

# Classical Density Functional Theory (cDFT) for Thermopack

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March 16, 2022

# 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 [14]. 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 Pick's-Yevick (PY) compressibility equation [13], equivalent to scaled particle theory.

### 2.1 The Rosenfeld functional

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

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

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

$$\frac{\partial \Phi^{\text{RF}}}{\partial n_1} = \frac{n_2}{1 - n_3} \quad (3)$$

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

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

$$\frac{\partial \Phi^{\text{RF}}}{\partial \vec{n}_1} = -\frac{\vec{n}_2}{1 - n_3} \quad (6)$$

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

## 2.2 Weight functions

Weight functions given by

$$w_3^i(\mathbf{r}) = \Theta(R_i - |\mathbf{r}|) \quad (8)$$

$$w_2^i(\mathbf{r}) = \delta(R_i - |\mathbf{r}|) \quad (9)$$

$$w_1^i(\mathbf{r}) = \frac{1}{4\pi R_i} w_2^i(\mathbf{r}) \quad (10)$$

$$w_0^i(\mathbf{r}) = \frac{1}{4\pi R_i^2} w_2^i(\mathbf{r}) \quad (11)$$

$$\mathbf{w}_2^i(\mathbf{r}) = \frac{\mathbf{r}}{|\mathbf{r}|} \delta(R_i - |\mathbf{r}|) \quad (12)$$

$$\mathbf{w}_1^i(\mathbf{r}) = \frac{1}{4\pi R_i} \mathbf{w}_2^i. \quad (13)$$

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 weight functions can be integrated for the  $x, y$  dimensions.

$$W_v(z) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dy w_v \left( \sqrt{x^2 + y^2 + z^2} \right) = 2\pi \int_{|z|}^{\infty} dr r w_v(r) \quad (14)$$

This can be integrated analytically to

$$w_3^i(z) = \pi (R_i^2 - z^2) \Theta(R_i - |z|) \quad (15)$$

$$w_2^i(z) = 2\pi R_i \Theta(R_i - |z|) \quad (16)$$

$$\mathbf{w}_2^i(z) = 2\pi z \mathbf{e}_z \Theta(R_i - |z|) \quad (17)$$

The planar weight functions are visualized in Figure 1.

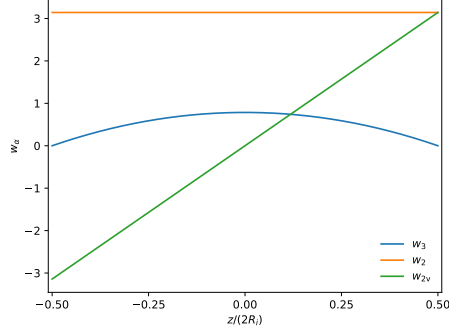


Figure 1: Planar weight functions.

### 2.2.2 Weight functions for spherical geometry

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

$$W_v(r) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dy w_v \left( \sqrt{x^2 + y^2 + z^2} \right) = 4\pi \int_{|r|}^{\infty} dr r^2 w_v(r) \quad (18)$$

TODO

## 2.3 The one body correlation function

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

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

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

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

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

## 2.4 Alternative FMT functionals

For the White Bear functional [15], the bulk phase properties are consistent with additive hard-sphere mixture compressibility of Boublík [1] and Mansoori-Carnahan-Starling-Leland (MCSL) [11].

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 [9].

## 2.5 The White Bear functional

$$\begin{aligned}\Phi^{\text{WB}} = & -n_0 \ln(1 - n_3) + \frac{n_1 n_2 - \vec{\mathbf{n}}_1 \cdot \vec{\mathbf{n}}_2}{1 - n_3} \\ & + (n_2^3 - 3n_2 \vec{\mathbf{n}}_2 \cdot \vec{\mathbf{n}}_2) \frac{n_3 + (1 - n_3)^2 \ln(1 - n_3)}{36\pi n_3^2 (1 - n_3)^2}\end{aligned}\quad (22)$$

$$\frac{\partial \Phi^{\text{WB}}}{\partial n_0} = -\ln(1 - n_3) \quad (23)$$

$$\frac{\partial \Phi^{\text{WB}}}{\partial n_1} = \frac{n_2}{1 - n_3} \quad (24)$$

