

Density Functional Theory: The Classical Hard-Core Gas

by

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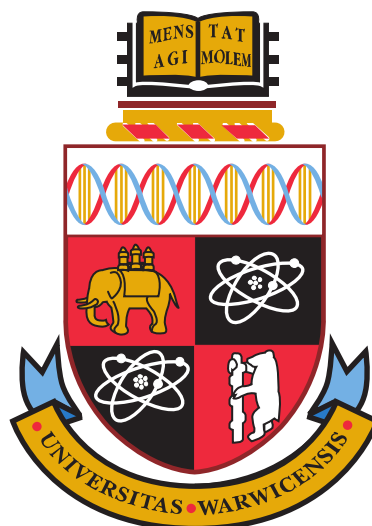
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Declarations

I, Simon Bignold, declare that to the best of my knowledge this work constitutes an original review compiled by the author except when otherwise specified by the references.

The material in this thesis has not to my knowledge been submitted for any other degree either at this university (the University of Warwick) or any other university.

Abstract

This paper gives a review of some problems in classical density functional theory using the canonical ensemble. We will introduce the concepts necessary for a basic understanding of this area and apply them to the exactly solvable model of the ideal gas. We will then use the one-dimensional hard-core model as a motivation in developing more generally applicable approximations.

Chapter 1

Introduction

1.1 The Importance of the Free Energy

An important quantity that will be the goal of most of our calculations is the Helmholtz free energy (hereafter known just as the free energy). This can be simply defined (see page 23 of [1]) as the canonical average of the Hamiltonian (see (2.6)) minus the product of temperature and the system entropy

$$A_{\beta}^{\Lambda N}[V] = E - TS_{\Lambda} \quad (1.1)$$

where the dependencies on the left-hand side will become clear in Chapter 2. Thus the free energy is the Legendre transform of the internal energy with respect to temperature.

The most important feature of the free energy from our point of view is that it can be shown (see for example Subsection 1.1.2 of [3]) that the free energy is minimised at equilibrium if the temperature is held constant. This means that if we find an expression for the free energy the configuration that minimises it will give the equilibrium configuration of our system.

To allow us to calculate a quantity similar to the free energy in the thermodynamic limit, where the system becomes infinite and thus so does our free energy, we define the free energy per particle. We also hope that this quantity will depend less on the number of particles within the system. Our free energy per particle is defined as

$$\mathcal{F}_{\beta}^{\Lambda N}[V] = \frac{1}{N}A_{\beta}^{\Lambda N}[V].$$

1.2 Density Functional Theory

One of the earliest recognised examples of Density Functional Theory (DFT) is the Thomas-Fermi theory and there exist many papers on DFT in a quantum context (see

for example [8], [13] for a high level of detail or [4] for a nice introduction). However in this paper we follow the first half of [7] and generally only consider DFT in a classical context.

The main idea of DFT for our purposes is that we can express the free energy as the sum of a functional of one-particle density only (see Chapter 3 for further details) and another term. This method is advantageous as we are now able to treat many problems “to a sufficiently high accuracy, as well as [the method] being computationally simple” (page 1 [7]). We hope to justify these claims in the latter parts of this paper.

We use the fact that the external potential that acts on each particle $V(x)$ is a conjugate variable to the one-particle density $\rho_{\Lambda^N}^{(1)}(x)$ (see page 11 of [7]). We first note that for a given system in the canonical and grand canonical ensemble, the free energy is a functional of the external potential. We can then use a Legendre transform to rewrite the free energy

$$A_{\beta}^{\Lambda^N}[V] = F_{HK}[\rho_{\Lambda^N}^{(1)}(x)] + \int_{\Lambda} V(x)\rho_{\Lambda^N}^{(1)}(x)dx \quad (1.2)$$

where F_{HK} is the Hohnberg-Kohn functional and is a unique functional of the one-particle density. The justification of this and the terminology used is given latter in this text (Section 4.2).

1.3 Outline

In this paper we wish to consider classical DFT in the canonical ensemble, due to the constraints of this paper we will only concentrate on two models the ideal gas and the hard-core model.

We begin by defining the basic concepts needed for classical DFT. As we are only considering the canonical ensemble, our first chapter is dedicated to introducing the statistical mechanical concepts necessary for this. We then introduce our most important concept the one-particle density, and give three ways of obtaining it. We conclude with a chapter where we introduce our main model the hard-core model and prove the Hohenberg-Kohn theorem which provides the theoretical justification for our later attempts to give the free energy as a functional of one-particle density plus an extra term (specifically the form given in (1.2)).

We then give our first attempt to formulate a DFT form of the free energy. To this end we consider the ideal gas a case were the internal potential is zero. This model has the advantage that we can formulate an exact expression for the free energy and will prove an important tool in our later approximations.

Having achieved a formula for the ideal gas we now move onto our second model the hard-core gas. We initially attempt to obtain an explicit formula using two techniques both of which are only applicable in the one-dimensional case. Our first technique requires the use of Laplace transforms and can be adapted for a range of potentials close to the hard-core potential which we also demonstrate. We take the zero distance limit of our hard-core model and show that in the thermodynamic limit we obtain the ideal gas case. This technique is however limited by the external potentials we can use, a topic discussed further in the first appendix. Therefore we consider a second technique where we start with a discrete approximation of our space obtain the free energy and take the continuum limit to obtain another formula.

So far our explicit formulations are only one-dimensional, we therefore develop an approximation which can be applied in higher dimension. Our approximation is based on a Mayer expansion and we hope that the techniques may be applicable to other internal potentials although for consistency we only consider the hard-core case. A brief appendix summarises some of the conditions needed such that our Mayer expansion can be curtailed.

We conclude this paper with a summary and an outlook. In the outlook we consider how this work could be extended to other applications in classical DFT. We first summarise the problems highlighted by this current work and how they might be dealt with. We finish with a summary of how we could consider more general internal potentials and thus a much greater number of classical DFT problems.

Chapter 2

Statistical Mechanics Background

2.1 Different Ensembles

In statistical mechanics there are three main ensembles that are commonly used: the micro-canonical, the canonical and the grand canonical (see [1] for more details). Most recent calculations are obtained using either of the latter two (see Section 4 [1]). For simplicity we choose to concentrate only on the canonical ensemble which we discuss below.

2.1.1 Canonical Ensemble

Here we confine our particles to a finite box $\Lambda \subset \mathbb{R}^d$ where d is the dimension of the space. In this case we have a strictly fixed positive integer number of particles N and each of the N particles has its momentum denoted by a d dimensional vector $p_i \in \mathbb{R}^d$. We choose a Hamiltonian depending on the boundary $H_{\Lambda^N}^V$. We also define

$$\beta = \frac{1}{k_B T} \tag{2.1}$$

where k_B is Boltzmann's constant and $\beta > 0$ since T is strictly positive. The N -body configuration of positions is denoted

$$X_N = (x_1, \dots, x_N) \in \Lambda^N \tag{2.2}$$

and the N -body configuration of momenta is denoted

$$P_N = (p_1, \dots, p_N) \in \mathbb{R}^{dN}. \tag{2.3}$$

Given the above N body position (2.2) and momentum (2.3) configuration we choose the Hamiltonian of such a static system to be given as

$$H_{\Lambda^N}^V(X_N, P_N) = \underbrace{\sum_{1 \leq i < j \leq N} W(x_i - x_j)}_{\text{inter-particle interaction } U} + \underbrace{\sum_{i=1}^N V(x_i)}_{\text{external potential}} + \underbrace{\sum_{i=1}^N \frac{p_i^2}{2m}}_{\text{Kinetic term } K} \quad (2.4)$$

where for simplicity we have chosen the external potential to depend only on the position of a particle and to act identically on all particles (they are indistinguishable). Also our internal potential (inter-particle interaction) is taken to depend only on the difference in position between any two particles.

Following Section 4.1 of [1] we define

Definition 1. *Canonical Gibbs Ensemble* is characterised by the probability measure $\gamma_{\Lambda, N}^\beta \in \mathcal{P}(\Lambda, \mathcal{B}_\Lambda)$ with density;

$$\rho_{\Lambda, N}^\beta(X_N, P_N) = \frac{\exp[-\beta H_{\Lambda^N}^V(X_N, P_N)]}{N! Z_\Lambda(\beta, N)} \quad (2.5)$$

with respect to the Lebesgue measure. \mathcal{B}_Λ is the Borel σ -algebra on Λ .

Compared to [1] we have introduced a divisor of $N!$ to account for the indistinguishability of the particles.

$Z_\Lambda(\beta, N)$ is a normalisation factor known as the partition function, we cover this in more detail in Section 2.2.

The canonical average of the Hamiltonian is then

$$\begin{aligned} E &= \langle H_{\Lambda^N}^V(X_N, P_N) \rangle_C \\ &= \frac{\int_{\mathbb{R}^d} \int_{\Lambda^N} H_{\Lambda^N}^V(X_N, P_N) \exp[-\beta H_{\Lambda^N}^V(X_N, P_N)] dX_N dP_N}{N! Z_\Lambda(\beta, N)} \end{aligned} \quad (2.6)$$

2.2 The Partition Function

In the canonical ensemble we define the partition function

$$\begin{aligned} Z_\Lambda(\beta, N) &= \frac{1}{N!} \int_{\mathbb{R}^{dN}} \int_{\Lambda^N} \exp[-\beta H_{\Lambda^N}^V(X_N, P_N)] dX_N dP_N \\ &= \frac{1}{N!} \left(\prod_{i=0}^N \int_{\mathbb{R}^d} \exp\left[-\beta \frac{p_i^2}{2m}\right] dp_i \right) \\ &\quad \times \int_{\Lambda^N} \prod_{i=1}^N \exp[-\beta V(x_i)] \prod_{1 \leq i < j \leq N} \exp[-\beta W(x_i - x_j)] dX_N \end{aligned} \quad (2.7)$$

$Z_\Lambda(\beta, N)$ is required for the normalisation of the probability measure in the canonical Gibbs ensemble. The momentum part is a Gaussian integral and is therefore easily calculated.

Following page 23 of [1] we can re-write the free energy as

$$A_\beta^{\Lambda^N}[V] = -\frac{1}{\beta} \ln [Z_\Lambda(\beta, N)] \quad (2.8)$$

and our free-energy per particle is

$$\mathcal{F}_\beta^{\Lambda^N}[V] = -\frac{1}{\beta N} \ln [Z_\Lambda(\beta, N)].$$

We note that using (2.7) the free energy can be written as:

$$\begin{aligned} A_\beta^{\Lambda^N}[V] &= -\frac{1}{\beta} \ln [Z_\Lambda(\beta, N)] \\ &= \underbrace{-\frac{1}{\beta} \ln \left[\prod_{i=0}^N \int_{\mathbb{R}^d} \exp \left[-\beta \frac{p_i^2}{2m} \right] dp_i \right]}_{\text{Kinetic free energy}} \\ &\quad + \underbrace{-\frac{1}{\beta} \ln \left[\frac{1}{N!} \int_{\Lambda^N} \prod_{i=1}^N \exp [-\beta V(x_i)] \prod_{1 \leq i < j \leq N} \exp [-\beta W(x_i - x_j)] dX_N \right]}_{\text{configurational free energy}}. \end{aligned}$$

We can thus see that the free energy can be written as the sum of a kinetic part which will be the same for all systems and a configurational part which will not. The same is obviously true of the free energy per particle. Thus we use the notation

$$\begin{aligned} Z_\Lambda(\beta, N) &= \underbrace{\left(\prod_{i=0}^N \int_{\mathbb{R}^d} \exp \left[-\beta \frac{p_i^2}{2m} \right] dp_i \right)}_{\text{kinetic partition function}} \\ &\quad \times \underbrace{\frac{1}{N!} \int_{\Lambda^N} \prod_{i=1}^N \exp [-\beta V(x_i)] \prod_{1 \leq i < j \leq N} \exp [-\beta W(x_i - x_j)] dX_N}_{\text{configurational partition function}}. \quad (2.9) \end{aligned}$$

For convenience we label the configurational free energy as $A_{\beta, \text{con}}^{\Lambda^N}[V]$, the configurational partition function as $Z_{\Lambda, \text{con}}(\beta, V)$ and the configurational free energy per particle as $\mathcal{F}_{\beta, \text{con}}^{\Lambda^N}[V]$.

Chapter 3

One-Particle Density

3.1 One-Particle Density

To undertake DFT we need to define the one (or single) particle density. This is our first concept specific to DFT as the concepts of Chapter 2 are applicable to a wide variety of statistical mechanics situations. This concept can be defined in three different ways, the method used will be chosen to be convenient for the specific problem we are trying to solve.

