An Introduction to Graph Theory, the Mayer Cluster Expansion and M.S. Wertheim's Multiple Density Approach
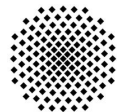
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An Introduction to Graph Theory, the Mayer Cluster Expansion and M.S. Wertheim's Multiple Density Approach

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Abstract

This abstract will explain the work's basic idea. And basic conclusions, if existent. And be superfunny, like, jokes and satirical remarks on current political debate and lots of references to VIPs unknown outside of the US and best to be forgotten immediately after reading a way too long wikipedia article on them.

1 Introduction

And we will introduce stuff here. Probably something with energy and mass. Physics, like grown-up people's physics.

This introductory article is meant to give the key ingredients to understanding M.S. Wertheim's theory, presented in references[?][?][?][?][?]. To that end, Section 2 will introduce the fundamental ideas of graph theory, which will be applied to the grand canonical partition function to derive the *Mayer Cluster Expansion* (MCE) in Section 3. Since Wertheim follows an analogous argumentation to the MCE, Section 4 will simply illustrate the major variations proposed by Wertheim and explain their advantages. Section 5 uses *Thermodynamic Perturbation Theory* (TPT) to yield approximations to compressibility values. These results are compared and fitted to simulation results. Section 6 gives concluding remarks.

2 Graph Theory

2.1 Basic Definitions

Fundamental to everything that follows is the basic notion of a graph. This section shall give a definition of various common elements of graphs and mention three important lemmas that are often used in graph theory. To simplify the application in the following sections, we will use physically interpretable function names. However, the theory is purely mathematical and does not require any physical argumentation.

The basic notion of a graph is described in a first definition.

Definition 1

Let $\mathbf{r} \in \Omega$ with a domain $\Omega \subset \mathbb{R}^d$. Let $z_i : \Omega \mapsto \mathbb{R}$ and $f_\mu : \Omega \times \Omega \mapsto \mathbb{R}$, $i, \mu \in \mathbb{N}$ be functions in one and two variables, respectively. We call z_i the properties *and f_μ the*

bonds. *With them, the following equations hold:*

i. *A* labelled point *with a property corresponds to a function in one variable:*

$$z_1 \underset{\mathbf{r}_1}{\bigcirc} = z_1(\mathbf{r}_1).\tag{1}$$

ii. *Two labelled points with a bond correspond to a function in two variables:*

$$z_1 \underset{\mathbf{r}_1}{\bigcirc} \overset{f_\mu}{\rule{3em}{0.4pt}} z_2 \underset{\mathbf{r}_2}{\bigcirc} = z_1(\mathbf{r}_1)f_\mu(\mathbf{r}_1, \mathbf{r}_2)z_2(\mathbf{r}_2).\tag{2}$$

iii. *This can be generalized as*
{*A graph with n labelled points and K bonds with $m(\mu, ij)$ bonds of type μ connecting points i and j*}

$$= \prod_{i=1}^{n} z_i(\mathbf{r}_i) \prod_{j>i}^{n} \prod_{\mu=1}^{K} \frac{1}{m(\mu, ij)!} f_\mu(\mathbf{r}_i, \mathbf{r}_j)^{m(\mu, ij)}.\tag{3}$$

A quick remark on the last item of the definition: if there is no bond of type μ present between points i and j, $m(\mu, ij)$ will be zero and the contribution of the bond-term in the product will be one. For all application we will discuss in this article, $m(\mu, ij)$ will be one or zero.

As a first advantage of graph theory, we can see that large products of functions can be simplified by replacing them with rather simple drawings. The true power within this ansatz is the easy manipulation of complicated (sums of) functions by set theoretic considerations on graphs.

Note that the label of a labelled point is not the property z_i but the fact that a fixed variable $\mathbf{r}$ is assigned to that point. For brevity, the property is often omitted when it is clear from the context. The same applies to bonds. Sometimes different

graphical representations are used to distinguish between bond types.

The next definition introduces integration into graph theory.

Definition 2

A field point is a filled point (usually without a label) and means integration over the coordinate:

i.
$$z_1 \bullet = \int_\Omega d\mathbf{r}_1 z_1(\mathbf{r}_1). \tag{4}$$

ii.
$$z_1 \bullet \!\!\frac{}{f_\mu}\!\! \bullet z_2 = \int_\Omega d\mathbf{r}_2 \int_\Omega d\mathbf{r}_1 z_1(\mathbf{r}_1) f_\mu(\mathbf{r}_1, \mathbf{r}_2) z_2(\mathbf{r}_2). \tag{5}$$

iii. And the general version:

$$\{A \text{ graph with } n \text{ labelled points and } m \text{ field points and arbirtrary bonds}\}$$
$$= \int_\Omega d\mathbf{r}_{n+m} \cdots \int_\Omega d\mathbf{r}_{n+1} \times \{the \text{ same graph with all} \tag{6}$$
$$field \text{ points carrying label } \mathbf{r}_{n+1} \text{ to } \mathbf{r}_{n+m}\}.$$

With graphs, the interdependences of integration variables are clearly visible. This helps to easily detect *steric incompatibilities*, e.g. graphs vanishing because their geometry always results in a value of zero. In the hard spheres case we will study, this is always due to overlapping spheres for those geometries where all bonds differ from 0.

2.2 Graph Symmetry

With the above definition, labels of field points can be set arbitrarily or omitted entirely, all resulting in the same graph. This is in agreement with the mathematical intuition that integration variables can be named arbitrarily as long as they stay well-defined and distinguishable. However, we will see in Section 3 that when using graphs to analyze the grand canonical ensemble, the prefactors of the arising graphs play an important role. Therefore, some authors (e.g. Morita & Hiroike in their definitions 3 and $3'$[?]) use a definition that distinguishes between graphs with labelled field points and graphs with unlabelled field points. We will also give this definition for completeness, but note that we will not stick to it. For a deeper understanding, we will consider the graph

$$:= \tag{7}$$

We will use the shorthand form on the left hand side of (7) to keep the overview. Obviously, we could label the field points

arbitrarily. It is, however, convenient to introduce an equivalency relation between two graphs with labelled (field) points: two graphs are *topologically indistinguishable* if field points with the same label i carry the same properties and pairs of points with labels i and j are linked by the same bonds in both graphs. For example,

$$\cong . \tag{8}$$

where the $\cong$ sign means topological indistinguishability. Conversely, two graphs are topologically distinguishable – indicated here by the $\not\cong$ sign – if the bonds or properties assigned to their points differ, as in

$$\not\cong , \tag{9}$$

The numerical value represented by all graphs in (8) and (9) is the same, and we did already note above that from a mathematical point of view the labelling of the integration variables is of no importance. So why is this distinction necessary at all?
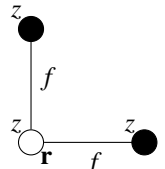
The answer to this question lies in the application of graph theory to problems of physics. When applying graph theory to the grand canonical partition function in Section 3, we will encounter sums over graphs. These will only contain topologically distinguishable graphs, and a graph of N points will be weighted by a factor of $(N!)^{-1}$. When only considering the graphs in the example above, the sum will contain the expression

$$\frac{1}{6}\left\{ + + \right\}$$
$$= \frac{1}{2}\left\{ \right\}. \tag{10}$$

The left hand side of (10) acould be shortened to a single expression because the values of all graphs on the left hand side are the same. The factor $\frac{1}{2}$ is an important property of the graph (7). It is the inverse of the *symmetry number s*. The symmetry number is given by the number of permutations of graph labels that lead to topologically indistinguishable graphs. In our example, this number is 2 according to (8). It is easily verified that the factor $(N!)^{-1}$ always reduces to s^{-1}: Assigning labels from 1 to N to the N field points of a graph leads to $N!$ graphs. For every type of topologically distinguishable graphs

there are s topologically indistinguishable versions. Omitting these leads to a total of $\frac{N!}{s}$ topologically distinguishable graphs. These all have the same value, so if we sum over them and divide by $N!$, we can choose any label assignment and multiply it by $\frac{1}{N!}\frac{N!}{s} = \frac{1}{s}$.

The symmetry number is an important property of a graph. Some authors include it directly in the basic definition of a graph, thereby distinguishing between graphs with labelled field points and graphs with unlabelled field points. We will not do so, which leads to different equations.

2.3 Derivatives of Graphs

While integration by definition turns a labelled point into a field point, turning a field point back into a labelled point requires a slight bit of analysis. For that purpose, we introduce the variational calculus, and thereby differentiation, into the graph theoretic framework.

