Classical Density Functional Theory For Fluids

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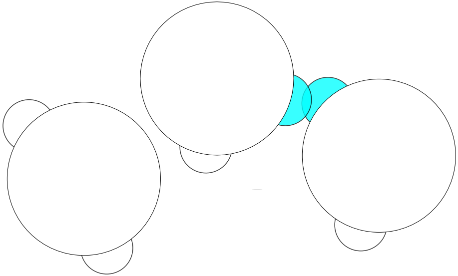
Statistical Associating Fluid Theory (SAFT)

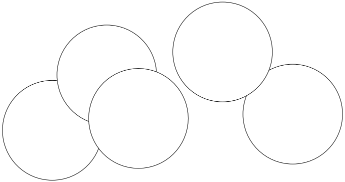
- 800 papers in the last four years
- Widely used by chemical engineers to treat chemical mixtures
- Hard sphere reference with interaction sites

$$A = A_{ideal} + A_{hs} + A_{chain} + A_{assoc} + A_{disp} \tag{1}$$



- Originally developed for homogeneous situations

Monte-Carlo simulations



- Exact in large limits
- Hard sphere interaction easy to compute
- Oversaw Patrick Kreitzberg editing code and running simulations
- Takes a long time and has statistical error

Classical Density Functional Theory

- Mermin's adaption of original density functional theory
- Treats molecules and finite tempuratures
- For given T, μ, and V_{ext}, Ω is minimized for the equilibrium density distribution:

$$\Omega = \min_{n(\mathbf{r})} \{\mathcal{F}[n] + \int d\mathbf{r}\, n(\mathbf{r})(V_{ext}(\mathbf{r}) - \mu)\} \tag{2}$$

- Primary task is to find functional form of $\mathcal{F}$

Fundamental Measure Theory

- Successful for systems of hard spheres
- Introduced by Rosenfeld in 1989
- Can predict the melting of hards spheres accurately
- Built with fundamental measures:

$$n_3(\mathbf{r}) = \int d^3\mathbf{r}' n(\mathbf{r}')\Theta(\sigma/2 - |\mathbf{r} - \mathbf{r}'|) \tag{3}$$

$$n_2(\mathbf{r}) = \int d^3\mathbf{r}' n(\mathbf{r}')\delta(\sigma/2 - |\mathbf{r} - \mathbf{r}'|) \tag{4}$$

$$\mathbf{n}_{2V}(\mathbf{r}) = \int d^3\mathbf{r}' n(\mathbf{r}')\delta(\sigma/2 - |\mathbf{r} - \mathbf{r}'|)\frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \tag{5}$$

Fundamental Measure Theory

- Makes appealing intuitive sense
- Mixtures are treated well (radii can be specified)
- Can reconstruct low density limit exactly
- Convolution theorem makes things easy computationally

$$n_3(\mathbf{r}) = \int d^3\mathbf{r}' n(\mathbf{r}')\Theta(\sigma/2 - |\mathbf{r} - \mathbf{r}'|) \tag{6}$$

$$n_2(\mathbf{r}) = \int d^3\mathbf{r}' n(\mathbf{r}')\delta(\sigma/2 - |\mathbf{r} - \mathbf{r}'|) \tag{7}$$

$$\mathbf{n}_{2V}(\mathbf{r}) = \int d^3\mathbf{r}' n(\mathbf{r}')\delta(\sigma/2 - |\mathbf{r} - \mathbf{r}'|)\frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \tag{8}$$

White Bear free energy functional

White Bear hard sphere free energy is

$$\mathcal{F} = \mathcal{F}^{id} + kT \int \Phi(\mathbf{r}) d\mathbf{r} \tag{9}$$

$$\Phi(\mathbf{r}) = -n_0 Ln(1 - n_3) + \frac{n_1 n_2 - \mathbf{n}_{1V} \cdot \mathbf{n}_{2V}}{1 - n_3} + (n_2^3 - 3 n_2 \mathbf{n}_{2V} \cdot \mathbf{n}_{2V}) \frac{n_3 + (1 - n_3)^2 Ln(1 - n_3)}{36\pi n_3^2 (1 - n_3)^2} \tag{10}$$