3.1.1 Integrating out $N - 1$ Variables

In Section 2.1 we defined a probability density for the canonical ensemble. This depends on the positions and momenta of N particles and so can be considered as a N -particle density (after integration over momentum phase space). Therefore a definition of a one-particle density could be obtained by integrating over $N - 1$ positions (and N momenta) to obtain a function that depends only on the position of one-particle. Since we have N particles there are N possible ways of doing this but since all the integrations we do are the same we can re-name the variables and obtain in the case of the canonical ensemble

Definition 2. Canonical One-particle Density

$$\rho_{\Lambda^N}^{(1)}(x) = \frac{N \int_{\mathbb{R}^{dN}} \int_{\Lambda^{N-1}} \exp[-\beta H_{\Lambda^N}^V(X_N, P_N)] dx_2 \dots dx_N dP_N}{N! Z_{\Lambda}(\beta, N)} \quad (3.1)$$

This definition has the advantage that in the canonical ensemble integrating the one particle density gives the total number of particles as expected

$$\begin{aligned} \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) dx &= \frac{N \int_{\Lambda^N} \int_{\mathbb{R}^N} \exp[-\beta H_{\Lambda^N}^V(X_N, P_N)] dX_N dP_N}{N! Z_{\Lambda}(\beta, N)} \\ &= N. \end{aligned}$$

3.1.2 Average over δ -functions

Following page 3 of [7] (which actually applies to the grand canonical ensemble) we can write one-particle density as the ensemble average over a sum of N δ -functions centered at the appropriate particle position.

$$\rho^{(1)}(x) = \left\langle \sum_{i=0}^N \delta(x - x_i) \right\rangle_E .$$

We can show that in the canonical ensemble this is equivalent to the definition given in the section above (Subsection 3.1.1). We have

$$\begin{aligned} \rho_{\Lambda^N}^{(1)}(x) &= \left\langle \sum_{i=0}^N \delta(x - x_i) \right\rangle_C \\ &= \frac{\int_{\mathbb{R}^{dN}} \int_{\Lambda^N} \sum_{i=0}^N \delta(x - x_i) \exp[-\beta H_{\Lambda^N}^V(X_N, P_N)] dX_N dP_N}{N! Z_{\Lambda}(\beta, N)} \\ &= \frac{N \int_{\mathbb{R}^{dN}} \int_{\Lambda^{N-1}} \exp[-\beta H_{\Lambda^N}^V(X_N, P_N)] dx_2 \dots dx_N dP_N}{N! Z_{\Lambda}(\beta, N)} \end{aligned} \quad (3.2)$$

where the third line follows by re-naming the integration variables. We can thus see that the results are equivalent to those in Subsection 3.1.1.

3.1.3 Functional Derivative

Again following [7] (page 3) we can in the canonical ensemble write the one-particle density as the functional derivative of the free energy with respect to the external potential.

We know that the functional derivative $\rho_{\Lambda^N}^{(1)} = \delta A_{\beta}^{\Lambda^N} / \delta V$ can be defined using a test function φ via

$$\left\langle \frac{\delta A_{\beta}^{\Lambda^N}[V]}{\delta V(x)}, \varphi(x) \right\rangle = \int_{\Lambda} \varphi(x) \frac{\delta A_{\beta}^{\Lambda^N}[V]}{\delta V(x)} dx.$$

Hence we can now find the one-particle density. Using the formula for free energy, (2.8) where we relabel the partition function to make the potential dependence clear, we have

$$\begin{aligned} \left\langle \frac{\delta A_{\beta}^{\Lambda^N}[V]}{\delta V(x)}, \varphi(x) \right\rangle &= \frac{d}{ds} \left(-\frac{1}{\beta} \log [Z_{\Lambda, N}(\beta, V + s\varphi)] \right) \Big|_{s=0} \\ &= \frac{-\frac{1}{\beta} \frac{d}{ds} Z_{\Lambda, N}(\beta, V + s\varphi) \Big|_{s=0}}{Z_{\Lambda}(\beta, N)}. \end{aligned} \quad (3.3)$$

Using the definition of the canonical partition function (2.7) we have

$$Z_{\Lambda,N}(V + s\varphi) = \frac{\int_{\Lambda^N} \prod_{i=1}^N \exp[-\beta(V(x_i) + s\varphi)] \prod_{1 \leq i < j \leq N} \exp[-\beta W(x_i - x_j)] dX_N}{N!} \\ \times \left(\int_{\mathbb{R}^d} \exp\left[\frac{-\beta p^2}{2m}\right] dp \right)^N$$

so with some appropriate re-naming of variables we have

$$\left. \frac{d}{ds} Z_{\Lambda,N}(\beta, V + s\varphi) \right|_{s=0} = \frac{\int_{\Lambda^N} \varphi(x_1) \prod_{i=1}^N \exp[-\beta(V(x_i))] \prod_{1 \leq i < j \leq N} \exp[-\beta W(x_i - x_j)] dX_N}{N!} \\ \times N(-\beta) \left(\int_{\mathbb{R}^d} \exp\left[\frac{-\beta p^2}{2m}\right] dp \right)^N. \quad (3.4)$$

We can now substitute this into (3.3) to give

$$\left\langle \frac{\delta A_{\beta}^{\Lambda^N}[V]}{\delta V(x)}, \varphi(x) \right\rangle = \frac{N \int_{\Lambda^N} \varphi(x_1) \prod_{i=1}^N \exp[-\beta(V(x_i))] \prod_{1 \leq i < j \leq N} \exp[-\beta W(x_i - x_j)] dX_N}{N! Z_{\Lambda}(\beta, N)} \\ \times \left(\int_{\mathbb{R}^d} \exp\left[\frac{-\beta p^2}{2m}\right] dp \right)^N.$$

Hence we can now find the one-particle density

$$\rho_{\Lambda^N}^{(1)}(x) = \frac{\delta A_{\beta}^{\Lambda^N}[V]}{\delta V(x)} \\ = \frac{N \int_{\Lambda^{N-1}} \prod_{i=1}^N \exp[-\beta(V(x_i))] \prod_{1 \leq i < j \leq N} \exp[-\beta W(x_i - x_j)] dx_2 \dots dx_N}{N! Z_{\Lambda}(\beta, N)} \\ \times \left(\int_{\mathbb{R}^d} \exp\left[\frac{-\beta p^2}{2m}\right] dp \right)^N.$$

Therefore all three of our formulas for the one-particle density are equivalent.

Chapter 4

Techniques

We now introduce various useful techniques. The hard-core model is introduced as an important test case which is more complicated than the ideal gas but may still be approachable analytically. The Hohenberg-Kohn Theorem is fundamental to DFT as it allows us to justify equation (1.2) and thus gives theoretical justification for our main goal of approximating the free energy by a functional of density.

4.1 The Hard-Core Model

In this model we consider N particles of equal mass m which move freely in the interval $[0, L]$. Any two particles are excluded from coming within a distance a of each other. Thus for any two particles with positions x_1 and x_2 we have the potential

$$\begin{cases} W_a(x_1 - x_2) = 0 & |x_1 - x_2| > a \\ W_a(x_1 - x_2) = \infty & |x_1 - x_2| \leq a \end{cases}.$$

We require that a the radius of the hard-core is less than the close-packing radius, which is the radius we would have if the line is filled by N particles with no space left over, which is equivalent to dividing the line into N segments

$$a \leq a_{cp} = \frac{L}{N}.$$

This concept of the hard core can be extended to M dimensions by using the interval $[0, L]^M$ the M -dimensional vectors $\mathbf{r}_i = (x_1^i, x_2^i \dots x_M^i)$ in place of x_1 and x_2 and the Euclidean norm in place of the modulus. The length of our box in each dimension need not necessarily be the same in which case our interval is

$$\Lambda \subset \mathbb{R}^M.$$

The close-packing density is calculated in a slightly different way depending on the dimension. For example in two dimensions we cover the plane with a triangular lattice where

the number of nodes is the smallest possible number greater than N , the diagonal distance between two nodes is the close-packing density. In three dimensions we cover the space with a body-centered cubic lattice where the number of nodes is the smallest possible number greater than N , the diagonal distance within the cube is then the close-packing density.

We can therefore define the d dimensional hard-core potential

$$\begin{cases} W_a(\mathbf{r}_i - \mathbf{r}_j) = 0 & \|\mathbf{r}_i - \mathbf{r}_j\| > a \\ W_a(\mathbf{r}_i - \mathbf{r}_j) = \infty & \|\mathbf{r}_i - \mathbf{r}_j\| \leq a \end{cases}$$

where $a < a_{cp}$.

Then the internal energy as defined in (2.4) is given as

$$U = \sum_{1 \leq i < j \leq N} W_a(x_i - x_j)$$

A summary of some of the results for DFT in the hard-core case are given in Section 4.3 of [9].

4.2 Hohenberg-Kohn Theorem

We now follow Section 4.2 of [15]. In contrast to [15] we use the canonical ensemble rather than the grand canonical ensemble.

We define

$$\hat{\rho}_V(x) = \sum_{i=1}^N \delta(x - x_i).$$

First we note that, following Section 3.1.2, the canonical average of this is the one-particle density. We then see that we can now re-write the total external potential of the system as the integral of $\hat{\rho}_V(x)$ multiplied by the external potential acting at the point x .

$$\begin{aligned} \int_{\Lambda} \hat{\rho}_V(x) V(x) dx &= \sum_{i=1}^N \int_{\Lambda} \delta(x - x_i) V(x) dx \\ &= \sum_{i=1}^N V(x_i). \end{aligned}$$

We can now redefine the probability density of the canonical ensemble using (2.5) to give:

$$p_V = \frac{\exp \left[-\beta \left(K + U + \int_{\Lambda} \hat{\rho}_V(x) V(x) dx \right) \right]}{N! Z_{\Lambda}(\beta, N)} \quad (4.1)$$

where K is the kinetic contribution and U is the internal energy.

We know from above ((1.1))

$$\begin{aligned} A_{\beta}^{\Lambda^N}[V] &= E - TS_{\Lambda} \\ &= \int_{\mathbb{R}^d} \int_{\Lambda^N} p_V \left(K + U + \int_{\Lambda} \hat{\rho}_V(x) V(x) dx + \beta^{-1} \ln p_V \right) dX_N dP_N \end{aligned} \quad (4.2)$$

where in the last line we use the definition of Shannon entropy from Notation 3.3 of [1]

$$S = -k_B \int_{\mathbb{R}^d} \int_{\Lambda^N} p_V \ln p_V dX_N dP_N.$$

Thus $A_{\beta}^{\Lambda^N}[V]$ is also a functional of p_V , $A[p_V]$. Given a new potential V' we can define a new probability density

$$p_{V'} = \frac{\exp \left[-\beta \left(K + U + \int_{\Lambda} \hat{\rho}_V(x) V'(x) dx \right) \right]}{N! Z'_{\Lambda}(\beta, N)} \quad (4.3)$$

where $Z'_{\Lambda}(\beta, N)$ is the appropriate normalisation, we do not have to change K and U as they are un-affected by the external potential. With this new probability density we are able to give a similar functional A

$$\begin{aligned} A[p_{V'}] &= \int_{\mathbb{R}^d} \int_{\Lambda^N} p_{V'} \left(K + U + \int_{\Lambda} \hat{\rho}_V(x) V(x) dx + \beta^{-1} \ln p_{V'} \right) dX_N dP_N \\ &= A[p_V] + \beta^{-1} \int_{\mathbb{R}^d} \int_{\Lambda^N} [p_{V'} \ln p_{V'} - p_{V'} \ln p_V] dX_N dP_N \end{aligned} \quad (4.4)$$

We now consider the last term. First we state the easily proved inequality

$$\ln[x] \leq x - 1 \quad \forall x > 0$$

which has equality if and only if $x = 1$. Using $x = p_{V'}/p_V$ then multiplying by $-p_V$ and integrating we can obtain the Gibbs' inequality after realising that both p_V and $p_{V'}$ are probability densities. The Gibbs' inequality is

$$- \int_{\mathbb{R}^d} \int_{\Lambda^N} p_V \ln p_V dX_N dP_N \leq - \int_{\mathbb{R}^d} \int_{\Lambda^N} p_V \ln p_{V'} dX_N dP_N \quad (4.5)$$

with equality if and only if $p_V = p_{V'}$. Thus we can see from (4.4)

$$A[p_V] < A[p_{V'}] \quad p_V \neq p_{V'}. \quad (4.6)$$

Using the definitions of p_V and $p_{V'}$ ((4.1) and (4.3)) as well as the equation for the free energy (2.8) we see that

$$\begin{aligned} -\beta^{-1} \int_{\mathbb{R}^d} \int_{\Lambda^N} p_V \ln p_V dX_N dP_N &= \int_{\mathbb{R}^d} \int_{\Lambda^N} p_V \left(K + U + \int_{\Lambda} V(x) \hat{\rho}_V(x) dx \right) dX_N dP_N \\ &\quad - A_{\beta}^{\Lambda^N} [V] + \beta^{-1} \ln[N!] \\ -\beta^{-1} \int_{\mathbb{R}^d} \int_{\Lambda^N} p_V \ln p'_{V'} dX_N dP_N &= \int_{\mathbb{R}^d} \int_{\Lambda^N} p_V \left(K + U + \int_{\Lambda} V'(x) \hat{\rho}_V(x) dx \right) dX_N dP_N \\ &\quad - A_{\beta}^{\Lambda^N} [V'] + \beta^{-1} \ln[N!] \end{aligned}$$

where the integral over p_V for the last two terms in both cases is ignored as they are not functions of p_V and p_V is normalised.

Hence using the Gibbs' inequality (4.5) we have

$$A_{\beta}^{\Lambda^N} [V'] \leq A_{\beta}^{\Lambda^N} [V] + \int_{\Lambda} [V'(x) - V(x)] \rho_{\Lambda^N}^{(1)}(x) dx$$

where we have used that the one particle density $\rho_{\Lambda^N}^{(1)}(x)$ is the ensemble average of $\hat{\rho}_V$. Changing the primed variables to un-primed and vice versa we have

$$A_{\beta}^{\Lambda^N} [V] \leq A_{\beta}^{\Lambda^N} [V'] + \int_{\Lambda} [V(x) - V'(x)] \rho_{\Lambda^N}^{(1)}(x) dx$$

for both these equations to hold we must have

$$V(x) = V'(x).$$

This means that for a given one particle density, the potential is unique.

Therefore given our equation for $A_{\beta}^{\Lambda^N}$ (4.2) and our definition of p_V we can see that A is a uniquely defined functional of the trial density $\rho_{\Lambda^N}^{(1)}$ or $\rho_{\Lambda^N}^{(1)'}$, $A = A[\rho_{\Lambda^N}^{(1)}(x)]$ and thus by (4.6) that the equilibrium density corresponds to the minimum value of the functional A .