Definition 3
Let z_i be defined as in Defintion 1 and let $\Lambda : z_i \mapsto \mathbb{R}$ be a functional. Then the functional derivative $\delta\Lambda/\delta z_i$ is defined via the variation $\delta\Lambda$ of Λ and δz_i of z_i by

$$\delta\Lambda = \int d\mathbf{r}\, \frac{\delta\Lambda}{\delta z_i(\mathbf{r})}\, \delta z_i(\mathbf{r}) \qquad (11)$$

Integration over the label of a labelled point is of course a functional of the property assigned to that labelled point. It is therefore an excellent candidate to use the above definition. We will use the relationship

$$\frac{\delta z_i(\mathbf{r})}{\delta z_{i'}(\mathbf{r}')} = \begin{cases} 0 & \text{for } z_i \text{ independent of } z_{i'}, \\ \delta(\mathbf{r}-\mathbf{r}') & \text{for } z_i \equiv z_{i'}. \end{cases} \qquad (12)$$

We will use these theorems on the situation given in equation (5) for $z_i \equiv z_{i'}$ and generalize the results found there:

$$\frac{\delta}{\delta z_i(\mathbf{r})}\;{}^{z_i}\!\!\bullet\!\!\underset{f_\mu}{\rule{1.2cm}{0.4pt}}\!\!\overset{z_i}{\bullet}$$

$$= \int d\mathbf{r}' \int d\mathbf{r}'' \frac{\delta}{\delta z_i(\mathbf{r})} \left[z_i(\mathbf{r}')f(\mathbf{r}',\mathbf{r}'')z_i(\mathbf{r}'') \right]$$

$$= \int d\mathbf{r}' \int d\mathbf{r}'' \left[\delta(\mathbf{r}-\mathbf{r}')f(\mathbf{r}',\mathbf{r}'')z_i(\mathbf{r}'') \right]$$
$$\quad + \int d\mathbf{r}' \int d\mathbf{r}''\delta(\mathbf{r}-\mathbf{r}'')f(\mathbf{r}',\mathbf{r}'')z_i(\mathbf{r}') \qquad (13)$$

$$= 2\int d\mathbf{r}' f(\mathbf{r},\mathbf{r}')z_i(\mathbf{r}')$$

$$= 2\;\;\underset{\mathbf{r}\;\;\;f_\mu}{\rule{1.2cm}{0.4pt}}\!\!\overset{z_i}{\bullet}.$$

The dashed lines around the left point indicate that there is no property assigned to it. Thus, the functional derivative of a

graph is identical to turning field points into labelled points. One can easily explain this in a straightforward way: the functional derivative of a graph Γ with respect to a property $z_i(\mathbf{r})$ is equal to the sum of all graphs obtained from Γ by turning a single field point with property z_i into a point labelled $\mathbf{r}$, and the point loses its property (or rather, adopts the new property $z^* \equiv 1$).

But as is the case in equation (13), this would result in summing many graphs with equal value. This redundancy stems from the aforementioned fact that our Definition 2 has no special treatment of graph symmetry. The derivative changes the symmetry number of the graph from 2 to 1. Devision by symmetry numbers yields a useful lemma, which we will give without a prove.

Lemma 4
Let z_i, $z_{i'}$ be properties and let Γ be a graph and let the set $\{\Gamma_\alpha\}_{1\leq\alpha\leq m}$ be the set of all topologically distinguishable graphs obtainable from Γ by turning one field point with property z_i into a labelled point with property $z_{i'}$. Let s be the symmetry number of Γ and let the set $\{s_\alpha\}_{1\leq\alpha\leq m}$ be the set of symmetry numbers corresponding to $\{\Gamma_\alpha\}$. Then

$$z_{i'}(\mathbf{r})\frac{\delta}{\delta z_i(\mathbf{r})}s^{-1}\,\Gamma = \sum_{\alpha=1}^{m} s_\alpha^{-1}\,\Gamma_\alpha. \qquad (14)$$

Note again that Lemma 4 would look differently if all graphs already contained division by symmetry number.

2.4 Articulation Points

Most considerations on graphs take only the topology of a graph into account. From the topology, it is possible to derive reductions which can ultimately result in huge simplifications of originally very complicated expressions.

For example, finding independent integration variables can be easily translated to a topological consideration. That is this subsection's purpose, and we will only need a short list of definitions to get there. The following properties are relevant in graph theory:

- *connected graph*: a graph Γ with two or more points is connected if for any points $A, B \in \Gamma$ there is a path of points and bonds connecting A to B.

- *doubly, triply, ... n-connected graph*: a graph Γ with two or more points is n-connected if for any points $A, B \in \Gamma$ there are n independent paths of points and bonds connecting A to B.

- *single-bonded graph*: a single-bond graph is a graph Γ where no double-bonds exist between points $A, B \in \Gamma$. Unconnected points are allowed.

- *singly connected graph*: a single-bonded connected graph.

- *articulation point*: a point A in a connected graph Γ. If one removes A and its adjacent bonds, the graph Γ will be divided into two or more separate graphs.

- *reducible graph*: a graph that contains articulation points or bonds that may be expressed in a more convenient way.

While these names are frequently used in graph theory, they may be understood differently in each context. For example, the vague definition of a reducible graph comes from the fact that it is up to the researcher which bonds they want to consider as fundamental for their graph. As one can see especially in the paper Wertheim III[?] , the correct definition in this matter is crucial to the types of graphs one ends up analyzing. Wertheim III also shows that careful characterizations of articulation points are fundamental to researches in graph theory.

Now, let us return to independent integration variables. Their treatment is easiest understood in a simple exemplatory calculation considering a three point singly connected graph. For simplicity, we will consider all properties to be z and all bonds to be f.

$$= \int_\Omega d\mathbf{r}' \int_\Omega d\mathbf{r}'' \, z(\mathbf{r})z(\mathbf{r}')z(\mathbf{r}'')f(\mathbf{r},\mathbf{r}')f(\mathbf{r},\mathbf{r}'')$$

$$= z(\mathbf{r}) \int_\Omega d\mathbf{r}' \int_\Omega d\mathbf{r}'' \, z(\mathbf{r}')f(\mathbf{r},\mathbf{r}')z(\mathbf{r}'')f(\mathbf{r},\mathbf{r}'') \qquad (15)$$

$$= z(\mathbf{r}) \left\{ \int_\Omega d\mathbf{r}' \, z(\mathbf{r}')f(\mathbf{r},\mathbf{r}') \right\}$$

$$\times \left\{ \int_\Omega d\mathbf{r}'' \, z(\mathbf{r}'')f(\mathbf{r},\mathbf{r}'') \right\}$$

$$= \quad \underset{\mathbf{r}}{\overset{z}{\bigcirc}} \times \left\{ \underset{\mathbf{r} \quad f}{\overset{z}{\longrightarrow}}\bullet \right\}^2 .$$
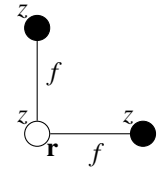
This simple example can be used to illuminate a few ideas. First of all, we used the independence of integration variables in line 3 to reach line 4. On the other hand, the original graph and the resulting graph can be linked with the following procedure if we consider that the labelled point is an articulation point: Separate the graph at the articulation point. Each of the resulting graphs may be computed with the articulation point replaced by a point without properties but with the same label as the labelled point. The original graph is the product of all graphs resulting from the separation times the articulation point with the corresponding property.

Another idea underlying the transformation in equation (15) is the fact that identifying independent subgraphs – independent in a sense that they are only linked by articultion points – can simplify graph computation.

A third remark concerns what simplifications may be made after arriving at the right hand side of equation (15). We did already reduce the number of integrations to be carried out. But we could also go further and define a new property according to

$$z^*(\mathbf{r}) := z(\mathbf{r}) \times \left\{ \underset{\mathbf{r} \quad f}{\overset{z}{\longrightarrow}}\bullet \right\}^2 , \qquad (16)$$

reducing the full graph altogether to

$$= \quad \underset{\mathbf{r}}{\overset{z^*}{\bigcirc}} . \qquad (17)$$

Systematically used, this simple trick is again capable of reducing large graphs in a straightforward way, and we will in fact use it in the Mayer cluster expansion.

In the above example, the articulation point was a labelled point. We chose this setting to clearly show the **r**-dependence in the reduced graphs. Of course, the same formalism can be used on a field articulation point, but some care has to be taken when treating the integration variable of the field point. If one turned all labelled points in equation (17) into field points, the equality would still hold, while when turning all labelled points in equation (15) into field points, the expressions would not necessarily be equal.

2.5   Exponentials of Graphs

At the end of this section, we give two very powerful lemmas which are crucial for many applications of graph theory. A proof can be found in Hiroike and Morita[?] (Lemmas 3 and 4), we will just give the basic idea behind it. The first lemma is

Lemma 5

Consider two sets of graphs of field points, $A := \{\Gamma_\alpha\}$ and $B := \{\Lambda_\beta\}$, with corresponding sets of symmetry numbers $\{s_\alpha\}$ and $\{\tilde{s}_\beta\}$. Let B contain all connected subgraphs of A and the single field point graph. If any $\Gamma_\alpha \subset A$ is a product of graphs $\Lambda_\beta \subset B$ (with a graph possibly appearing multiple times or not at all), and any product of graphs $\Lambda_\beta \subset B$ is represented by exactly one $\Gamma_\alpha \subset A$, then

$$1 + \sum_{\alpha \mid \Gamma_\alpha \in A} s_\alpha^{-1} \Gamma_\alpha = \exp\left(\sum_{\beta \mid \Lambda_\beta \in B} \tilde{s}_\beta^{-1} \Lambda_\beta \right). \qquad (18)$$

Note that a set A, in order to fulfill the prerequisites of the previous lemma, has to be infinite. This does not apply to the set B.

To understand Lemma 5, we consider the exponential function. If one does not consider factors, the exponential function is 1 plus a sum of all powers of the exponent. The 1 is already on the left hand side of (18), so only the sum remains. Since each graph in A is a product of graphs in B, and A contains all products of graphs in B, summing over all graphs in A must contain the same graphs as the exponential function of a sum of all graphs in B. One can prove that the sums are exactly the same if one examines the factors resulting from the symmetry numbers and the factors $(N!)^{-1}$ in the exponential series.

