Abstract: The current article completes our investigation of the hard-particle interaction by determining their distribution functionals. Beginning with a short review of the perturbation expansion of the free-energy functional, we derive two representations of the correlation functionals in rooted and unrooted Mayer diagrams, which are related by a functional derivative. This map allows to transfer the mathematical methods, developed previously for unrooted diagrams, to the current representation in rooted graphs. Translating then the Mayer to Ree-Hoover diagrams and determining their automorphism groups, yields the generic functional for all r-particle distributions. From this we derive the examples of 2- and 3-particle correlations up to four intersection centers and show that already the leading order reproduces the Wertheim, Thiele, Baxter solution for the contact probability of spheres. Another calculation shows the failure of the Kirkwood superposition approximation for any r-particle correlation.

Key words. integral geometry, fundamental measure theory, correlation functionals

1. Introduction

Density functional theory (DFT) for classical particles introduces direct correlation and distribution functionals. These two classes form the building blocks not only for the grand canonical potential and its perturbative expansion but also for the Enskog integrals in non-equilibrium thermodynamics and the background potential in quantum mechanical calculations [7,8,17]. But contrary to the correlation functions, which can be derived from molecular dynamic or Monte Carlo simulations, the correlation functionals are not readily available by numerical methods, which explains why so much less is known about this essential part of classical DFT.

The two types of correlations derive from the free energy and the grand canonical potential respectively and are therefore canonically conjugate variables of their Legendre-dual potentials. This connection allows, at least in principal, to write any
thermodynamic expression in only one class of correlations and to use integral
equations to substitute the other [17]. But solving these identities is a difficult task as the
Ornstein-Zernike equation shows, whose only known analytic solution has been ob-
tained by Wertheim, Thiele, and Baxter for the interaction of hard spheres [1,33,35
36]. But despite its accuracy for low to medium packing fractions and its extension to
the mean spherical approximation [17], its solution is of limited use for more general
geometries as the underlying mathematical methods do not generalize to non-spherical
interactions. Another and even more fundamental restriction for the use of integral equa-
tions is their dependence on the correlation functions instead of the functionals, which
excludes their application for inhomogeneous fluids.

To gain some insight into the structure of the correlation functionals, the current ar-
ticle follows a different strategy and starts from the virial expansion in rooted Mayer
diagrams [11,12]. For a general potential this ansatz with its infinite number of integrals
is inaccessible. But for the hard-particle interaction it has recently been shown that the
free-energy functional expands in a fast converging series of intersection kernels, gen-
eralizing previous results from Rosenfeld’s fundamental measure theory [23,24,25,26
31], the transformation from Mayer to Ree-Hoover diagrams [13,19,20], Wertheim’s
derivation of the third virial coefficient [37,38,39,40], and the Blaschke, Santalo, Chern
equation from integral geometry [2,4,5,6,29]. Its leading contribution coincides with
the Rosenfeld functional, which has been shown to accurately predict the phase diagram
of spheres and polyhedrons from low to medium packing fractions [3,9,10,14,15,16
27,28,30]. It is therefore a natural step to generalize these methods to the more general
correlations functionals.

As the direct correlation functionals derive from the free energy, they will be ignored
in the following discussion. The same applies to the intersection kernels, whose derivation
is independent of the virial expansion. This leaves us to transfer the diagrammatic
methods from the unrooted Ree-Hoover graphs to its rooted form, which will be done
in Sec. 2 where the generic distribution functional is derived. Examples will then be
presented in Sec. 3 where the 2- and 3-particle distributions for up to four intersection
centers are given. It is then shown that already the leading term of the contact proba-
bility between equally sized spheres agrees with the solution from Wertheim, Thiele,
and Baxter. We conclude with a final comment on the applicability of the Kirkwood
superposition approximation.

2. The Generic Distribution Functional for Hard Particles

The main difference between the free-energy and the distribution functionals is their re-
spective virial expansion in Mayer clusters. Once this is known, it is a mere technicality
to identify their intersection classes and to write the functional in intersection kernels. In
the following, we will therefore first derive the Mayer representation of the r-particle
distribution functionals $\rho_{i_1...i_r}$, or more conveniently of their normalized form $g_{i_1...i_r}$,
translate them into Ree-Hoover diagrams, from which follows the generic correlation
functional.

