# Classical Density Functional Theory (cDFT) for Thermopack

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# 1 Introduction

The Jupiter notebooks of Mary K. Coe cDFT is a great recourse for understanding classical DFT. Her PhD thesis also contains a lot of information [3].

# 2 Fundamental Measure Theory

Fundamental measure theory for hard sphere mixtures was developed by Rosenfeld [9]. The name "measure" relates to the fundamental geometrical measures (volume, surface area, mean radius of curvature and the Euler characteristic) of a sphere particle. The fundamental geometrical measures are recovered when integrating the weight functions defined in Section 2.2.

For bulk phases this functional reduces to the Percus-Yevick (PY) compressibility equation [8], equivalent to scaled particle theory.

## 2.1 The Rosenfeld functional

$$\Phi^{\mathrm{RF}} = -n_0 \ln(1-n_3) + \frac{n_1 n_2 - \vec{\mathbf{n}}_1 \cdot \vec{\mathbf{n}}_2}{1-n_3} + \frac{n_2^3 - 3n_2 \vec{\mathbf{n}}_2 \cdot \vec{\mathbf{n}}_2}{24\pi(1-n_3)^2} \tag{1}$$

The differentials needed when searching for the Grand potential and the equilibrium density profile:

$$\frac{\partial \Phi^{\mathrm{RF}}}{\partial n_0} = -\ln(1-n_3) \tag{2}$$

$$\frac{\partial \Phi^{\mathrm{RF}}}{\partial n_1} = \frac{n_2}{1-n_3} \tag{3}$$

$$\frac{\partial \Phi^{\mathrm{RF}}}{\partial n_2} = \frac{n_1}{1-n_3} + \frac{n_2^2 - \vec{\mathbf{n}}_2 \cdot \vec{\mathbf{n}}_2}{8\pi(1-n_3)^2} \tag{4}$$

$$\frac{\partial \Phi^{\mathrm{RF}}}{\partial n_3} = \frac{n_0}{1-n_3} + \frac{n_1 n_2 - \vec{\mathbf{n}}_1 \cdot \vec{\mathbf{n}}_2}{(1-n_3)^2} + \frac{n_2^3 - 3n_2 \vec{\mathbf{n}}_2 \cdot \vec{\mathbf{n}}_2}{12\pi(1-n_3)^3} \tag{5}$$

$$\frac{\partial \Phi^{\mathrm{RF}}}{\partial \vec{\mathbf{n}}_1} = -\frac{\vec{\mathbf{n}}_2}{1-n_3} \tag{6}$$

$$\frac{\partial \Phi^{\mathrm{RF}}}{\partial \vec{\mathbf{n}}_2} = -\frac{\vec{\mathbf{n}}_1}{1-n_3} - \frac{n_2 \vec{\mathbf{n}}_2}{4\pi(1-n_3)^2} \tag{7}$$

## 2.2 Weight functions

Weight functions given by

$$w_3^i(\mathbf{r}) = \Theta(R_i - |\mathbf{r}|) \tag{8}$$
$$w_2^i(\mathbf{r}) = \delta(R_i - |\mathbf{r}|) \tag{9}$$
$$w_1^i(\mathbf{r}) = \frac{1}{4\pi R_i} w_2^i(\mathbf{r}) \tag{10}$$
$$w_0^i(\mathbf{r}) = \frac{1}{4\pi R_i^2} w_2^i(\mathbf{r}) \tag{11}$$
$$\mathbf{w}_2^i(\mathbf{r}) = \frac{\mathbf{r}}{|\mathbf{r}|}\delta(R_i - |\mathbf{r}|) \tag{12}$$
$$\mathbf{w}_1^i(\mathbf{r}) = \frac{1}{4\pi R_i}\mathbf{w}_2^i. \tag{13}$$

Where $\Theta$ is the Heaviside function, and $\delta$ are the Dirac delta function.

