_0(\mathbf{r})\}}\right) = \frac{\delta}{\delta\psi_0(\mathbf{r})}\left(\frac{1}{\lambda^3}\int d\mathbf{r}'\,e^{\psi_0(\mathbf{r}')}\right)\\ &= \frac{1}{\lambda^3}e^{\psi_0(\mathbf{r})},\end{aligned}$$

so that for an ideal gas in an external potential,

$$\psi_0[\mathbf{r},\rho_0(\mathbf{r})] = \ln\left(\lambda^3\rho_0(\mathbf{r})\right).$$

- Recall that since

$$\frac{\delta F_0}{\delta\rho_0(\mathbf{r})} = \psi_0(\mathbf{r}) = \ln\left(\lambda^3\rho_0(\mathbf{r})\right),$$

by integrating the expression above, we have that the free energy F for the ideal gas system is

$$F_0[\rho_0(\mathbf{r})] = \int d\mathbf{r}\,\rho_0(\mathbf{r})\left(\ln\left(\lambda^3\rho_0(\mathbf{r})\right) - 1\right).$$

  - Note that this is a non-linear functional of the density $\rho_0(\mathbf{r})$.

- Recall that since $\beta A = F + \beta\langle\phi\rangle$,

$$\beta A_0 = \int d\mathbf{r}\,\rho_0(\mathbf{r})\left(\ln\left(\lambda^3\rho_0(\mathbf{r})\right) - 1 + \beta\phi(\mathbf{r})\right).$$

  - Since $\beta\langle\phi\rangle$ is the energy contribution to βA_0, we see that F_0 is really the entropic contribution.

- In light of the ideal gas result, we *define* the quantity $C[r;\rho(\mathbf{r})]$ so that

$$\rho(\mathbf{r}) = \frac{1}{\lambda^3}e^{\psi(\mathbf{r})+C(\mathbf{r})}.$$

  - Meaning: If ideal gas was in an external field $\psi(\mathbf{r}) + C(\mathbf{r})$, its average density would be same as an interacting system in potential field $\psi(\mathbf{r})$.

- We now define the *excess free energy* $\Delta F = F - F_0$ so that

$$\begin{aligned}\frac{\delta F}{\delta\rho(\mathbf{r})} &= \frac{\delta F_0}{\delta\rho(\mathbf{r})} + \frac{\delta\Delta F}{\delta\rho(\mathbf{r})} = \psi(\mathbf{r}) = \ln\left(\lambda^3\rho(\mathbf{r})\right) - C(\mathbf{r}) \quad \text{so}\\ \frac{\delta\Delta F}{\delta\rho(\mathbf{r})} &= -C[\mathbf{r};\rho(\mathbf{r})].\end{aligned}$$

- In some instances, we can functionally expand $C(\mathbf{r})$ around a uniform reference system of density ρ if $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho$ is small:

$$\begin{aligned}C[\mathbf{r};\rho(\mathbf{r})] &= C(\mathbf{r};\rho) + \int d\mathbf{r}'\left(\frac{\delta C(\mathbf{r})}{\delta\rho(\mathbf{r}')}\right)_{\rho(\mathbf{r}')=\rho}\Delta\rho(\mathbf{r}') + \cdots\\ &= C(\mathbf{r};\rho) + \int d\mathbf{r}'\,\bar{c}(\mathbf{r},\mathbf{r}')\,\Delta\rho(\mathbf{r}') + \cdots\end{aligned}$$

where

$$\bar{c}(\mathbf{r},\mathbf{r}') = \left(\frac{\delta C(\mathbf{r})}{\delta\rho(\mathbf{r}')}\right)_{\rho(\mathbf{r}')=\rho} = \left(\frac{\delta^2\Delta F}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right)_{\rho}.$$

- Note that for a uniform system of density ρ,

$$C(\mathbf{r};\rho) = \ln\left(\lambda^3\rho\right) - \psi(\mathbf{r}) = \ln\left(\lambda^3\rho\right) - \beta\mu,$$

  which is not a function of $\mathbf{r}$.