A convenient starting point for the derivation of the Mayer representation is the per-
turbation expansion of the grand canonical potential [17]. Introducing the hard $\phi^H$ and
soft $\phi^S$ contributions of the interaction potential $\phi_{ij} = \phi^H_{ij} + \phi^S_{ij}$ results in a correspond-
ing splitting of the Boltzmann functions

$$e_{ij} = e^H_{ij} + e^H_{ij} F_{ij} = e^H_{ij} + \lambda F_{ij} \quad \text{for} \quad \lambda = 1,$$  (1)
where we introduced the auxiliary variable $\lambda$ for counting the number of $F$-terms. Next observe that the partition function of $N$ particles is a fully $e$-bonded cluster integral of $N$ labeled nodes $I_j(e)$ and that the expansion of the product $\prod_{j} e_{ij}^\beta + \lambda F_{ij}$ yields a sum of products, with a subset of $e$-bonds replaced by $F$-bonds. Using the invariance of the partition function under relabeling of particle numbers, it is always possible to define a unique, labeled subgraph $I_{rk}(e,F)$ of $r$ nodes and counting index $k$, such that each node is linked to at least one $F$-bond. The Taylor expansion of the partition function in $\lambda$ can now be written as a functional derivative of cluster diagrams

$$D_k = \sum_{r=2}^{\infty} \sum_{k=1}^{\frac{N}{r}} \frac{\lambda^{[r_k]}}{[r_k]!} \frac{\sigma_{r_k}}{r_k} I_{rk}(e^\beta, F) \frac{\delta}{\delta I_i(e)} \bigg|_{\lambda=0},$$

where $[I_{rk}]$ denotes the number of $F$-bonds, $[I_k]$ the total number of $I_{rk}$ diagrams, and $\sigma_{r_k}$ the number of inequivalent particle labelings.

The Taylor expansion of the partition function $\Xi_k$ up to second order includes the three leading diagrams, whose functional derivatives

$$\Xi_k = \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_{i,j=1}^{N} (e_{ij}^\beta + \lambda F_{ij}) d\gamma_{i_1...i_N} = \sum_{N=0}^{\infty} \frac{1}{N!} \Xi_N(0) \left[ 1 + D_k \frac{\Xi_N(\lambda)}{\Xi_N(0)} \right]$$

$$= \Xi_0[1+\lambda \int \frac{1}{2} e_{i_1i_2}^\beta S_{i_1} S_{i_2} d\gamma_{i_1i_2} + \lambda^2 \int \frac{1}{2} \rho_{i_1i_2i_3}^\beta S_{i_1} S_{i_2} S_{i_3} + \frac{1}{4} \rho_{i_1i_2i_3i_4}^\beta S_{i_1} S_{i_2} S_{i_3} S_{i_4} d\gamma_{i_1i_2i_3i_4} + O(\lambda^3)]$$

introduces the grand-canonical $r$-particle distribution functionals $\rho_{i_1...i_r}^\beta$. Expanding its logarithm and setting $\lambda = 1$ reproduces the well known perturbation expansion of the grand-canonical potential $\Xi^{[2]}$

$$\beta \Omega = \beta \Omega^{[2]} - \frac{1}{2} \int \rho_{i_1i_2}^\beta S_{i_1} S_{i_2} d\gamma_{i_1i_2} - \frac{1}{2} \int \rho_{i_1i_2i_3}^\beta S_{i_1} S_{i_2} S_{i_3} d\gamma_{i_1i_2i_3}$$

$$- \frac{1}{8} \int (\rho_{i_1i_2i_3i_4}^\beta S_{i_1} S_{i_2} S_{i_3} S_{i_4}) d\gamma_{i_1i_2i_3i_4} - \cdots$$

where an implicit sum over paired indices is understood. Higher order corrections are determined likewise by successive insertion of further $F$-bonds into the cluster diagrams.

