



# AN ABSTRACT OF THE DISSERTATION OF

Jeff B. Schulte for the degree of Doctor of Philosophy in Physics presented on  
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David Roundy

We did some cDFT and then I simulated some minD.

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cDFT and MinD

by

Jeff B. Schulte

A DISSERTATION

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APPROVED:

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Major Professor, representing Physics

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Chair of the Department of Physics

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Dean of the Graduate School

I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

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Jeff B. Schulte, Author

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Thank Dr. Roundy and people who helped, undergrads. The department as a whole, and family?

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## 1 Introduction

ghghgh

rhello

## 2 Introduction to cDFT papers

Going to reverse engineer the explanation of DFT:

Talk about why need functionals to deal with inhomogenous situations. Then talk about how functional derivatives are taken.

### 2.1 Classical Density Functional Theory

A statistical ensemble is a collection of an arbitrary number of systems that have the same macroscopic properties and internal restrictions, but have positions and momenta that are otherwise distributed randomly. In the canonical ensemble, the number of particles  $N$ , the total volume of the system  $V$ , and the temperature  $T$  are taken as constant. In this ensemble the free energy, defined as  $F = U - TS$ , where  $U$  is the internal energy and  $S$  is the entropy of the system, is minimized in thermodynamic equilibrium. In the grand canonical ensemble, the number of particles is allowed to vary while  $V$ ,  $T$  and the chemical potential  $\mu$  are held constant. In this ensemble it is the grand potential, defined as  $\Omega = F - \mu N$ , that

is minimized in thermodynamic equilibrium.

In the case of inhomogenous fluids, an inhomogenous external potential  $\phi(\mathbf{r})$  restricts the particles in the system and takes the place of the volume  $V$  in the thermodynamic equations. In such a system, a change in the internal energy is given by

$$\delta U = T\delta S + \int \rho^{(1)} \delta \phi(\mathbf{r}) d(\mathbf{r}) + \mu \delta N \quad (2.1)$$

In the grand canonical ensemble, the probability density  $f_0(\mathbf{r}^N, \mathbf{p}^N; N)$  is defined so that  $f_0(\mathbf{r}^N, \mathbf{p}^N; N) d\mathbf{r}^N$  is the probability that there are  $N$  particles in the system and that those particles are found within the infinitesimal range of positions  $\mathbf{r}^N$  and momenta  $\mathbf{p}^N$ . It's definition is

$$f_0(\mathbf{r}^N, \mathbf{p}^N; N) = \frac{\exp(-\beta(\mathcal{H} - N\mu))}{\Xi} \quad (2.2)$$

where

$$\Xi = \sum_{N=0}^{\infty} \frac{\exp(N\beta\mu)}{h^{3N} N!} \int \int \exp(\beta\mathcal{H}) d\mathbf{r}^N d\mathbf{p}^N \quad (2.3)$$

is the partition function of the grand canonical ensemble. Eq. 2.2 is structured as the boltzmann constant with an energy argument comprised of the Hamiltonian and chemical potential, divided by the grand partition function.

Classical Density Functional Theory assumes that the hamiltonian can be split

into linearly combined parts:

$$\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = K_N(\mathbf{p}^N) + V_N(\mathbf{r}^N) + \Phi(\mathbf{r}^N) \quad (2.4)$$

The three terms on the right are the kinetic energy, potential interaction between particles, and external potential, respectively. The kinetic energy depends solely on the momenta of the particles, and the two potentials solely on their positions.

Substituting this into the Hamiltonian term in Eq. 2.2 and taking the natural logarithm, we have:

$$\ln f_0 = \beta\Omega - \beta K_N - \beta V_N - \beta\Phi_N + N\beta\mu \quad (2.5)$$

where we have used the relation

$$\Omega = -k_B T \ln \Xi \quad (2.6)$$

which is the basic connection between thermodynamics and statistical mechanics in the grand canonical ensemble.