- The same sort of Taylor expansion can be carried out for the excess free energy $\Delta F[\rho(\mathbf{r})]$,

$$\begin{aligned}
\Delta F[\rho(\mathbf{r})] &= \Delta F(\rho) + \int d\mathbf{r} \left(\frac{\delta \Delta F}{\delta\rho(\mathbf{r})}\right)_\rho \Delta\rho(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}d\mathbf{r}' \left(\frac{\delta^2\Delta F}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}\right)_\rho \Delta\rho(\mathbf{r})\Delta\rho(\mathbf{r}') + \cdots \\
&= \Delta F(\rho) - \int d\mathbf{r}\; C(\rho)\,\Delta\rho(\mathbf{r}) - \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\; \bar{c}(\mathbf{r},\mathbf{r}';\rho)\,\Delta\rho(\mathbf{r})\,\Delta\rho(\mathbf{r}') + \cdots
\end{aligned}$$

- What is this function $\bar{c}(\mathbf{r},\mathbf{r}')$ for the uniform reference system? Claim: $\bar{c}(\mathbf{r},\mathbf{r}') = c(\mathbf{r},\mathbf{r}')$, the direct correlation function defined earlier. Recall that $-C(\mathbf{r}) = -\ln(\lambda^3\rho(\mathbf{r})) + \psi(\mathbf{r})$ so

$$-\frac{\delta C(\mathbf{r})}{\delta\rho(\mathbf{r}')} = -\bar{c}(\mathbf{r},\mathbf{r}') = -\frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho(\mathbf{r})} + \frac{\delta\psi(\mathbf{r})}{\delta\rho(\mathbf{r}')}.$$

To establish the connection to the direct correlation function, recall that this function is defined through the Ornstein-Zernike equation

$$\begin{aligned}
h(\mathbf{r},\mathbf{r}') &= c(\mathbf{r},\mathbf{r}') + \int d\mathbf{r}''\; c(\mathbf{r},\mathbf{r}'')\,\rho(\mathbf{r}'')h(\mathbf{r}'',\mathbf{r}') \quad \text{where} \\
\rho(\mathbf{r})\rho(\mathbf{r}')h(\mathbf{r},\mathbf{r}') &= \rho^{(2)}(\mathbf{r},\mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}') = \chi(\mathbf{r},\mathbf{r}') - \rho(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') \\
&= \frac{\delta\rho(\mathbf{r})}{\delta\psi(\mathbf{r}')} - \rho(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}').
\end{aligned}$$

Inserting the relation for $h(\mathbf{r},\mathbf{r}')$ into the O-Z equation gives

$$\begin{aligned}
\frac{1}{\rho(\mathbf{r})\rho(\mathbf{r}')}\frac{\delta\rho(\mathbf{r})}{\delta\psi(\mathbf{r}')} &= \frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho(\mathbf{r})} + c(\mathbf{r},\mathbf{r}') + \int d\mathbf{r}''\; c(\mathbf{r},\mathbf{r}'')\rho(\mathbf{r}'')\left(\frac{1}{\rho(\mathbf{r}'')\rho(\mathbf{r}')}\frac{\delta\rho(\mathbf{r}'')}{\delta\psi(\mathbf{r}')} - \frac{\delta(\mathbf{r}''-\mathbf{r}')}{\rho(\mathbf{r}'')}\right) \\
&= \frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho(\mathbf{r})} + \int d\mathbf{r}''\; \frac{c(\mathbf{r},\mathbf{r}'')}{\rho(\mathbf{r}')}\frac{\delta\rho(\mathbf{r}'')}{\delta\psi(\mathbf{r}')} \quad \text{hence} \\
\frac{1}{\rho(\mathbf{r})}\frac{\delta\rho(\mathbf{r})}{\delta\psi(\mathbf{r}')} &= \delta(\mathbf{r}-\mathbf{r}') + \int d\mathbf{r}''\; c(\mathbf{r},\mathbf{r}'')\frac{\delta\rho(\mathbf{r}'')}{\delta\psi(\mathbf{r}')}
\end{aligned}$$