The operator $D_k$ provides a compact notation for the correlation functionals, where each diagram $I_{rk}(e^\beta, F)$ corresponds to exactly one $\rho_{i_1...i_r}^\beta$. To change the representation into Mayer diagrams, one only has to insert $F = e^\beta f^\delta$, $e^\beta = f^\delta + 1$ and to expand the graph in the virial series

$$I_{rk}(f^\delta + 1, F) = [f^\delta] I_{rk} \sum_{n\geq r} \Gamma_n^{(r)}(f^\delta, e^\beta),$$

which yields a corresponding representation in terms of $r$-rooted Mayer diagrams $I_n^{(r)}$

$$g_r(r_1,..,r_r) = \sum_{n\geq r} \sum_k \frac{\sigma_n^{(r)}}{(n-r)!} \int \Gamma_n^{(r)}(f, e) \rho_{i_{n+1}} ... \rho_{i_n} d\gamma_{i_{n+1}} ... d\gamma_{i_n},$$
The fourth virial order of the 2-particle correlation function in a) Mayer and b) Ree-Hoover diagrams. The continuous lines denote f-bonds, while the dashed lines correspond to e-bonds. The rooted points are always mutually e-bonded.

where we omitted the hard-particle index and introduced the symmetry factor $\sigma_{n,k}$, transforming from labeled to unlabeled graphs [22,34].

An alternative representation can be derived by observing that completely e- and f-bonded graphs are uniquely related $\tilde{\Gamma}_r(e) \sim \tilde{\Gamma}_r(f)$ by the substitution $e = f + 1$ and ignoring all diagrams of lower order $|\Gamma_{r,k}| < |\Gamma_r|$:

$$\Gamma_r(e) = \Gamma_r(f) + \sum_k \Gamma_{r,k}(f).$$

This relation allows to replace $\Gamma_r(e)$ in (2) by $\Gamma_r(f)$ and to change the representation of $D_1$ from the fully connected e-bonded graphs to Mayer diagrams. The resulting operator then applies to the virial expansion of $\Omega$, where the functional derivative substitutes any subgraph $\Gamma_r(f) \subset \Gamma_{n,k}(f)$ in a Mayer diagram by $\Gamma_r(e)$

$$g_r = \Gamma_r(e) \frac{\delta}{\delta \Gamma_r(f)} \Omega,$$

which reproduces the definition of the normalized r-particle functional. At the level of individual diagrams, this operation can also be written as

$$\Gamma_{n,k}^{(r)}(f,e) = \Gamma_r(e) \frac{\delta}{\delta \Gamma_r(f)} \Gamma_{n,k}(f).$$

Examples for the 2-rooted diagrams of fourth virial order are shown in Fig. 1a).

In the following, we will use the close relationship between the virial expansion (6) and the functional derivative (8) to transfer the methods previously developed for the free energy to derive the r-particle correlation functionals. This approach is divided into two steps: the first one translates the Mayer into intersection diagrams, while the second determines their intersection probabilities. Let us first summarize the central ideas and notations from [12]:

The approximation method for the free-energy functional uses an expansion in the number of intersection centers, whereas the virial series is an expansion in increasing powers of the particle density. Both are uniquely related by Ree-Hoover (RH) diagrams $\tilde{\Gamma}_{n,k}$, which derive from Mayer graphs $\Gamma_{n,k}$ by inserting $1 = ei - fj$ for each pair $i,j$ of nodes not bonded by an f-function [18,19,20]. Their respective cluster integrals are related by the “star-content” $a_{n,k}$ as introduced in [18]:

$$\Gamma_n = \sum_{k'} \Gamma_{n,k'} = \sum_k a_{n,k} \tilde{\Gamma}_{n,k}.$$
which satisfies the recursion relations

$$\pi^{-1}(\Gamma_n) = (n-2) \Gamma_{n-1} , \quad a_{n,k} = (-1)^{n-1}(n-2)a_{n-1,k}$$

under removal of a node and its associated f-bonds from a labeled diagram $\pi^{-1} : \Gamma_{n,k} \rightarrow \Gamma_{n-1,k'}$. This map can be reversed for a nontrivial RH-graph by adding a node and bonding it by f-functions to all previous vertices $\pi : \Gamma_{n-1,k} \rightarrow \Gamma_{n,k'}$. For any lowest element $\pi^{-1}(\Gamma_{n,k}) = 0$, this defines a unique RH-class

$$\tilde{\Lambda}_{n,k} = \bigcup_{m=0}^{\infty} \pi^m(\Gamma_{n,k}) ,$$

whose intersection networks can be contracted into a common pattern with an equal number of intersection centers. Each intersection diagram therefore belongs to a unique RH-class, whose elements can be summed up into a generic functional, weighted by the numerical prefactors of the virial expansion

$$\tilde{\sigma}_{n,k} = -\frac{1}{n!} \sigma_{n,k} a_{n,k} , \quad \sigma_{n,k} = \frac{|S_n|}{|\text{Aut}(\Gamma_{n,k})|} ,$$

where the symmetry factor $\sigma_{n,k}$ counts the number of inequivalent labelings, determined by the coset of permutations $S_n$ and the automorphism group $\text{Aut}(\Gamma_{n,k})$.