Because the external potential and  $\mu$  both don't change and  $\rho^{(1)}(\mathbf{r})$  is the average ensemble equilibrium density at  $\mathbf{r}$ , it's true that

$$\langle \Phi_N \rangle = \int \rho^{(1)}(\mathbf{r}) \phi(\mathbf{r}) d\mathbf{r} \text{ and } \langle N\mu \rangle = \mu \int \rho^{(1)}(\mathbf{r}) d\mathbf{r} \quad (2.7)$$

Using these relations and switching terms around in Eq. results in the equation

$$\langle K_N + V_N + k_B T \ln f_0 \rangle = \Omega - \int \rho^{(1)}(\mathbf{r}) \phi(\mathbf{r}) d\mathbf{r} + \mu \int \rho^{(1)}(\mathbf{r}) d\mathbf{r} \quad (2.8)$$

Switching around the definition of the thermodynamic grand potential gives us  $F = \Omega + \mu N$ . We can see the right hand side of Eq. 2.8 is analougous to the free energy of the inhomogenous system minus the part given by the external potetnial. We call this function the 'intrinsic free energy'  $\mathcal{F}$  since it addresses the interactions between the particles within the system:

$$\mathcal{F} = \Omega - \int \rho^{(1)}(\mathbf{r}) \phi(\mathbf{r}) d\mathbf{r} + \mu \int \rho^{(1)}(\mathbf{r}) d\mathbf{r} = \langle K_N + V_N + k_B T \ln f_0 \rangle \quad (2.9)$$

It can be shown that for a given  $\mu$ ,  $T$ , and defined function  $V_N$  describing the potential interaction between particles, there is a one-to-one relation between the external potential function and the equilibrium density profile  $\rho^{(1)}$  at thermodynamic equilibrium. The grand canonical density function  $f_0$  (Eq. 2.2) for a given function  $V_N$ ,  $\mu$ , and  $T$  is a function of external potential, so that the right hand side of Eq. 2.8 is a function of external potential and therefore also of  $\rho^{(1)}$ . Thus intrinsic free energy  $\mathcal{F}$  is dependent on  $\rho^{(1)}$ .

We can thus write

$$\Omega_\phi[n] = \mathcal{F}[n] + \int n(\mathbf{r}) \phi(\mathbf{r}) d\mathbf{r} - \mu \int n(\mathbf{r}) d\mathbf{r} \quad (2.10)$$

At equilibrium, this grand potential is minimized.

The first step in Classical Density Functional Theory is to design the functional form of the intrinsic free energy  $iF$ , which is conceptually equal to the free energy ignoring the external potential. We then set the temperature  $T$ , chemical potential  $\mu$ , and external potential  $\phi(\mathbf{r})$ , and adjust the density profile until we have found the global minimum of this grand potential. The result is the density and grand potential in equilibrium.

(the statistical average of  $V_N$  depends on  $\rho^{(1)}$  since  $V_N$  initially defined by  $V_N(r^N)$  in Eq. 2.4, so a function of positions of particles, so statistical average version is above).

Is the configuration integral, it's the potential's contribution to the partitionn function

This is the functional version of grand potential, dependent upon  $n(\mathbf{r})$ , not neccesarly the equilibrium  $n(\mathbf{r})$ , and this will be minimized in the case of thermodynamic equilibrium.

$$\Omega_\phi[n] = \mathcal{F}[n] + \int n(\mathbf{r})\phi(\mathbf{r})d\mathbf{r} - \mu \int n(\mathbf{r})d\mathbf{r} \quad (2.11)$$

n-particle density in the grand canonical ensemble is:

$$\rho_N^{(n)}(\mathbf{r}^n) = \frac{1}{\Xi} \sum_{N=n}^{\infty} \frac{\exp(N\beta\mu)}{\Lambda^3(N-n)!} \int \exp(-\beta V_N) d\mathbf{r}^{(N-n)} \quad (2.12)$$

where the spatial integral of the Boltzmann factor is taken over all the potential interaction with all the other particles  $N$  in the system, and all the possible  $N$ s are

considered. The  $\exp(N\beta\mu)$  boltzmann term accounts for the chemical potential's regulation of the average number of particles in the system. It is defined so that an integral of the single particle density gives the average number of particles:

$$\rho_N^{(1)}(\mathbf{r})d\mathbf{r} = \langle N \rangle \quad (2.13)$$

canonical ensemble:

$$F = U - TS \quad (2.14)$$

grand canonical ensemble:

$$\Omega = F - N\mu \quad (2.15)$$

The second term on the right hand side normally vanishes, since the external potential is usually a wall, so either infinity or zero, and if it's infinity, then  $n(\mathbf{r})$  there is zero.

