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

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

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

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

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

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

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

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

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

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 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 weigth functions can be integrated for the x, y dimensions.

$$W_v(z) = \int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty} dxdyw_v\left(\sqrt{x^2+y^2+z^2}\right) = 2\pi\int\limits_{|z|}^{\infty} drrw_v(r) \tag{14}$$

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 Alternative FMT functionals

For the White Bear functional [8], the bulk phase properties are consistent with additive hard-sphere mixture compressibillity 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

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

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

$$\frac{\partial \Phi^{\mathrm{WB}}}{\partial n_1} = \frac{n_2}{1-n_3} \tag{21}$$

$$\frac{\partial \Phi^{\mathrm{WB}}}{\partial n_2} = \frac{n_1}{1-n_3} + \left(n_2^2 - \vec{\mathbf{n}}_2 \cdot \vec{\mathbf{n}}_2\right) \frac{n_3 + (1-n_3)^2 \ln(1-n_3)}{12\pi n_3^2 (1-n_3)^2} \tag{22}$$

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

$$\frac{\partial \Phi^{\mathrm{WB}}}{\partial \vec{\mathbf{n}}_1} = -\frac{\vec{\mathbf{n}}_2}{1-n_3} \tag{24}$$

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

2.5 The White Bear Mark II functional

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

with,

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

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

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

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

$$\frac{\partial \Phi^{\mathrm{WBII}}}{\partial n_0} = -\ln\left(1-n_3\right) \tag{31}$$

$$\frac{\partial \Phi^{\mathrm{WBII}}}{\partial n_1} = \frac{n_2\left(1+\frac{1}{3}\phi_2\right)}{1-n_3} \tag{32}$$

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

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

$$\frac{\partial \Phi^{\mathrm{WBII}}}{\partial \vec{\mathbf{n}}_1} = -\frac{\vec{\mathbf{n}}_2\left(1+\frac{1}{3}\phi_2\right)}{1-n_3} \tag{35}$$

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

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