The approximate free-energy functional derives from the sum over all contracted intersection diagrams $\gamma^i_0$ of a RH-class, where the particle domains $D_{i_1}, \ldots, D_{i_m} \subset \mathbb{R}^N$ of index $I = (i_1, \ldots, i_m)$ intersect in the center $r_a \in D_{i_1} \cap \cdots \cap D_{i_m}$. Its functional then factorizes into a convolute of integral kernels $K$, satisfying the rules

$$K(\gamma^i_0 + \gamma^j_0) = K(\gamma^i_0) + K(\gamma^j_0) , \quad K(\gamma^i_0 \gamma^j_0) = K(\gamma^i_0)K(\gamma^j_0) ,$$

$$K(\gamma^i_0[e \ldots e]) = K(\gamma^i_0)[e \ldots e]$$

for the intersection networks $\gamma^i_0$, $\gamma^j_0$, and the product of Boltzmann functions $[e \ldots e]$.

The integral kernel for $N$-dimensional particles in the $N$-dimensional, Euclidean space $\mathbb{R}^N$ is a combination of $N+1$ weight functions $w_k^{i_1 \ldots i_l}$, determined by the functional derivative with respect to the weight function of the particle domain $w_0^i$.

$$K(\gamma^i_0 \ldots \gamma^{i_n}) = \varrho_a w_0^i(r_{ai_1}) \ldots w_0^{i_n}(r_{ai_n}) ,$$

where the derivative at intersection point $r_{ai} = r_a - r_i$ is defined by

$$\varrho_a = \sum_{k=1}^{N} \sum_{i \in (i)} \frac{1}{k!} w_k^{i_1 \ldots i_k}(r_{ai_1}, \ldots, r_{ai_k}) \frac{\delta^k}{\delta w_0^{i_1}(r_{ai_1}) \ldots \delta w_0^{i_k}(r_{ai_k})} .$$

These definitions provide a set of rules, which are sufficient to derive approximations of the free-energy functional for any number of intersection centers. And, as will be shown in the following, they also apply to the correlation functionals, replacing star-diagrams by rooted graphs and a corresponding change in their automorphism groups.
bonded by $f$-functions, resulting in a change of the virial series from Mayer to $r$-rooted RH-diagrams $\tilde{\Gamma}_{n,k}^{(r)}$ [19,21]. Examples for 2-rooted graphs of the fourth virial order are shown in Fig. 1b).

Following the conventions of [12], we define the notation for rooted diagrams:

**Definition 1.** Let $\Gamma_{n,k}^{(r)}$ denote a labeled $r$-rooted Mayer diagram with $r$ white and $n-r$ black nodes. The rooted points are mutually $e$-bonded, while the black points are 1-path connected in the subset of $f$-bonds.

A black node can be removed by deleting its vertex and all associated $f$-bonds $\pi^{-1}$: $\Gamma_{n,k}^{(r)} \rightarrow \{\Gamma_{n-1,k'}, \Gamma_{n-1,k'}^{(r)}\}$, leaving a residual diagram, which is either a new $r$-rooted Mayer graph $\Gamma_{n-1,k}^{(r)}$, or a sum of disjunct diagrams with articulation points $\Gamma_{n-1,k}$.

**Definition 2.** Let $\tilde{\Gamma}_{n,k}^{(r)}$ denote a labeled $r$-rooted RH-diagram with $r$ white and $n-r$ black nodes. The rooted points are mutually $e$-bonded, while the black points are 1-path connected in the subset of $f$-bonds.

A black node without $e$-bonds can be removed by deleting its vertex and all associated $f$-bonds $\pi^{-1}$: $\tilde{\Gamma}_{n,k}^{(r)} \rightarrow \{\tilde{\Gamma}_{n-1,k'}, 0\}$, leaving either a new or the trivial RH-graph.