I am citing a source [1]

Important to note that the functional your minimizing is not the grand potential until its minimized

## 2.2 Introduction to SAFT and explanation of first free energy term

Work on classical Density Functional Theory for fluids involves creating intrinsic density functionals of the density profile. These are comprised of a sum of terms that individually address different conceptual aspects of the system. terms that treat different types of interaction between particles are added to terms that describe reference system. For example, the functional for the version of SAFT that we use in our work, is defined as

$$iF_{SAFT} = F_{ideal} + F_{hardsphere} + F_{something} \quad (2.16)$$

We will discuss in much more detail the meaning of these terms below, but write it down now to illustrate the general structure of the total functional.

While our contributions described in the next chapters could certainly be applied to many different types of fluid functionals, we specifically worked towards improving the very popular SAFT versions functionals in current development. Indeed in one of the papers described, we use the function we've created within a SAFT functional to test it's affect upon the results of the that functional. Therefore while describing the general background and origin of the ideas we use, I'll



speak directly to the build up of the SAFT functional, the pieces of which (developed and verified by others) and the general structure are found in many other functionals.

The first two terms,  $F_{ideal}$  and  $F_{hardsphere}$  define the reference system. The rest of the terms address different approximations of interactions (which we describe below). In inhomogeneous fluids, each one of these terms is itself a functional of the density profile.

Many times different approaches will use the same reference systems and even the exact functional form of the reference system free energy terms while, when treating other forms of interaction, will use different conceptual models and implementation in order to construct those terms. SAFT itself departs from other theories in its last three terms. The first 'ideal' term it uses is ubiquitous, and the second is a particularly common reference system for fluids. I give a detailed introduction to the particular functional that we use for it below (that of the White Bear free energy), because while we don't actually modify it in our implementation of inhomogeneous SAFT, we do draw heavily from its ideas when creating the function that we do.

The first term in the SAFT functional is the ideal free energy term  $F_{ideal}$ . This term treats a system of particles that do not interact with each other. This is an obvious place to start if one is to build the description of particle interaction terms upon a reference system. Its lack of interaction actually causes this term to be the only one that we can construct exactly, with no approximations. To see why, we point out that a system of non interacting spheres is able to satisfy the local

density approximation (only here it is not an approximation!) The local density approximation states that a free energy functional can be written as an integral of a completely local function of the density profile. For example,

$$\mathcal{F}_{local\ density}[\rho^{(1)}] = \int f(\rho^{(1)}) d\mathbf{r} \quad (2.17)$$

where  $f(\rho^{(1)})$  is the free energy per unit volume of the homogenous fluid at a density  $\rho^{(1)}$ . This approximation neglects any interaction between the particles, so that any spatial variation in the density will be due entirely to the varying external potential. In essence, each bit of volume becomes it's own thermodynamic system, with a free energy equal that of a homogenous density of particles, and the free energies from all the bits of volume are added up to get the total. This approximation has also been used to construct entire intrinsic free energy functional (cite). In fact it does apply to external potentials that modulate the density slowly over space, much more slowly than correlation lengths. The approximation breaks down rather quickly, however, near hard walls for interacting systems, where often the spheres will stack up in 'layers' (should see some figure) and the densities are higher than bulk freezing densities (cite).

However, the ideal term can be constructed in this fashion, so all we need to do is integrate the free energy of an ideal homogenous system at the local density. Going back to basic thermodynamics and statistical mechanics, we have:

$$F = -k_B T \ln Q_N = -k_B T \ln \left( \frac{V}{N! \Lambda^3} \right) \quad (2.18)$$

where  $Q_N$  is the partition function and  $\Lambda$  is de Broglie thermal wavelength. Using the Stirling approximation for  $N!$ , we have

$$F^{id} = Nk_B T (\ln \Lambda^3 \rho - 1) \quad (2.19)$$

Taking this as the free energy per unit volume and integrating, we have

$$\beta \mathcal{F}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) (\ln(\Lambda^3 \rho(\mathbf{r})) - 1) \quad (2.20)$$

Because this term is in fact an exact one for the ideal gas, it is ubiquitous in the use of classical density functional theory for inhomogeneous and homogeneous fluids.