We therefore know that:

$$\frac{\delta A[\rho_{\Lambda^N}^{(1)}(x)]}{\delta \rho_{\Lambda^N}^{(1)}(x)} = 0.$$

The trial density and therefore implicitly our free energy depend on $V'(x)$ to avoid this we define a new quantity

$$F_{HK}[\rho_{\Lambda^N}^{(1)}(x)] = A_{\beta}^{\Lambda^N}[\rho_{\Lambda^N}^{(1)}(x)] - \int_{\Lambda} V(x) \rho_{\Lambda^N}^{(1)}(x) dx$$

for a given system p_V is uniquely determined by $\rho_{\Lambda^N}^{(1)}(x)$ (see equation 68 [15]). So F_{HK} is a unique functional of density and our formula (1.2) is justified.

Although in principle this means that we can express the free energy as a functional of the one-particle density and an additional term in any case, in reality analytical forms of F_{HK} are rarely known and we have to approximate this functional.

Chapter 5

The Ideal Gas

5.1 The Ideal Gas in the Canonical Ensemble

We now consider the case of the ideal gas which has the simplest possible internal interactions (i.e. none). In this case unusually we can find a relatively uncomplicated analytical form of the free energy as a functional of the one particle density.

This follows pages 24-25 of [1]. Consider a non-interacting gas of N identical particles of mass m in d dimensions contained in a box $\Lambda \subset \mathbb{R}^d$ of finite volume. If an external force V acts on the system then the Hamiltonian of this system is (using again (2.2) and (2.3))

$$H_{\Lambda}^V(X_N, P_N) = \frac{1}{2m} \sum_{i=1}^N p_i^2 + \sum_{i=1}^N V(x_i) \quad (X_N, P_N) \in \Gamma_{\Lambda} \quad (5.1)$$

following (2.4) where

$$\Gamma_{\Lambda} = (\Lambda \times \mathbb{R}^d)^N. \quad (5.2)$$

We have for the partition function (comparing to the calculations in [1] we have set $h = 1$)

$$\begin{aligned} Z_{\Lambda}(\beta, N) &= \frac{1}{N!} \int_{\Gamma_{\Lambda}} \exp[-\beta H_{\Lambda}^V(X_N, P_N)] dX_N dP_N \\ &= \frac{1}{N!} \left(\int_{\Lambda} \exp[-\beta V(x)] dx \right)^N \left(\int_{\mathbb{R}^d} \exp\left[-\frac{\beta p_1^2}{2m}\right] dp_1 \right)^N \end{aligned}$$

where we have used the property of the exponential to split up the integrals to a spatial integral and a momentum integral. We can also use this to split up the momentum integrals, which means we can use any of the d -dimensional momentum vectors so we choose to use p_1 .

We can then define

$$z_{\beta}(dx_i) = dx_i \exp[-\beta V(x_i)] \quad (5.3)$$

thus

$$z_{\beta}^{(N)}(dX_N) = z_{\beta}(dx_1) \dots z_{\beta}(dx_N) \quad (5.4)$$

and we define

$$\begin{aligned} z(\Lambda)^N &= \int_{\Lambda^N} z^{(N)}(dX_N) \\ &= \left(\int_{\Lambda} z_{\beta}(dx) \right)^N. \end{aligned} \quad (5.5)$$

We thus find

$$Z_{\Lambda}(\beta, N) = \frac{1}{N!} z(\Lambda)^N \left(\frac{2\pi m}{\beta} \right)^{\frac{1}{2}Nd} \quad (5.6)$$

where we have used for each component of the momentum the appropriately rescaled standard formula for the Gaussian integral. We define

$$\lambda = \left(\frac{\beta}{2\pi m} \right)^{\frac{1}{2}}.$$

We can now write the partition function in a simpler form

$$Z_{\Lambda}(\beta, N) = \frac{1}{N!} \left(\frac{z(\Lambda)}{\lambda^d} \right)^N. \quad (5.7)$$

We use this to derive the free-energy

$$\begin{aligned} A_{\beta}^{\Lambda^N}[V] &= -\frac{1}{\beta} \ln [Z_{\Lambda}(\beta, N)] \\ &= \beta^{-1} (\ln [N!] + Nd \ln \lambda - N \ln [z(\Lambda)]). \end{aligned} \quad (5.8)$$

5.2 The Density Functional Form

Given the Hohenberg-Kohn theorems we seek a free energy of the form

$$A_{\beta}^{\Lambda^N}[V] = F_{HK} \left[\rho_{\Lambda^N}^{(1)}(x) \right] + \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) V(x) dx. \quad (5.9)$$

Using the definition of the one-particle density as the functional derivative of the free energy (see Subsection 3.1.3), we have

$$\rho_{\Lambda^N}^{(1)}(x) = \frac{N \exp[-\beta V(x)]}{z(\Lambda)}.$$

This relation allows us to re-write the external potential as a function of the density we state it here for clarity

$$V(x) = -\beta^{-1} \ln \left[\frac{\rho_{\Lambda^N}^{(1)}(x) z(\Lambda)}{N} \right].$$

Thus we can find an expression for external potential dependent term in the expression for the free energy (5.9)

$$\begin{aligned} \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) V(x) dx &= -\beta^{-1} \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) \ln \left[\frac{\rho_{\Lambda^N}^{(1)}(x) z(\Lambda)}{N} \right] dx \\ &= -\beta^{-1} \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) \ln \left[\rho_{\Lambda^N}^{(1)}(x) \right] dx - \beta^{-1} N \ln \left[\frac{z(\Lambda)}{N} \right] \end{aligned}$$

where in the second line we have used that z and N are independent of x and that the integral of the density over the phase space is N .

We can thus now re-write the free energy

$$\begin{aligned} A_{\beta}^{\Lambda^N}[V] &= \beta^{-1} (\ln [N!] + Nd \ln \lambda) + \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) V(x) dx + \beta^{-1} \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) \ln \left[\rho_{\Lambda^N}^{(1)}(x) \right] dx \\ &\quad - \beta^{-1} N \ln N \\ &= \beta^{-1} \left(Nd \ln \lambda + \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) \ln \left[\rho_{\Lambda^N}^{(1)}(x) \right] dx - N + O(\ln N) \right) \\ &\quad + \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) V(x) dx \end{aligned}$$

where in the second line we have used Stirling's approximation [10]

$$\sqrt{2\pi N} N^N \exp[-N] \exp \left[\frac{1}{12N+1} \right] \leq N! \leq \sqrt{2\pi N} N^N \exp[-N] \exp \left[\frac{1}{12N} \right] \quad (5.10)$$

to give

$$\ln N! = N \ln N - N + O(\ln N). \quad (5.11)$$

If we normalise the density

$$\begin{aligned} \tilde{\rho}(x) &= \frac{\rho_{\Lambda^N}^{(1)}(x)}{\int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) dx} \\ &= \frac{\rho_{\Lambda^N}^{(1)}(x)}{N} \end{aligned} \quad (5.12)$$

then we can give the free energy per particle

$$\mathcal{F}_{\beta}^{\Lambda^N}[V] = \beta^{-1} \left(d \ln \lambda + \int_{\Lambda} \tilde{\rho}(x) \ln [\tilde{\rho}(x) N] dx - 1 + O\left(\frac{\ln N}{N}\right) \right) + \int_{\Lambda} \tilde{\rho}(x) V(x) dx.$$

As we know that N can be written as the integral of $\rho_{\Lambda^N}^{(1)}(x)$ over Λ (Subsection 3.1.1) so

we can now remove all reference to N in the leading order terms

$$A_{\beta}^{\Lambda N}[V] = \beta^{-1} \int_{\Lambda} \rho_{\Lambda N}^1(x) (\ln [\rho_{\Lambda N}^1(x)] + d \ln \lambda - 1) dx + \int_{\Lambda} \rho_{\Lambda N}^1(x) V(x) dx + O(\ln N)$$

and the free energy per particle is

$$\begin{aligned} \mathcal{F}_{\beta}^{\Lambda N}[V] &= \beta^{-1} \left(d \ln \lambda + \int_{\Lambda} \tilde{\rho}(x) \ln [\rho_{\Lambda N}^{(1)}(x)] dx - 1 \right) + \int_{\Lambda} \tilde{\rho}(x) V(x) dx \\ &\quad + O\left(\frac{\ln N}{N}\right) \end{aligned}$$

In the thermodynamic limit $N \rightarrow \infty$ the final term vanishes. This means that although we are able to express $A_{\beta}^{\Lambda N}[V]$ as a functional of $\rho_{\Lambda N}^{(1)}(x)$ plus an extra term, even in this case a simple form exists only in the thermodynamic limit.

Chapter 6

Tonks Gas

6.1 General Case

Given our success in obtaining a DFT form of the free energy in the ideal gas case we now consider a slightly more complicated internal energy. To this end in this chapter we consider a way of obtaining the configurational part of the free energy for a hard-core gas in one dimension. The main objective of this chapter is to show that even in this case we have to make major simplifications.

Following pages 120-124 of [14] we define a pair potential W_a such that

$$W_a(x_i - x_j) = \begin{cases} \infty & \text{for } |x_i - x_j| < a \text{ (hard-core)} \\ \psi(x_i - x_j - a) & \text{for } a < |x_i - x_j| < 2a \\ 0 & \text{for } |x_i - x_j| > 2a \end{cases}$$

In the case $\psi = 0$ this reduces to the Tonks (hard-core) gas. However we retain this formula to allow greater generality. A more general form of ψ (which we call the decreasing potential) that we could also use is

$$\psi(x_i - x_j - a) = \frac{1}{(|x_i - x_j| - a)^m} \quad m > 0.$$

This has the advantage that it covers a larger range of potentials and can be chosen to more closely mimic the Lennard-Jones potential which is a commonly used potential (equation 3 of [2]).

Since we are in one dimension the particles lie along a line. Since the particles have diameter a the distance between nearest neighbours is at least a and thus the final line ensures that the contributions from next nearest and further neighbours vanish. This statement relies on the one-dimensional nature of our product.

We now give the general formula for the configurational partition function (which we write as $Z_{\Lambda, \text{con}}(\beta, V) = \mathfrak{Z}(L)$):

$$\mathfrak{Z}(L) = \frac{1}{N!} \int_0^L \cdots \int_0^L \prod_{1 \leq i < j \leq N} \exp[-\beta W_a(x_i - x_j)] \prod_{i=1}^N \exp[-\beta V(x_i)] dx_1 \cdots dx_N$$

The integral (i.e. $\mathfrak{Z}N!$) is just $N!$ times the integral over the regions $0 \leq x_1 \leq x_2 \leq \cdots \leq x_N \leq L$ which is obtained by placing the particles in order and re-naming to obtain the $N!$. Such a partitioning only exists in one dimension as this is the only time we can order particles along a line.

We now know the configurational partition function can be written as

$$\begin{aligned} \mathfrak{Z}(L) &= \int_{(N-1)a}^L \int_{(N-2)a}^{x_N - a} \cdots \int_0^{x_2 - a} \prod_{i=1}^N \exp[-\beta \psi(x_i - x_{i-1} - a)] \\ &\quad \times \prod_{i=1}^N \exp[-\beta V(x_i)] dx_1 \cdots dx_N \end{aligned}$$

since the j th particle cannot be in the region from 0 to $(j-1)a$ since at least this region must be occupied by the first $j-1$ particles. W_a has reduced to ψ as we have eliminated the possibility that particles over-lap. We now only consider particles that are adjacent as next neighbour and higher neighbour interactions are excluded.

We now introduce the local variables

$$y_j^a = x_j - (j-1)a, \quad l^a = L - (N-1)a. \quad (6.1)$$

Since our external potential is translation invariant we have

$$V(x_j) = V(y_j^a).$$

In these variables we can re-write the configurational partition function as

$$\begin{aligned} \mathfrak{Z}(l^a) &= \int_0^{l^a} dy_N^a \exp[-\beta V(y_N^a)] \int_0^{y_N^a} dy_{N-1}^a \exp[-\beta V(y_{N-1}^a)] \exp[-\beta \psi(y_N^a - y_{N-1}^a)] \cdots \\ &\quad \int_0^{y_2^a} dy_1^a \exp[-\beta V(y_1^a)] \exp[-\beta \psi(y_2^a - y_1^a)]. \end{aligned} \quad (6.2)$$

We now introduce a co-ordinate system that depends only on the difference between the positions of the particles in the local co-ordinate system

$$\lambda_N^a = l^a - y_N^a, \quad \lambda_i = y_{i+1}^a - y_i^a. \quad (6.3)$$

From these equations we can deduce that

$$y_i^a = l^a - \sum_{j=0}^i \lambda_{N-j}^a.$$

In this system the configurational partition function can be written as

$$\begin{aligned} \mathfrak{Z}(l^a) &= \int_0^{l^a} d\lambda_N^a \exp[-\beta V(l^a - \lambda_N^a)] \int_0^{l^a - \lambda_N^a} d\lambda_{N-1}^a \exp[-\beta V(l^a - \lambda_N^a - \lambda_{N-1}^a)] \\ &\times \exp[-\beta\psi(\lambda_{N-1}^a)] \dots \int_0^{l^a - \sum_{i=2}^N \lambda_i^a} d\lambda_1^a \exp\left[-\beta V\left(l^a - \sum_{j=0}^{N-1} \lambda_{N-j}^a\right)\right] \\ &\times \exp[-\beta\psi(\lambda_1^a)] \end{aligned} \quad (6.4)$$

It is unclear how to proceed in the case of a general external potential, however in the case of zero external potential this can be seen to be the convolution integral of $N - 1$ exponentials and two constant functions 1. Where the convolution of f and g is defined as

$$(f * g)(t) = \int_0^t f(\tau)g(t - \tau)d\tau.$$

Remark 1. *We can also make some progress in the case of the-load potentials, this is considered in Appendix A.1*

We now use the definition of the Laplace transform of a function f (see equation (1) Chapter 1 of [12]). If $f(t)$ is piece-wise continuous on $0 \leq t \leq \infty$ and $f(s)$ is of exponential order i.e.

$$\exists \mathcal{K}, \mathcal{A} > 0 \text{ s.t. } |f(t)| \leq \mathcal{K} \exp[\mathcal{A}t]$$

then the Laplace transform is given

$$F(s) = \int_0^\infty \exp[-st]f(t)dt \quad s > 0.$$

The Laplace transform of the convolution is denoted $H(s)$ where $h = (f * g)(t)$

$$H(s) = F(s)G(s) \quad (6.5)$$

where $G(s)$ is the Laplace transform of $g(t)$ (see page 55 of [12]).