We now define a function $d(\mathbf{r},\mathbf{r}')$ so that $c(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')/\rho(\mathbf{r}) - d(\mathbf{r},\mathbf{r}')$, and then

$$\begin{aligned}
\frac{1}{\rho(\mathbf{r})}\frac{\delta\rho(\mathbf{r})}{\delta\psi(\mathbf{r}')} &= \delta(\mathbf{r}-\mathbf{r}') + \frac{1}{\rho(\mathbf{r})}\frac{\delta\rho(\mathbf{r})}{\delta\psi(\mathbf{r}')} - \int d\mathbf{r}''\; d(\mathbf{r},\mathbf{r}'')\frac{\delta\rho(\mathbf{r}'')}{\delta\psi(\mathbf{r}')} \quad \text{or} \\
d(\mathbf{r},\mathbf{r}'') &= \frac{\delta\psi(\mathbf{r})}{\delta\rho(\mathbf{r}'')} \qquad \text{and} \qquad c(\mathbf{r},\mathbf{r}') = \frac{\delta(\mathbf{r}-\mathbf{r}')}{\rho(\mathbf{r})} - \frac{\delta\psi(\mathbf{r})}{\delta\rho(\mathbf{r}'')} \quad \text{so finally} \\
\bar{c}(\mathbf{r},\mathbf{r}') &= c(\mathbf{r},\mathbf{r}') \quad \text{the direct correlation function.}
\end{aligned}$$

- Many formulations exist to calculate $c(\mathbf{r},\mathbf{r}')$ for uniform liquids in equilibrium: integral equation theory such as the Percus-Yevick equation.
  - Simplest approximation that captures the short-ranged nature of $c(\mathbf{r},\mathbf{r}')$ is:

$$c(\mathbf{r},\mathbf{r}') = e^{-\beta u(|\mathbf{r}-\mathbf{r}'|)} - 1 \approx -\beta u(|\mathbf{r}-\mathbf{r}'|).$$

- Putting everything together:

$$\begin{aligned}
\psi(\mathbf{r}) &= \beta\mu - \beta\phi(\mathbf{r}) = \ln(\lambda^3\rho(\mathbf{r})) - c(\rho) + \int d\mathbf{r}'\, c(\mathbf{r},\mathbf{r}')\Delta\rho(\mathbf{r}') + \cdots \\
\ln(\lambda^3\rho(\mathbf{r})) &= -\beta\phi(\mathbf{r}) + \beta(\mu-\mu_0)\ln(\lambda^3\rho) + \int d\mathbf{r}'\, c(\mathbf{r},\mathbf{r}')\Delta\rho(\mathbf{r}') + \cdots \\
\ln\frac{\rho(\mathbf{r})}{\rho} &= -\beta\phi(\mathbf{r}) + \beta\,(\mu-\mu_0) + \int d\mathbf{r}'\, c(\mathbf{r},\mathbf{r}')\Delta\rho(\mathbf{r}') + \cdots
\end{aligned}$$

  or

$$\boxed{\rho(\mathbf{r}) = \rho_0 \exp\left\{-\beta\phi(\mathbf{r}) + \beta\,(\mu-\mu_0) + \textstyle\int d\mathbf{r}'\, c(\mathbf{r},\mathbf{r}')\Delta\rho(\mathbf{r}')\right\}}$$

  - The last result is known as the *General Hypernetted Chain Equation.*
  - Equation is non-linear, and self-consistent for $\rho(\mathbf{r})$.
  - Non-linearity allows for multiple solutions for $\rho(\mathbf{r})$ depending on parameters.
  - Phase transitions with spontaneous symmetry breaking can be examined when $\mu = \mu_0$ and $\phi(\mathbf{r}) = 0$.
  - Need criterion for deciding which of multiple solutions is the physical one.

2 Variational Principal

- Recall that $\beta A = F + \beta\langle\phi\rangle = F + \beta\int d\mathbf{r}'\,\phi(\mathbf{r}')\rho(\mathbf{r}')$.

- Consider a general functional of $\bar{\rho}(\mathbf{r})$, where $\bar{\rho}(\mathbf{r})$ is not necessarily equal to $\rho(\mathbf{r})$.

$$\frac{\delta F}{\delta\bar{\rho}(\mathbf{r})} = \psi(\mathbf{r}) \qquad \text{so} \qquad \frac{\delta\beta A}{\delta\bar{\rho}(\mathbf{r})} = \psi(\mathbf{r}) + \beta\phi(\mathbf{r}) = \beta\mu.$$

- If we restrict ourselves to variations of $\bar{\rho}(\mathbf{r})$ such that $\int d\mathbf{r}\,\bar{\rho}(\mathbf{r}) = \langle N\rangle$ and hence $\int d\mathbf{r}\,\delta\bar{\rho}(\mathbf{r}) = 0$, we see that

$$\delta(\beta A) = \int d\mathbf{r}\left(\frac{\delta\beta A}{\delta\bar{\rho}(\mathbf{r})}\right)_{\bar{\rho}=\rho}\delta\bar{\rho}(\mathbf{r}) = \beta\mu\int d\mathbf{r}\,\delta\bar{\rho}(\mathbf{r}) = 0.$$

- The above equation implies that $\beta A[\bar{\rho}(\mathbf{r})]$ *is stationary at* $\bar{\rho}(\mathbf{r}) = \rho(\mathbf{r})$ with respect to variations of the density that conserve the total number of particles.