## 2.3 Virial Equation, Mayer functions, and the Carnahan Starling Equation

The second term in the SAFT intrinsic free energy functional,  $f_{hard\ sphere}$ , is also a reference term and is used in many other functionals besides the one described here. I'll introduce the term and the theory behind it in some detail below because it is so widely used and, more importantly, because an understanding of the ideas involved is necessary for an understanding of our own work. Before describing the term itself, however, I'll explain here some important things that lead up to this theory, namely the Virial equation, Mayer functions, and the Carnahan Starling Equation.

The Virial Equation applies to homogeneous fluids. It equates a thermodynamic, intensive quantity (likes the pressure) with an expansion of the homogeneous density of the fluid. It's standard form is

$$\frac{\beta P}{\rho} = 1 + \sum_{i=1}^{\infty} \beta_i \eta^i. \quad (2.21)$$

The expansion comes out of a formulation of the partition function that is most often expressed as a series of diagrams that have well defined rules of construction. I won't explain the diagrams or their rules here, but Figure(REF) shows an example so that if the reader sees them somewhere she'll know what they are. A single term (or diagram) in this expansion of the partition function is in fact a spatial integral of an integrand composed of particle densities multiplied by a number of what are

called Mayer Functions. To explain, I'll start with the partition function:

$$\Xi = \sum_{N=0}^{\infty} \frac{\exp(N\beta\mu)}{h^{3N}N!} \int \dots \int \exp(\beta\mathcal{H}) d\mathbf{r}^N d\mathbf{p}^N \quad (2.22)$$

$$= \sum_{N=0}^{\infty} \frac{\exp(N\beta\mu)}{h^{3N}N!} \int \dots \int \exp(-\beta(V_N + \phi(\mathbf{r}))) d\mathbf{r}^N d\mathbf{p}^N \quad (2.23)$$

where  $V_N$  is the interaction potential between all the particles in the system and  $\phi(\mathbf{r})$  is the external potential. If the the interaction potential can be written as a summation of pairwise superposable interactions, i.e.

$$V_N = \sum_{\substack{\text{all particles} \\ i < j}} v(i, j) \quad (2.24)$$

than the partition function can be written as

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \int \dots \int \left( \prod_{i < j}^N f(i, j) \right) \left( \prod_{i=1}^N \frac{\exp(\beta(\mu - \phi(\mathbf{r}_i)))}{\Lambda^3} \right) d\mathbf{r}^N \quad (2.25)$$

where  $f(i, j) = \exp(-\beta v(i, j))$  is the Mayer function between two particles. With the help of the diagrams, one can take the natural logarithm of this function to get the grand potential, and then derivatives to find what are called direct correlation functions (which I won't explain here). The use of an identity yields a relationship between the chemical potential and the density:

$$\beta\mu = \beta\mu^{id} - \sum_{i=1}^{\infty} \beta_i \rho^i \quad (2.26)$$

Then the use of the following relation from thermodynamics:

$$\left(\frac{\partial P}{\partial \rho}\right)_T = \rho \left(\frac{\partial \mu}{\partial \rho}\right)_T \quad (2.27)$$

allows one to express the pressure as

$$\frac{\beta P}{\rho} = 1 + \sum_{i=1}^{\infty} \beta_i \eta^i \quad (2.28)$$

where

$$\beta_i = \left(\frac{6}{\pi d^3}\right)^i B_{i+1} \quad (2.29)$$

(REWRITE BELOW) The above formulation of a thermodynamic property is useful, but it requires an expansion of coefficients, which can be a nuisance computationally. Caranahan and Starling (cite) were able to develop a rule for coefficient generation that approximates Eq. 2.29, but that results in integers, and ones that one can allow for a geometric the one written above, based on and then multiple terms of a The virial coefficients  $\beta_i$  based on the procedure above are not integers, so in order to get get to a thermodynamic property the series must be expanded. Carnahan Starllng constructed a method that allows them to approximate each coefficient by a very close integer in a sysematic fashion that allows them to create a geometric series. This series yields a simple, analytic approximation of the pressure in the homogenous fluid as a function of density 3.9.17

$$\frac{\beta P}{\rho} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (2.30)$$

or for the free energy:

$$\frac{\beta F^{ex}}{N} = \frac{\eta(4 - 3\eta)}{(1 - \eta)^2} \quad (2.31)$$

Its is very successful in predicting pressure of homogenous hard sphere fluid at different densities.