### 2.2.1 Weight functions for planar geometry

For the planar geometry $\rho(\mathbf{r}) = \rho(z)$, and the weigth functions can be integrated for the $x, y$ dimensions.

$$W_v(z) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dxdy w_v\left(\sqrt{x^2+y^2+z^2}\right) = 2\pi\int_{|z|}^{\infty} drr w_v(r) \tag{14}$$

This can be integrated analytically to

$$w_3^i(z) = \pi\left(R_i^2 - z^2\right)\Theta(R_i - |z|) \tag{15}$$
$$w_2^i(z) = 2\pi R_i \Theta(R_i - |z|) \tag{16}$$
$$\mathbf{w}_2^i(z) = 2\pi z \mathbf{e}_z \Theta(R_i - |z|) \tag{17}$$

### 2.2.2 Weight functions for spherical geometry

For the shperical geometry $\rho(\mathbf{r}) = \rho(r)$, and the weigth functions can be integrated for the angle dimensions.

$$W_v(r) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dxdy w_v\left(\sqrt{x^2+y^2+z^2}\right) = 4\pi\int_{|r|}^{\infty} drr^2 w_v(r) \tag{18}$$

TODO

## 2.3 The one body correlation function

The one body correlation functions is given from the Helmholtz free energy functional as,

$$c^{(1)}(\mathbf{r}) = \beta\frac{\partial \mathcal{F}_{\text{ex}}[\rho]}{\partial\rho(\mathbf{r})} = -\sum_{\alpha}\int d\mathbf{r}'\frac{\partial\Phi_\alpha}{\partial n_\alpha}\frac{\partial n_\alpha}{\partial\rho}. \tag{19}$$

In a planar geometry, the one body correlation function simply becomes,

$$\frac{\partial n_\alpha(z')}{\partial\rho(z)} = \frac{\partial}{\partial\rho(z)}\int dz''\rho(z'')\,w_\alpha(z'-z'') = w_\alpha(z'-z), \tag{20}$$

$$c^{(1)}(z) = -\sum_{\alpha}\int dz'\frac{\partial\Phi_\alpha}{\partial n_\alpha}w_\alpha(z'-z). \tag{21}$$

## 2.4 Alternative FMT functionals

For the White Bear functional [10], the bulk phase properties are consistent with additive hard-sphere mixture compressibillity of Boublík [1] and Mansoori-Carnahan-Starling-Leland (MCSL) [6].

The BMCSL equation of state leads to a excess free energy density that is slightly inconsistent, and a new generalization of the Carnahan- Starling [2] equation of state to mixtures was derived, the White Bear Mark II [4].

## 2.5 The White Bear functional

$$\begin{aligned}\Phi^{\text{WB}} =& -n_0\ln(1-n_3) + \frac{n_1n_2 - \vec{\mathbf{n}}_1\cdot\vec{\mathbf{n}}_2}{1-n_3} \\ &+ \left(n_2^3 - 3n_2\vec{\mathbf{n}}_2\cdot\vec{\mathbf{n}}_2\right)\frac{n_3 + (1-n_3)^2\ln(1-n_3)}{36\pi n_3^2(1-n_3)^2}\end{aligned} \tag{22}$$

$$\frac{\partial \Phi^{\mathrm{WB}}}{\partial n_0} = -\ln\left(1-n_3\right) \tag{23}$$

$$\frac{\partial \Phi^{\mathrm{WB}}}{\partial n_1} = \frac{n_2}{1-n_3} \tag{24}$$

$$\frac{\partial \Phi^{\mathrm{WB}}}{\partial n_2} = \frac{n_1}{1-n_3} + \left(n_2^2 - \vec{\mathbf{n}}_2 \cdot \vec{\mathbf{n}}_2\right) \frac{n_3 + (1-n_3)^2 \ln\left(1-n_3\right)}{12\pi n_3^2 \left(1-n_3\right)^2} \tag{25}$$

$$\begin{aligned}\frac{\partial \Phi^{\mathrm{WB}}}{\partial n_3} = &\frac{n_0}{1-n_3} + \frac{n_1 n_2 - \vec{\mathbf{n}}_1 \cdot \vec{\mathbf{n}}_2}{\left(1-n_3\right)^2} \\ &+ \left(n_2^3 - 3 n_2 \vec{\mathbf{n}}_2 \cdot \vec{\mathbf{n}}_2\right) \left( \frac{n_3 \left(5-n_3\right) - 2}{36\pi n_3^2 \left(1-n_3\right)^3} - \frac{\ln\left(1-n_3\right)}{18\pi n_3^3} \right)\end{aligned} \tag{26}$$