- $\Phi(\mathbf{r})$ here is a *local* function
- Reduces to Carnahan Starling in homogeneous situations
- Widely used functional

Two SAFT terms that we focus on are

$$\frac{A_{chain}}{kT} = -(m-1)n(Ln(ng_\sigma) - 1) \tag{11}$$

$$\frac{A_{assoc}}{kT} = \sum_j n(LnX_j - \frac{1}{2}X_j + \frac{1}{2}) \tag{12}$$

$$X_i = \frac{1}{1 + \sum_j n g_\sigma X_j \kappa_{ij}(e^{\beta\epsilon_{ij}} - 1)} \tag{13}$$

- Important variable in these functionals is radial distribution function at contact g_σ

Radial distribution functions of Gross and of Yu and Wu

Radial Distribution Function of Gross

$$g_\sigma^{Gross}(\mathbf{r}) = \frac{1 - \frac{\eta(\mathbf{r})}{2}}{(1-\eta(\mathbf{r}))^3}$$

$$\eta(\mathbf{r}) = \frac{1}{8}\int n(\mathbf{r}')\Theta(\sigma - |\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'$$

- Uses the Carnahan Starling equation for Radial Distribution

Radial distribution function of Yu and Wu

$$g_\sigma^{Yu}(\mathbf{r}) = \zeta^2\left(\frac{1}{1-n_3} + \frac{1}{4}\frac{\sigma n_2 \zeta}{(1-n_3)^2} + \frac{1}{72}\frac{\sigma^2 n_2^2 \zeta}{(1-n_3)^3}\right)$$

$$\zeta = 1 - \frac{\mathbf{n}_{2V}\cdot\mathbf{n}_{2V}}{n_2^2}$$

- There is yet to be a careful study of g_σ on it's own

Defining radial distribution at contact g_σ; asymmetric

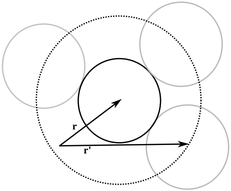
Pair distribution function defined as

$$g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \equiv \frac{n^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{n(\mathbf{r}_1)n(\mathbf{r}_2)} \tag{14}$$

and we define an average

$$n_A(\mathbf{r})g_\sigma^A(\mathbf{r}) = \frac{1}{n(\mathbf{r})}\int n^{(2)}(\mathbf{r}, \mathbf{r}+\mathbf{r}')\frac{\delta(\sigma - |\mathbf{r}'|)}{4\pi\sigma^2}d\mathbf{r}' \tag{15}$$

$$n_A(\mathbf{r}) = \int n(\mathbf{r}')\frac{\delta(\sigma - |\mathbf{r}-\mathbf{r}'|)}{4\pi\sigma^2}d\mathbf{r}' \tag{16}$$



- Gross' g_σ is of this type

Defining radial distribution at contact g_σ; symmetric

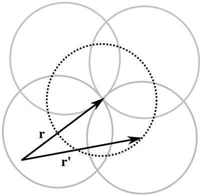
Pair distribution function defined as

$$g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \equiv \frac{n^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{n(\mathbf{r}_1)n(\mathbf{r}_2)} \tag{17}$$

and we define an average

$$g_\sigma^S(\mathbf{r}) = \frac{1}{n_0(\mathbf{r})^2} \int n^{(2)}(\mathbf{r} - \mathbf{r}', \mathbf{r} + \mathbf{r}') \frac{\delta(\sigma/2 - |\mathbf{r}'|)}{\pi\sigma^2} d\mathbf{r}' \tag{18}$$

$$n_0(\mathbf{r}) = \int n(\mathbf{r}') \frac{\delta(\sigma/2 - |\mathbf{r} - \mathbf{r}'|)}{\pi\sigma^2} d\mathbf{r}' \tag{19}$$