A similar lemma which uses articulation points is

Lemma 6

Consider two sets of connected graphs $A := \{\Gamma_\alpha\}$ and $B := \{\Lambda_\beta\}$ with corresponding sets of symmetry numbers $\{s_\alpha\}$ and $\{\tilde{s}_\beta\}$. The graphs in A and B do all contain a fixed number of labelled points without property and an arbitrary number of field points. Let B contain all the subgraphs of A that stay connected if the labelled points are removed. If any $\Gamma_\alpha \subset A$ can be uniquely dissected into (possibly identical) graphs belonging to B by separating Γ_α at the labelled points, and any graph obtained by joining together (possibly identical) graphs from B at the labelled points uniquely belongs to A, then

$$1 + \sum_{\alpha \,|\, \Gamma_\alpha \in A} s_\alpha^{-1} \, \Gamma_\alpha = \exp\left(\sum_{\beta \,|\, \Lambda_\beta \in B} \tilde{s}_\beta^{-1} \, \Lambda_\beta \right). \quad (19)$$

The proof for this lemma is exactly the same as for Lemma 5, since the process of joining together graphs at labelled points without property is again a simple graph multiplication, so the arguments for the power series in the exponential function and the inclusion of symmetry numbers need not be changed.

An infinite sum of graphs can therefore be expressed by the exponential of a sum of elemental subgraphs, which may be finite. This result will prove useful in the following sections.

3 The Mayer Cluster Expansion

3.1 Fundamentals

The MCE uses graph theory to tackle statistical mechanics. Our task is to acquire thermodynamic properties of a system of identical particles moving in the fixed volume V at the fixed temperature T and the fixed chemical potential μ. The system is to be considered uniform, that is all properties have the same value in the entire system. The properties of interest may for example be the *pressure p* or the *density* ρ. To that end, we consider the graph theoretical approach to obtain a useful expression for the *grand canonical partition function* Ξ,

$$\Xi(\mu, V, T) = \sum_{N \geq 0} e^{N\mu/k_B T} Q(N, V, T) \quad (20)$$

with the *Boltzmann constant k_B* and the *canonical partition function Q*. The sum runs over all *numbers of particles N* contained in V. A common replacement is

$$\beta := \frac{1}{k_B T}, \quad (21)$$

and we can define the *fugacity* by

$$\tilde{z} := e^{\beta\mu}. \quad (22)$$

The canonical partition function is given by

$$Q(N, V, T) = \underbrace{\frac{V^N}{N! \lambda_{\text{th}}^{3N}}}_{Q^{(ig)}(N,V,T)} \frac{1}{V^N} \int d\mathbf{r}^N \, \exp\left[-\beta U_N(\mathbf{r}^N) \right], \quad (23)$$

with a *potential U_N* in which the particles move. The prefactor contains the value of the canonical partition function of the ideal gas $Q^{(ig)}(N, V, T)$, with the *thermal wavelength*

$$\lambda_{\text{th}} = \sqrt{\frac{h^2}{2\pi m k_B T}}, \quad (24)$$

where m is a particle's mass and h is *Planck's constant*. Note that the potential U_N does not depend on particle velocity, that is the particles move in a *force field*.

For all that follows, we will only consider two-body interaction potentials of the form

$$U_N = \sum_{i=1}^{N} \sum_{j>i} \phi(ij), \quad (25)$$
$$\phi(ij) := \phi(\mathbf{r}_i, \mathbf{r}_j) = \phi(\mathbf{r}_j, \mathbf{r}_i).$$

For now, we do not need to know any further details on the interaction potential.

In order to adjust the upper equations to their use in graph theory, we make a change to the definition of the fugacity in equation (22) and give it the new form

$$z := \frac{\tilde{z}}{\lambda_{\text{th}}^3}. \quad (26)$$

In all that follows, we will refer to the quantity z when talking about fugacity, ignoring that $\tilde{z}$ and z have different dimensions. In the framework of graph theory, our points carry property functions. We will therefore treat the fugacity as a constant function

$$z(\mathbf{r}) :\equiv z. \quad (27)$$

We can also use the functions

$$e(ij) := e^{-\beta\phi(ij)},$$
$$f(ij) := e(ij) - 1. \tag{28}$$

These will proof helpful if we insert (25) into the integral in (23). Without factors, the integral then takes the form

$$\int d\mathbf{r}^N \exp(-\beta\sum_{j>i}\phi(ij))$$
$$= \int d\mathbf{r}^N \prod_{j>i} e(ij) = \int d\mathbf{r}^N \prod_{j>i}(f(ij)+1) \tag{29}$$
$$= \int d\mathbf{r}^N [\, 1 + f(12) + \ldots + f(12)f(23) + \ldots$$
$$+ f(12)f(23)f(34) + \ldots \,].$$

So, we have our functions $f(ij)$ and $z(i)$. Using all reformulations of this chapter, we can start from equation (20) to reach a simplified expression

$$\Xi = \sum_{N\geq 0} \tilde{z}^N Q(N,V,T)$$
$$= \sum_{N\geq 0} \frac{\tilde{z}^N V^N}{N!\lambda_{\mathrm{th}}^{3N}} \frac{1}{V^N} \int d\mathbf{r}^N \exp(-\beta\sum_{j>i}\phi(ij))$$
$$= \sum_{N\geq 0} \frac{z^N}{N!} \int d\mathbf{r}^N \prod_{j>i}(f(ij)+1) \tag{30}$$
$$= \sum_{N\geq 0} \frac{1}{N!} \int d\mathbf{r}^N z(1)\cdots z(N)\,[1+f(12)+\ldots].$$

This sum still contains many graphs of equal value. These can be removed by arguments outlined in Section 2.2. We drop the labels and include symmetry numbers for every graph in (30). It is therefore possible to express Ξ in terms of graphs according to

$$\tag{31}$$

We can now go on to use the results of the previous section to further simplify the sum given here. To do so, we have a closer look at (31). It has the form of a sum over sums of N-point graphs. Each sum of N-point graphs contains the unconnected N-point graph, a graph with 1 connection, graphs with 2 connections, $\ldots$, a graph connecting all N points. All of them are weighted with the corresponding symmetry number. For $N \geq 2$, these graphs are not all connected. But they can all be constructed by combining connected subgraphs. On closer

examination, it appears that this does exactly amount to the prerequisite of Lemma 5, where the set B is the set of all connected graphs with $N \geq 1$. Using (18) on (31) yields

$$= \{\text{Sum of all connected graphs with } N \geq 1$$
$$\text{points. All points are } z \text{ field points and are}$$
$$\text{connected by } f\text{-bonds. All graphs are weigh-}$$
$$\text{ted by symmetry numbers } 1/s.\} \tag{32}$$

The property $\ln\Xi$ is of great importance to thermodynamic descriptions of our system, since it yields a thermal equation of state (EOS) for the pressure p by

$$\beta p V = \ln\Xi. \tag{33}$$

We do also know from thermodynamics that the *grand canonical potential* Ω is given by

$$\beta\Omega = -\ln\Xi. \tag{34}$$

The differential of Ω is

$$d\Omega = -SdT - pdV - \bar{N}d\mu. \tag{35}$$

Here, S is the *entropy* of the system. We wrote $\bar{N}$ to indicate the expectation value of the number N of particles in the system, which must not be confused with N in the sums of (20) and similar expressions. We will need (35) later on.

Another important property is the number density ρ. It is the probability of finding a particle at a given position while ignoring the positions of all other particles. To get a good representation, we can write Ξ by

$$\Xi = \sum_{N=0}^{\infty} \int d\mathbf{r}^N P(N, \mathbf{r}^N) \tag{36}$$

with the probability distribution

$$P(N, \mathbf{r}^N) = \frac{1}{N!} z^N \exp(-\beta V(\mathbf{r}^N)). \tag{37}$$

ρ is then given by the grand canonical average of the delta peak, yielding

$$\rho(1) = \frac{1}{\Xi} \sum_{N=1}^{\infty} N \int d(2)\cdots d(N) P(N, \mathbf{r}^N)$$
$$= z \frac{1}{\Xi}\frac{\partial\Xi}{\partial z} = z\frac{\partial\ln\Xi}{\partial z}. \tag{38}$$

The factor N in the integral equation includes indistinguishalbe particles. There are higher order number density functions, to which we will come back at the very end of this section. The

expectation value of the number N of particles in the system depends on ρ by

$$\bar{N} = \int d(1)\rho(1). \tag{39}$$

We can also express ρ in terms of graphs. Remember that we assigned a constant function to z in (27). We can similarly replace z by $z(1)$ in (38) and replace $\ln\Xi$ by the sum of graphs in (31). If we apply Lemma 4 to each graph, we can express the number density $\rho(1)$ by graphs:

$$\tag{40}$$

= {Sum of all graphs obtained from (32) by

turning a field point into a labelled point.

The graphs are weighted by the correct

symmetry numbers $1/s$.}

The equations (32) and (40) are the two first major results of the MCE. Their further simplification is one of the general goals of graph theory. Wertheim's approach[?] also starts developing its main advantages at this point. However, we will not directly proceed with Wertheim's reasoning but rather introduce a more "classical" way to reduce equation (40), the Mayer formalism. Wertheim's equations closely resemble those obtained by the Mayer formalism, and we can later explain them by mostly analogous arguments.