$$\frac{\partial \Phi^{\mathrm{WB}}}{\partial \vec{\mathbf{n}}_1} = -\frac{\vec{\mathbf{n}}_2}{1-n_3} \tag{27}$$

$$\frac{\partial \Phi^{\mathrm{WB}}}{\partial \vec{\mathbf{n}}_2} = -\frac{\vec{\mathbf{n}}_1}{1-n_3} - n_2 \vec{\mathbf{n}}_2 \frac{n_3 + (1-n_3)^2 \ln\left(1-n_3\right)}{6\pi n_3^2 \left(1-n_3\right)^2} \tag{28}$$

## 2.6 The White Bear Mark II functional

$$\begin{aligned}\Phi^{\mathrm{WBII}} = &-n_0 \ln\left(1-n_3\right) + \left(n_1 n_2 - \vec{\mathbf{n}}_1 \cdot \vec{\mathbf{n}}_2\right) \frac{1 + \frac{1}{3}\phi_2\left(n_3\right)}{1-n_3} \\ &+ \left(n_2^3 - 3 n_2 \vec{\mathbf{n}}_2 \cdot \vec{\mathbf{n}}_2\right) \frac{1 - \frac{1}{3}\phi_3\left(n_3\right)}{24\pi \left(1-n_3\right)^2}\end{aligned} \tag{29}$$

with,

$$\phi_2\left(n_3\right) = \frac{1}{n_3}\left(2n_3 - n_3^2 + 2\left(1-n_3\right)\ln\left(1-n_3\right)\right) \tag{30}$$

$$\phi_3\left(n_3\right) = \frac{1}{n_3^2}\left(2n_3 - 3n_3^2 + 2n_3^3 + 2\left(1-n_3\right)^2 \ln\left(1-n_3\right)\right) \tag{31}$$

$$\frac{\mathrm{d}\phi_2}{\mathrm{d}n_3} = -1 - \frac{2}{n_3} - \frac{2\ln\left(1-n_3\right)}{n_3^2} \tag{32}$$

$$\frac{\mathrm{d}\phi_3}{\mathrm{d}n_3} = -\frac{4(1-n_3)\ln\left(1-n_3\right)}{n_3^3} - \frac{4}{n_3^2} + \frac{2}{n_3} + 2 \tag{33}$$

$$\frac{\partial \Phi^{\mathrm{WBII}}}{\partial n_0} = -\ln\left(1-n_3\right) \tag{34}$$

$$\frac{\partial \Phi^{\mathrm{WBII}}}{\partial n_1} = \frac{n_2\left(1+\frac{1}{3}\phi_2\right)}{1-n_3} \tag{35}$$

$$\frac{\partial \Phi^{\mathrm{WBII}}}{\partial n_2} = \frac{n_1\left(1+\frac{1}{3}\phi_2\right)}{1-n_3} + \frac{\left(n_2^2-\vec{\mathbf{n}}_2\cdot\vec{\mathbf{n}}_2\right)\left(1-\frac{1}{3}\phi_3\right)}{8\pi\left(1-n_3\right)^2} \tag{36}$$

$$\begin{aligned}\frac{\partial \Phi^{\mathrm{WBII}}}{\partial n_3} = {} & \frac{n_0}{1-n_3} + \left(n_1 n_2 - \vec{\mathbf{n}}_1\cdot\vec{\mathbf{n}}_2\right)\left(\frac{\frac{1}{3}\frac{\mathrm{d}\phi_2}{\mathrm{d}n_3}}{1-n_3} + \frac{1+\frac{1}{3}\phi_2}{\left(1-n_3\right)^2}\right) \\ & + \frac{\left(n_2^3 - 3n_2\vec{\mathbf{n}}_2\cdot\vec{\mathbf{n}}_2\right)}{24\pi\left(1-n_3\right)^2}\left(-\frac{1}{3}\frac{\mathrm{d}\phi_3}{\mathrm{d}n_3} + \frac{2\left(1-\frac{1}{3}\phi_3\right)}{1-n_3}\right)\end{aligned} \tag{37}$$

