

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 [7]. 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 [6], 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 Θ is the Heaviside function, and δ 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

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

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

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

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 Alternative FMT functionals

For the White Bear functional [8], the bulk phase properties are consistent with additive hard-sphere mixture compressibility of Boublík [1] and Mansoori-Carnahan-Starling-Leland (MCSL) [5].

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].

2.4 The White Bear functional

$$\begin{aligned} \Phi^{\text{WB}} = & -n_0 \ln(1 - n_3) + \frac{n_1 n_2 - \vec{n}_1 \cdot \vec{n}_2}{1 - n_3} \\ & + (n_2^3 - 3n_2 \vec{n}_2 \cdot \vec{n}_2) \frac{n_3 + (1 - n_3)^2 \ln(1 - n_3)}{36\pi n_3^2 (1 - n_3)^2} \end{aligned} \quad (19)$$

$$\frac{\partial \Phi^{\text{WB}}}{\partial n_0} = -\ln(1 - n_3) \quad (20)$$

$$\frac{\partial \Phi^{\text{WB}}}{\partial n_1} = \frac{n_2}{1 - n_3} \quad (21)$$

$$\frac{\partial \Phi^{\text{WB}}}{\partial n_2} = \frac{n_1}{1 - n_3} + (n_2^2 - \vec{n}_2 \cdot \vec{n}_2) \frac{n_3 + (1 - n_3)^2 \ln(1 - n_3)}{12\pi n_3^2 (1 - n_3)^2} \quad (22)$$

$$\begin{aligned} \frac{\partial \Phi^{\text{WB}}}{\partial n_3} &= \frac{n_0}{1 - n_3} + \frac{n_1 n_2 - \vec{n}_1 \cdot \vec{n}_2}{(1 - n_3)^2} \\ &\quad + (n_2^3 - 3n_2 \vec{n}_2 \cdot \vec{n}_2) \left(\frac{n_3(5 - n_3) - 2}{36\pi n_3^2 (1 - n_3)^3} - \frac{\ln(1 - n_3)}{18\pi n_3^3} \right) \end{aligned} \quad (23)$$

$$\frac{\partial \Phi^{\text{WB}}}{\partial \vec{n}_1} = -\frac{\vec{n}_2}{1 - n_3} \quad (24)$$

$$\frac{\partial \Phi^{\text{WB}}}{\partial \vec{n}_2} = -\frac{\vec{n}_1}{1 - n_3} - n_2 \vec{n}_2 \frac{n_3 + (1 - n_3)^2 \ln(1 - n_3)}{6\pi n_3^2 (1 - n_3)^2} \quad (25)$$

2.5 The White Bear Mark II functional

$$\begin{aligned} \Phi^{\text{WBII}} &= -n_0 \ln(1 - n_3) + (n_1 n_2 - \vec{n}_1 \cdot \vec{n}_2) \frac{1 + \frac{1}{3}\phi_2(n_3)}{1 - n_3} \\ &\quad + (n_2^3 - 3n_2 \vec{n}_2 \cdot \vec{n}_2) \frac{1 - \frac{1}{3}\phi_3(n_3)}{24\pi (1 - n_3)^2} \end{aligned} \quad (26)$$

with,

$$\phi_2(n_3) = \frac{1}{n_3} (2n_3 - n_3^2 + 2(1 - n_3) \ln(1 - n_3)) \quad (27)$$

$$\phi_3(n_3) = \frac{1}{n_3^2} (2n_3 - 3n_3^2 + 2n_3^3 + 2(1 - n_3)^2 \ln(1 - n_3)) \quad (28)$$

$$\frac{d\phi_2}{dn_3} = -1 - \frac{2}{n_3} - \frac{2\ln(1 - n_3)}{n_3^2} \quad (29)$$

$$\frac{d\phi_3}{dn_3} = -\frac{4(1 - n_3) \ln(1 - n_3)}{n_3^3} - \frac{4}{n_3^2} + \frac{2}{n_3} + 2 \quad (30)$$

$$\frac{\partial \Phi^{\text{WBII}}}{\partial n_0} = -\ln(1 - n_3) \quad (31)$$

$$\frac{\partial \Phi^{\text{WBII}}}{\partial n_1} = \frac{n_2(1 + \frac{1}{3}\phi_2)}{1 - n_3} \quad (32)$$

$$\frac{\partial \Phi^{\text{WBII}}}{\partial n_2} = \frac{n_1(1 + \frac{1}{3}\phi_2)}{1 - n_3} + \frac{(n_2^2 - \vec{n}_2 \cdot \vec{n}_2)(1 - \frac{1}{3}\phi_3)}{8\pi(1 - n_3)^2} \quad (33)$$

$$\begin{aligned} \frac{\partial \Phi^{\text{WBII}}}{\partial n_3} &= \frac{n_0}{1 - n_3} + (n_1 n_2 - \vec{n}_1 \cdot \vec{n}_2) \left(\frac{\frac{1}{3} \frac{d\phi_2}{dn_3}}{1 - n_3} + \frac{1 + \frac{1}{3}\phi_2}{(1 - n_3)^2} \right) \\ &\quad + \frac{(n_2^3 - 3n_2 \vec{n}_2 \cdot \vec{n}_2)}{24\pi(1 - n_3)^2} \left(-\frac{1}{3} \frac{d\phi_3}{dn_3} + \frac{2(1 - \frac{1}{3}\phi_3)}{1 - n_3} \right) \end{aligned} \quad (34)$$

$$\frac{\partial \Phi^{\text{WBII}}}{\partial \vec{n}_1} = -\frac{\vec{n}_2(1 + \frac{1}{3}\phi_2)}{1 - n_3} \quad (35)$$

$$\frac{\partial \Phi^{\text{WBII}}}{\partial \vec{n}_2} = -\frac{\vec{n}_1(1 + \frac{1}{3}\phi_2)}{1 - n_3} - \frac{n_2 \vec{n}_2(1 - \frac{1}{3}\phi_3)}{4\pi(1 - n_3)^2} \quad (36)$$

References

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