- Considering the second variational derivative,

$$\frac{\delta^2\beta A}{\delta\bar{\rho}(\mathbf{r})\delta\bar{\rho}(\mathbf{r}')} = \frac{\delta\psi(\mathbf{r})}{\delta\bar{\rho}(\mathbf{r}')} = \chi^{-1}(\mathbf{r},\mathbf{r}') > 0 \quad \text{since} \quad \chi(\mathbf{r},\mathbf{r}') > 0.$$

  - Thus we conclude that $\beta A[\bar{\rho}(\mathbf{r})]$ is *minimized* by $\bar{\rho}(\mathbf{r}) = \rho(\mathbf{r})$. The equilibrium destribution is the one that minimizes the free energy.

- Equivalently, we can define a variational criterion in the Grand Canonical Ensemble by noting that if $W = -\Omega = F - \int d\mathbf{r}\,\bar{\rho}(\mathbf{r})\psi(\mathbf{r})$:

$$\left(\frac{\delta W}{\delta\bar{\rho}(\mathbf{r})}\right)_{\bar{\rho}=\rho} = \left(\frac{\delta F}{\delta\bar{\rho}(\mathbf{r})}\right)_{\bar{\rho}=\rho} - \psi(\mathbf{r}) = 0 \qquad \left(\frac{\delta^2 W}{\bar{\rho}(\mathbf{r})\bar{\rho}(\mathbf{r}')}\right)_{\bar{\rho}=\rho} = \left(\frac{\delta^2\beta A}{\delta\bar{\rho}(\mathbf{r})\delta\bar{\rho}(\mathbf{r}')}\right)_{\bar{\rho}-\rho} > 0.$$

3 Application of DFT: Solid-Liquid Equilibria

- Phase equilibria requires the equality of temperature, chemical potentials and pressure: $W^\alpha = W^\beta$.
- Equilibrium density field is the $\rho(\mathbf{r})$ that minimizes $W[\bar{\rho}(\mathbf{r})]$.
- First approach: look for solutions of general hypernetted chain equation with $\mu^\alpha = \mu_\beta$ and $\phi(\mathbf{r}) = 0$, where α is the liquid phase with uniform density ρ_l, and find solution with minimum W:

$$\rho(\mathbf{r}) = \rho_l \exp\left\{\int d\mathbf{r}'\, c(|\mathbf{r}-\mathbf{r}'|)\Delta\rho(\mathbf{r}')\right\},$$

  where $\Delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_l$ and $c(r)$ is the direct correlation function for the uniform liquid system.

- Second approach: solve directly the $\rho(\mathbf{r})$ from the equations:

$$\frac{\delta W}{\delta \bar{\rho}(\mathbf{r})} = 0 \qquad \text{and} \qquad W[\rho(\mathbf{r})] = W[\rho_l].$$

- What is an approximate form for W?

$$\begin{aligned} W[\bar{\rho}(\mathbf{r})] &= F[\bar{\rho}(\mathbf{r})] - \int d\mathbf{r}\, \psi(\mathbf{r})\bar{\rho}(\mathbf{r}) = F_0 + \Delta F - \int d\mathbf{r}\, \bar{\rho}(\mathbf{r}) \Big(\ln(\lambda^3\bar{\rho}(\mathbf{r})) - C(\mathbf{r};\bar{\rho}(\mathbf{r}))\Big) \\ &= \int d\mathbf{r}\, \bar{\rho}(\mathbf{r}) \Big(\ln(\lambda^3\bar{\rho}(\mathbf{r})) - 1\Big) + \Delta F[\bar{\rho}(\mathbf{r})] - \int d\mathbf{r}\, \bar{\rho}(\mathbf{r}) \Big(\ln(\lambda^3\bar{\rho}(\mathbf{r})) - C(\mathbf{r};\bar{\rho}(\mathbf{r}))\Big) \\ &= \Delta F[\bar{\rho}(\mathbf{r})] + \int d\mathbf{r}\, \bar{\rho}(\mathbf{r}) \left(C(\mathbf{r};\bar{\rho}(\mathbf{r})) - 1\right). \end{aligned}$$