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

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

$$\frac{\partial \Phi^{\text{WB}}}{\partial \vec{\mathbf{n}}_1} = -\frac{\vec{\mathbf{n}}_2}{1 - n_3} \quad (27)$$

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

## 2.6 The White Bear Mark II functional

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

with,

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

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

$$\frac{d\phi_2}{dn_3} = -1 - \frac{2}{n_3} - \frac{2\ln(1-n_3)}{n_3^2} \quad (32)$$

$$\frac{d\phi_3}{dn_3} = -\frac{4(1-n_3)\ln(1-n_3)}{n_3^3} - \frac{4}{n_3^2} + \frac{2}{n_3} + 2 \quad (33)$$

$$\frac{\partial \Phi^{\text{WBII}}}{\partial n_0} = -\ln(1-n_3) \quad (34)$$

$$\frac{\partial \Phi^{\text{WBII}}}{\partial n_1} = \frac{n_2(1 + \frac{1}{3}\phi_2)}{1-n_3} \quad (35)$$

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

$$\begin{aligned}\frac{\partial \Phi^{\text{WBII}}}{\partial n_3} = & \frac{n_0}{1-n_3} + (n_1 n_2 - \vec{\mathbf{n}}_1 \cdot \vec{\mathbf{n}}_2) \left( \frac{\frac{1}{3}\frac{d\phi_2}{dn_3}}{1-n_3} + \frac{1 + \frac{1}{3}\phi_2}{(1-n_3)^2} \right) \\ & + \frac{(n_2^3 - 3n_2 \vec{\mathbf{n}}_2 \cdot \vec{\mathbf{n}}_2)}{24\pi(1-n_3)^2} \left( -\frac{1}{3} \frac{d\phi_3}{dn_3} + \frac{2(1 - \frac{1}{3}\phi_3)}{1-n_3} \right)\end{aligned}\quad (37)$$

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

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

### 3 Numerics

Solving of the convolution integrals in the FMT and cDFT in real space uses  $O(N^2)$  operations, however according to the convolution theorem the integrals can be done by Fourier transformations, leading to only  $O(N \ln N)$  operations [16, 10]. 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,  $\tilde{\rho}^{(i)} \rightarrow \rho^{(i)}$ , a mixing of the new density with the original density is used to dampen the effect of the new value, accordign to,

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

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 [16] suggest using a simple quadratic line search. Roth [16] used the Grand Potential  $\Omega$ , when evaluating the line search. [10] evaluated the  $\|\tilde{\rho}^{(i)} - \rho^{(i)}\|$  as a function of  $\alpha$  and found the minimum of a quadratic polynomial.

One simple way of accelerate the solution of the equilibrium density profile is by extrapolation as used by Ng [12].

[10] 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....

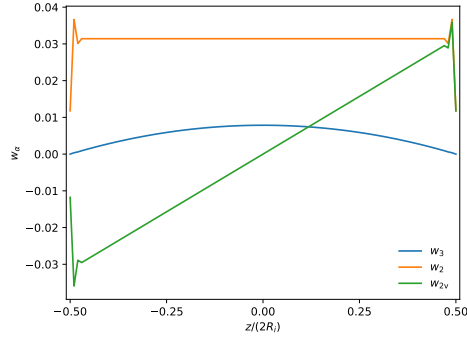


Figure 2: Actual planar weight functions.

### 3.0.1 Quadratures for the weight functions

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

Cite

,

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

The quadrature is implemented by multiplying the end weights with by the quadrature weights.

The actual planar weight functions are visualized in Figure 2.

