IV. DENSITY FUNCTIONAL THEORY OF FLUID-FLUID INTERFACES

For fluid-fluid interfaces, the density gradients are small enough to be described by local density functional theory. For fluid-solid interfaces, the density gradients are large enough to require nonlocal density functional theory. In this section, we discuss local density functional theory.

van der Waals Model

The partition function of a van der Waals fluid has a hard-sphere component and a long-range attractive component.

$$Q_N^{VDW} = Q_N^{HS} e^{-\beta U_{AA}} \tag{3.1}$$

The Helmholtz free energy of the fluid is

$$F^{VDW} = F^{HS} + U_{AA} \tag{3.2}$$

In the VDW approximation, the fluid is assumed to be structureless in computing U_{AA}. This means that the pair correlation function is unity for the long-range attractive component, so

$$U_{AA} = \frac{1}{2}\int n^{(1)}(\underline{r}) n^{(1)}(\underline{r}') U_{ij}(|\underline{r} - \underline{r}'|) d^3r d^3r' \tag{3.3}$$

The next assumption of the VDW theory is that the local Helmholtz free energy density of hard spheres, $f^{HS}(\underline{r})$, depends only on the local density $n^{(1)}(\underline{r})$ at position $\underline{r}$.

We can write the free energy of the hard sphere system as a functional of the singlet density distribution:

$$F^{HS} = \int f^{HS}(n^{(1)}(\underline{r})) d^3r \tag{3.4}$$

Substituting equations (3.3) and (3.4) into equation (3.2) yields

$$F^{VDW} = \int f^{HS}(n^{(1)}(\underline{r})) d^3r + \frac{1}{2}\int n^{(1)}(\underline{r}) n^{(1)}(\underline{r}') U_{ij}(|\underline{r} - \underline{r}'|) d^3r d^3r' \tag{3.5}$$

We can rearrange equation (3.5) to give us a form with more physical insight. To do this, we first use the relations

$$\left[n^{(1)}(\underline{r}') - n^{(1)}(\underline{r})\right]^2 = n^{(1)}(\underline{r}')^2 - 2n^{(1)}(\underline{r}) n^{(1)}(\underline{r}') + n^{(1)}(\underline{r})^2$$

$$n^{(1)}(\underline{r})n^{(1)}(\underline{r}') = \frac{-\left[n^{(1)}(\underline{r}') - n^{(1)}(\underline{r})\right]^2 + n^{(1)}(\underline{r}')^2 + n^{(1)}(\underline{r})^2}{2}$$

Substituting into the integral of equation (3.5) we have

$$\begin{aligned}
&\frac{1}{2}\int n^{(1)}(\underline{r})n^{(1)}(\underline{r}')U_{ij}(|\underline{r}-\underline{r}'|)d^3r d^3r' \\
&= \frac{1}{4}\int\left\{-\left[n^{(1)}(\underline{r}') - n^{(1)}(\underline{r})\right]^2 + n^{(1)}(\underline{r}')^2 + n^{(1)}(\underline{r})^2\right\}U_{ij}(|\underline{r}-\underline{r}'|)d^3r d^3r' \\
&= -\frac{1}{4}\int\left[n^{(1)}(\underline{r}') - n^{(1)}(\underline{r})\right]^2 U_{ij}(|\underline{r}-\underline{r}'|)d^3r d^3r' + \frac{1}{4}\int\left[n^{(1)}(\underline{r}')^2 + n^{(1)}(\underline{r})^2\right]U_{ij}(|\underline{r}-\underline{r}'|)d^3r d^3r' \qquad (3.6) \\
&= -\frac{1}{4}\int\left[n^{(1)}(\underline{r}') - n^{(1)}(\underline{r})\right]^2 U_{ij}(|\underline{r}-\underline{r}'|)d^3r d^3r' + \frac{1}{2}\int n^{(1)}(\underline{r})^2 U_{ij}(|\underline{r}-\underline{r}'|)d^3r d^3r' \\
&= -\frac{1}{4}\int\left[n^{(1)}(\underline{r}') - n^{(1)}(\underline{r})\right]^2 U_{ij}(|\underline{r}-\underline{r}'|)d^3r d^3r' + \frac{1}{2}\int n^{(1)}(\underline{r})^2 U_{ij}(s)d^3r d^3s
\end{aligned}$$

where

$$s = |\underline{r}-\underline{r}'|$$

so that equation (3.5) becomes

$$F^{VDW} = \int f^{HS}(n^{(1)}(\underline{r}))d^3r + \frac{1}{2}\int n^{(1)}(\underline{r})^2 U_{ij}(s)d^3r d^3s - \frac{1}{4}\int\left[n^{(1)}(\underline{r}') - n^{(1)}(\underline{r})\right]^2 U_{ij}(|\underline{r}-\underline{r}'|)d^3r d^3r' \qquad (3.7)$$