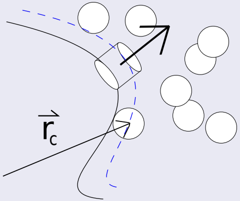
- Yu and Wu's g_σ is of this type

Creating our own approximation for g_σ

- Adapt homogeneous derivation of g_σ to inhomogenoues systems
- Homogeneous derivation starts with the Contact Value Theorem

Pressure on Solvant Accessable Surface

$$p(\mathbf{r_c}) = k_B T n(\mathbf{r}_c)$$



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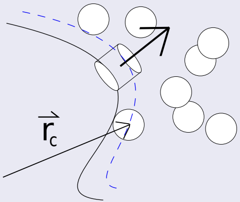
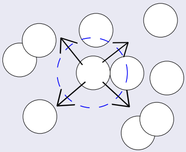


Pressure on SAS of Sphere

$$p_{SAS} = k_B T n g_\sigma$$



Pressure is also force divided by area!

Getting to the pressure for homogeneous hard spheres

Carnahan-Starling Free Energy for homogeneous hard spheres

$$A_{HS} = Nk_B T \frac{4\eta - 3\eta^2}{(1-\eta)^2} \tag{20}$$

where η is the filling fraction

$$\eta \equiv \frac{\pi}{6}\sigma^3 n \tag{21}$$

Getting to the pressure for homogeneous hard spheres

Now start with a more direct definition of pressure on a sphere

$$p_{SAS} = \frac{1}{N4\pi\sigma^2}\frac{dA_{HS}}{dR} \tag{22}$$

$$= k_B T n \frac{1-\frac{\eta}{2}}{(1-\eta)^3} \tag{23}$$

$$= k_B T n g_\sigma \tag{24}$$

which gives us

$$g_\sigma = \frac{1-\frac{\eta}{2}}{(1-\eta)^3} \tag{25}$$

Inhomogeneous derivation of assymetric case

In the inhomogeneous situation

Homogeneous equation

$$p_{SAS} = \frac{1}{N4\pi\sigma^2}\frac{dA_{HS}}{dR}$$

Inhomogeneous equation

$$p_{SAS}(\mathbf{r}) = \frac{1}{n(\mathbf{r})4\pi\sigma^2}\frac{1}{2}\frac{\delta A_{HS}}{\delta\sigma(\mathbf{r})}$$

and similar to the homogeneous

$$p_{SAS}(\mathbf{r}) = k_B T n_A(\mathbf{r}) g_\sigma^A(\mathbf{r}) \tag{26}$$

$$g_\sigma^A(\mathbf{r}) = \frac{1}{n(\mathbf{r})n_A(\mathbf{r})}\frac{1}{k_B T 4\pi\sigma^2}\frac{1}{2}\frac{\delta A_{HS}}{\delta\sigma(\mathbf{r})} \tag{27}$$

- Use White Bear free energy approximation A_{HS}

Derivation of symmetric

Similar concepts lead to symmetric radial distribution

Symmetric g_σ^S

$$g_\sigma^S(\mathbf{r}) = \frac{1}{n_0(\mathbf{r})^2}\frac{1}{4\pi\sigma^2}\frac{1}{2}\frac{\partial\Phi(\mathbf{r})}{\partial\sigma}$$

Asymmetric g_σ^A

$$g_\sigma^A(\mathbf{r}) = \frac{1}{n(\mathbf{r})n_A(\mathbf{r})}\frac{1}{k_B T 4\pi\sigma^2}\frac{1}{2}\frac{\delta A_{HS}}{\delta\sigma(\mathbf{r})}$$

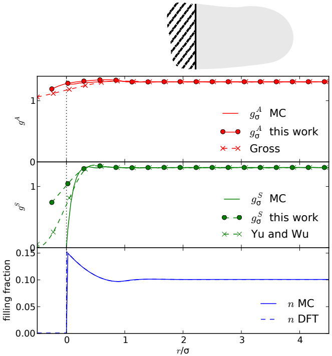
- Utilized that White Bear uses a local function and integrates to arrive at A_{HS}