White Bear uses MCSL equation of state, which is the generalization to the multi component mixture of hard spheres of the Carnahan-Starling equation of state. We describe the Carnahan-Starling equation of state here because we use it in the first chapter.

## 2.4 Fundamental Measure Theory and the White Bear intrinsic free energy functional

Some of the intial attempts to get around this included expanding this local free energy in powers of dereivitives of the density with respect to positions (but maybe not mention this?). Also some of the initial attempts included what was called weighted density approximation

A weighted density  $\bar{\rho}$  is created through a convolution of the  $\rho^{(1)}$ :

$$\bar{\rho}(\mathbf{r}) = \int w(|\mathbf{r} - \mathbf{r}'|) \rho^{(1)}(\mathbf{r}') d\mathbf{r}' \quad (2.32)$$

and then the intrinsic free energy is defined as

$$\mathcal{F}[\rho^{(1)}] = \int \frac{f^{ex}(\bar{\rho})}{\bar{\rho}} \rho^{(1)}(\mathbf{r}') d\mathbf{r}' \quad (2.33)$$

This hard sphere reference is described by an interaction potential that discontinuously jumps from zero to infinity when the spheres are within a certain range (the diameter of the hard sphere). This reference system potential is meant to approximate the 'hard core' repulsions that are common to all particles. It seems to do some stuff well (WHAT DOES IT DO WELL) Together with the ideal free energy term (described below),

Fundamental measure Theory, created by Rosenfeld in 1989, is based on convolutions, but represents a considerable departure.

Percis-Yevik have an involved derivation of an equation of state, which once again allows one to write thermodynamic properties in terms of densities for homogeneous systems. Comparing this theory (and using properties of correlation functions, which we will once again not get into) with the derivations of another theory call Scaled Particle Theory, which once again we will not explain but will say that it has to do with a system of spheres where one sphere is slowly growing, Rosenfeld recognized that the density sides of these equations can be reformulated in terms of combinations of convolutions of weighting functions that are



constructed to describe the geometric properties of spheres. He then discovered that for inhomogeneous systems, he could write down the intrinsic free energy in terms of convolutions of densities in a way so that as the system approached the homogeneous limit, the correct terms for the Perkis-Yevik homogeneous density expansion are reproduced.

It originates from the fact that the mayer function that goes into describing the virial expansions can itself be deconvolved into a sum of products of convolutions of weighting functions that are designed with geometry of the hard sphere in mind.(should probably describe the virial equation before this, actually). The resulting expression for the excess free energy (excess to the ideal free energy) can be formulated in terms of a series of closely related fundamental measures, that also reflect the geometry of the hard sphere reference system. They are the following:

The White Bear free energy is thus

$$A_{HS}[n] = k_B T \int (\Phi_1(\mathbf{r}) + \Phi_2(\mathbf{r}) + \Phi_3(\mathbf{r})) d\mathbf{r} , \quad (2.34)$$

with integrands

$$\Phi_1 = -n_0 \ln(1 - n_3) \quad (2.35)$$

$$\Phi_2 = \frac{n_1 n_2 - \mathbf{n}_{V1} \cdot \mathbf{n}_{V2}}{1 - n_3} \quad (2.36)$$

$$\Phi_3 = (n_2^3 - 3n_2 \mathbf{n}_{V2} \cdot \mathbf{n}_{V2}) \frac{n_3 + (1 - n_3)^2 \ln(1 - n_3)}{36\pi n_3^2 (1 - n_3)^2}, \quad (2.37)$$

using the fundamental measures

$$n_3(\mathbf{r}) = \int n(\mathbf{r}') \Theta(\sigma/2 - |\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' \quad (2.38)$$

$$n_2(\mathbf{r}) = \int n(\mathbf{r}') \delta(\sigma/2 - |\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' \quad (2.39)$$

$$\mathbf{n}_{2V}(\mathbf{r}) = \int n(\mathbf{r}') \delta(\sigma/2 - |\mathbf{r} - \mathbf{r}'|) \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2.40)$$

$$\mathbf{n}_{V1} = \frac{\mathbf{n}_{V2}}{2\pi\sigma}, \quad n_1 = \frac{n_2}{2\pi\sigma}, \quad n_0 = \frac{n_2}{\pi\sigma^2} \quad (2.41)$$

where  $\delta$  is the direct delta function and  $\Theta$  is the Heaviside step function.