$$\frac{\partial \Phi^{\mathrm{WBII}}}{\partial \vec{\mathbf{n}}_1} = -\frac{\vec{\mathbf{n}}_2\left(1+\frac{1}{3}\phi_2\right)}{1-n_3} \tag{38}$$

$$\frac{\partial \Phi^{\mathrm{WBII}}}{\partial \vec{\mathbf{n}}_2} = -\frac{\vec{\mathbf{n}}_1\left(1+\frac{1}{3}\phi_2\right)}{1-n_3} - \frac{n_2\vec{\mathbf{n}}_2\left(1-\frac{1}{3}\phi_3\right)}{4\pi\left(1-n_3\right)^2} \tag{39}$$

# 3 Numerics

Solving of the convolution integrals in the FMT and cDFT in real space uses $O\left(N^2\right)$ operations, however according to the convolution theorem the integrals can be done by Fourier transformations, leading to only $O\left(N\ln N\right)$ operations [11, 5]. Different options for solving the discrete fast Fourier transform (FFT) is available, FFTW (GNU General Public License), FFTPACK (MIT) and Python FFT.

The common approach used when solving classical DFT problems is Picard iterations. Instead of using a successive substituting iteration, $\tilde{\rho}^{(i)} \to \rho^{(i)}$, a mixing of the new density with the original density is used to dampen the effect of the new value, accordign to,

$$\tilde{\rho}^{(i+1)}\left(z\right) = \alpha\rho^{(i)}\left(z\right) + \left(1-\alpha\right)\tilde{\rho}^{(i)}\left(z\right). \tag{40}$$

The main reason is to avoid $n_3$ values exceeding unity.

Often the Picard parameter is set to a fixed low value, typically $\alpha = 0.1$, resulting in slow convergence. However using a line search requiring some decay in error

is probably the best way to implement the Picard iterations. Roth [11] suggest using a simple quadratic line search. Roth [11] used the Grand Potential $\Omega$, when evaluating the line search. [5] evaluated the $\|\tilde{\rho}^{(i)} - \rho^{(i)}\|$.

One simple way of accelerate the solution of the equilibrium density profile is by extrapolation as used by Ng [7].

[5] tested a Newton solver (using numerical approximations for the differentials), but they report linear convergence through most of the iteration steps. The use of inefficient generation of differentials was also reported as an issue.

Looking at Equation 20 and 21 we see that differentiating Equation 21 will require convolution of the $\Phi_{\alpha\gamma}$ with $w_\alpha(z'-z_1)\,w_\gamma(z'-z_2)$. The latter will become a matrix constant matrix requiering a convolution integral per element in the banded Jacobian. The matrix is constant and only the inverse Fourier transform will require computuational effort. Each of these elements will require CPU time similar to one half Picard iteration. For example if there are 1000 grid cells over the diameter of a particle, the generation of one Jacobian instance will be similar to 500 Picard iterations.

Parallel solution for the Fourier transforms are simple using the FFTW library....

### 3.0.1 Quadratures for the weight functions

Integrating on a regular grid the integral can be made more accurate using a qudrature formula

Cite

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$$\begin{aligned}\int_{z_N}^{z_1} dz' f\left(z'\right) g\left(z'-z\right) =& \Delta z\left(\frac{3}{8}f_1 g_{i-1} + \frac{7}{6}f_2 g_{i-2} + \frac{23}{24}f_3 g_{i-3} + f_4 g_{i-4}\right.\\ &+ \cdots + f_{N-3} g_{i-N+3} + \frac{23}{24}f_{N-2} g_{i-N+2}\\ &\left.+ \frac{7}{6}f_{N-1} g_{i-N+1} + \frac{3}{8}f_{N-2} g_{i-N+2}.\right) \end{aligned} \tag{41}$$

The qudarature is implemeted by multipying the end weights with by the quadrature weights.

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