To rewrite the virial integrals [6] in rooted RH-diagrams, observe that the rooting-process (9) only exchanges fully $f$-bonded subdiagrams $\Gamma_{r}^{(f)} \subseteq \Gamma_{n,k}$ by its corresponding $e$-bonded graph $\Gamma_{r}^{(e)}$, whereas the Ree-Hoover transformation only operates on pairs of un bonded nodes. The two operations are therefore mutually exclusive and commute. From this follows that the same functional derivative (9), which transforms star-diagrams into rooted Mayer graphs, also applies to RH-diagrams

$$\frac{\delta}{\delta \Gamma_{r}^{(f)}} \tilde{\Gamma}_{n,k}^{(r)} = \Gamma_{n,k}^{(r)}.$$  \hspace{1cm} (17)

The previously derived results for unrooted RH-graphs therefore remain valid for its rooted forms.

This connection can be immediately applied to rewrite the transformation between Mayer and RH-diagrams

$$\tilde{\Gamma}_{n,k}^{(r)} = \sum_{k'} \Gamma_{n,k'}^{(r)} - \sum_{k'} (-1)^{|\Gamma_{n,k'}| - |\tilde{\Gamma}_{n,k'}^{(r)}|} \tilde{\Gamma}_{n,k'}^{(r)}$$  \hspace{1cm} (18)

and to express the sum over rooted RH-diagrams

$$\tilde{\Gamma}_{r}^{(r)} = \sum_{k} \Gamma_{n,k}^{(r)} - \sum_{k} (-1)^{|\Gamma_{n,k}| - |\tilde{\Gamma}_{r}^{(r)}|} \tilde{\Gamma}_{n,k}^{(r)}$$  \hspace{1cm} (19)

in terms of the “root-content”

$$\tilde{e}_{n,k}^{(r)} = \sum_{k} (-1)^{|\Gamma_{n,k}| - |\tilde{\Gamma}_{n,k}^{(r)}|}.$$  \hspace{1cm} (20)
which satisfies an analogous recursion relation as the star-content \( \mathbf{11} \) under removal of a black node. This is readily seen by commuting \( \pi^{-1} \) with the functional derivative \( \delta \) and using \( \mathbf{11} \)

\[
\pi^{-1}(\Gamma_n^{(r)}) = \Gamma_\pi(e) \frac{\delta}{\delta \Gamma_\pi(f)} \pi^{-1}(\Gamma_n) = \Gamma_\pi(e) \frac{\delta}{\delta \Gamma_\pi(f)} (n-2) \Gamma_{n-1} = (n-2) \Gamma_{n-1}^{(r)}, \quad (21)
\]

with the corresponding relation for RH-diagrams, where the removal of a black node and its \( n-1 \) f-bonds

\[
\pi^{-1}(\Gamma_n^{(r)}) = \sum_k \pi^{-1}(a_{n,k}^{(r)} \tilde{\Gamma}_n^{(r)}) = (-1)^{n-1} \sum_{k'} a_{n,k'}^{(r)} \tilde{\Gamma}_{n-1,k'}^{(r)}
\]

\[
= (n-2) \Gamma_{n-1} = (n-2) \sum_{k'} a_{n-1,k'}^{(r)} \tilde{\Gamma}_{n-1,k'}^{(r)} \quad (22)
\]

yields the recursion relation

\[
a_{n,k}^{(r)} = (-1)^{n-1} (n-2) a_{n-1,k}. \quad (23)
\]

The successive application of \( \pi^{-1} \) traces each diagram to a unique lowest element \( \pi^{-1}(\Gamma_{n_0,k}^{(r)}) = 0 \), which is the first element of the RH-class

\[
\tilde{\Lambda}_{n_0,k}^{(r)} = \bigcup_{m=0}^{\infty} \pi^m(\tilde{\Gamma}_{n_0,k}^{(r)}), \quad (24)
\]

defined by the inverse map \( \pi : \tilde{\Gamma}_{n-1,k}^{(r)} \rightarrow \tilde{\Gamma}_{n,k}^{(r)} \) which attaches a node to the previous \( n-1 \) vertices by f-bonds. The set of rooted RH-diagrams therefore separates into RH-classes, whose root-contents can be recursively calculated by \( \mathbf{23} \), proving