We recall that the Laplace transform of one is given as

$$\begin{aligned} \int_0^{\infty} \exp[-st] ds &= \left[\frac{\exp[-st]}{-s} \right] \\ &= \frac{1}{s}. \end{aligned}$$

Using this and that our initial variable is spatially dependent, this suggests that our variable s is proportional to density.

Defining the Laplace transform of the configurational partition function $\mathfrak{Z}(l^a)$ as $Z(s)$ and the Laplace transform of $\exp[-\beta\psi(\lambda^a)]$ as $K(s)$ then using (6.5) we have:

$$\begin{aligned} Z(s) &= \int_0^{\infty} \exp[-sl^a] \mathfrak{Z}(l^a) dl^a \\ &= \int_0^{\infty} \exp[-sl^a] (1 * 1 * \exp[-\beta\psi(\lambda^a)] * \exp[-\beta\psi(\lambda^a)] \dots \exp[-\beta\psi(\lambda^a)]) dl^a \\ &= s^{-2} [K(s)]^{N-1} \end{aligned} \tag{6.6}$$

More explicitly

$$K(s) = \int_0^{\infty} \exp[-s\lambda^a] \exp[-\beta\psi(\lambda^a)] d\lambda^a. \tag{6.7}$$

A large selection of possible Laplace transforms is given in, for example, Appendix B of [12].

From Chapter 7 of [12] we know that the inverse of the Laplace transform can be given as:

$$f(t) = \frac{1}{2\pi i} \oint_C \exp[st] F(s) ds \quad \text{if } \exists M > 0, k > 0 \text{ s.t. } |F(s)| \leq \frac{M}{R^k} \text{ given } R = |s| \tag{6.8}$$

where \oint is the contour integral and C is the Bromwich contour (defined on page 201 of [12]). The conditions on $|F(s)|$ are required to use this contour integral form of the inverse. Thus we can write a new form for the partition function

$$\mathfrak{Z}(l^a) = \frac{1}{2\pi i} \oint_C \exp[sl^a] s^{-2} [K(s)]^{N-1} ds. \tag{6.9}$$

Comparing to (6.8) we see that

$$\begin{aligned} \left| s^{-2} [K(s)]^{N-1} \right| &= |F(s)| \\ &\leq \frac{M}{R^k}. \end{aligned}$$

Hence

$$\left| [K(s)]^{N-1} \right| \leq MR^{2-k}. \quad (6.10)$$

Thus we require that $[K(s)]^{N-1}$ increases at a less than quadratic rate.

Remark 2. *This is not what [14] says but the calculations in (6.10) suggests this less restrictive requirement*

We now re-write the integrand of (6.9) as an exponential of a function g so that

$$\begin{aligned} g(s) &= \ln \left[\exp[sl] s^{-2} [K(s)]^{N-1} \right] \\ &= sl + (N-1) \ln K(s) - 2 \ln s. \end{aligned} \quad (6.11)$$

We expand g around its saddle-point (s_0) up to second order (this assumes that we are not far from the saddle point $|s - s_0| < 1$). Given that s is proportional to density this is equivalent to our density being close to the uniform density ρ_0 .

$$\begin{aligned} g(s) &= g(s_0) + g'(s_0)(s - s_0) + \frac{g''(s_0)(s - s_0)^2}{2} + O(s - s_0)^2 \\ &= g(s_0) + \frac{g''(s_0)(s - s_0)^2}{2} + O(s - s_0)^2 \end{aligned}$$

where in the second line we have used that at the saddle point the first derivative ($g'(s_0)$) vanishes.

We can now derive the saddle-point condition (using (6.11))

$$\begin{aligned} g'(s_0) &= l + (N-1) \frac{K'(s_0)}{K(s_0)} - \frac{2}{s_0} \\ &= 0 \end{aligned} \quad (6.12)$$

and the second derivative of g

$$g''(s_0) = (N-1) \left(\frac{K''(s_0)}{K(s_0)} - \frac{K'(s_0)^2}{K(s_0)^2} \right) + \frac{2}{s_0^2}. \quad (6.13)$$

Following Section 4.6 of [14] we consider the method of steepest descent. We will demonstrate that $g(s)$ has a minimum along the real-axis in the cases we are considering.

If we assume g is complex differentiable, which is equivalent to assuming $K(s)$ is complex differentiable (which can be shown in all the cases we are considering), then by the Cauchy-Riemann equations the minimum along the real-axis is a maximum along the imaginary axis and thus we have a saddle-point. We can write $s = x_s + iy_s$ and thus

$s_0 = x_{s_0} + iy_{s_0}$ shifting the contour so that it is parallel to the y_s axis we have

$$\begin{aligned} \mathfrak{Z}(l^a) &= \frac{1}{2\pi i} \oint_C \exp[g(s)] ds \\ &\approx \frac{1}{2\pi i} \exp[g(s_0)] \int_{x_{s_0}-i\infty}^{x_{s_0}+i\infty} \exp\left[\frac{g''(s_0)(s-s_0)^2}{2}\right] ds \end{aligned} \quad (6.14)$$

using the contour parallel to the y_s axis

$$\begin{aligned} &\approx \frac{1}{2\pi} \exp[g(s_0)] \int_{-\infty}^{\infty} \exp\left[-\frac{g''(s_0)y_s^2}{2}\right] dy_s && \text{using } s - s_0 = iy_s \\ &\approx \frac{\exp[g(s_0)]}{\sqrt{2\pi g''(s_0)}} \left(1 + O\left(\frac{1}{N}\right)\right) \end{aligned}$$

where the form of the error can be seen, at least in the hard-core case, by appropriate use of the formula in [5] and the formula becomes exact in the thermodynamic limit.

To obtain the configurational free-energy we need

$$\begin{aligned} A_{\beta,con}^{\Lambda^N}[V] &= -\beta^{-1} \ln[\mathfrak{Z}(l^a)] \\ &\approx -\beta^{-1} \left(g(s_0) - \frac{1}{2} \ln[2\pi g''(s_0)] + \ln\left[1 + O\left(\frac{1}{N}\right)\right] \right) \end{aligned} \quad (6.15)$$

6.2 Hard-Core Calculation

Using (6.13) and (6.11) in (6.15) and the definition of l^a (6.1) we have an expression for the configurational free energy (which we relabel $A_a^{N,L} = A_{\beta,con}^{\Lambda^N}$ so the a and N dependence is clear)

$$\begin{aligned} A_a^{N,L} &\approx -\beta^{-1} \left(s_0 L + (N-1) [-s_0 a + \ln K(s_0)] - 2 \ln s_0 - \frac{1}{2} \ln[2\pi] \right. \\ &\quad \left. - \frac{1}{2} \ln \left[(N-1) \frac{K''(s_0)K(s_0) - K'(s_0)^2}{K(s_0)^2} + \frac{2}{s_0^2} \right] + \ln \left[1 + O\left(\frac{1}{N}\right) \right] \right). \end{aligned} \quad (6.16)$$

We can use the definition of l^a to re-write the stationary point condition ((6.12)) is

$$L + (N-1) \left[-a + \frac{K'(s_0)}{K(s_0)} \right] - \frac{2}{s_0} = 0 \quad (6.17)$$

If we consider the hard core gas then $\psi = 0$ and thus

$$\begin{aligned} K(s) &= \int_0^{\infty} \exp[-st] dt \\ &= \frac{1}{s} \end{aligned} \quad (6.18)$$

which clearly satisfies our assumption of complex differentiability. Thus using (6.11) we have

$$g(s) = ls - (N + 1) \ln s$$

since along the real axis $s = x_s$ we can graph this and show there is a minimum. Alternatively we can see that at low s the logarithm dominates so $g(s) \rightarrow \infty$ as $s \rightarrow 0$ and at high s the linear term dominates so $g(s) \rightarrow \infty$ as $s \rightarrow \infty$ at $g(1) = l < \infty$ so somewhere in the range $s > 0$ there is a minimum.

We state here for reference the first and second derivatives of K evaluated at s_0

$$K'(s_0) = \frac{-1}{s_0^2}$$

$$K''(s_0) = \frac{2}{s_0^3}$$

using these and (6.17) we can re-write the stationary point equation as

$$L - a(N - 1) = \frac{N + 1}{s_0}$$

which allows us to give an equation for the stationary point

$$s_0 = \frac{N + 1}{L - a(N - 1)}. \quad (6.19)$$

Using the derivatives of K we can see

$$\frac{K''(s_0)K(s_0) - K'(s_0)^2}{K(s_0)^2} = \frac{\frac{2}{s_0^4} - \left(\frac{-1}{s_0^2}\right)^2}{\left(\frac{1}{s_0}\right)^2}$$

$$= \frac{1}{s_0^2}.$$

Hence using (6.13)

$$g''(s_0) = \frac{N - 1}{s_0^2} + \frac{2}{s_0^2}$$

$$= \frac{N + 1}{s_0^2}.$$

With this, the equation for K (6.18), the equation for free energy (6.16) and (6.19) we can give an expression for the configurational free energy

$$\begin{aligned}
A_a^{N,L} &\approx -\beta^{-1} \left(s_0 L + (N-1) [-s_0 a - \ln s_0] - 2 \ln s_0 - \frac{1}{2} \ln[2\pi] - \frac{1}{2} \ln \left[\frac{(N+1)}{s_0^2} \right] \right. \\
&\quad \left. + \ln \left[1 + O \left(\frac{1}{N} \right) \right] \right) \\
&\approx -\beta^{-1} \left(s_0 [L - (N-1)a] - (N+1) \ln s_0 - \frac{1}{2} \ln[2\pi] - \frac{1}{2} \ln \left[\frac{N+1}{s_0^2} \right] \right. \\
&\quad \left. + \ln \left[1 + O \left(\frac{1}{N} \right) \right] \right) \\
&\approx -\beta^{-1} \left(s_0 [L - (N-1)a] - N \ln s_0 - \frac{1}{2} \ln[2\pi] - \frac{1}{2} \ln[N+1] + \ln \left[1 + O \left(\frac{1}{N} \right) \right] \right) \\
&\approx -\beta^{-1} \left(N+1 - N \ln[N+1] + N \ln[L - a(N-1)] - \frac{1}{2} \ln[2\pi] - \frac{1}{2} \ln[N+1] \right. \\
&\quad \left. + \ln \left[1 + O \left(\frac{1}{N} \right) \right] \right)
\end{aligned}$$

the limit of zero hard-core is given as

$$\begin{aligned}
\lim_{a \rightarrow 0} A_a^{N,L} &\approx -\beta^{-1} \left(N+1 - N \ln[N+1] + N \ln[L] - \frac{1}{2} \ln[2\pi] - \frac{1}{2} \ln[N+1] \right. \\
&\quad \left. + \ln \left[1 + O \left(\frac{1}{N} \right) \right] \right) \\
&\approx -\beta^{-1} \left(N+1 - N \ln \left[\frac{N+1}{L} \right] - \frac{1}{2} \ln[2\pi] - \frac{1}{2} \ln[N+1] + \ln \left[1 + O \left(\frac{1}{N} \right) \right] \right).
\end{aligned} \tag{6.20}$$

We wish to consider the ideal gas, with no external potential, we expect the configurational free energy (following (5.8)) to be given as

$$A_0^{N,L} = \beta^{-1} (\ln[N!] - N \ln[|\Lambda|]).$$

We recall Stirling's formula (which is exact in the thermodynamic limit) (5.11). We see that this should lead to an approximate formula as

$$A_0^{N,L} = -\beta^{-1} \left(N - N \ln \left[\frac{N}{L} \right] - \frac{1}{2} \ln[2\pi] - \frac{1}{2} \ln[N] \right) + O \left(\frac{1}{N} \right).$$

We now calculate the approximate configurational free energy per particle for the ideal gas

$$\begin{aligned}
\mathcal{F}_0^{N,L} &= \frac{1}{N} A_0^{N,L} \\
&= -\beta^{-1} \left(1 - \ln \left[\frac{N}{L} \right] - \frac{1}{2N} \ln[2\pi] - \frac{1}{2N} \ln[N] \right) + O \left(\frac{1}{N^2} \right).
\end{aligned}$$

We take the thermodynamic limit, this means $N, L \rightarrow \infty$ and N/L becomes the density ρ . We therefore have the exact formula in the thermodynamic limit

$$\begin{aligned}\mathcal{F}_0^{th} &= \lim_{\substack{N \rightarrow \infty \\ L \rightarrow \infty}} \mathcal{F}_0^{N,L} \\ &= -\beta^{-1} (1 - \ln[\rho]).\end{aligned}\tag{6.21}$$

We now look at the zero hard-core limit of the configurational free energy per particle using (6.20)

$$\begin{aligned}\lim_{a \rightarrow 0} \mathcal{F}_a^{N,L} &= \lim_{a \rightarrow 0} \frac{1}{N} A_a^{N,L} \\ &\approx -\beta^{-1} \left(\frac{N+1}{N} - \ln \left[\frac{N+1}{L} \right] - \frac{1}{2N} \ln [2\pi] - \frac{1}{2N} \ln [N+1] + \frac{\ln \left[1 + O\left(\frac{1}{N}\right) \right]}{N} \right).\end{aligned}$$

We can now find the thermodynamic limit

$$\lim_{\substack{N \rightarrow \infty \\ L \rightarrow \infty}} \lim_{a \rightarrow 0} \mathcal{F}_a^{N,L} = -\beta^{-1} (1 - \ln[\rho])$$

which is exactly the same as the ideal gas (6.21).