3.2 The Mayer Formalism and Topological Reduction

A defect of the theory we established so far is the great importance of the fugacity z. This quantity is more difficult to measure than other quantities that are also easier to comprehend by intuition – as for example the number density ρ. Our goal in this subsection is to determine equations for $\ln\Xi$ and the *Helmholtz free energy A* that do not depend on z but on ρ. This would be straightforward if we could replace all occurences of z by ρ, so it seems a good idea to investigate the connection between those two. We already have equation (38), which can be put as

$$\frac{\rho(1)}{z(1)} = \frac{\partial\ln\Xi}{\partial z(1)}. \tag{41}$$

We will see that reducing the right hand side of this equation leads to the desired relation. Similar to (40), we get

$$\tag{42}$$

This sum falls under the prerequisites of Lemma 6: all graphs contained can be uniquely expressed as products of graphs where the labelled point 1 is not an articulation point, and if one joins any graphs where 1 is not an articulation point together, the result is exactly one graph in the sum. We can use (19) and define a new function $c(1)$, which is sometimes referred to as the *correlation function* (also called $h(1)$ by some authors[?]). It is given by

$$c(1) := \ln\left[\frac{\rho(1)}{z(1)}\right], \tag{43}$$

and using the above simplifications, it is

$$\tag{44}$$

= {Sum of all graphs with one labelled point 1,

$N_z \geq 1$ z field points connected by f-bonds

such that the labelled point is no articulation

point. The graphs are weighted by the correct

symmetry numbers 1/s.}

Equation (44) contains all of the graphs with $N \leq 3$ points in $c(1)$ and some of those with $N = 4$ points. We chose them to illustrate the next step in our reduction. We already used the fact that in some graphs of ρ the labelled point is an articulation point. However, there are also numerous graphs where at least one field point is an articulation point. These are still contained in $c(1)$, in (44) they are in the second, forth, fifth and sixth graph. These graphs can all be constructed from a at least doubly connected subgraph containing the labelled point and a graph from ρ in (40) attached to each field point such that the field point is replaced by the labelled point in ρ and turned into a field point. The attached graph may be the one point graph. One can group all the graphs in $c(1)$ into equivalence classes by defining the *maximal connected subgraph Γ_m* for any graph Γ: it is the subgraph with the most field points in

the set of subgraphs free of articulation field points that contain the labelled point. Since the labelled point is not an articulation point in the graphs of $c(1)$, Γ_m is unique for any Γ in $c(1)$. If we know look at all the graphs contained in one of the equivalence classes defined by Γ_m, we see that it contains exactly all graphs obtainable by attaching graphs from ρ to the field points in the manner described above. We can therefore use the idea of changing the property of a point we described in Section 2.4 and change the property of the field points from $z(1)$ to $\rho(1)$. Then, we can express $c(1)$ by

$$\begin{aligned}
&= \{\text{Sum of all graphs with one labelled point 1,}\\
&\quad N_\rho \geq 1 \ \rho \text{ field points connected by } f\text{-bonds}\\
&\quad \text{such that none of the points is an articulation}\\
&\quad \text{point. The graphs are weighted by the correct}\\
&\quad \text{symmetry numbers } 1/s.\}
\end{aligned}$$

This equation contains all of the graphs with $N \leq 4$ points in $c(1)$. We use blue points to mark ρ field points. Using the definition of $c(1)$ and the fact that we can express $c(1)$ purely ρ dependent, we can now express $z(1)$ with respect to ρ by inserting (45) into (43), which yields

$$\ln z(1) = \ln \rho(1) - c(1). \qquad (46)$$

With these equations, we are able to give a ρ dependent version of $\ln \Xi$. We start with the variation given by (11), which is for $\ln \Xi$

$$\begin{aligned}
\delta \ln \Xi &= \int d(1) \frac{\delta \ln \Xi}{\delta z(1)} \, \delta z(1)\\
&= \int d(1) \rho(1) \frac{\delta z(1)}{z(1)}\\
&= \int d(1) \rho(1) \, \delta [\ln z(1)] \qquad (47)\\
&= \int d(1) \rho(1) \, \delta [\ln \rho(1) - c(1)]\\
&= \int d(1) \left[\delta \rho(1) - \delta [\rho(1)c(1)] + c(1) \, \delta \rho(1) \right].
\end{aligned}$$

If there were a function $c^{(0)}$ with the property

$$c(1) = \frac{\delta c^{(0)}}{\delta \rho(1)}, \qquad (48)$$

then (47) could be written

$$\delta \ln \Xi = \delta \left[\int d(1) \rho(1) - \int d(1) \rho(1) c(1) + c^{(0)} \right]. \qquad (49)$$

This implies

$$\ln \Xi = \int d(1) \rho(1) - \int d(1) \rho(1) c(1) + c^{(0)}, \qquad (50)$$

where we ignored the possible addition of a constant, as it is unimportant in a thermodynamic potential. The only chore left is to find the missing graph sum $c^{(0)}$. It is however easy to guess from (45). It must be

$$\begin{aligned}
&= \{\text{Sum of all connected graphs with } N \geq 2 \qquad (51)\\
&\quad \rho \text{ field points connected by } f\text{-bonds such}\\
&\quad \text{that none of the points is an articulation point.}\\
&\quad \text{The graphs are weighted by the correct}\\
&\quad \text{symmetry numbers } 1/s.\}
\end{aligned}$$

Since the symmetry numbers are changed adequately by the process of derivation, $c^{(0)}$ given by (51) satisfies (48). From an expression for $\ln \Xi$, which gives us an equation of state by the relation (33), we can also derive an expression for the free energy A. It is related to the grand canonical potential Ω by

$$\beta A = \beta \Omega + \beta \mu \bar{N} = -\ln \Xi + \ln \left(z \lambda_{\text{th}}^3 \right) \bar{N}. \qquad (52)$$

We can do some rearrangments by remembering that $z(1) \equiv z$ is constant and using equation (39), (46) and (49), which leads to

$$\begin{aligned}
\beta A &= -\int d(1) \rho(1) + \int d(1) \rho(1) c(1) - c^{(0)}\\
&\quad + \int d(1) \rho(1) \ln \left(z(1) \lambda_{\text{th}}^3 \right) \qquad (53)\\
&= \int d(1) \rho(1) \left[\ln \left(\rho(1) \lambda_{\text{th}}^3 \right) - 1 \right] - c^{(0)}.
\end{aligned}$$

We have therefore reached the goal of this section and derived equations for $\ln \Xi$ and βA that do not depend on the possibly disadvantageous property z but on the number density ρ. Before proceeding, we want to introduce a different class of functions that are often of interest to thermodynamic models.

3.3 *s*-Particle Distribution and Correlation Functions

The function $\rho(1)$ describes the particle density at location 1 (possibly including orientation). Obviously, there may be functions $\rho(1 \cdots s)$ that describe the density of s particles – or, in that case more accurately, their distribution – at the locations

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$1, \ldots, s$. They are described by a more general form of (38),

$$\rho(1 \cdots s) = \sum_{N=s}^{\infty} \int d(s) \cdots d(N) \frac{N!}{(N-s)!} P(N, \mathbf{r}^N), \qquad (54)$$

which again is the result for calculating the canonical average of delta peaks. We can simplify (54) to

$$\rho(1 \cdots s) = \frac{1}{\Xi} \prod_{i=1}^{s} z(i) \frac{\delta^s \Xi}{\prod_{i=1}^{s} \delta z(i)}. \qquad (55)$$

This time, we can not jump straight to the logarithm for which we have a representation by connected graphs. However, we can define the *Ursell functions*

$$u(1 \cdots s) := \prod_{i=1}^{s} z(i) \frac{\delta^s \ln \Xi}{\prod_{i=1}^{s} \delta z(i)} \qquad (56)$$

that are in close relation to $\rho(1 \cdots s)$. Obviously,

$$u(1) = \rho(1). \qquad (57)$$

And also

$$\begin{aligned} u(12) =& z(1)z(2) \frac{\delta}{z(2)} \frac{1}{\Xi} \frac{\partial \Xi}{\partial z(1)} \\ =& z(1)z(2) \left[\frac{1}{\Xi} \frac{\delta^2 \Xi}{\delta z(1) \delta z(2)} - \frac{1}{\Xi^2} \frac{\partial \Xi}{\partial z(1)} \frac{\partial \Xi}{\partial z(2)} \right] \\ =& \rho(12) - \rho(1)\rho(2). \end{aligned} \qquad (58)$$

It becomes evident that by an analogous procedure any $\rho(1 \cdots s)$ can be described by $u(1 \cdots r)$ with $r \le s$. Since the $u(1 \cdots s)$ are all sums of graphs obtained from $\ln \Xi$ by turning s field points into labelled points, $\rho(1 \cdots s)$ will have a similar form. Even better, it is possible to express an s-particle distribution entirely by 1-particle distribution functions times so-called *correlation functions*. We will explain this with the example of the two-particle correlation functions $g(12)$ and $h(12)$. Let us look closer at $u(12)$. It contains

$$\qquad (59)$$

The approach presented here is rather general, since we have not committed to any forms of the interaction potential $\phi(12)$.

Of course, when choosing a specific class of $\phi(12)$, it may be advisable to also undertake variations to the process of graph reduction we outlined in this section. One of these variations was presented by M. S. Wertheim in 1983[?], and the following section will describe its main ideas.

4 Wertheim's Multiple Density Formalism

4.1 Revisiting the Fundamentals

Most of what follows is part of Wertheim's first paper on the topic[?], which we will simply call I. The three subsequent publications II[?], III[?] and IV[?] will only be briefly visited. Wertheim submitted an additional paper on thermodynamic perturbation theory[?], which we will especially consider in the next section. We will refer to it by V. Since the papers III and IV are generalizations to the papers I and II that go beyond the limit of complexity within the scope of this summary, we will not discuss their technical details but only give remarks on the way they generalize the results of I and II.