Rearrangement yields:

$$F^{VDW} = \int\left[f^{HS}(n^{(1)}(\underline{r})) + \frac{1}{2}\int n^{(1)}(\underline{r})^2 U_{ij}(s)d^3s\right]d^3r - \frac{1}{4}\int\left[n^{(1)}(\underline{r}') - n^{(1)}(\underline{r})\right]^2 U_{ij}(|\underline{r}-\underline{r}'|)d^3r d^3r' \qquad (3.8)$$

The first term is the integral of the Helmholtz free energy density of a homogeneous VDW fluid, $f^{\circ}(n^{(1)}(\underline{r}))$,

$$f^{\circ}(n^{(1)}(\underline{r})) = \left[f^{HS}(n^{(1)}(\underline{r})) + \frac{1}{2}\int n^{(1)}(\underline{r})^2 U_{ij}(s)d^3s\right] \qquad (3.9)$$

The second term contains all of the free energy due to fluid density inhomogeneities. If there was an external potential, we would add a third term to equation (3.8)

$$F^{X}(n^{(1)}(\underline{r})) = \int n^{(1)}(\underline{r})U_{AP}(\underline{r})d^3\underline{r} \qquad (3.10)$$

The chemical potential is equal to the functional derivative of F

$$\mu = \frac{\delta F}{\delta n(\underline{r})} \tag{3.11}$$

For the VDW theory,

$$\mu(\underline{r}) = \mu^{\circ}(n^{(1)}(\underline{r})) + \int \left[n^{(1)}(\underline{r}') - n^{(1)}(\underline{r}) \right] U_{ij}(|\,\underline{r} - \underline{r}'\,|) d^3r' + U_{AP}(\underline{r}) \tag{3.12}$$

where $\mu^{\circ}(n(\underline{r}))$ is the chemical potential of a homogeneous fluid at density n.

$$\mu^{\circ}(n^{(1)}(\underline{r})) = \frac{\delta f^{\circ}(n)}{\delta n(\underline{r})} \tag{3.13}$$

What can this model give us?

1. Single-component single-phase bulk behavior

The van der Waals theory gives the density inhomogeneities of a bulk fluid in the presence of an external potential. If we specify the chemical potential of interest, we can find the density distribution using equation (3.12). The equation is a nonlinear integral equation.

If there is no external potential, then the bulk fluid is homogeneous and the singlet density distribution is a constant. In this case, we have an equation of state for the VDW gas, an equation which relates density to chemical potential. Equation (3.12) becomes

$$\mu = \mu^{\circ}(n^{(1)}) \tag{3.15}$$

Whoever imagined solving the VDW equation of state could be so much fun?

2. Single-component two-phase interfacial behavior

As we know, the van der Waals theory allows for phase equilibria so the above equations can be used to describe the density inhomogeneities (spatial variation of density) of equilibrium vapor-liquid interfaces. The inhomogeneities occur in one dimension if the interface is planar. They occur in 3 dimensions, if not. In that case, one derives the free energy of the interface and takes the functional derivative of that with respect to the liquid and vapor density distributions. A fair amount of work is involved in rearranging these equations.

3. Multicomponent behavior

The above derivation can be extended to multicomponent mixtures. (In fact in his book, Davis derives only the multicomponent equations for single-phase bulk and two-phase interfacial behavior.)

Other Local Density Functional Theories

In addition to the van der Waal’s theory, there are other common local density functional theories.

1. Modified VDW Model

Replace the hard sphere partition function by the repulsive part of a soft sphere fluid. As before, use the reference pair correlation function of the soft sphere reference fluid rather than unity to computer that average repulsive energy. Derive free energies based on these assumptions.

2. Density Gradient Theory

Use VDW or Modified VDW free energy functional. Expand free energy functional in Taylor series. Truncate after a few terms. The equations controlling equilibrium distributions become nonlinear differential equations rather than nonlinear integral equations. (This only works well for small gradients, i.e. gradients due to gravity.)

V. DENSITY FUNCTIONAL THEORY OF SOLID-FLUID INTERFACES

For fluid-solid interfaces, the density gradients are large enough that the local DFT models described above do not work well. The free energy functionals can no longer be considered as functions. The free energy at a given point depends upon the density at other neighboring points. Solid-fluid interfaces require nonlocal density functional theory. In this section, we discuss nonlocal density functional theory. We drive the simplest model and then give qualitative descriptions of the nature of the improvement presented by other models.