6.3 The Decreasing Potential Case

We now refer to our other potential choice of $\psi(\lambda^a)$

$$\psi(x_i - x_j - a) = \frac{1}{(|x_i - x_j| - a)^m} \quad m > 0.$$

The Laplace transform we seek is then

$$K(s) = \int_0^\infty \exp[-s\lambda^a] \exp\left[-\frac{\beta}{(\lambda^a)^m}\right] d\lambda^a$$

It can be shown that

$$\exp[-\beta] H(\lambda^a - 1) \leq \exp\left[-\frac{\beta}{(\lambda^a)^m}\right] \leq 1$$

where

$$H(x) = \begin{cases} 0 & \text{if } x < 0 \\ 1 & \text{if } x > 0 \end{cases}.$$

This means we can formulate bounds for the modulus, real and imaginary parts of $K(s)$

$$\begin{aligned} \exp[-\beta] \left| \int_1^\infty \exp[-s\lambda^a] d\lambda^a \right| &\leq |K(s)| \leq \left| \int_0^\infty \exp[-s\lambda^a] d\lambda^a \right| \\ \exp[-\beta] \left| \left[\frac{\exp[-s\lambda^a]}{-s} \right]_1^\infty \right| &\leq |K(s)| \leq \left| \left[\frac{\exp[-s\lambda^a]}{-s} \right]_0^\infty \right| \\ \frac{\exp[-\beta - s_x]}{|s|} &\leq |K(s)| \leq \frac{1}{|s|}. \end{aligned}$$

We now know (from (6.11))

$$g(s) = ls - 2lns + (N - 1) \ln K(s)$$

as $s \rightarrow 0$ the logarithmic terms dominate and $g(s) \rightarrow 0$. We can see that $g(1) < \infty$. As $s \rightarrow \infty$ the linear term dominates and $g(s) \rightarrow \infty$. This means that at some point we have a turning point i.e. a stationary point.

We can also see this by directly graphing the function. Below we give the graph for $m = 2$ where we have taken a system of $N = 99$ particles with $l^a = 1$ (obtained using Mathematica).

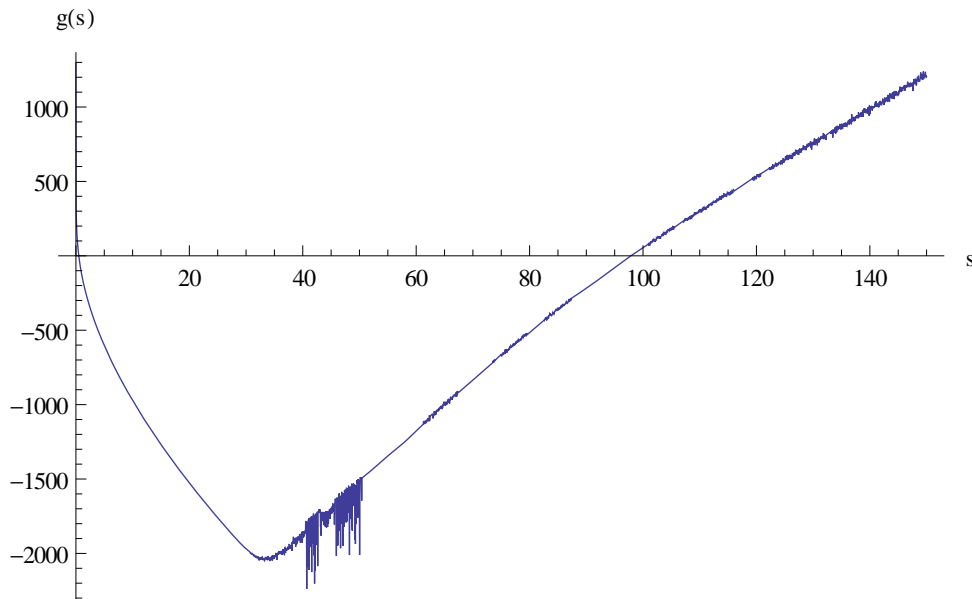


Figure 6.1: graph of $g(s)$ for the decreasing potential where we have chosen $m = 2$, $N = 99$ and $l^a = 1$. The existence of a minimum is clear. As we know the function is smooth the distortions visible may be a result of numerical issues or too low resolution.

We have shown how hard it is to obtain an explicit formula even when the potential chosen is very simple and we have confined ourselves to one dimension.

Chapter 7

One-Dimensional Hard Core System

So far we have only made progress in a direct analysis of the hard-core case for a limited number of external potentials, thus we present another attempt to obtain the explicit free energy in the one-dimensional hard-core case. We start by considering a discrete formulation and take a continuum limit to obtain a continuous formula. Again we have to constrain to one dimension to make any progress. In this section we are again considering only the configurational free energy.

7.1 Discrete Analogue

In line with Section 3.1 of [11] we start with a discrete system in one-dimension. In this case we have a line in one-dimension with a finite number (M) of sites along the line. We also have a finite number of particles (N). In general we want to calculate the probability of obtaining a configuration of the fluid system with the particles occurring at site s acted upon by the external potential V_s . This is denoted by

$$Z_{\Lambda,con}(\beta, N)^{-1} \exp \left(-\beta \sum_s \rho_s V_s \right)$$

where the probability of finding a particle at s is given by ρ_s (the occupation number).

7.1.1 Uniform System

In the uniform system with no interaction, where the particles have zero length. The probability of finding a particle at s is the same for all s i.e.

$$\begin{aligned} \rho_s &= \rho & \forall s \\ &= \frac{N}{M} & \forall s. \end{aligned}$$

We can now construct the probability of a configuration of the fluid with uniform occupation number. To do this since our particles have zero dimension and are uniformly

distributed, each site is either occupied or un-occupied with a probability independent of the occupancy of the adjacent sites. Thus the system follows a binomial distribution of N particles over the M sites

$$\begin{aligned} Z_{\Lambda,con}(\beta, N)^{-1} \exp[-\beta NV] &= \frac{1}{N!} \rho^N (1 - \rho)^{M-N} \\ &= \frac{1}{N!} [\rho^\rho (1 - \rho)^{1-\rho}]^M. \end{aligned}$$

7.1.2 Non-Uniform System

We wish to consider a non-uniform system where each site can have a different density. Our system of M sites is now a product over all the sites, where each site is either occupied or unoccupied independent of adjacent sites. This means that each site can be chosen as a binomial system with number of particles ρ_s i.e.

$$\rho_s^{\rho_s} (1 - \rho_s)^{1-\rho_s}$$

taking the product over all the M sites is

$$Z_{\Lambda,con}(\beta, N)^{-1} \exp\left(-\beta \sum_s \rho_s V_s\right) = \frac{1}{N!} \prod_{s=0}^{M-1} \rho_s^{\rho_s} (1 - \rho_s)^{1-\rho_s}.$$

7.1.3 Finite Range System

We now want to consider the case where our particles have a finite size m . This means that if a particle is at site s then the sites $s - m$ to $s + m$ can-not be occupied as particles on those sites would over-lap with the current particle. This means a total of $2m + 1$ sites are un-occupied for each particle. Our sites are now no longer occupied independently of each other, if we wish to construct a binomial distribution as above we must find two independent probabilities that sum to one. Since we are building up from the left we only need to condition on the sites to the left of our site. For a site s to be occupied we need sites $s - 1$ to $s - m$ to be empty. Since a site can either be occupied or unoccupied, the probability of having a hole at s is

$$\rho_h(s) = 1 - \rho_s.$$

We can build this up iteratively by subtracting the probability of a particle at each site until we reach the site $s - m$. So the probability of having un-occupied sites from $s - 1$ to $s - m$ denoted \mathbb{P}_{s-1}^{s-m} [unoccupied] is

$$\mathbb{P}_{s-1}^{s-m} [\text{unoccupied}] = 1 - \sum_{l=1}^m \rho_{s-l}.$$

We now consider the probability of the site s being occupied given that the sites $s - m$ to $s - 1$ are un-occupied. This is independent of the probability of its conjugate (i.e. one minus this probability) and is given using conditional probability by

$$\frac{\rho_s}{\mathbb{P}_{s-1}^{s-m}[\text{unoccupied}]} = \frac{\rho_s}{1 - \sum_{l=1}^m \rho_{s-l}}.$$

Thus if we take the number of successful site occupations as ρ_s and the total number as $1 - \sum_{l=1}^m \rho_{s-l}$. We have the binomial distribution for each site.

$$\begin{aligned} & \left(\frac{\rho_s}{1 - \sum_{l=1}^m \rho_{s-l}} \right)^{\rho_s} \left(1 - \frac{\rho_s}{1 - \sum_{l=1}^m \rho_{s-l}} \right)^{1 - \sum_{l=1}^m \rho_{s-l} - \rho_s} \\ &= \left(\frac{\rho_s}{1 - \sum_{l=1}^m \rho_{s-l}} \right)^{\rho_s} \left(\frac{1 - \sum_{l=0}^m \rho_{s-l}}{1 - \sum_{l=1}^m \rho_{s-l}} \right)^{1 - \sum_{l=0}^m \rho_{s-l}} \\ &= \frac{\rho_s^{\rho_s}}{(1 - t_{m-1}(s))^{1-t_{m-1}(s)}} (1 - t_m(s))^{1-t_m(s)} \end{aligned}$$

where

$$t_i(s) = \sum_{l=0}^i \rho_{s-m+l}. \quad (7.1)$$

We can then take the product over all M to give:

$$Z_{\Lambda, \text{con}}(\beta, N)^{-1} \exp \left(-\beta \sum_s \rho_s V_s \right) = \frac{1}{N!} \prod_{s=0}^{M-1} \frac{\rho_s^{\rho_s}}{(1 - t_{m-1}(s))^{1-t_{m-1}(s)}} (1 - t_m(s))^{1-t_m(s)} \quad (7.2)$$

which is similar to equation 28 of [11].

Using (2.8) we can now find the free energy of the discrete system. To do this we first re-arrange (7.2) to give the configurational partition function

$$Z_{\Lambda, \text{con}}(\beta, N) = \left(\frac{1}{N!} \prod_{s=0}^{M-1} \frac{\rho_s^{\rho_s}}{(1 - t_{m-1}(s))^{1-t_{m-1}(s)}} (1 - t_m(s))^{1-t_m(s)} \right)^{-1} \exp \left(-\beta \sum_s \rho_s V_s \right).$$

We can now easily calculate the configurational free-energy

$$\begin{aligned}
A_{\beta,con}^{\Lambda N}[V] &= -\beta^{-1} \ln [Z_{\Lambda}(\beta, N)] \\
&= -\beta^{-1} \ln \left[\left(\frac{1}{N!} \prod_{s=0}^{M-1} \frac{\rho_s^{\rho_s}}{(1-t_{m-1}(s))^{1-t_{m-1}(s)}} (1-t_m(s))^{1-t_m(s)} \right)^{-1} \right. \\
&\quad \left. \times \exp \left(-\beta \sum_s \rho_s V_s \right) \right] \\
&= \beta^{-1} \left(\sum_s \rho_s [\beta V_s + \ln \rho_s] + (1-t_m(s)) \ln [1-t_m(s)] \right. \\
&\quad \left. - (1-t_{m-1}(s)) \ln [1-t_{m-1}(s)] - \ln N! \right). \tag{7.3}
\end{aligned}$$

7.2 The Explicit Case

We now have a formula (7.2) for finding the partition function and we wish to find the limit in the continuous case. In this case the density is still a bounded function but both the number of sites and the number of particles are now infinite. We note that (7.2) can be re-written

$$\begin{aligned}
Z_{\Lambda,con}(\beta, N)^{-1} \exp \left(-\beta \sum_s \rho_s V_s \right) &= \frac{1}{N!} \prod_{s=0}^{M-1} \left(\frac{\rho_s}{(1-t_{m-1}(s))} \right)^{\rho_s} \left(\frac{1-t_m(s)}{1-t_{m-1}(s)} \right)^{1-t_m(s)} \\
&= \frac{1}{N!} \prod_{s=0}^{M-1} \left(\frac{\rho_s}{(1-t_{m-1}(s))} \right)^{\rho_s} \left(1 - \frac{\rho_s}{1-t_{m-1}(s)} \right)^{1-t_m(s)}
\end{aligned}$$

which we for convenience now re-arrange as

$$Z_{\Lambda,con}(\beta, N)^{-1} = \exp \left(\beta \sum_s \rho_s V_s \right) \frac{1}{N!} \prod_{s=0}^{M-1} \left(\frac{\rho_s}{(1-t_{m-1}(s))} \right)^{\rho_s} \left(1 - \frac{\rho_s}{1-t_{m-1}(s)} \right)^{1-t_m(s)}.$$

If we assume that the limit of the sum is the integral and the limit of the discrete ρ_s is a continuous $\rho_{\Lambda N}^{(1)}(x)$ then the formula splits into the product of three parts. One that is largely un-altered

$$\exp \left(\beta \sum_s \rho_s V_s \right) \prod_{s=0}^{M-1} \left(\frac{\rho_s}{(1-t_{m-1}(s))} \right)^{\rho_s}, \tag{7.4}$$

one which depends only on N

$$\frac{1}{N!}, \tag{7.5}$$

and the final part, a product of parts that depends on the probability that site s is occupied given that sites $s-1$ to $s-m$ are un-occupied.

$$\left(1 - \frac{\rho_s}{1-t_{m-1}(s)} \right)^{1-t_m(s)}. \tag{7.6}$$

We now consider each part separately.