**Lemma 1.** The root-content of \( \tilde{\Gamma}_{n,k}^{(r)} \in \tilde{\Lambda}_{n_0,k}^{(r)} \) with lowest element \( \tilde{\Gamma}_{n_0,k}^{(r)} \) is determined by

\[
a_{n,k}^{(r)} = (-1)^{\left\lfloor \frac{n}{2} \right\rfloor - \left\lfloor \frac{r}{2} \right\rfloor} \frac{(n-2)!}{(n_0-2)!} a_{n_0,k}. \quad (25)
\]

The last step in rewriting the correlation function \( \mathbf{6} \) in RH-graphs is the transition from labeled to unlabeled diagrams. As for the star-diagrams \( \mathbf{13} \), the symmetry factor \( \sigma_{n,k}^{(r)} \) counts the number of inequivalent permutations of particle indices, determined by the coset of the permutation and automorphism group of rooted diagrams.

**Lemma 2.** Let \( \tilde{\Gamma}_{n,k}^{(r)} \in \tilde{\Lambda}_{n_0,k}^{(r)} \) denote an element of the RH-class with lowest element \( \tilde{\Gamma}_{n_0,k}^{(r)} \). Its inequivalent labelings of the \( r \) white and \( n-r \) black nodes are permuted by the coset group

\[
S_r \times S_{n-r}/\text{Aut}(\tilde{\Gamma}_{n,k}^{(r)}) \quad (26)
\]

whose automorphism group factorizes into the direct product

\[
\text{Aut}(\tilde{\Gamma}_{n,k}^{(r)}) = S_{n-n_0} \times \text{Aut}(\tilde{\Gamma}_{n_0,k}^{(r)}). \quad (27)
\]
This is shown as follows: The white and black nodes are labeled independently, resulting in the decoupling of the permutation group $S_e \times S_{n-r}$, proving (25). Whereas the automorphism group factorizes, because each of the $m_0$ nodes is linked to at least one $e$-bond, while the residual $n-n_0$ nodes are completely $f$-bonded. Any exchange of labels between these two groups therefore results in an inequivalent permutation, leaving the $n-n_0$ vertices as an invariant set under relabeling, proving (27).

To rewrite the virial expansion (6) in RH-diagrams, let us define the symmetry factor of RH-integrals

$$\tilde{\sigma}_{n,k}^{(r)} = \frac{1}{(n-r)!} \sigma_{n,k}^{(r)} d_{n,k}^{(r)},$$

combining the root-content (25) and the number of inequivalent labelings

$$\sigma_{n,k}^{(r)} = \frac{|S_r \times S_{n-r}|}{|\text{Aut}(\tilde{I}_{n,k}^{(r)})|} = \frac{r!(n-r)!}{(n-n_0)!} \frac{1}{|\text{Aut}(\tilde{I}_{n_0,k}^{(r)})|},$$

which yields the numerical prefactor of the rooted RH-class:

**Corollary 1.** The symmetry factor of the r-rooted RH-diagram $\tilde{I}_{n,k}^{(r)} \in \tilde{A}_{n_0,k}^{(r)}$ with lowest element $\tilde{I}_{n_0,k}^{(r)}$ for $r \geq 2$ is determined by

$$\tilde{\sigma}_{n,k}^{(r)} = (-1)^{(\frac{r}{2})-\frac{n}{2}} \left( \begin{array}{c} n-2 \\ n_0-2 \end{array} \right) \frac{r! d_{n,k}^{(r)}}{|\text{Aut}(\tilde{I}_{n_0,k}^{(r)})|}.$$  (30)

This result follows by inserting (25), (29) into (28).

Up to now, no approximation has been made on the virial expansion (6). The next step is therefore to simplify the integrals by restricting the number of intersection centers in which the particles are allowed to overlap. A useful observation is the following property of intersection diagrams of a RH-class:

**Lemma 3.** The intersection network of the class $\tilde{A}_{n_0,k}^{(r)}$ is defined by its lowest subgraph.

The proof begins with the intersection diagram of the lowest element. Any further particle, added by $\pi$, can then be chosen to overlap with the previous intersection centers. This shows that a new particle can be added without changing their number. Repeated operation with $\pi$ then completes the proof.

