Introduction

Classical Density-Functional Theory to Describe Spherical Solutes in Water

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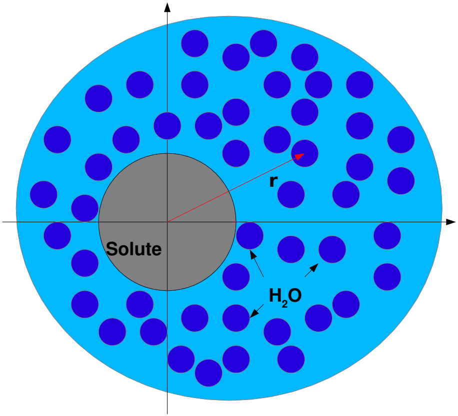
Hard Solutes



Question:

- How can we describe water surrounding a hard spherical solute?

Method

- Insert a hard spherical solute at the origin
- Determine density, n(r)
- Determine Free Energy, F(T)

"Classical" Density-Functional Theory (DFT)

Mermin Theorem (Generalized Hohenberg-Kohn Thm.)

$$F(T) = \min_{n(r)} \left\{ F_{un}[n(r), T] + \int V_{ext}(r)n(r)\, d^3r \right\}$$

Method

- Find a universal functional $F_{un}[n(r), T]$
- Minimize F_{un} to find Helmholtz free energy $F(T)$
- Apply it "Classically"

What is in a functional?

The Universal Functional

$$F_{un}[n(r)] = F_{id}[n(r)] + F_{exc}[n(r)] + \mu \int n(r) d^3 r$$

Ideal Gas Free Energy

$$F_{id}[n(r)] = k_B T \int n(r) \log[n(r)] d^3 r$$

F_{hs} is purely repulsive
F_{att} is purely attractive

$\longrightarrow$

Excess Free Energy

$$F_{exc}[n(r)] = F_{hs}[n(r)] + F_{att}[n(r)]$$

Hard Sphere and Attractive Functionals

Hard Sphere Functional

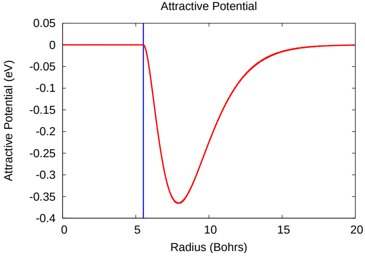
Rosenfeld's Fundamental-Measure Theory (FMT) functional

- Reduces to Scaled-Particle Theory in the homogeneous limit
- Reduces to Percus-Yevick correlation in the homogeneous limit
- Exact in the 1-D limit of hard spheres in a narrow pore
- Exact in the 0-D limit, cavities that can only hold one sphere

Attractive Functional

Requirements

- Similar to Lenard-Jones interaction
- 2 Variational parameters



Empirical Parameters

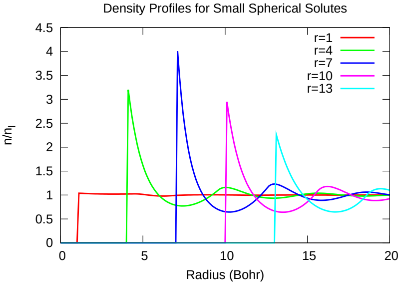
Known Input Parameters

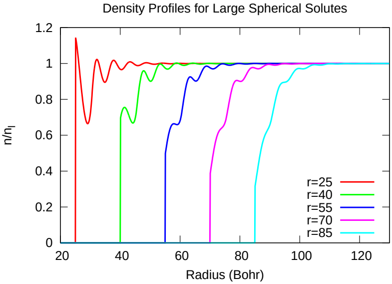
- Liquid Density
- Vapor Density (not used)
- Liquid-Vapor Coexistence
- Bulk Modulus
- Standard Temperature
- Surface Tension

Variational Parameters

- Attractive Potential Depth
- Attractive Potential Width
- Chemical Potential
- Hard-Sphere Radius

Density Profiles





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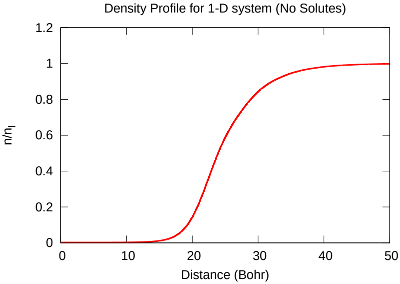

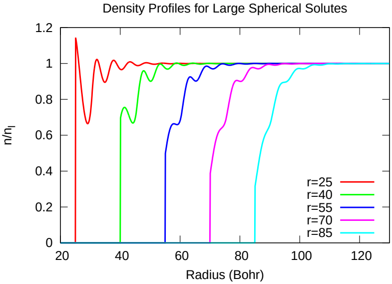

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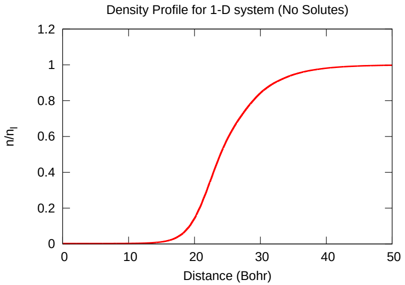
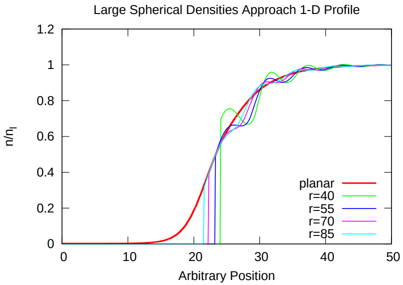
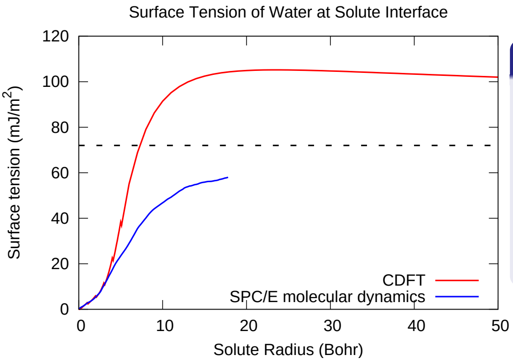




Surface Tension



Notes

- For large cavity radii, the surface tension should approach the 1-D limit.
- For small radii, our results match MD calculations

Conclusion

Summary

- "Classical" Functional Using FMT and an Attractive Potential
- Tunable Parameters for Reasonable Physics
- No Microscopic Input Parameters
- Reliable model for small spherical solutes

Future Work

- Find Lower Surface Tension for Radial System
- Use Vapor Density
- Include Individual Atoms
- Electromagnetic Interactions