7.2.1 Un-altered Part

As M tends to infinity the number of sites s tends to infinity. This means that the sum is now an infinite sum i.e. an integral over the real numbers in one dimension ($\int_{\Lambda} dx$). Our discrete functions ρ_s and V_s would in this case now depend on the continuous variable x so if $\rho_{\Lambda^N}^{(1)}(x)$ and $V(x)$ are continuous we can use them to replace ρ_s and V_s .

Thus the left-hand side of (7.4) becomes:

$$\exp \left(\beta \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) V(x) dx \right).$$

From (7.1) we know that in the discrete case

$$t_i(s) = \sum_{l=0}^i \rho_{s-m+l}.$$

which is the sum of the probabilities of sites being occupied from $s - m$ to s . Thus the continuous version (for a particle at x) is

$$t^m(x) = \int_{x-m}^x \rho_{\Lambda^N}^{(1)}(y) dy.$$

Since we now have an infinite number of sites the difference between $t_{m-1}(s)$ and $t_m(s)$ vanishes in the limit (provided the density is continuous). This is because in the discrete case the two sums differ only by the density at s and since this is now only a difference at an infinitesimal point it can safely be discarded provided ρ is continuous.

We choose not to evaluate (7.4) directly in the limit but instead evaluate the logarithm and take the limit, the logarithm of (7.4) is

$$\ln \left[\exp \left(\beta \sum_{s=0}^M \rho_s V_s \right) \prod_{s=0}^M \left(\frac{\rho_s}{1 - t_{m-1}(s)} \right)^{\rho_s} \right] = \beta \sum_{s=0}^M \rho_s V_s + \sum_{s=0}^M \rho_s \ln \left[\frac{\rho_s}{1 - t_{m-1}(s)} \right]$$

The limit of this can then be taken to be

$$\beta \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) V(x) dx + \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) \ln \left[\frac{\rho_{\Lambda^N}^{(1)}(x)}{(1 - t^m(x))} \right] dx. \quad (7.7)$$

7.2.2 N Dependent Part

To approximate (7.5) we first use (5.10) which we re-state for convenience

$$\sqrt{2\pi N} \left(\frac{N}{e}\right)^N \exp\left[\frac{1}{12N+1}\right] \leq N! \leq \sqrt{2\pi N} \left(\frac{N}{e}\right)^N \exp\left[\frac{1}{12N}\right]$$

We can invert this equation and use the fact that ρ is a density to give the limit from (7.5) as

$$\frac{1}{N!} = \frac{1}{\sqrt{2\pi N}} \left(\frac{e}{N}\right)^{\int_{\Lambda} \rho_{\Lambda N}^{(1)}(x) dx} \left(1 + O\left(\frac{1}{N}\right)\right). \quad (7.8)$$

7.2.3 Probability Dependent Part

In this case we consider each part of the product separately using the formula in (7.6) for each of these we take the ρ_s -th root to give.

$$\left(1 - \frac{\rho_s}{1 - t_{m-1}(s)}\right)^{\frac{(1-t_m(s))}{\rho_s}} = \left(1 - \frac{\rho_s}{1 - t_{m-1}(s)}\right)^{\frac{(1-t_{m-1}(s))}{\rho_s}} \left(1 - \frac{\rho_s}{1 - t_{m-1}(s)}\right)^{-1}.$$

For a linear system the probability of site s being occupied if the sites $s - m$ to $s - 1$ are unoccupied is clearly inversely proportional to the number of sites (M). Since this probability is given by:

$$\frac{\rho_s}{1 - t_m}$$

and thus in the limit of large M by rescaling we can see

$$\left(1 - \frac{\rho_s}{1 - t_{m-1}(s)}\right)^{\frac{(1-t_{m-1}(s))}{\rho_s}} \rightarrow \exp[-1]$$

and

$$\left(1 - \frac{\rho_s}{1 - t_{m-1}(s)}\right)^{-1} \rightarrow 1.$$

Thus (7.6) becomes simply the exponential function evaluated at minus one. i.e.

$$\left(1 - \frac{\rho_s}{1 - t_{m-1}(s)}\right)^{\frac{(1-t_m(s))}{\rho_s}} \rightarrow \exp[-1].$$

Since in our term for the configurational free energy we wish to take the product of N of these factors. The term we wish to add is

$$(\exp(-1))^N = \exp\left(-\int_{\Lambda} \rho_{\Lambda N}^1(x) dx\right) \quad (7.9)$$

where we have used that the integral of the density over the space Λ is equal to N .

7.2.4 Explicit Free Energy

We can now recombine the limits we obtained above ((7.7) , (7.8) and (7.9)) to obtain a formula for the logarithm of the inverse of the partition function, explicitly

$$\begin{aligned}
\ln Z_{\Lambda,con}(\beta, N)^{-1} &= \beta \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) V(x) dx + \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) \ln \left[\frac{\rho_{\Lambda^N}^{(1)}(x)}{(1 - t^m(x))} \right] dx \\
&\quad + \ln \left[\frac{1}{\sqrt{2\pi N}} \left(\frac{e}{N} \right)^{\int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) dx} \left(1 + O\left(\frac{1}{N}\right) \right) \exp \left[- \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) dx \right] \right] \\
&= \beta \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) V(x) dx + \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) \ln \left[\frac{\rho_{\Lambda^N}^{(1)}(x)}{(1 - t^m(x))} \right] dx \\
&\quad + \left(\int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) dx \right) \ln \left[\left(\frac{1}{N} \right) \right] - \frac{1}{2} \ln N - \frac{1}{2} \ln[2\pi] + O\left(\frac{1}{N}\right)
\end{aligned}$$

Using (2.8) we can now calculate the free energy.

$$\begin{aligned}
A_{\beta,con}^{\Lambda^N}[V] &= \beta^{-1} \ln [Z_{\Lambda}(\beta, N)^{-1}] \\
&= \beta^{-1} \left(\beta \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) V(x) dx + \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) \ln \left[\frac{\rho_{\Lambda^N}^{(1)}(x)}{(1 - t^m(x))} \right] dx \right. \\
&\quad \left. - \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) \ln [N] dx - \frac{1}{2} \ln N - \frac{1}{2} \ln[2\pi] + O\left(\frac{1}{N}\right) \right) \\
&= \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) \left(V(x) + \beta^{-1} \ln \left[\frac{\rho_{\Lambda^N}^{(1)}(x)}{N} \right] - \beta^{-1} \ln [1 - t^m(x)] \right) dx \\
&\quad - \frac{\beta^{-1}}{2} \ln N - \frac{\beta^{-1}}{2} \ln[2\pi] + O\left(\frac{1}{N}\right). \tag{7.10}
\end{aligned}$$

using the normalised one-particle density (5.12) we have for the free-energy per particle

$$\mathcal{F}_{\beta,con}^{\Lambda^N}[V] = \int_{\Lambda} \tilde{\rho}(x) (V(x) + \beta^{-1} \ln [\tilde{\rho}(x)] - \beta^{-1} \ln [1 - t^m(x)]) dx - \frac{\beta^{-1} \ln N}{2} \frac{1}{N} + O\left(\frac{1}{N^2}\right)$$

In the thermodynamic limit the final term vanishes and Stirling's approximation becomes exact.

We also note that if we replace N by the integral over space of the one-particle density then our expression is a functional of the one-particle plus another term as per (1.2).

7.3 Problems

We now note several problems with the formula (7.10) there are three problems we shall focus on

- This method only works in one dimension.

- What is the influence of assuming large N ?
- Are our limits precise?

The first of these problems is fundamental in the sense that we would really like a higher-dimensional form for free energy especially for the more realistic case of two or three dimensions and this excludes us from using the same method to derive such a free energy. This problem comes from the fact that in one-dimension we can partition the line into regions that are occupied by particles and those that are not using a grid structure. The problem comes that in two-dimensions we are looking at particles that exclude a circular region rather than a region of a straight line, this means we cannot approximate the region on a finite grid.

The other two problems can be assessed in more detail.

7.3.1 Influence of large N

In Subsection 7.2.2 we considered an approximation of the inverse of $N!$ that is valid at large N . An alternative way to deal with this is that since our final formula in (7.10) is N depend we could just alleviate the approximation and use $N!$. Using (7.7) and (7.9)

$$\begin{aligned}
\ln [Z_{\Lambda,con}(\beta, N)^{-1}] &= \beta \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) V(x) dx + \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) \ln \left[\frac{\rho_{\Lambda^N}^{(1)}(x)}{(1-t^m(x))} \right] dx + \ln \left[\frac{1}{N!} \right] \\
&\quad + \ln \left[\exp \left[- \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) dx \right] \right] \\
&= \beta \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) V(x) dx - \ln [N!] + \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) \ln \left[\frac{\rho_{\Lambda^N}^{(1)}(x)}{(1-t^m(x))} \right] dx \\
&\quad - \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) dx.
\end{aligned}$$

Using (2.8) we can now calculate the configurational free energy

$$\begin{aligned}
A_{\beta,con}^{\Lambda^N}[V] &= \beta^{-1} \ln [Z_{\Lambda,con}(\beta, N)^{-1}] \\
&= \beta^{-1} \left(\beta \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) V(x) dx - \ln [N!] + \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) \ln \left[\frac{\rho_{\Lambda^N}^{(1)}(x)}{(1-t^m(x))} \right] dx \right. \\
&\quad \left. - \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) dx \right) \\
&= \int_{\Lambda} \rho_{\Lambda^N}^{(1)}(x) \left(V(x) + \beta^{-1} \ln \left[\rho_{\Lambda^N}^{(1)}(x) \right] - 1 - \beta^{-1} \frac{\ln N!}{N} - \beta^{-1} \ln [1 - t^m(x)] \right) dx
\end{aligned} \tag{7.11}$$

However as realistic particle systems are likely to have a very large number of particles usually around 6×10^{23} (see page 1 of [1]) and because it has a slightly nicer form we will generally use (7.10). Also in the thermodynamic limit, for the associated free energy

per particle, the difference between the two approximations vanish as do the explicitly N dependent terms in the free energy per particle associated with (7.10).

7.3.2 Precision of the Limits

While the choice of $\rho_{\Lambda^N}^{(1)}(x)$, $t^m(x)$ and $V(x)$ are appropriate as limits of their discrete analogues provided that these are continuous functions. It is also true that the discrete analogue of the sum over the sites can be reasonable approximated by the integral.

However the splitting procedure we have used seems rather ad hoc it would be nice to have a better explanation of this. It seems clear that separating of the $N!$ is reasonable since this does not depend on M but only on N . However we need to consider the other separation used.

Although this problem gives us an insight into the hard-core problem it again only works in one-dimension. We now consider an approximation method which we hope will be more universally applicable.

Chapter 8

Mayer Expansion

As we noted at the end of the previous chapter the method we used to find an explicit formula in one dimension for the configurational free energy in the hard-core case will not work in higher dimensions. Therefore as a first course we will consider an expansion that we hope will give a good approximation of the partition function. The expansion we will consider is the Mayer expansion. To demonstrate the use of this expansion we will also calculate the expansion in the one-dimensional case.

8.1 Mayer Expansion

We know from (2.7) that the partition function can be re-written as a product of the exponentials of the potentials. We also know from (5.3) and (5.4) that the product of the exponentials containing the external potential can be re-written using simpler notation. Thus we note that the configurational partition function (see (2.9)) can be re-written (using (5.4))

$$Z_{\Lambda,con}(\beta, N) = \frac{1}{N!} \int_{\Lambda^N} z_{\beta}^N(dX_N) \prod_{1 \leq i < j \leq N} \exp[-\beta W(x_i - x_j)]. \quad (8.1)$$

Now we consider a way to expand the right-hand side exponential product

$$\begin{aligned} \prod_{1 \leq i < j \leq N} \exp[-\beta W(x_i - x_j)] &= \prod_{1 \leq i < j \leq N} \left(\underbrace{(\exp[-\beta W(x_i - x_j)] - 1) + 1}_{f(x_i - x_j)} \right) \\ &= \sum_{G \in \mathcal{G}_N} \prod_{\{i,j\} \in G} f(x_i - x_j) \end{aligned}$$

where \mathcal{G}_N denotes the power set (the set of all subsets) of the set of all pairs in $\{1, \dots, N\}$ and we call f the Mayer cluster. \mathcal{G}_N gives us the empty set which gives the one that in the first line comes from the product of all ones, it then gives all the individual pairs of numbers 1 to N (where $i < j$) which comes from multiplying the Mayer cluster in one of

the products and one in all the others. We can continue this for all the other pairs, two pairs come from the product of the Mayer cluster in two products with the ones in all the others and so on until N pairs come from the product of the Mayer clusters.