## 4 Perturbation theory

The canonical partition function,

$$Q_N = \frac{1}{h^{3N} N!} \int d\mathbf{p}^N \int d\mathbf{r}^N e^{-\beta \mathcal{H}} \quad (42)$$



Relation between Helmholtz energy and partition function,

$$F = -k_B T \ln Q_N \quad (43)$$

Using a Hamiltonian,

$$\mathcal{H} = \Phi(\mathbf{r}^N) + K(\mathbf{p}^N) + V_{\text{ext}}(\mathbf{r}^N), \quad (44)$$

where the kinetic energies is given from the moments,

$$K(\mathbf{p}^N) = \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2m} \quad (45)$$

the partition function can be integrated with respect to the moments,

$$\begin{aligned} Q_N &= \frac{1}{h^{3N} N!} \int d\mathbf{p}^N e^{-\beta K(\mathbf{p}^N)} \int d\mathbf{r}^N e^{-\beta(\Phi(\mathbf{r}^N) + V_{\text{ext}}(\mathbf{r}^N))} \\ &= \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^N e^{-\beta(\Phi(\mathbf{r}^N) + V_{\text{ext}}(\mathbf{r}^N))} \\ &= \frac{Z_N}{\Lambda^{3N} N!} \end{aligned} \quad (46)$$

where  $Z_N$  is the configurational integral, and  $\Lambda$  is the thermal de Broglie wavelength.

Having the perturbation potential

$$\phi_\lambda(\mathbf{r}, \mathbf{r}') = \phi_0(\mathbf{r}, \mathbf{r}') + \lambda \phi_{\text{att}}(\mathbf{r}, \mathbf{r}') \quad 0 \leq \lambda \leq 1, \quad (47)$$

where  $\lambda$  is the perturbation strength, the potential energy felt between all particles is given by

$$\Phi(\mathbf{r}^N) = \sum_{j=1}^N \sum_{k>j}^N \phi_\lambda(\mathbf{r}_j, \mathbf{r}_k) \quad (48)$$

The excess Helmholtz energy can be differentiated with respect to  $\lambda$  using Equation 43,

$$\beta \frac{\partial F_{\text{ex}}}{\partial \lambda} = -\frac{1}{Z_N} \frac{\partial Z_N}{\partial \lambda} = \frac{\beta}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho_\lambda^{(2)}(\mathbf{r}, \mathbf{r}') \phi_{\text{att}}(\mathbf{r}, \mathbf{r}') \quad (49)$$

we can also describe the Helmholtz energy using ensemble average,  $\langle \dots \rangle_\lambda$ , for a system described by  $\phi_\lambda$ ,

$$\beta \frac{\partial F_{\text{ex}}}{\partial \lambda} = \langle \Phi' \rangle_\lambda \quad (50)$$

where  $\frac{\partial \Phi_\lambda}{\partial \lambda} = \Phi'_\lambda$ . Integration yields,

$$\beta F_{\text{ex}} = \beta F_0 + \int_{\lambda=0}^{\lambda=1} d\lambda \langle \Phi' \rangle_\lambda \quad (51)$$

In order to get ensemble averages over the reference system  $\lambda = 0$ , the average can be expanded in  $\lambda$  around  $\lambda = 0$ .

Leading to

$$\beta F_{\text{ex}} = \beta F_0 + \beta F_1 + \beta F_2 + \beta F_3 + O(\beta^4) \quad (52)$$

where

$$\beta F_1 = \beta \langle \Phi_{\text{att}} \rangle_0 \quad (53)$$

$$\beta F_2 = -\frac{\beta^2}{2} \left[ \langle \Phi_{\text{att}}^2 \rangle_0 - \langle \Phi_{\text{att}} \rangle_0^2 \right] \quad (54)$$

$$\beta F_3 = \frac{\beta^3}{3!} \left\langle \Phi_{\text{att}} - \langle \Phi_{\text{att}} \rangle_0 \right\rangle^3 \quad (55)$$

For pair-wise additive potentials we have,

$$\frac{\beta F_1}{N} = \frac{\beta \rho}{2} \int g_\lambda(r) \phi_{\text{att}}(r) dr \quad (56)$$

and to first order  $g_\lambda = g_0$ .