As we mentioned at the end of the last section, the Mayer Cluster Expansion in its generality may not be the most adequate way to treat special forms of the interaction potential $\phi(12)$. The form Wertheim chose to analyze is

$$\phi(12) = \phi_R(12) + \sum_{A,B} \phi_{AB}(|\mathbf{r}_2 + \mathbf{d}_\beta(\Omega_2) - \mathbf{r}_1 - \mathbf{d}_\alpha(\Omega_1)|). \qquad (60)$$

α and β are labels for interaction sites on each particle, the position of which is described by $\mathbf{d}(\Omega_i)$, dependent on the orientation Ω_i of each particle. The potentials ϕ_{AB} are considered to be purely attractive, that is

$$\phi_{AB} \le 0 \qquad \forall A, B. \qquad (61)$$

The rest of the interaction is purely repulsive, preferably strong enough to make a lot of graphs vanish later in the expansion. A classical example is the *hard sphere potential* ϕ_R^{HS}, which strictly forbids core overlap by

$$\phi_R^{HS}(12) = \begin{cases} \infty, & r_{12} \le D, \\ 0, & r_{12} > D, \end{cases} \qquad (62)$$

where D is the hard sphere diameter.

Wertheim I focusses on the case that there is only one interaction site per particle, turning (60) into

$$\phi(12) = \phi_R(12) + \phi_A(|\mathbf{r}_2 + \mathbf{d}_\beta(\Omega_2) - \mathbf{r}_1 - \mathbf{d}_\alpha(\Omega_1)|). \qquad (63)$$

The binding site A is situated at the edge of the repulsive core. In the hard sphere example, this may be of the form

$$\phi_A(x) = \begin{cases} < 0 & x < a, \\ = 0 & x > a. \end{cases} \qquad (64)$$

The position of the site defined by $\mathbf{d}(\Omega_i)$ has to be chosen so that the site is within the particle but close enough to the edge to avoid that the attractive region is cancelled out by the infinite core repulsion. A case of special interest would be short-ranged interaction leading to glue spots such that a site can only interact attractively with one other site. In that case, a would have to be much smaller than D.

Potentials of the form (60) can obviously be clearly separated into their attractive and their repulsive contributions. So it seems adequate to maintain this separation when considering $e(12)$ and $f(12)$. We can define

$$\left.\begin{array}{l} e_i(12) := \exp(-\beta\phi_i(12)) \\ f_i(12) = e_i(12) - 1 \end{array}\right\} i \in \{R,A\}, \qquad (65)$$

leading to

$$e(12) = e_R(12)e_A(12), \qquad (66)$$

which means for $f(12)$ as in (28) that

$$\begin{aligned} f(12) &= e_R(12)(e_A(12) - 1 + 1) - 1 \\ &= [e_R(12) - 1] + e_R(12)[e_A(12) - 1] \qquad (67) \\ &=: f_R(12) + F(12). \end{aligned}$$

We can use this new definition to change (32) and (40). The resulting graphs should contain either f_R-bonds and F-bonds. However, it is more convenient to define a subset of graphs with the help of which all graphs in $\ln\Xi$ can be constructed. Wertheim introduces the s-mer graphs, which are the graphs of s points in which all points are connected by F-bonds. Note that there may also be f-bonds present. Because of this, the set of pure s-mer graphs can be further simplified, which we can illustrate by the example of all trimer graphs, which would be in a sum

(68)

The zigzag connections are here (and in the following) F-bonds, the straight continuous lines are f_R-bonds and the dashed lines are e_R-bonds. It is clear that when replacing all f-bonds by $F + f_R$, a replacement like in (68) will be possible for any graph already connected by F-bonds, since the sum includes F-connected graph and no other bond and the F-connected graph plus an f_R-bond, plus two f_R-bonds etc. The replacement procedure will also not change the symmtery numbers. We do not give a clean mathematical explanation here, but it is at least evident that one can imagine the replacement to take place "symmetrically" on all bonds.

Therefore, we state

Definition 7

A (pure) s-mer graph is an s-point graph of z field points where all points are connected by F-bonds. All pairs of points not directly connected by an F-bond are connected by an e_R-bond.

This leads us straight to an expression for

$$\begin{aligned} \ln\Xi = \{&\text{Sum of all connected graphs consisting of} \\ &\text{s-mer graphs, } s \geq 1, \text{ and } f_R\text{-bonds between} \qquad (69) \\ &\text{pairs of points in distinct s-mer graphs.}\} \end{aligned}$$

$\rho(1)$ can be derived from $\ln\Xi$ in the same way as before, it is still the sum over all graphs obtained from $\ln\Xi$ by turning a field point into a point labelled 1.

The e_R-bonds within s-mers are considered irreducible, that is it is not allowed to exchange an e_R-bond by the sum of an f_R-bond and no bond. This has the important consequence that a pure s-mer graph does not contain articulation points of any sorts. This means that neither can an s-mer graph be broken down into two or more independent subgraphs at a labelled point nor can an s- and an s'-mer graph with $s,s' \geq 2$ be joined together into an $(s + s' - 1)$-mer graph at a labelled point since there would be at least one e_R-bond missing. You could say that by Definition 7, all s-mer graphs are closed in a sense that it is impossible to obtain a higher s-mer graph by appending a new graph to a single point.

This last remark makes the following approach seem interesting: it could be useful to separate the graphs in $\rho(1)$ into those where an s-mer with $s \geq 2$ can be attached to the labelled point and those where this is not possible. This idea and its consequences are the next section's focus.

4.2 The Two Density Approach

We decompose $\rho(1)$ by

$$\rho(1) = \rho_0(1) + \rho_1(1). \qquad (70)$$

Here, $\rho_0(1)$ contains all graphs where the labelled point is in a monomer, that is it has no adjacent F-bonds. $\rho_1(1)$ contains all the other graphs, i.e. the graphs where the labelled point is in an s-mer with $s \geq 2$. We can call $\rho_0(1)$ the *monomer density*. Like in Section 3.2, $\rho_0(1)/z$ is the exponential of the subgraphs of ρ_0/z that have no articulation labelled point. In analogy, we define

$$c_0(1) := \ln\left[\frac{\rho_0(1)}{z(1)}\right]. \qquad (71)$$

Since an arbitrary number of f_R-bonds can be attached to the labelled point (in fact, any point) in $\rho_1(1)$, it must contain $\rho_0(1)$ as a factor. It is therefore convenient to define

$$c_1(1) := \frac{\rho_1(1)}{\rho_0(1)}, \qquad (72)$$

the sum of all graphs with a property-free labelled point 1 in an s-mer ($s \geq 2$) in which 1 is not an articulation point.

In the Mayer formalism, the next step would be to change the property of the field points from z to ρ to get an articulation point free representation of $c(1)$ and a ρ dependent expression for z. The Wertheim approach continues analogously, but there is a slight variation necessary.

We did already elaborate in the remarks on Definition 7 that we can not add F-bonds to a field point that is already in an s-mer with $s \geq 2$. Therefore, those points within doubly connected graphs in $c_0(1)$ and $c_1(1)$ that do belong to such an s-mer can only carry graphs from $\rho_0(1)$. For monomeric points within the doubly connected graphs it is still possible to attach any graph from $\rho(1)$ to the point. Therefore, we change the property from $z(1)$ to either $\rho(1)$ or $\rho_0(1)$. We consider only the at least doubly connected graphs in $c_0(1)$ and $c_1(1)$, where points in monomers carry the property $\rho(1)$ and points in s-mers for $s \geq 2$ carry the property $\rho_0(1)$. For example,

$$c_0(1) = \text{graphs}$$
(73)

Here, the blue point are still ρ field points and the green points are ρ_0 field points.

So what happens to $\ln \Xi$? We can use (71) and then (72) to find for the variation of $\ln \Xi$ that

$$
\begin{aligned}
\delta \ln \Xi &= \int d(1) \rho(1)\, \delta \left[\ln z(1)\right] \\
&= \int d(1) \rho(1)\, \delta \left[\ln \rho_0(1) - c_0(1)\right] \\
&= \int d(1) \frac{\rho(1)}{\rho_0(1)} \delta \rho_0(1) - \int d(1) \delta \left[\rho(1)\, c_0(1)\right] \\
&\quad + \int d(1) c_0(1)\, \delta \rho(1) \\
&= \int d(1) \delta \rho_0(1) - \int d(1) \delta \left[\rho(1)\, c_0(1)\right] \\
&\quad + \int d(1) \left[c_0(1)\, \delta \rho(1) + c_1(1) \delta \rho_0(1)\right].
\end{aligned}
$$
(74)

Again, the similarity to (47) is strong. This time, we need a function $c^{(0)}$ that saitsfies

$$c_0(1) = \frac{\delta c^{(0)}}{\delta \rho(1)}, \qquad c_1(1) = \frac{\delta c^{(0)}}{\delta \rho_0(1)}.$$
(75)

Then, we have

$$\delta c^{(0)} = \int d(1) \left[c_0(1)\, \delta \rho(1) + c_1(1) \delta \rho_0(1)\right],$$
(76)

and therefore, again ignoring addition of a constant,

$$\ln \Xi = \int d(1) \rho_0(1) - \int d(1) \rho(1) c_0(1) + c^{(0)}.$$
(77)

, or the equivalent

$$\ln \Xi = \int d(1) \left[\rho(1) - c_1(1) \rho_0(1) - c_0(1) \rho(1)\right] + c^{(0)}.$$
(78)

Finding $c^{(0)}$ is fairly obvious from $c_0(1)$ and $c_1(1)$. It should be the sum of the graphs in $c_0(1)$ and $c_1(1)$ where the labelled point is turned into a ρ field point or a ρ_0 field point, respectively. All graphs resulting from this manipulation are only counted once (despite the fact that the derivative of the graph may appear in both $c_0(1)$ and $c_1(1)$) and weighted with the correct symmetry number. The straightforward definition can be found in Wertheim I.