Fundamental Measure theory comes out of a similar result of the Percus-Yevick equation of state and the result of scaled particle theory

There are very accurate equations

I think do introduction to what the fundamental theory does, here, with the weighted densities based on geometry.

Based on the geometry of particles in question. Can deal with mixtures... Below we will describe in more detail the White Bear functional, which is what we use for our term that approximated hard spheres.

The derivation of Fundamental Measure Theory is inspired by a similarity between the results of a homogeneous theory called scaled particle theory and an equation of state called the Percus-Yevick equation. I won't explain the derivation, but we will mention some things about the Percus-Yevick equation

When constructing a functional theory that will be appropriate for inhomoge-

nous fluids, Rosenfeld had the freedom to dictate what the functional would say in the limit of a homogenous fluid. A great deal of work has been done with homogenous fluids and fluids mixtures. This work results in equations of state, which relate thermodynamic properties of homogenous fluids such as free energy pressure or free energy to the density. Rosenfeld chose to build up his intrinsic free energy functional so that in the limit of homogenous distribution it approached that given by the Percus-Yevik equation of state. This is a successful equation of state.

The result was the very successful Fundamental Measure Theory (in what ways was it successful?)

Later Roth et al. created there own fundamental measure functional that is in the limit of homogeneous density approaches not the Percis Yevik equation but instead the Carnahan-Starling equation of state. They do so because for the hard sphere fluid at high densities, approaching freezing, the pressure is over estimated in Percis Yevik. FMT follows the contact theorem, that  $\rho_w = \beta p$  where  $\rho_w$  is the contact density of spheres in contact with a hard wall, which means that this value is consequently overestimated. White Bear people keep many of the ideas in place, but replace the Percus-Yevik underlying equation of state to that of Mansoori-Carnahan-Starling-Leland: (reference below) As a consequence, the White Bear functional is extremely successful in predicting the density profiles of inhomogenous collections of hard spheres (examples?).

The diagramatic expression approach gives the virial equation and it's exact in low-density limit

The percis-Yevik equation of state that the original FMT is based on is not the

low density limit, say that the excess free energy function itself is built so that the thermodynamic equation of state of hard spheres is that given by the Perkis-Yevik equation of state.

This is the FMT that we use in our functionals so it is the one that we will briefly describe. Fill the first part of this out a bit more, or just explain more how you'd be able to get these things.

## 2.5 The convolution theorem

One of the largest advantages to using Fundamental Measure Theory, and one that is not immediately obvious, is that the convolutions that combine to construct the functional allow for very efficient computation. This is not very intuitive, since an integral of a convolution integral must integrate over two dimensions, e.g.

$$\int (f * g)(\mathbf{x}) d\mathbf{x} = \int \int f(\mathbf{y}) g(\mathbf{x} - \mathbf{y}) d\mathbf{y} d\mathbf{x} \quad (2.42)$$

so that it may seem that the size of the computation would scale as  $N^2$ , where  $N$  is the size of the system. It is true that in the case of FMT, the weighting functions cut off the integrals at the size on the order of a sphere of particle radius, but this can still be a large enough volume so that a double integral for which one of the volumes is this size and the other is the size of the whole system would be too costly for practical computation. FMT is saved, however, by what is called the Convolution Theorem. The Convolution Theorem states that when one takes the

Fourier Transform on a spatial convolution of two functions (a double integral in space), the result is two separate integrals over  $\mathbf{k}$ -space that are simply multiplied together. (SHOW IN EQ FORM) When minimizing our functional, after taking a Fourier Transform of the convolutions, we have merely to integrate once over the one variable  $\mathbf{k}$ . Wait! You may say. This is a cheat, since the Fourier Transform is itself an integral, so at the end of the day we're still performing two integrals. This would be true if it were not for the computational technique known as Fast Fourier Transforms, developed by (cite). I won't explain how it works here, but its effect is to perform the transform, which would normally have a computational cost on the order of  $N$ , with a computational cost on the order of  $\ln N$  instead. Thus, when we Fourier Transform the convolutions in the functional and proceed to take the single integral over the result (in  $\mathbf{k}$ -space), the computational cost scales as  $N \ln N$ . For large systems (we simulate systems with hundreds or even thousands of particles) this can certainly be the difference between practically possible and impossible computations. The proof is short and pretty so I'll relate it here:

$$\hat{h}(\mathbf{k}) = \hat{f}(\mathbf{k})\hat{g}(\mathbf{k}) \tag{2.43}$$

Is the convolution theorem. Proof:

$$h(\mathbf{x}) = (f * g)(x) = \int f(\mathbf{y})g(\mathbf{x} - \mathbf{y})d\mathbf{y} \quad (2.44)$$

$$\hat{f}(\mathbf{k}) = \int f(\mathbf{y})\exp(-i2\pi\mathbf{k} \cdot \mathbf{y})d\mathbf{y} \quad (2.45)$$

$$\hat{g}(\mathbf{k}) = \int g(\mathbf{y})\exp(-i2\pi\mathbf{k} \cdot \mathbf{y})d\mathbf{y} \quad (2.46)$$

$$\int h(\mathbf{r})\exp(-i2\pi\mathbf{k} \cdot \mathbf{z})d\mathbf{z} = \int \int f(\mathbf{y})g(\mathbf{z} - \mathbf{y})\exp(-i2\pi\mathbf{k} \cdot \mathbf{z})d\mathbf{y}d\mathbf{z} \quad (2.47)$$

because the two integrals are necessarily over all space,

$$\mathbf{x} = \mathbf{z} - \mathbf{y} \quad (2.48)$$

$$\hat{h}(\mathbf{k}) = \int \int f(\mathbf{y})\exp(-i2\pi\mathbf{k} \cdot \mathbf{y})d\mathbf{y}g(\mathbf{x})\exp(-i2\pi\mathbf{k} \cdot \mathbf{x})d\mathbf{x} \quad (2.49)$$

$$= \hat{f}(\mathbf{k})\hat{g}(\mathbf{k}) \quad (2.50)$$

## 2.6 Contact Value Theorem

Fixed number of particles:

$$F = U - TS \quad (2.51)$$

$$dU = TdS - pdV \quad (2.52)$$

$$dF = dU - TdS - SdT = -SdT - pdV \quad (2.53)$$

picture a fixed volume except a little protrusion into it, so call  $F_{out}$  and  $F_{flat}$ . So looking at partition functions:

$$Z_{flat} = \int_V \dots \int_V \exp(-\phi\{\mathbf{r}^N\}) d\mathbf{r}^N Z_{out} = \int_{V-dV} \dots \int_{V-dV} \exp(-\phi\{\mathbf{r}^N\}) d\mathbf{r}^N \quad (2.54)$$

Writing  $Z_{flat}$  in terms of  $Z_{out}$ :

$$\begin{aligned} Z_{flat} = & \int_{V-dV} \dots \int_{V-dV} \exp(-\phi\{\mathbf{r}^N\}) d\mathbf{r}^N \\ & + \int_V \dots \int_V \int_{V-dV} \exp(-\phi\{\mathbf{r}^N\}) d\mathbf{r}^N + \int_V \dots \int_{V-dV} \int_V \exp(-\phi\{\mathbf{r}^N\}) d\mathbf{r}^N \dots \\ & + \int_V \dots \int_V \int_{V-dV} \int_{V-dV} \exp(-\phi\{\mathbf{r}^N\}) d\mathbf{r}^N + \int_V \dots \int_{V-dV} \int_V \int_{V-dV} \exp(-\phi\{\mathbf{r}^N\}) d\mathbf{r}^N \dots \end{aligned} \quad (2.55)$$