Remark 3. *The same formulation of $f(x_i - x_j)$ is used in Chapters 6 and 7 of [6]. In Section 7.2 they even consider the hard-core gas. However their work is more concerned with expressions for pressure, although it contains graphical formulations of $f(x_i - x_j)$ which could prove useful in later work.*

Remark 4. *We would hope that we could extend this methodology to n -body potentials. In the case of an n -body external potential we could replace $f(x_i - x_j)$ with $f_{i\dots n}$ where the indices correspond to the indices of the particles in the potential. We would also replace \mathcal{G}_N by \mathcal{G}_N^n , where \mathcal{G}_N^n denotes the power set of the set of all n -tuples in $\{1, \dots, N\}$. Then using $\{i, \dots, n\} \in G$ in the product we would hope that the formula would be the same. However we have not verified this as for clarity we have chosen to focus on two-body potentials which are also very commonly used ([6] only uses two-body potentials).*

Using this we can now formulate the configurational partition function using (8.1) to give

$$Z_{\Lambda, \text{con}}(\beta, N) = \frac{1}{N!} \int_{\Lambda^N} z_{\beta}^N(dX_N) \sum_{G \in \mathcal{G}_N} \prod_{\{i,j\} \in G} f(x_i - x_j). \quad (8.2)$$

So far all we have written is without approximation and is also true for all potentials, we now wish to use the hard-core potential. Using the formulation of W_a given in Section 4.1 and the fact that the exponential of W_a is unity at zero and vanishes at minus one. Thus the Mayer cluster is a step function

$$\begin{aligned} f(x_i - x_j) &= \exp[-\beta W_a(x_i - x_j)] - 1 \\ &= -\mathbb{I}_{[0,a]}(|x_i - x_j|). \end{aligned}$$

We can now find a simpler expression for the configurational partition function (8.2)

$$\begin{aligned} Z_{\Lambda, \text{con}}(\beta, N) &= \frac{1}{N!} \int_{\Lambda^N} z_{\beta}^N(dX_N) \sum_{G \in \mathcal{G}_N} \prod_{\{i,j\} \in G} -\mathbb{I}_{[0,a]}(|x_i - x_j|) \\ &= \frac{1}{N!} \sum_k \int_{\Lambda^N} z_{\beta}^N(dX_N) \sum_{\substack{G \in \mathcal{G}_N \\ |G|=k}} (-1)^k \prod_{\{i,j\} \in G} \mathbb{I}_{[0,a]}(|x_i - x_j|) \\ &= \frac{1}{N!} \sum_{k=0}^N I_k \end{aligned} \quad (8.3)$$

where we can decompose the integral as a sum due to the linearity of integrals.

So we can approximate the configurational partition function using the form given above,

we would like to be able to discount higher order terms in I_k . Ideally this would mean $|I_k|$ is a decreasing sequence for our purposes we just require that $|I_0 + I_1| \gg |\sum_{k=1}^N I_k|$. This is discussed further in the Appendix B.1.

8.2 Expansion of First Two Terms

We consider the first two terms of the Mayer expansion I_0 and I_1 . As stated above (using (5.5) and (8.3))

$$\begin{aligned} I_0 &= \int_{\Lambda^N} z^N(dX_N) \\ &= z(\Lambda)^N \end{aligned}$$

this is the no interaction term and thus is the entire expansion (given the preceding divisor of $N!$) in the case of ideal gas. We note that this means that in all our cases our configurational partition function is the sum of the ideal gas term and extra terms. This highlights the importance of the ideal gas case and shows that if it dominates we already have a good density functional approximation.

We now consider the I_1 term, this gives the interaction between two particles

$$\begin{aligned} I_1 &= - \int_{\Lambda^N} z^N(dX_N) \sum_{i \neq j} \mathbb{I}_{[0,a]}(|x_i - x_j|) \\ &= - \binom{N}{2} z(\Lambda)^{N-2} \int_{\Lambda^2} z(dx_1) z(dx_2) \mathbb{I}_{[0,a]}(|x_1 - x_2|). \end{aligned}$$

If we have translational invariance we obtain

$$I_1 = - \binom{N}{2} z(\Lambda)^{N-2} \int_{\Lambda} z_{\beta}(dx) \int_{|h| \leq a} d(x+h) \exp[-\beta V(x+h)]$$

where we have taken that $x_2 = x + h$ where h is a d -dimensional vector and using (5.3) to recover the exponential in $z_{\beta}(dx_2)$. The higher order terms in k are of higher order in $|B_a|$, the volume of a ball of radius a and we have thus discarded terms of order $O(|B_a|^2)$, this assumes that the hard core occupies a small proportion of the volume of $|\Lambda|$. $V(x+h)$ depends on h which is of order $|B_a|$. It therefore makes sense to expand V as a power series in h and discard terms of order h^3 or higher

$$V(x+h) = V(x) + \nabla V(x)h + \frac{1}{2} \nabla^2 V(x)h^2 + O(|h|^3).$$

We can thus write

$$\exp[-\beta V(x+h)] = \exp[-\beta V(x)] \exp\left[-\beta\left(\nabla V(x)h + \frac{1}{2}\nabla^2 V(x)h^2\right) + O(|h|^3)\right].$$

Using the power series expansion of the exponential we can discard more terms due to their dependence on high powers of h , thus discarding all terms higher than h^2 we have

$$\begin{aligned} \exp[-\beta V(x+h)] &= \exp[-\beta V(x)] \\ &\times \left(1 - \beta\nabla V(x)h + \frac{1}{2}(\beta\nabla V(x)h)^2 - \frac{\beta}{2}\nabla^2 V(x)h^2 + O(|h|^3)\right). \end{aligned}$$

We can now give an approximation for the configurational partition function

$$\begin{aligned} Z_{\Lambda, \text{con}}(\beta, N) &= z(\Lambda)^N - z(\Lambda)^{N-2} \binom{N}{2} \int_{\Lambda} z_{\beta}(\text{d}x) \exp[-\beta V(x)] \int_{|h|\leq a} \text{d}h \\ &\times \left(1 - \beta\nabla V(x)h + \frac{1}{2}(\beta\nabla V(x)h)^2 - \frac{\beta}{2}\Delta V(x)h^2 + O(|h|^3)\right) + O(|B_a|^2). \end{aligned}$$

The zeroth order term in h is

$$\begin{aligned} \int_{\Lambda} z_{\beta}(\text{d}x) \exp[-\beta V(x)] \int_{|h|\leq a} \text{d}h &= \int_{\Lambda} z_{\beta}(\text{d}x) \exp[-\beta V(x)] |B_1| a^d \\ &= \underbrace{z_{2\beta}(\Lambda)}_{c_1} |B_1| a^d \end{aligned}$$

the first order term in h vanishes using that the integral over the modulus of h of an odd power of h vanishes.

Finally we can give the second order term in h

$$\begin{aligned} &\int_{\Lambda} z_{\beta}(\text{d}x) \exp[-\beta V(x)] \int_{|h|\leq a} \text{d}h \left(\frac{1}{2}(\beta\nabla V(x)h)^2 - \frac{\beta}{2}\Delta V(x)h^2\right) \\ &= \frac{\beta}{2} \int_{\Lambda} z_{2\beta}(\text{d}x) (\beta|\nabla V(x)|^2 - \Delta V(x)) \int_{|h|\leq a} \text{d}h h^2. \end{aligned}$$

So we now need to evaluate the h integral

$$\begin{aligned} \int_{|h|\leq a} \text{d}h h^2 &= |B_1| \int_{|h|\leq a} \text{d}|h| |h|^{d-1} \\ &= \underbrace{\frac{|B_1|}{d+2}}_{c_2} a^{d+2}. \end{aligned}$$

We can now define two functions

$$J_1(\Lambda) = z(\Lambda)^{N-2} \binom{N}{2} c_1$$

$$J_2(\Lambda) = \frac{\beta}{2} z(\Lambda)^{N-2} \binom{N}{2} c_2 \int_{\Lambda} z_{2\beta}(\mathrm{d}x) (\beta |\nabla V(x)|^2 - \Delta V(x)).$$

Then we can re-write the configurational partition function as

$$Z_{\Lambda, \text{con}}(\beta, N) = z(\Lambda)^N - a^d J_1 - a^{d+2} J_2(V) + O(a^{3+d} + a^{2d}).$$

Therefore using (2.8) we can find the free energy

$$\begin{aligned} A_{\beta, \text{con}}^{\Lambda N}[V] &= -\beta^{-1} \ln [Z_{\Lambda}(\beta, N)] \\ &= -\beta^{-1} \ln [z(\Lambda)^N] \\ &\quad - \beta^{-1} \ln \left[1 - \frac{\binom{N}{2}}{z(\Lambda)^2} \left(c_1 a^d + a^{d+2} c_2 \frac{\beta}{2} \int_{\Lambda} z_{2\beta}(\mathrm{d}x) (\beta |\nabla V(x)|^2 - \Delta V(x)) \right) \right] \\ &\quad \left. + O(a^{3+d} + a^{2d}) \right] \end{aligned}$$

Using that to first order in $x \ln[1-x] = -x$ (to make this assumption we are discarding higher order terms in a , which are again of order $|B_a|$, the integral does not depend on a and will be constant for a given external potential) then we have

$$\begin{aligned} A_{\beta, \text{con}}^{\Lambda N}[V] &= -\frac{N}{\beta} \left(\ln [z(\Lambda)] - \frac{N-1}{2z(\Lambda)^2} \left(c_1 a^d + \frac{\beta}{2} a^{d+2} c_2 \int_{\Lambda} z_{2\beta}(\mathrm{d}x) (\beta |\nabla V(x)|^2 - \Delta V(x)) \right) \right) \\ &\quad + O(a^{3+d} + a^{2d}). \end{aligned} \tag{8.4}$$

The advantage of this form is that we have isolated the potential dependent term and thus by curtailing the expansion we can obtain an approximate expression for the one-particle density using the expression given in Subsection 3.1.3.

We also note that using Subsection 3.1.3

$$\begin{aligned} \left\langle \frac{\delta A_\beta^{\Lambda N}[V]}{\delta V(x)}, \varphi(x) \right\rangle &= \frac{-\beta^{-1}}{Z_\Lambda(\beta, N)} \frac{d}{ds} Z_{\Lambda, \text{con}, N}(V + s\varphi(x)) \Big|_{s=0} \\ &= \frac{-\beta^{-1} \sum_{k=0}^N \frac{d}{ds} I_k[V + s\varphi(x)] \Big|_{s=0}}{\sum_{k=0}^N I_k}. \end{aligned}$$

Where following (5.8) the momentum part of the free energy is independent of the external potential.

If we define ρ_k by

$$\langle \rho_k(x), \varphi \rangle = \frac{-\beta^{-1} \frac{d}{ds} I_k[V + s\varphi(x)] \Big|_{s=0}}{\sum_{k=0}^N I_k}$$

and thus in this case we can write the one particle density (which following Subsection 3.1.3 is the functional derivative of the free energy with respect to the external potential) as

$$\rho_{\Lambda^N}^{(1)}(x) = \sum_{k=0}^N \rho_k(x). \quad (8.5)$$

We can see using (8.4) that it is likely that our higher order approximations of the configurational free energy will depend on first and higher order derivatives in V . The methods used in Subsection 3.1.3 imply that in our evaluation of the functional derivative of the free energy we will obtain first and higher order derivatives of the test function which may be problematic as we wish to obtain an equation of the form of an integral multiplying the product of a function and $\varphi(x)$. However since our test function is arbitrary we can choose $\varphi(x)$ so that it and its derivatives vanish on the boundary and then use this and the divergence theory to move the derivatives onto the other term in our integral.

Given our formula (8.5) we can now in principle calculate the one-particle density as the functional derivative of the free energy. This will lead to a one-particle density that depends on the external potential, which we can re-arrange to make this dependence obvious. Given our formula for free energy (8.4) we should then be able to re-cast it as a functional of the one-particle density and an extra term (the form given in (1.2)). In practice however this may be very difficult as the one-particle density will have a very complex dependence on the external potential and the eventual functional may even depend on the density non-locally and thus further approximations may be needed to find a suitable functional form.

This method has the advantage that unlike our previous examples it is applicable in all dimensions. We hope that this method may also be applicable to other internal potentials.

Chapter 9

Conclusion

9.1 Summary

We here give a synopsis of the content of this paper. We begin the paper with a brief summary of the statistical mechanical techniques and definition of the one particle density required for a consideration of classical DFT in the canonical ensemble. We follow this with a description of the hard-core model which is our principle example in this paper. Our introduction concludes with a proof of the Hohenberg-Kohn theorem which states that we can give the free energy as a functional of the one-particle density and another term (as in (1.2)) which justifies our attempts to gain a DFT formulation of the free energy.

Our first example is the ideal gas, here we can find an explicit formula for the free energy. Our attempts to find an explicit formulation in the hard-core case follows two main routes both of which are only applicable in one dimension. The first method relies on the Laplace transform whereas the second method involves computing the free energy in a discrete case and then taking the continuum limit.

Given that our explicit formula are limited to one dimension and in our Laplace case are even more limited (see Chapter 6), we attempt an approximation that is applicable in all dimensions. This approximation is based on the Mayer expansion and we hope that it will be more generally applicable to different potentials.

9.2 Current Problems

9.2.1 Curtailing the Expansion of $g(s)$

To obtain our explicit form of the free energy in Chapter 6 we wish to write the function g as a constant term plus a term which is quadratic in s we wish to explore further in which situations such an approximation is possible. Manipulation of the formula given in [5] is anticipated to be useful in estimating the error of using the form (6.14) in the

thermodynamic limit.

9.2.2 The Mayer Expansion

After doing the Mayer expansion we obtain a neat form of the free energy and gave a way of obtaining the one-particle density. However we have not expressed the free energy as a functional of the one particle density which is what we would desire. It would be much better if we could obtain such a formulation. However it is anticipated that this may require further approximations.

9.3 Further Applications

9.3.1 Grand Canonical Ensemble

We have confined all our considerations to the canonical ensemble, however it should be relatively straight-forward to adapt our techniques to the grand canonical ensemble.