  - Expanding ΔF and $C(\mathbf{r})$ around the uniform fluid density with $\Delta\bar{\rho}(\mathbf{r}) = \bar{\rho}(\mathbf{r}) - \rho_l$:

$$\begin{aligned} \Delta F[\bar{\rho}(\mathbf{r})] &= \Delta F(\rho_l) + \int d\mathbf{r} \left(\frac{\delta \Delta F}{\delta \bar{\rho}(\mathbf{r})}\right)_{\rho_l} \Delta\bar{\rho}(\mathbf{r}) + \int d\mathbf{r} d\mathbf{r}' \left(\frac{\delta^2 \Delta F}{\delta \bar{\rho}(\mathbf{r})\delta\bar{\rho}(\mathbf{r}')}\right)_{\rho_l} \Delta\bar{\rho}(\mathbf{r})\Delta\bar{\rho}(\mathbf{r}') + \ldots \\ C[\mathbf{r};\bar{\rho}(\mathbf{r})] &= C(\rho_l) + \int d\mathbf{r}'\, c(|\mathbf{r}-\mathbf{r}'|;\rho_l)\Delta\bar{\rho}(\mathbf{r}') + \ldots \end{aligned}$$

- Inserting these expansions into W gives (homework):

$$\Delta W = W[\bar{\rho}(\mathbf{r})] - W(\rho_l) = V\rho_l + \int d\mathbf{r}\, \bar{\rho}(\mathbf{r}) \left(\ln \bar{\rho}(\mathbf{r})/\rho_l - 1\right) - \frac{1}{2}\int d\mathbf{r} d\mathbf{r}' \Delta\bar{\rho}(\mathbf{r}) c(|\mathbf{r}-\mathbf{r}'|;\rho_l)\Delta\bar{\rho}(\mathbf{r}').$$

- Defining the function $\omega[\bar{\rho}(\mathbf{r})] = \Delta W/(V\rho_l)$, at co-existence the density must satisfy:

$$\left(\frac{\delta\omega[\bar{\rho}(\mathbf{r})]}{\delta\bar{\rho}(\mathbf{r})}\right)_{\bar{\rho}=\rho} = 0 \qquad \text{and} \qquad \omega[\rho(\mathbf{r})] = 0.$$

  - Note that the first equation is just the general hypernetted chain equation for the phase transition.

- Must search for solutions to these equations of a specific lattice type.
- Minimize free energy with respect to density profile in cell as well as cell size.