After finding $\ln \Xi$, we can again find βA by (53),

$$
\begin{aligned}
\beta A &= -\int d(1) \rho_0(1) + \int d(1) \rho(1) c_0(1) - c^{(0)} \\
&\quad + \int d(1) \rho(1) \ln \left(z(1) \lambda_{\text{th}}^3\right) \\
&= \int d(1) \left[\rho(1) \ln \left(\rho(1) \lambda_{\text{th}}^3\right) - \rho_0(1)\right] - c^{(0)}.
\end{aligned}
$$
(79)

The two density formalism stays therefore very close to the Mayer formalism.

4.3 Multiple Densities

The two density formalism is designed for cases where the attractive interaction between particles is only governed by a single site per particle. While the creation of s-meric compounds with arbitrary values for s is possible with potentials of that kind, the structure of the compounds has very little degrees of freedom. For example, a system containing chains of particles can not be modelled by this approach, the chains would require at least two sites per particle. To meet this new challenge, it is possible to generalize the two density formalism to a multiple density formalism which can deal with an arbitrary number of sites per particle. This section shall briefly outline the main ideas of this generalization. We revisit the four steps we covered for the two density case, namely to define a potential, to define the topolgy including s-mer graphs, to introduce new densities ρ_α and to find reduced funtions c_α, and finally to express the EOS and βA in terms of the definitions we made.

New potential. We now consider potentials of the form (60) without the restriction of (63). The set of all sites on one particle shall be denoted by Γ. We still use the functions $e_R(12)$ and $f_R(12)$ for the repulsive interaction and for the attractive interaction

$$
\left.
\begin{aligned}
e_{AB}(12) &:= \exp(-\beta \phi_{AB}(12)) \\
f_{AB}(12) &= e_{AB}(12) - 1
\end{aligned}
\right\} A, B \in \Gamma.
$$
(80)

This means for the full $e(12)$ and $f(12)$ that

$$e(12) = e_R(12) \prod_{A,B} e_{AB}(12),$$

$$f(12) = f_R(12) + e_R(12) \left\{ \prod_{A,B} [f_{AB}(12) + 1] - 1 \right\}. \tag{81}$$

If we set $\phi_{AA} = 0$ for all $A \in \Gamma$, then $f(12)$ is of the form

$$\begin{aligned} f(12) =& f_R(12) + e_R(12) \{ f_{AB}(12) + f_{AC}(12) + \ldots \\ & + f_{AB}(12)f_{AC}(12) + f_{AC}(12)f_{BC}(12) + \ldots \}. \end{aligned} \tag{82}$$

Introducing bonds of type $F(12) = e_R(12)f_{AB}(12)$ only made sense if there were a maximum of one bond of this type between two partciles, in the situation with more than one site per particle and therefore the possibility of multiple attractive bonds between particles, this would lead to higher powers of $e_R(12)$, which would not be true to (81). Indeed, it is now important to clearly distinguish bonds between (attractive) inter-action sites from bonds between (repulsive) particles. There may be more than one bond $f_{AB}(12)$ between two particles while there can still only be one bond of type $e_R(12)$ or $f_R(12)$. As in Wertheim I, the attractive f_{AB}-bonds between sites are still paired with repulsive e_R-bonds between particles, so it remains possible to use the advantage of identifying s-mers by their interconnection with e_R-bonds. However, the question of the additional e_R-bonds resulting from combining the graph with an f_R-bond between a pair of points and the graph where there is no bond present should be discussed again.

Toplogy and s-mers. We need to introduce some additional terminology. This is best done with some explanatory graphs. We can draw a point with 2 sites by

$$\tag{83}$$

Adopting Wertheim's definition, we call the big circle a *hyperpoint* and the small black circles are the sites. If not stated otherwise, the hyperpoint is a field point despite it not being filled black. It has to be made clear beforehand which site is which.

Now, consider how the following graphs differ in connection:

$$\tag{84a}$$

$$\tag{84b}$$
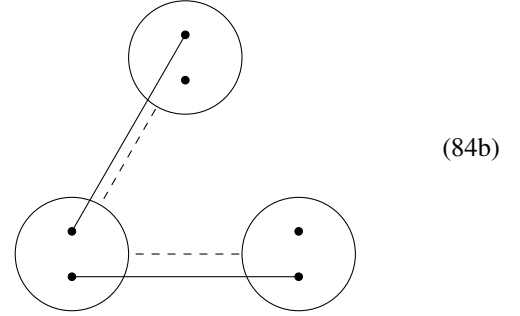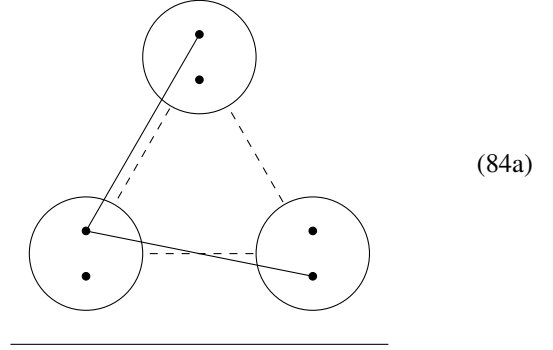
The e_R-bonds already anticipate Wertheim's generalization, which we will now explain.

One would consider both graphs to be connected. The connection in (84a) is clearer, the sites are connected by direct attraction bonds. The connection in (84b) comes from attraction bonds and the fact that sites are connected because they belong to the same hyperpoint. Wertheim calls the sites that are connected by a path of attraction bonds and sites *bond-connected*, while he calls sites belonging to the same hyperpoint *constraint-connected*. The hyperpoints of bond-connected sites are all additionally interconnected by e_R-bonds, while in the case of constraint-connection no further e_R-bonds are added.

An s-mer graph would therefore be a graph in which all hyperpoints are connected by e_R-bonds. There may be pairs of points without an e_R-bond. Those may carry either no bond or an f_R-bond, which may not be reduced to an e_R-bond. Therefore, the e_R-connection may not be as interwoven as in the two density case. It is possible, as for example at the left hyperpoint in (84b), that a hyperpoint is an articulation point. We call such a point a *constraint-articulation point* (c-AP). A hyperpoint is a c-AP if deleting the constraint connection of the sites within the hyperpoint and all incident f_R and e_R-bonds leads to two or more separate graphs.

In terms of f_R-bonds, Wertheim introduces the *bare s-mer* graphs as those s-mer graphs where no f_R-bonds are present and the *hindered s-mer* graphs as those where at least one f_R-bond is present. The two sets are disjoint and the set of all pure

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s-mer graphs is the union of both.

Finally, a quick remark on the purpose of using the third e_R-bond in (84a) and not in (84b). Especially when progressing to TPT, Wertheim uses steric incompatibilities between hyperpoints – that is hard core overlap – to further treat the equations this section is concerned with. In (84a) one site is connected to two sites in different hyperpoints. If one identifies sites with valence electrons, this type of bonding becomes physically dubious. To ensure the cancellation of graphs of this kind, Wertheim demands the e_R-bond. The graph (84a) will always vanish: either at least one of the f_{AB}-bonds is zero because the pertaining sites are too far apart, or if both the attractive bonds are non-vanishing, the hard core overlap between the hyperpoints forbids this structure, which mathematically means that the e_R-bond between the upper and the right hyperpoint in (84a) becomes zero. Including the bond and considering it irreducible will ensure that it stays intact after the process of topological reduction and that therefore no information about steric incompatibility is lost. One can later use it to further simplify the results.

We did now introduce a variety of new definitions and conventions into the former framework of the two density formalism. The new definitions do not change the main form for $\ln \Xi$ as stated by (69), where only the transition from points to hyperpoints has to be kept in mind. $\rho(1)$ is again obtained by turning field hyperpoints in $\ln \Xi$ into labelled hyperpoints.

Defining densities. While we had ρ_0 for the graphs with no site-site interaction at the labelled point and ρ_1 for those with at least one, we can now generally introduce ρ_α for the graphs where the labelled point has (possibly multiple) attraction bonds at all sites in the set α. If we call the set of all sites per particle Γ, this leads to

$$\rho(1) = \sum_{\alpha \subseteq \Gamma} \rho_\alpha(1). \tag{85}$$

The set $\rho_0(1)$ stays basically the same, so, in the spirit of (71), we can define

$$c_0(1) := \ln \left[\frac{\rho_0(1)}{z(1)} \right]. \tag{86}$$

$c_0(1)$ contains all graphs of $\rho_0(1)/z$ where 1 is not a c-AP. Again, any $\rho_\alpha(1)$ must contain $\rho_0(1)$ as a factor. We can define for $\alpha \neq \emptyset$

$$c_\alpha(1) := \{\text{Sum of all graphs of } \rho_\alpha(1)/\rho_0(1) \text{ such} \\ \text{that 1 is not a c-AP.}\} \tag{87}$$

$\rho_\alpha(1)/\rho_0(1)$ does not only contain $c_\alpha(1)$, but also products of $c_\gamma(1)$, where γ is part of partitions of α. An example: When turning the left point in (84b) into a labelled point, the resulting graph belongs to ρ_{AB}. However, it does not belong to $\rho_0(1)c_{AB}(1)$ but to $\rho_0(1)c_A(1)c_B(1)$ since 1 is a c-AP.