The definition of the grand canonical ensemble can be found in Section 4 of [1] and the definitions of the one-particle density are relatively similar in this case. In [7] they give a demonstration of obtaining the free energy in the ideal gas case.

Re-working our techniques in the case of the grand canonical ensemble may prove useful because as we mentioned in Section 2.1 this ensemble is often used in current calculations.

9.3.2 Further Potentials

So far we have only considered two model potentials. For our work to be applicable to real chemistry problems we need to be able to consider a wider degree of potentials.

Our first attempt to go beyond the hard-core potential is in Chapter 6. We have already constrained our potential so that the Laplace transform of the exponential of $\exp[-\beta\psi(\lambda)]$ exists and is less than a stated power of $|R|$. However there may be greater constraints, that we have yet to discover, since we have explored the relation between the free energy and the one-particle density in a few example cases and not in generality.

The second area where we could consider different internal potentials is in the Mayer expansion. The formulation of the configurational partition function in Subsection 8.1 as a summation should be more generally applicable. We suggest that the principle problem in this case may be whether the series can be curtailed and when they can what is the error associated with curtailing the series.

9.3.3 Quantum Problems

As mentioned in the introduction DFT was developed in a quantum context and there is still a great deal of work being currently undertaken on quantum DFT.

We suggest that as in the quantum case the constituent terms of the Hamiltonian are replaced by their corresponding operators it should be simple to obtain an ideal gas approximation by simply removing the associated operator for the internal energy. The hard-core gas should also be relatively simple to obtain. The advantage of doing quantum DFT from our point of view would be that we could obtain a benchmark which would allow us to compare these two different types of DFT.

Appendix A

Dead-Load Potentials

A.1 The Dead-Load Potential

In this case we assume that each particle has a position x_i which is centered around an equilibrium position \hat{x}_i and we further assume that its displacement from this equilibrium position is very small i.e. $\|x_i - \hat{x}_i\| \ll 1$. In this case we can approximate the external potential at each point by

$$V(x_i) = V(\hat{x}_i) + V'(x_i)(x_i - \hat{x}_i) + O((x_i - \hat{x}_i)^2).$$

If we further assume that close to \hat{x}_i our potential is approximately linear then $V(\hat{x}_i) = V'(\hat{x}_i)\hat{x}_i$ and we can re-write the potential as

$$V(x_i) \approx V'(\hat{x}_i)x_i$$

thus we can approximate the external potential by

$$\sum_{i=1}^N V(x_i) \approx \sum_{i=1}^N \chi_i x_i \quad \text{where } \chi_i = V'(\hat{x}_i).$$

Writing

$$\chi_i = \xi_i - \xi_{i-1} \quad \xi_0 = 0$$

we have

$$\begin{aligned} \sum_{i=1}^N V(x_i) &\approx \sum_{i=1}^N (\xi_i - \xi_{i-1})x_i \\ &\approx \xi_N x_N - \xi_{N-1} x_N + \xi_{N-1} x_{N-1} - \xi_{N-2} x_{N-1} + \cdots + \xi_2 x_2 - \xi_1 x_2 + \xi_1 x_1 \\ &\approx \xi_N x_n + \xi_{N-1}(x_{N-1} - x_N) + \cdots + \xi_1(x_1 - x_2) \\ &\approx \sum_{i=1}^N \xi_i(x_i - x_{i+1}) \quad \text{where } x_{N+1} = 0. \end{aligned}$$

A.2 The Configurational Free Energy

Given our equation (6.4) we seek to consider

$$\begin{aligned}
\exp \left[-\beta \sum_{i=1}^N V(x_i) \right] &= \exp \left[-\beta \sum_{i=1}^N \xi_i (x_i - x_{i+1}) \right] \\
&= \exp \left[-\beta \sum_{i=1}^N \xi_i (y_i^a - y_{i+1}^a + a) \right] && \text{using (6.1)} \\
&= \exp \left[-\beta \sum_{i=1}^N \xi_i (a - \lambda_i^a) \right] && \text{using (6.3).}
\end{aligned}$$

Using this we can re-write (6.4) as

$$\begin{aligned}
\mathfrak{Z}(l^a) &= \exp \left[-\beta \sum_{i=1}^N \xi_i a \right] \int_0^{l^a} d\lambda_N^a \exp[\beta \xi_N \lambda_N^a] \int_0^{l^a - \lambda_N^a} d\lambda_{N-1}^a \exp[\beta \xi_{N-1} \lambda_{N-1}^a] \\
&\quad \times \exp[-\beta \psi(\lambda_{N-1}^a)] \dots \int_0^{l^a - \sum_{i=2}^N \lambda_i^a} d\lambda_1^a \exp[\beta \xi_1 \lambda_1^a] \exp[-\beta \psi(\lambda_1^a)].
\end{aligned}$$

As in Chapter 6 we see that this is the a constant multiplying a convolution of a constant function 1 a exponential function $\exp[\beta \xi_N \lambda_N^a]$ and $N - 1$ exponential functions $\exp[\beta \xi_i \lambda_i^a] \exp[-\beta \psi(\lambda_i^a)]$.

If $F(s)$ is the Laplace transform of $f(t)$ the Laplace transform has the property that the Laplace transform of $\exp[at]f(t)$ is $F(s - a)$ (see Appendix A of [12]). We now find using (6.6) that the Laplace transform of the configurational partition function is

$$Z(s) = \exp \left[-\beta \sum_{i=1}^N \xi_i a \right] \frac{\prod_{i=1}^{N-1} K(s - \beta \xi_i)}{s(s - \beta \xi_N)}$$

using (6.7). The methods of Chapter 6 should now be applicable except that $g(s)$ will become

$$sl - \ln s - \ln[s - \beta \xi_N] + \sum_{i=1}^{N-1} \ln K(s - \beta \xi_i) - \beta \sum_{i=1}^N \xi_i a$$

and thus we expect that the thermodynamic limit may be hard to obtain.

Appendix B

Validity of the Mayer Expansion

B.1 The Validity of Curtailing the Mayer Expansion

For ease of calculation we first explicitly state the formula for I_k using (8.3)

$$I_k = \int_{\Lambda^N} z_\beta^N(dX_N) \sum_{\substack{G \in \mathcal{G}_N \\ |G|=k}} (-1)^k \prod_{\{i,j\} \in G} \mathbb{I}_{[0,a]}(|x_i - x_j|). \quad (\text{B.1})$$

Since we have chosen an external potential (V) that split into separate potentials for each spatial co-ordinates we can write

$$\int_{\Lambda^N} z_\beta^N(dX_N) = \left(\int_{\Lambda} z_\beta(dx_1) \right)^N.$$

This can also be seen to be I_0 . For a given k all integrals higher than k are unaffected as we only have identity functions for k variables and since all variables are treated the same by integration we can rename and re-arrange. Thus we can re-write I_k as:

$$I_k = C_N^k \left(\int_{\Lambda} z_\beta(dx_N) \right)^{N-k} \int_{\Lambda^k} z_\beta^k(dX_k) (-1)^k \prod_{\substack{\{i,j\} \in G \\ G \in \mathcal{G}_N \\ |G|=k}} \mathbb{I}_{[0,a]}(|x_i - x_j|).$$

where X_k is the space of k d -dimensional vectors constrained to Λ and C_N^k is the number of subsets of the pairs of numbers $1, \dots, N$ of length k . We have used one of the $G \in \mathcal{G}_N$ $|G| = k$ as by re-arrangement all configurations are the same. We have re-named the variable that does not see the indicator functions as x_N as this will never be involved.

C_N^k is easily calculated since we are pick subsets of length k from the number of pairs N_P then

$$C_N^k = \binom{N_P}{k}.$$

The number of pairs is just the number of sets length two taken from the total number of particles N_p which is given by

$$N_p = \binom{N}{2}.$$

Since we are only interested in the modulus of I_k we are only interested in

$$|I_k| = C_N^k \left(\int_{\Lambda} z_{\beta}(dx_N) \right)^{N-k} \int_{\Lambda^k} z_{\beta}^k(dX_k) \prod_{\substack{\{i,j\} \in G \\ G \in \mathcal{G}_N \\ |G|=k}} \mathbb{I}_{[0,a]}(|x_i - x_j|).$$

Thus to prove $|I_k| < |I_{k-1}|$ all we have to show is

$$\begin{aligned} & C_N^k \int_{\Lambda^k} z_{\beta}^k(dX_k) \prod_{\substack{\{i,j\} \in G \\ G \in \mathcal{G}_N \\ |G|=k}} \mathbb{I}_{[0,a]}(|x_i - x_j|) < \\ & C_N^{k-1} \int_{\Lambda} z_{\beta}(dx_N) \int_{\Lambda^{k-1}} z_{\beta}^{k-1}(dX_{k-1}) \prod_{\substack{\{i,j\} \in G \\ G \in \mathcal{G}_N \\ |G|=k-1}} \mathbb{I}_{[0,a]}(|x_i - x_j|). \end{aligned}$$

The ratio of the coefficients is

$$\begin{aligned} \frac{C_N^k}{C_N^{k-1}} &= \frac{(k-1)!(N_p - (k-1))!}{k!(N_p - k)!} \\ &= \frac{N_p + 1}{k} - 1. \end{aligned}$$

We can thus bound the ratio

$$\frac{1}{N_p} \leq \frac{C_N^k}{C_N^{k-1}} \leq N_p \quad 1 \leq k \leq N_p.$$

This decreases as $k \rightarrow N_p$ suggesting we may be able to discount higher order terms in k as N_p will be larger.

We want to show that

$$\begin{aligned} & \frac{C_N^k}{C_N^{k-1}} \int_{\Lambda^k} z_{\beta}^k(dX_k) \prod_{\substack{\{i,j\} \in G \\ G \in \mathcal{G}_N \\ |G|=k}} \mathbb{I}_{[0,a]}(|x_i - x_j|) < \\ & \int_{\Lambda} z_{\beta}(dx_1) \int_{\Lambda^{k-1}} z_{\beta}^{k-1}(dX_{k-1}) \prod_{\substack{\{i,j\} \in G \\ G \in \mathcal{G}_N \\ |G|=k-1}} \mathbb{I}_{[0,a]}(|x_i - x_j|). \end{aligned}$$

which is equivalent to

$$\begin{aligned} & \frac{C_N^k}{C_N^{k-1}} \int_{\Lambda^k} z_\beta^k(dX_k) \prod_{\substack{\{i,j\} \in G \\ G \in \mathcal{G}_N \\ |G|=k}} \mathbb{I}_{[0,a]}(|x_i - x_j|) < \\ & N_p \int_{\Lambda^k} z_\beta^k(dX_k) \prod_{\substack{\{i,j\} \in G \\ G \in \mathcal{G}_N \\ |G|=k}} \mathbb{I}_{[0,a]}(|x_i - x_j|) < \\ & \int_{\Lambda} z_\beta(dx_N) \int_{\Lambda^{k-1}} z_\beta^{k-1}(dX_{k-1}) \prod_{\substack{\{i,j\} \in G \\ G \in \mathcal{G}_N \\ |G|=k-1}} \mathbb{I}_{[0,a]}(|x_i - x_j|). \end{aligned}$$

We begin by giving the formula for a d -sphere of radius a which is

$$C_d a^d$$

where

$$C_d = \frac{\pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2} + 1)}.$$

Since our d -spheres are all hard and we desire to have them within the space Λ . Thus we have

$$N \ll \frac{|\Lambda|}{C_d a^d}$$

this can be inverted to give

$$\frac{C_d a^d}{|\Lambda|} \ll \frac{1}{N}.$$

We know

$$N_p = \frac{N(N-1)}{2}.$$

If we are in a sufficiently dilute system then

$$\frac{C_d a^d}{|\Lambda|} \ll \frac{1}{N^2}$$

and thus

$$\frac{C_d a^d}{|\Lambda|} \ll \frac{1}{N_p}.$$

If we have the indicator function $\mathbb{I}_{[0,a]}(|x_i - x_j|)$ then the maximum amount of the volume $|\Lambda|$ that can be occupied is $C_d a^d$. If the external potential is equally distributed across Λ

then

$$\begin{aligned}
 & \frac{C_N^k}{C_N^{k-1}} \int_{\Lambda^k} z_\beta^k(dX_k) \prod_{\substack{\{i,j\} \in G \\ G \in \mathcal{G}_N \\ |G|=k}} \mathbb{I}_{[0,a]}(|x_i - x_j|) < \\
 & N_p \int_{\Lambda^k} z_\beta^k(dX_k) \prod_{\substack{\{i,j\} \in G \\ G \in \mathcal{G}_N \\ |G|=k}} \mathbb{I}_{[0,a]}(|x_i - x_j|) < \\
 & N_p \frac{1}{N_p} \int_{\Lambda} z_\beta(dx_1) \int_{\Lambda^{k-1}} z_\beta^{k-1}(dX_{k-1}) \prod_{\substack{\{i,j\} \in G \\ G \in \mathcal{G}_N \\ |G|=k-1}} \mathbb{I}_{[0,a]}(|x_i - x_j|) < \\
 & \int_{\Lambda} z_\beta(dx_1) \int_{\Lambda^{k-1}} z_\beta^{k-1}(dX_{k-1}) \prod_{\substack{\{i,j\} \in G \\ G \in \mathcal{G}_N \\ |G|=k-1}} \mathbb{I}_{[0,a]}(|x_i - x_j|).
 \end{aligned}$$

and thus $|I_{k-1}| < |I_k|$. Therefore in a dilute system the terms become successively smaller in k and we will be able to curtail the series.

Remark 5. *We can also say that higher I_k depend on higher powers of the volume of the d -spheres so if they are sufficiently small the terms will vanish.*

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