3.1 Freezing of a hard sphere system

- We will look for solutions $rho(\mathbf{r})$ that are periodic on a FCC lattice: $\rho(\mathbf{r}) = \sum_{\mathbf{R}} \rho(\mathbf{r}-\mathbf{R}|\mathbf{R})$ with $\mathbf{R} = l\mathbf{e}_1 + m\mathbf{e}_2 + n\mathbf{e}_3$ with lattice vectors
$$\mathbf{e}_1 = \frac{a}{\sqrt{2}}(1,0,1) \qquad \mathbf{e}_2 = \frac{a}{\sqrt{2}}(1,1,0) \qquad \mathbf{e}_3 = \frac{a}{\sqrt{2}}(0,1,1),$$
where a is the lattice spacing.
- The volume of the cell $\Delta = \mathbf{e}_1 \cdot (\mathbf{e}_2 \times \mathbf{e}_3) = 1/(4a^3)$, and the density of the solid is $\rho_s = \langle N\rangle/V = 1/\Delta = 4a^3$.
- We will assume that $\rho(\mathbf{r}-\mathbf{R}|\mathbf{R})$ vanishes outside of cell centered at $\mathbf{R}$.
- Using Fourier transforms:
$$\hat{\rho}(\mathbf{G}) = \int_\Delta d\mathbf{r}\, e^{-i\mathbf{G}\cdot\mathbf{r}}\rho(\mathbf{r}|0) \qquad \rho(\mathbf{r}|0) = \frac{1}{\Delta}\sum_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}\hat{\rho}(\mathbf{G})$$
and
$$\hat{c}(\mathbf{k}) = \int_V d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}}c(r),$$
the free energy diffence to minimize is (homework):
$$\begin{aligned}\omega = 1 \quad &+ \quad \frac{\rho_s}{\rho_l}\int_\Delta d\mathbf{r}\rho(\mathbf{r}|0)\left(\ln\rho(\mathbf{r}|0)/\rho_l - 1\right) + \rho_s\hat{\rho}(0)\hat{c}(0) - \frac{1}{2}\rho_l\hat{c}(0)\\ &-\frac{\rho_s^2}{2\rho_l}\sum_{\mathbf{G}}\hat{c}(\mathbf{G})\hat{\rho}(\mathbf{G})\hat{\rho}(-\mathbf{G}).\end{aligned}$$
- Simplest approach is to represent $\rho(\mathbf{r}|0)$ as a Gaussian density, based on our derived results using elasticity theory:
$$\rho(\mathbf{r}|0) = \left(\frac{1}{\sqrt{\pi}\epsilon}\right)^3 e^{-r^2/\epsilon^2} \qquad \hat{\rho}(\mathbf{G}) = e^{-G^2\epsilon^2/4}.$$
so that
$$\begin{aligned}\omega(\epsilon, a, \rho_l) = 1 \quad &+ \quad \rho_s/\rho_l\left[-\frac{5}{2} - \ln\rho_l - 2\ln\left(\sqrt{\pi}\epsilon\right)\right]\\ &+\rho_s\hat{c}(0) - \frac{1}{2}\rho_l\hat{c}(0) - \frac{\rho_s^2}{2\rho_l}\sum_{\mathbf{G}}\hat{c}(\mathbf{G})\hat{\rho}(\mathbf{G})\hat{\rho}(-\mathbf{G}).\end{aligned}$$
- Input required for direct correlation function $\hat{c}(\mathbf{G})$.
  - For hard spheres of diameter σ, the Percus-Yevick theory provides excellent results:
  $$c(r/\sigma) = \begin{cases} b_0 + b_1(r/\sigma) + b_2(r/\sigma)^3 & 0 \le r/\sigma \le 1 \\ 0 & 1 < r/\sigma \end{cases}$$
  where
  $$\begin{aligned} b_0 &= -\frac{(1+2\eta)^2}{(1-\eta)^4} \qquad b_1 = \frac{6\eta(1+\eta/2)^2}{(1-\eta)^4} \\ b_2 &= -\frac{\eta(1+2\eta)^2}{(1-\eta)^4} \qquad \eta = \pi\rho_l/6.\end{aligned}$$

- Minimization conditions are:

$$\frac{\partial \omega}{\partial \epsilon} = 0 \qquad \frac{\partial \omega}{\partial \rho_l} = 0 \qquad \frac{\partial \omega}{\partial a} = 0$$

  - Coupled non-linear equations to be solved by numerical methods: Newton-Raphson, conjugate gradient, Monte-Carlo,...
  - Result (homework):

$$\begin{array}{lll} \text{Theory:} & \rho_l \sigma^3 = 0.968 & \rho_s \sigma^3 = 1.5 \\ \text{Simulation:} & \rho_l \sigma^3 = 0.94 - 0.96 & \rho_s \sigma^3 = 1.04 - 1.05 \end{array}$$

  - Can use infinite basis representation of $\rho(\mathbf{r}|0)$ as in:

$$\rho(\mathbf{r}) = \rho_l \left[1 + \eta_s + \sum_n \mu_n e^{i\mathbf{k}_n \cdot \mathbf{r}} \right] \qquad \eta_s = (\rho_s - \rho_l)/\rho_l,$$

    where $\{\mathbf{k}_n\}$ is the set of reciprical lattice vectors.
  - $\eta_s = 0$ and μ_n always a solution of general hypernetted chain equation.
  - Find non-trivial solutions for $\rho_l \sigma^3 \approx 0.93$ and $\omega = 0$ at $\rho_l \sigma^3 \approx 0.965$ and $\rho_s \sigma^3 = 1.148$.
  - Quadratic expansion method of ΔF and $C[\mathbf{r}; \rho(\mathbf{r})]$ works for this transition to within a few percent.