This leads to

$$\rho_\alpha(1) = \rho_0(1) \sum_{\{\gamma\} \in P(\alpha)} \prod_\gamma c_\gamma(1). \tag{88}$$

$P(\alpha)$ is the partition of α into nonempty subsets. Especially, $\{\alpha\} \in P(\alpha)$. (88) is simply the mathematical illustration that any graph belonging to $\rho_\alpha(1)$ is constructed by repulsive bonds between the hyperpoint 1 and other *s*-mers ($\rho_0(1)$) and combinations of irreducible *s*-mers such that exactly all sites in α are bonded at the hyperpoint 1 (product over $c_\gamma(1)$).

As before, we can reduce all the $c_\gamma(1)$ by considering which graphs can still be attached to the hyperpoints of all irreducible subgraphs and their sites without violating the *s*-mer construction conditions dictated by e_R-bonds. For two densities, either $\rho_0(1)$ or the full $\rho(1)$ could be attached. The density $\rho_1(1)$ is only indirectly included since $\rho(1) = \rho_0(1) + \rho_1(1)$. And indeed, whenever a graph of $\rho_1(1)$ can be appended to 1, then it must also be possible to append a graph of $\rho_0(1)$ to it. This can be expanded to a case of multiple sites: if it is possible to add a graph from some $\rho_\alpha(1)$ to a point 1 – that is, a graph in which all sites of α are bonded in at least one *s*-mer – then it must be possible to append a graph from any $\rho_\gamma(1)$ with $\gamma \subseteq \alpha$ to 1. We define

$$\sigma_\alpha(1) := \sum_{\gamma \subseteq \alpha} \rho_\gamma(1), \tag{89}$$

especially

$$\sigma_0(1) = \rho_0(1), \qquad \sigma_\Gamma(1) = \rho(1). \tag{90}$$

By $\sigma_\alpha(1)$ we can reduce the graphs $c_\alpha(1)$ as we did in the previous section. This yields

$$
\begin{aligned}
c^{(0)} = \{&\text{Sum of all at least doubly connected graphs} \\
&\text{constructed by } s\text{-mer graphs of field hyper-} \\
&\text{points interconnected by } f_R\text{-bonds. If } \alpha \text{ is} \\
&\text{the set of all attraction bonded sites of a} \\
&\text{hyperpoint, then the hyperpoint carries the} \\
&\text{property } \sigma_{\Gamma-\alpha}.\}
\end{aligned}
\tag{91}
$$

The properties $c_\alpha(1)$ are again obtained by differentiation via

$$c_\alpha(1) = \frac{\delta c^{(0)}}{\delta \sigma_{\Gamma-\alpha}}. \tag{92}$$

Finding the EOS. The remainder is just a longer calculation. We break it into smaller pieces, starting from the very begin-

ning with

$$\delta \ln \Xi = \int d(1)\rho(1)\delta\left[\ln z(1)\right]$$

$$\stackrel{(86)}{=} \int d(1)\frac{\rho(1)}{\rho_0(1)}\delta\rho_0(1) - \int d(1)\rho(1)\delta c_0(1)$$

$$= \underbrace{\int d(1)\frac{\rho(1)}{\rho_0(1)}\delta\rho_0(1) - \int d(1)\delta\rho(1)}_{(A)} \tag{93a}$$

$$\underbrace{- \int d(1)\rho(1)\delta c_0(1)}_{(B)} + \underbrace{\int d(1)\delta\rho(1)}_{(C)}.$$

We inserted the term (C) to get closer to the variation of (78). We can leave (C) and (B) as they are and focus on the term (A). Also, to keep equations slim, we drop the arguments in the integrand.

$$(A) = \int \left\{\frac{\rho}{\rho_0}\delta\rho_0 - \delta\rho\right\}$$

$$\stackrel{(85)}{=} \int \left\{\left[1 + \sum_{\gamma \subseteq^* \Gamma}\frac{\rho_\gamma}{\rho_0}\right]\delta\rho_0 - \delta\rho\right\}$$

$$= \int \left\{\sum_{\gamma \subseteq^* \Gamma}\frac{\rho_\gamma}{\rho_0} - \delta\left[\rho - \rho_0\right]\right\} \tag{93b}$$

$$= \int \sum_{\gamma \subseteq^* \Gamma}\left\{\frac{\rho_\gamma}{\rho_0} - \delta\rho_\gamma\right\}.$$

The notation $\gamma \subseteq^* \Gamma$ shall indicate that only the nonempty subsets of Γ are summed over. For the quotient ρ_γ/ρ_0 we can use (88) to find

$$(A) = \int \sum_{\gamma \subseteq^* \Gamma}\sum_{M \in P(\gamma)}\left\{\left[\prod_{\alpha \in M}c_\alpha\right]\delta\rho_0 - \delta\left[\rho_0\prod_{\alpha \in M}c_\alpha\right]\right\}$$

$$= \int \sum_{\gamma \subseteq^* \Gamma}\sum_{M \in P(\gamma)}\left\{\left[\prod_{\alpha \in M}c_\alpha\right]\delta\rho_0 - \left[\prod_{\alpha \in M}c_\alpha\right]\delta\rho_0 \right.$$

$$\left. - \rho_0\delta\left[\prod_{\alpha \in M}c_\alpha\right]\right\} \tag{93c}$$

$$= -\int \sum_{\gamma \subseteq^* \Gamma}\sum_{M \in P(\gamma)}\sum_{\alpha \in M}\rho_0\left[\prod_{\alpha' \in M\setminus\{\alpha\}}c_{\alpha'}\right]\delta c_\alpha.$$

This long equation will reduce to a rather simple one by a re-arrangement of sums. We want to get the sum over α to the very left. We first have to exchange it with the sum over M. Since M counts all the partitions of γ into subsets and α runs over all subsets contained in M, we can express the sum over all subsets contained in all partitions of γ as the sum over all

nonempty subsets $\alpha \subseteq^* \gamma$ and the partitions M of γ containing the subset. That is,

$$(A) = -\int \sum_{\gamma \subseteq^* \Gamma}\sum_{\alpha \subseteq^* \gamma}\sum_{\substack{M \in P(\gamma)\\M \ni \alpha}}\rho_0\left[\prod_{\alpha' \in M\setminus\{\alpha\}}c_{\alpha'}\right]\delta c_\alpha. \tag{93d}$$

We can investigate the sets M appearing in (93d) further. Taking all partitions of γ and then selecting those containing α yields the same set as taking all partitions of $\gamma\setminus\alpha$ and uniting them with $\{\alpha\}$, or expressed mathematically:

$$P(\gamma) \cap \{M \mid \alpha \in M\} = P(\gamma\setminus\alpha) \cup \{\alpha\}. \tag{93e}$$

The appearance of both the set α and the set containing α, $\{\alpha\}$, is due to the fact that M is a set of subsets of γ while γ and α are simply sets of binding sites, making the separation necessary. For all that follows, we will use the simple terminology $\gamma - \alpha$ whenever we want to express that the set α is not included. Since we can construct the sets M from $P(\gamma - \alpha)$ as in (93e), we do not need the partition of the full set γ in (93d). This is especially useful since the product over α' can then be simplified via (88). We calculate

$$(A) = -\int \sum_{\gamma \subseteq^* \Gamma}\sum_{\alpha \subseteq^* \gamma}\sum_{M \in P(\gamma-\alpha)}\rho_0\left[\prod_{\alpha' \in M}c_{\alpha'}\right]\delta c_\alpha$$

$$= -\int \sum_{\gamma \subseteq^* \Gamma}\sum_{\alpha \subseteq^* \gamma}\rho_{\gamma-\alpha}\delta c_\alpha \tag{93f}$$

$$= -\int \sum_{\alpha \subseteq^* \Gamma}\sum_{\substack{\gamma \subseteq^* \Gamma\\\gamma \supseteq \alpha}}\rho_{\gamma-\alpha}\delta c_\alpha.$$

On the last line, we swapped the sums over α and γ, where we now sum over all the subsets of Γ and then all sets containing these subsets. If we consider all summands multiplied by c_α for some fixed α, we find sums of the form

$$\rho_{\alpha-\alpha} + \rho_{\alpha+A-\alpha} + \rho_{\alpha+B-\alpha} + \ldots + \rho_{\alpha+A+B-\alpha} + \ldots$$

$$= \rho_0 + \rho_A + \rho_B + \ldots + \rho_{AB} + \ldots, \tag{93g}$$

with $A, B \in (\Gamma - \alpha)$. This is exactly $\sigma_{\Gamma-\alpha}$ by (89). Therefore, we find when including (B) and (C) again

$$\delta \ln \Xi = -\int \sum_{\alpha \subseteq^* \Gamma}\sigma_{\Gamma-\alpha}\delta c_\alpha - \int \sigma_\Gamma \delta c_0 + \int \delta\rho$$

$$= -\int \sum_{\alpha \subseteq \Gamma}\sigma_{\Gamma-\alpha}\delta c_\alpha + \int \delta\rho$$

$$= -\int \sum_{\alpha \subseteq \Gamma}\delta\left[\sigma_{\Gamma-\alpha}c_\alpha\right] + \int c_\alpha\delta\sigma_{\Gamma-\alpha} + \int \delta\rho \tag{93h}$$

$$\stackrel{(92)}{=} \delta\left\{\int \rho - \int \sum_{\alpha \subseteq \Gamma}\sigma_{\Gamma-\alpha}c_\alpha + c^{(0)}\right\}.$$