The term on the first line is just  $Z_{out}$ . The terms on the second line treat one particle being in the bit of volume and the others being integrated over the rest of the volume. Because every particle is identical, it doesn't matter which is in the little bit of volume, each of these terms is the same. So they can be replaced by one of them multiplied by  $N$ . The terms on the last line or any line after are of order 2 or higher in  $dV$ . We will throw away these terms, and there are two arguments that allow us to do this. The simplest one is that  $dV$  is small, and so terms with a two  $dV$ s multiplied together will be small. One must be careful with this, however, because one is really integrating over the boltzmann factor over these volumes. If the interaction potential between the particles is constructed so that they are highly attracted to each other, than a state in which there are two

particles in the bit of volume can have the same order of magnitude probability as the one in which there is just one. In this case we would not be able to say for certain that these terms are so much smaller than the order 1  $dV$  terms on the second line that we could reasonably ignore them. Thus the validity of the derivation has to do with the size of your smallest measurement along the wall, and the nature of the attractive potential between the particles. In our case we deal with an interaction between hard spheres, which simply exclude other spheres from being too close to them. Thus it's reasonable for us to imagine that if there is one hard sphere in the bit of volume, then there is only the one, and any terms that address the situation in which there are two in the bit of volume can be ignored. After applying these arguments we have:

$$Z_{flat} = Z_{out} + N \int_V \dots \int_V \int_{V-dV} \exp(-\phi\{\mathbf{r}^N\}) d\mathbf{r}^N \quad (2.56)$$

Now we consider the statistical mechanical definition of the particle density,

$$n(\mathbf{r}) = \frac{N \int_V \dots \int_V \exp(-\phi\{\mathbf{r}^N\}) d\mathbf{r}^{N-1}}{\int_V \dots \int_V \exp(-\phi\{\mathbf{r}^N\}) d\mathbf{r}^N} \quad (2.57)$$

Which is the sum of the boltzmann factors of all the states for which a particle is at position  $\mathbf{r}$ , divided by the partition function for the system. Comparing this with the right-most term in the Eq. 2.56 we see that:

$$N \int_V \dots \int_V \int_{V-dV} \exp(-\phi\{\mathbf{r}^N\}) d\mathbf{r}^N = Z_{flat} \int_{dV} n(\mathbf{r}) d\mathbf{r} \approx Z_{flat} n(\mathbf{r}) dV \quad (2.58)$$



where on the right we make the approximation that because the volume is small  $n(\mathbf{r})$  is constant over it. Thus we have

$$Z_{flat} = Z_{out} + Z_{flat}n(\mathbf{r})dV \quad (2.59)$$

$$Z_{out} = Z_{flat}(1 - n(\mathbf{r})dV) \quad (2.60)$$

We have

$$\begin{aligned} dF = F_{out} - F_{flat} &= -kT \ln \left( \frac{Z_{out}}{Z_{flat}} \right) \\ &= -kT \ln \left( \frac{Z_{flat}(1 - n(\mathbf{r})dV)}{Z_{flat}} \right) \\ &= -kT \ln (1 - n(\mathbf{r})dV) \\ &= kTn(\mathbf{r})dV \end{aligned} \quad (2.61)$$

Then relating back to thermodynamics:

$$pdV = dF = kTn(\mathbf{r})dV \quad (2.62)$$

$$p = kTn(\mathbf{r}) \quad (2.63)$$

Eq. 2.63 is the standard formulation of the contact value theorem.

Another equation for the particle density is:

$$n(\mathbf{r}) = \frac{\delta \mathcal{F}}{\delta V_{ext}} \quad (2.64)$$

## 2.7 Remaining terms in SAFT

## 3 Correlation Functionat Contact

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## 4 Introduction to MinD Paper

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## 5 Conclusion

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## Bibliography

- [1] Kerwyn Casey Huang, Yigal Meir, and Ned S Wingreen. Dynamic structures in escherichia coli: spontaneous formation of mine rings and mind polar zones. *Proceedings of the National Academy of Sciences*, 100(22):12724–12728, 2003.

Figure 3.1: Smart 2nd figure

Table 3.1: Smart 2nd table

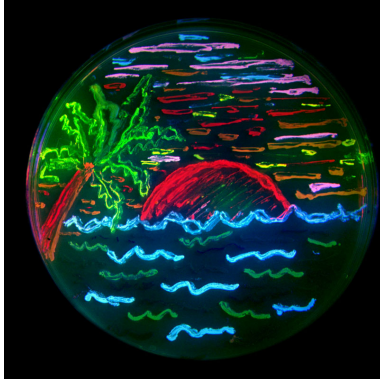


Figure 4.1: Smart third figure

## APPENDIX

### A First stuff in the appendix

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