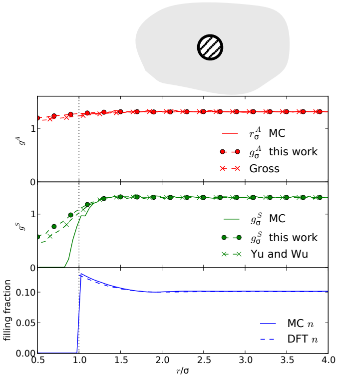
$$\Phi(\mathbf{r}) = \Phi_1(\mathbf{r}) + \Phi_2(\mathbf{r}) + \Phi_3(\mathbf{r}) \tag{28}$$

$$= -n_0 Ln(1-n_3) + \frac{n_1 n_2 - \mathbf{n}_{1V}\cdot\mathbf{n}_{2V}}{1-n_3}\ldots \tag{29}$$

- Begins as an approximation while assymetric does not

Low density comparisons with Gross, Yu and Wu, and Monte-Carlo





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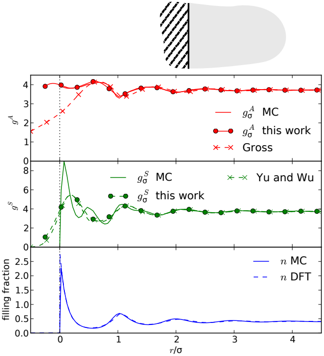
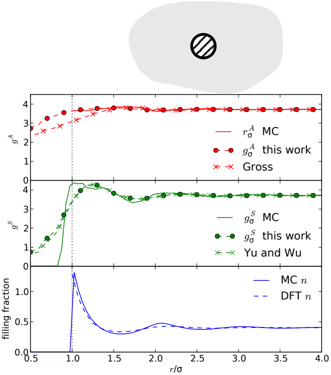


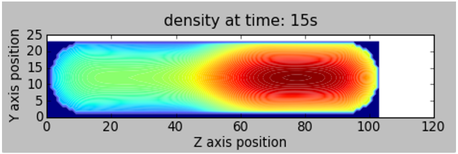


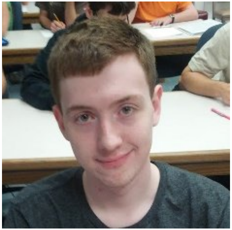
Summary

- Radial distribution function g_σ is a key function in SAFT
- Developed two approximations for g_σ
- Compared against functions of Gross, Yu and Wu, and of Monte-Carlo
- Our g_σ^A achieves almost perfect resemblence to Monte-Carlo version

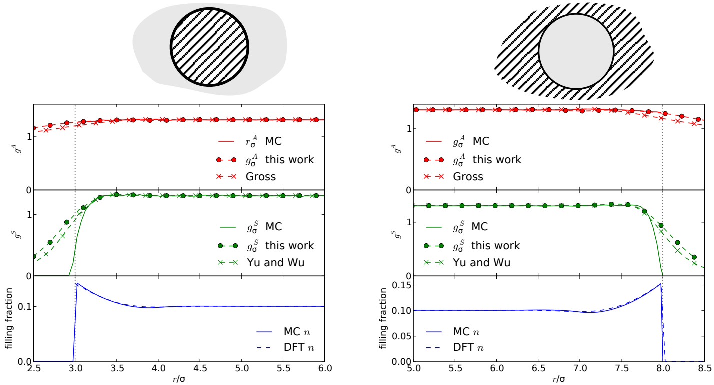
Future research

- Apply g_σ^A to new SAFT functional
- Approximate $g^{(2)}(\mathbf{r_1}, \mathbf{r_2})$ using g_σ^A
- Treating Dielectric Interactions
  - Hard sphere reference system and electrostatic energy term
- Analyzing protein dynamics in Escherichia coli
  - Modelling the interaction of Min proteins in bacteria
  - Look at the cell shape limits of oscillation
  - Overseeing Rene Zeto





Appendix low density comparisons with Gross, Yu and Wu, and Monte-Carlo



Appendix high density comparisons with Gross, Yu and Wu, and Monte-Carlo