One-dimensional hard-rods at a hard wall

The density distribution of one-dimensional hard rods (1DHR) at a hard wall has an exact solution, obtainable through statistical mechanics. (See Davis, Chapter 10). However, we consider the local DFT approximation of the 1DHR system here to introduce ourselves to local DFT .

Consider a hard wall at x=0 and hard rods of length d. The external potential the wall exerts on the fluid particles (the hard rods) is

$$v(x) = \begin{cases} \infty & x < d/2 \\ 0 & x > d/2 \end{cases} \tag{3.16}$$

The density distribution is

$$n(x) = \begin{cases} 0 & x < d/2 \\ n^{bulk} & x >> d/2 \end{cases} \tag{3.17}$$

In the range of positions where x>d/2, the fluid is inhomogeneous, due to the external potential caused by the presence of the wall.

It is convenient to split the potential into a reference system and the excess (everything not in the reference fluid). Most modern Nonlocal DFT theories use a reference system of repulsive short-ranged interactions.

$$U_{AA} = U_{AA,R} + \lambda U_{AA,A} \tag{3.18}$$

In our system λ is one, but we explicitly include the factor in the equation (3.18) because it is necessary to define the free energy.

You construct a free energy functional of the form

$$F = F^{\circ} + F_A \tag{3.19}$$

where we split the free energy into the reference (not repulsive) contribution and the additional contribution, which contains everything not in F°. The additional component of the free energy contains all explicit functionality of both $U_{AA,R}$ and $\lambda U_{AA,A}$. The configuration Helmholtz free energy of a system with arbitrary lambda in the N-particle canonical ensemble is given by

$$e^{-\beta F_N} = \int \ldots \int e^{-\beta U_{AA,R} - \beta \lambda U_{AA,A}} d^3 r_1 d^3 r_N \tag{3.20}$$

Differentiate with respect to λ. Integrate the derivative taking grand canonical ensemble average

$$F_A = \frac{1}{2} \int_0^1 \int n(\underline{r}) n(\underline{r}') g(\underline{r}, \underline{r}') U_{AA,A}(|\,\underline{r} - \underline{r}'\,|) d^3 r d^3 r' d\lambda \tag{3.21}$$

The reference free energy functional can itself be decomposed into contributions due to the external potential, the ideal gas, and the excess term.

$$F^{\circ} = F_X + F_I + F_{ex} \tag{3.22}$$

For a one-component system, the free energy contribution due to the external potential is

$$F_X = \int n(\underline{r}) U_{AP}(\underline{r}) d^3 r \tag{3.23}$$

The free energy contribution due to the ideal gas is

$$F_I = \int n(\underline{r}) \left\{ \mu^{o}(T) + kT \left[\ln(n(\underline{r})) - 1 \right] \right\} d^3 r \tag{3.24}$$

The free energy contribution due to the excess term needs to be constructed. Percus (1981) defined a generic free energy functional for the excess free energy of the form

$$F_{ex} = \int \bar{n}^{\sigma}(\underline{r}) F_P(\bar{n}^{\tau}(\underline{r}))\, d^3 r \tag{3.25}$$

where F_P is the excess free energy per particle of a homogeneous hard sphere fluid of density n. The quantities $\bar{n}^{\sigma}(\underline{r})$ and $\bar{n}^{\tau}(\underline{r})$ are called coarse grain densities that are linear functionals of density and are related to the local density by weighting functions:

$$\bar{n}^{\sigma}(\underline{r}) \equiv \int \sigma(\underline{r} - \underline{r}'; \{n\}) n(\underline{r}') d^3 r' \tag{3.26}$$

$$\bar{n}^{\tau}(\underline{r}) \equiv \int \tau(\underline{r} - \underline{r}'; \{n\}) n(\underline{r}') d^3 r' \tag{3.27}$$

The constraint that the course grain densities must yield the constant density n in the limit of a homogeneous fluid can be expressed as

$$\int \sigma(\underline{r}-\underline{r}';\{n\})d^3r' = \int \tau(\underline{r}-\underline{r}';\{n\})d^3r' = 1 \tag{3.28}$$

At this point, we need to find approximations to σ, τ, F_P, and $g(\underline{r},\underline{r}')$. Equation (3.25) is the starting point for most nonlocal DFT.