## 5 Approaches used when extending classical DFT to attractive fluids

### 5.1 Mean Field Theory (MFT)

Under the MFT approximation,  $g \approx 1$ , and Equation 56 simply becomes

$$\frac{\beta F_1}{N} = \frac{\beta \rho}{2} \phi_{\text{att}}(r) dr \quad (57)$$

For some reason it is common to use the WCA perturbation potential, however the hard-sphere diameter seem to be independent of density.

Check if cDFT\_Package uses sigma=1 with WCA simulation....

## 5.2 Local density approximation (LDA)

Under the LDA assumption the Helmholtz energy density of an inhomogeneous system with density profile  $\rho(r)$  is calculated using the bulk phase Helmholtz energy density evaluated at the value of the local density. This often work for surface tension calculations, however adjacent to walls where the density oscillate strongly and the local density can exceed the maximum packing fractions this will be a problem.

## 5.3 Weighted density approximation (WDA)

The WDA uses locally weighted densities and evaluates the Helmholtz energy functional with these densities. This methodology have proven successful even for fluid to wall interacting systems.

Sauer and Gross [17] Tarazona [18], Tarazona and Evans [19]

## 5.4 Nonlocal perturbation theory (NLP)

Gloor et al. [4] Gross [6]

# 6 The PCP-SAFT classical DFT

Sauer and Gross [17]

PC-SAFT Gross and Sadowski [7] Polar extensions Quadrupole-Quadrupole:Gross [5] Dipole-dipole:Gross and Vrabec [8] Dipole-Quadrupole: Vrabec and Gross [20]

# 7 Analytical Fourier transforms of the weight functions

Knepley et al. [10, Appendix B] derives the analytical Fourier transform for the weight functions.

## 7.1 Planar geometry

The weight functions in a planar geometry is derived in section 2.2.1. The weight functions can be transformed to Fourier space according to the definition,

$$\begin{aligned}\hat{w}_\alpha^i(k) &= \mathcal{F}(w_\alpha^i(z)) = \int_{-\infty}^{\infty} dz w_\alpha^i(z) e^{-ikz} \\ &= \int_{-\infty}^{\infty} dz w_\alpha^i(z) \cos(kz) + i \int_{-\infty}^{\infty} dz w_\alpha^i(z) \sin(kz)\end{aligned}\quad (58)$$

Since  $w_3^i$  and  $w_2^i$  are even functions, the Fourier transform will be purely real valued, while  $w_1^i$  is odd and therefore purely imaginary,

$$\begin{aligned}\hat{w}_3^i &= \int_{-\infty}^{\infty} dz \pi (R_i^2 - z^2) \Theta(R_i - |z|) \cos(kz) \\ &= \pi \int_{-R_i}^{R_i} dz (R_i^2 - z^2) \cos(kz) \\ &= \frac{4\pi}{k^3} \left( \sin(kR_i) - kR_i \cos(kR_i) \right)\end{aligned}\quad (59)$$

$$\begin{aligned}\hat{w}_2^i &= \int_{-\infty}^{\infty} dz 2\pi R_i \Theta(R_i - |z|) \cos(kz) \\ &= 2\pi R_i \int_{-R_i}^{R_i} dz \cos(kz) \\ &= \frac{4\pi R_i}{k} \sin(kR_i)\end{aligned}\quad (60)$$

$$\begin{aligned}
\hat{\mathbf{w}}_2^i &= i \int_{-\infty}^{\infty} dz 2\pi \mathbf{z} \Theta(R_i - |z|) \cos(\mathbf{k} \cdot \mathbf{z}) \\
&= 2\pi i \int_{-R_i}^{R_i} dz \mathbf{z} \cos(\mathbf{k} \cdot \mathbf{z}) = -2\pi i \mathbf{e}_k \int_{-R_i}^{R_i} dz z \cos(kz) \\
&= -\frac{4\pi i}{k^2} \left( \sin(kR_i) - kR_i \cos(kR_i) \right) \mathbf{e}_k
\end{aligned} \tag{61}$$

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