If we ignore and additive constant and properly spell the integrals, this yields the desired equation

$$\ln \Xi = \int d(1)\rho(1) - \int d(1) \sum_{\alpha \subseteq \Gamma} \sigma_{\Gamma-\alpha}(1)c_\alpha(1) + c^{(0)}. \quad (94)$$

This can be paired with (53) to find an expression for

$$
\begin{aligned}
\beta A &= \int d(1)\ln\left(z(1)\lambda_{th}^3\right)\rho(1) - \int d(1)\rho(1) \\
&\quad + \int d(1) \sum_{\alpha \subseteq \Gamma} \sigma_{\Gamma-\alpha}(1)c_\alpha(1) - c^{(0)} \\
&= \int d(1)\left[\ln\left(\rho_0(1)\lambda_{th}^3\right) - 1\right]\rho(1) \\
&\quad + \int d(1) \sum_{\substack{\alpha \subseteq \Gamma \\ \alpha \neq \emptyset}} \sigma_{\Gamma-\alpha}(1)c_\alpha(1) - c^{(0)}.
\end{aligned}
\quad (95)
$$

There is also a representation of A entirely independent of $c_\alpha(1)$. It can be derived from (95) by inserting a reformulation of c_α in terms of the σ_γ for $\gamma \subseteq \alpha$. The approach prominently features dual numbes?, which favor some rather elegant manipulations of graph sums, yet they are more technical than what we used so far. We will not go into the details here and simply name the final result that

$$\beta A = \int d(1)\left[\sigma_\Gamma(1)\ln\left(\sigma_0(1)\lambda_{th}^3\right) + Q(1)\right] - c^{(0)}, \quad (96)$$

with

$$
\begin{aligned}
Q(1) = &-\sum_{A \in \Gamma} \sigma_{\Gamma-A}(1) \\
&+ \sigma_0(1) \sum_{\substack{\{\gamma\} \in P(\Gamma) \\ \#\{\gamma\}=M \geq 2}} (-1)^M (M-2)! \prod_\gamma \frac{\sigma_\gamma(1)}{\sigma_0(1)}.
\end{aligned}
\quad (97)
$$

Here, $\#\{\gamma\}$ is the cardinality of the set $\{\gamma\}$, so the improper partition $\{\gamma\} = \{\Gamma\}$ is not included. With (96) it is possible to express $\ln \Xi$ independent of $c_\alpha(1)$ as well. We can use the *Gibbs free energy G*, which is related to A by

$$G = E - TS + pV = A + pV = \mu N. \quad (98)$$

With the differential of A,

$$dA = -SdT - pdV + \mu dN, \quad (99)$$

we arrive at

$$\left.\frac{\partial A}{\partial N}\right|_{T,V} = \mu. \quad (100)$$

This also means

$$G = N \left.\frac{\partial A}{\partial N}\right|_{T,V} = \rho \left.\frac{\partial A}{\partial \rho}\right|_{T,V}, \quad (101)$$

leading to a graph representation of (98) by

$$\ln \Xi = \beta G - \beta A = \int d(1)\sigma_\Gamma(1)\frac{\delta(\beta A)}{\delta \sigma_\Gamma(1)} - \beta A. \quad (102)$$

We consider the variables $\sigma_\alpha(1)$ to be independent from one another, which yields

$$\ln \Xi = -\int d(1)Q(1) + c^{(0)} - \int d(1)\sigma_\Gamma(1)\frac{\delta c^{(0)}}{\delta \sigma_\Gamma(1)}. \quad (103)$$

(94) and (95) or (103) and (96) are the two fundamental equations of the multiple density formalism. Of course, the two density formalism remains a special case. The advantages of multiple densities over the one density approach of the Mayer formalism are discussed in Wertheim I and III. Especially the topic of steric incompatibility is approached systematically. Instead, we are now interested in putting the equations obtained so far straight to use.

5 Thermodynamic Perturbation Theory

5.1 TPT Equations for the Multiple Density Approach

For the following, we will consider a system with the potential (60) with only two sites A and B per particle and with the additional condition

$$\phi_{AA} = \phi_{BB} = 0. \quad (104)$$

The repulsive part of the potential will be of spherical form, as given by (62) with the hard sphere diameter D. (104) ensures that only one unique type of attractive bond f_{AB} can link two particles. Furthermore, the system is in a grand canonical ensemble within the volume V at temperature T and density ρ. We call this system the *real system* and are interested in calculating its pressure p.

In TPT, we are interested in systematically approaching the calculation of properties like the pressure p or the Helmholtz free energy A – for which we have expressions with infinite sums of graphs – by equations containing only a finite amount of graphs. This usually means that the remainder of the infinite sum is considered negligible in the system being examined. For example, when decreasing the density of our real system, graphs of more than two hyperpoints will soon contribute only very insignificantly to $\ln \Xi$, and when further decreasing the density, all site-site interaction will become completely negligible. The hyperpoint-hyperpoint interaction remains important, since it reduces the effective volume the particles are contained in. This means that a hard sphere fluid will eventually describe the system accurately.

Since the hard sphere fluid is easy to treat and there are indeed sophisticated analytical expressions for its various properties, we can use it as a *reference system* in the study at hand. It is described by the purely repulsive potential of the reference system without any attraction. It has the same particle density ρ and Temperature T as the real system. Its pressure p_R can be reasonably well described by the *Carnahan-Starling* EOS[?]

$$\frac{\beta p_R}{\rho} = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3} \tag{105}$$

with the *packing density*

$$\eta = \frac{1}{6}\pi\rho D^3. \tag{106}$$

The pressure in the real system is described by (103), with the Since they both obey (103) (with $Q_R(1) = 0$), we can quantify the difference between the real system and the reference system by

$$\beta(p - p_R)V = \int d(1) \left[-\sigma_\Gamma(1) + \sigma_A(1) + \sigma_B(1) \right. \\ \left. - \frac{\sigma_A(1)\sigma_B(1)}{\sigma_0(1)} \right] + \Delta c^{(0)} \\ - \int d(1)\sigma_\Gamma \frac{\delta \Delta c^{(0)}}{\delta \sigma_\Gamma(1)}, \tag{107}$$

where we inserted the result for $Q(1)$ with two sites and (104). Obviously, a new quantity of interest is

$$\Delta c^{(0)} = c^{(0)} - c_R^{(0)}. \tag{108}$$

$c_R^{(0)}$ is the graph sum we defined in (51). The $\Delta c^{(0)}$ is the sum of all graphs in $c^{(0)}$ not purely interacting by repulsion. Equation (107) contains three unknowns, σ_0, σ_A and σ_B along with $\Delta c^{(0)}$, which is itself a function of the latter. This function contains infinite sums of graphs, so we are not able to obtain results without simplifications. To that end, let us have a look at the first graphs in $\Delta c^{(0)}$

$$\tag{109}$$

Helmholtz free energy A of our system, which reduces with the knowledge of the reference Helmholtz free energy A_R to the task of finding the *excess Helmholtz free energy $A - A_R$* of our system. The reference system is just described by the equations we already derived for the Mayer formalism in (53), but in the language of the multiple density formalism:

$$\beta A_R = \int d(1)\sigma_\Gamma(1) \left[\ln\left(\sigma_\Gamma(1)\lambda_{th}^3\right) - 1 \right] - c_R^{(0)}. \tag{110}$$

$c_R^{(0)}$ is the graph sum we defined in (51). Instead of also using the corresponding result (50) for the reference EOS, we rather We will only consider the case of two sites per particle, so we have

$$\beta A = \int d(1)\sigma_\Gamma(1) \ln\left(\sigma_0(1)\lambda_{th}^3\right) - \int d(1)\sigma_A(1) \\ - \int d(1)\sigma_B(1) + \int d(1)\frac{\sigma_A(1)\sigma_B(1)}{\sigma_0} - c^{(0)}. \tag{111}$$

The excess energy is then simply

$$\beta(A - A_R) = \int d(1)\sigma_\Gamma(1) \ln\left(\frac{\sigma_0(1)}{\sigma_\Gamma(1)}\right) + \sigma_\Gamma(1) \\ - \sigma_A(1) - \sigma_B(1) + \frac{\sigma_A(1)\sigma_B(1)}{\sigma_0} - \Delta c^{(0)}. \tag{112}$$

The $\Delta c^{(0)}$ is the sum of all graphs in $c^{(0)}$ not purely interacting by repulsion, since

$$\Delta c^{(0)} = c^{(0)} - c_R^{(0)}. \tag{113}$$

We also want an expression for the excess pressure. We can use (103) to that end, yielding

$$\beta(p - p_R)V = \int d(1) \left[-\sigma_\Gamma(1) + \sigma_A(1) + \sigma_B(1) \right. \\ \left. - \frac{\sigma_A(1)\sigma_B(1)}{\sigma_0(1)} \right] + \Delta c^{(0)} \\ - \int d(1)\sigma_\Gamma \frac{\delta \Delta c^{(0)}}{\delta \sigma_\Gamma(1)}. \tag{114}$$

The reference system contains only hard spheres with diameter D as in (62) at the density ρ of the real system. It can be reasonably well described by the *Carnahan-Starling* EOS[?]

$$\frac{\beta p_R}{\rho} = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3} \tag{115}$$

with the *packing density*

$$\eta = \frac{1}{6}\pi\rho D^3 \tag{116}$$

6   Conclusions