As an example, consider the one-dimensional hard rod fluid with length a and nominal density n, and where x designates the spatial position.

$$\bar{n}^{\sigma}(x) = \frac{1}{2}\left[n\left(x+\frac{a}{2}\right)+n\left(x-\frac{a}{2}\right)\right] = \frac{1}{2}\int \delta\left(|x-x'|-\frac{a}{2}\right)n(x')dx' \tag{3.29}$$

where $\delta(x)$ is the Dirac delta function. Where did equation (3.29) come from? Basically it came from someone who knew the analytical solution to the one-dimensional hard rod fluid and used their intuition and experience to construct it. (In other words, I can't derive it at the moment.) What does it physically say? Equation (3.29) says the course-grained density of the 1DHR fluid is the average of the density of the fluid at either end of the rod.

$$\bar{n}^{\tau}(x) = \frac{1}{a}\int_{x-\frac{a}{2}}^{x+\frac{a}{2}} n(x')dx' = \frac{1}{a}\int \left[n\left(x+\frac{a}{2}\right)+n\left(x-\frac{a}{2}\right)\right] = \frac{1}{2}\int \eta\left(\frac{a}{2}-|x-x'|\right)n(x')dx' \tag{3.30}$$

where η is the step function. This course grained density says that the space between -a/2 and a/2 is occupied by a hard rod of length a. So the density weighting functionals are

$$\sigma(x-x') = \frac{1}{2}\delta\left(|x-x'|-\frac{a}{2}\right) \tag{3.31}$$

and

$$\tau(x-x') = \frac{1}{a}\eta\left(\frac{a}{2}-|x-x'|\right) \tag{3.32}$$

The corresponding formula for F_P is

$$F_P(n) = -kT\ln(1-na) \tag{3.33}$$

Equation (3.33) came from the analytical solution to the 1DHR system.

With these definitions of the density functionals and F_P, the free energy of a homogeneous fluid at the local density n, we can evaluate equation (3.25). It turns out for the 1DHR case, that these definitions yield the exact results. They form the basis for later approximations.

Connection between local DFT and nonlocal DFT

One can obtain the VDW local density functional approximation by choosing

$$\sigma(r) = \tau(r) = \delta(r) \tag{3.34}$$

and using the Clausius approximation

$$P^R(n) = \frac{nkT}{(1-nb)} \tag{3.35}$$

so that

$$F_P(n) = -kT\ln(1-nb) \tag{3.36}$$

Other Nonlocal Density Functional Theories

In addition to the One-dimensional hard-rods at a hard wall theory, there are other nonlocal density functional theories.

1. Generalized VDW Model

$$\sigma(r) = \delta(r) \tag{3.37}$$

and

$$\tau(x - x') = \frac{1}{\frac{4}{3}\pi\left(\frac{d}{2}\right)^3}\eta(d - |r|) \tag{3.38}$$

So that the course-grained density $\overline{n}^{\sigma}(r) = n(r)$ is the local density and $\overline{n}^{\tau}(r)$ is the density locally averaged over a volume equal to the volume excluded by a particle centered at r.

2. Generalized Hard Sphere Model

This follows from 1DHR theory,

$$\sigma(r) = \frac{1}{4\pi\left(\frac{d}{2}\right)^2}\delta\left(\frac{d}{2} - |r|\right) \tag{3.39}$$

and

$$\tau(r) = \frac{1}{\frac{4}{3}\pi\left(\frac{d}{2}\right)^3}\eta\left(\frac{d}{2} - |r|\right) \tag{3.40}$$

So that we have locally averaged density first over the surface of the hard sphere and second over the volume of the hard sphere.

3. Tarazona Model

In the above two examples, the weighting functions were obtained heuristically. Tarazona presented a less heuristic method for obtaining the weighting functions. $\overline{n}^{\sigma}(r) = n(r)$ but $\overline{n}^{\tau}(r)$ is the solution to an integral equation which provides a weighted density functional based on the weighting function. The function τ which defines $\overline{n}^{\tau}(r)$ is a power-series expansion in $\overline{n}^{\tau}(r)$. If you keep only the zero-order term you obtain the generalized VDW model. Tarazona kept terms up to and including the second-order term.

4. Curtin-Ashcroft Model

Followed Tarazona's lead but used the exact relation for the direct correlation function in the homogeneous fluid limit to obtain the weighting functional τ. It is a computationally more expensive way to obtain τ but is more rigorous. (I know nothing about the relative accuracy of the two methods.)

5. Meister-Kroll Model

"This theory takes advantage of exact DFT in a way that can be systematically improved if homogeneous fluid theory improves."