The intersection diagram with the lowest number of intersection centers therefore defines the “backbone” diagram for the entire RH-class. This is the basic idea for the resummation of RH-diagrams of a given RH-class and the approximation transferring the virial series (6) to the generic r-particle correlation functional:

**Theorem 1.** Let $\tilde{I}_{n_0,k}^{(r)}$ denote the lowest element of the RH-class $\tilde{A}_{n_0,k}^{(r)}$. The generic r-particle correlation functional of the intersection network $\gamma_{i_1}^{d_1} \ldots \gamma_{i_p}^{d_p} [e \ldots e]$ with particle indices $I \in (i_1, \ldots, i_n)$ is determined by

$$g_{I_{i_1} \ldots i_p} (r_{i_1}, \ldots, r_{i_p} | r_{i_1}, \ldots, r_{i_p}) = \tilde{I}_{i_1}^{(r)} (e) \delta_{i_1,r_1} \delta_M + \frac{1}{|\text{Aut}(\tilde{I}_{n_0,k}^{(r)})|} \frac{r! d_{n_0,k}^{(r)}}{d_{n_0,k}^{(r)}} \sum_{n \geq n_0} \sum_{I} \left( \begin{array}{c} n-2 \\ n_0-2 \end{array} \right) \int K^{(d_1)}(\gamma_{i_1}^{d_1} \ldots \gamma_{i_p}^{d_p} [e \ldots e]) \prod_{j=1}^{n_0} d_{i_j}$$  (31)
with the notation $\delta_l = \delta(r_{a_1}) \ldots \delta(r_{a_i}) \delta(r_{a_{i+1}}) \ldots \delta(r_{a_p})$ for the product of delta-functions.

This result follows from inserting (30) into the cluster expansion (6) and the cancelation of signs due to the identity

\[
|\tilde{T}^{(r)}_{n,k}| = |\tilde{T}^{(r)}_{n_0,k}| + \binom{n}{2} - \binom{n_0}{2},
\]

which leaves an overall constant, depending only on the lowest element of the RH-class and an $n$-dependent binomial coefficient. An exception provides the leading diagram $n_0 = r$ of each $r$-correlation functional. Without an f-bond, its intersection probability vanishes and therefore has to be included separately. Finally, the delta-functions $\delta_l$ have been added in (31) to achieve a symmetric formulation of the integrals

\[
[g_{i_1i_2}f_{i_1i_2}](r_{i_1}, r_{i_2}) = \int g_{i_1i_2} \tilde{\gamma}_a \gamma_{i_3} \ldots \gamma_{i_n} \gamma_b \gamma_{j_3} \ldots \gamma_{l_n} d\gamma_a d\gamma_b d\gamma_c,
\]

\[
[g_{i_1i_2}f_{i_1i_2}](r_a, r_b, r_c) = \int g_{i_1i_2} \tilde{\gamma}_a \gamma_{i_3} \ldots \gamma_{i_n} \gamma_b \gamma_{j_3} \ldots \gamma_{l_n} d\gamma_a d\gamma_b d\gamma_c
\]

in the particle and intersection coordinates, which proves useful in later applications.

### 3. Examples of R-Particle Correlation Functionals

This last section presents four examples. We begin with the explicit derivation of the 2-particle correlation functional with two intersection centers and compare its contact probability with the Ornstein-Zernike solution of Wertheim, Baxter, and Thiele. The 2- and 3-particle correlations are then calculated for up to four intersection centers and compared to the Kirkwood superposition approximation.

The first f-bonded RH-diagram of the 2-particle correlation functional $g_{i_1i_2}$ is $\tilde{\Lambda}^{(2)}_{2,1}$, whose two white and one black nodes define a backbone diagram with two intersection centers. All further networks of the same RH-class can then be contracted to the pattern

\[
\tilde{\Lambda}^{(2)}_{2,1} : \quad e_{i_1i_2} + e_{i_1i_2} \tilde{\gamma}_{i_3} \gamma_{i_4} \gamma_{j_3} \ldots \gamma_{l_n}.
\]

Applying the rules (14) and (15) for the representation of the intersection kernel and introducing the notation $w_{a} = w_{0}(r_{a})$ for the volume weight, the virial series sums up to the generating function

\[
g_{i_1i_2}[z(r_{i_1}, r_{i_2})/a_{i_1}, b_{i_2}] = e_{i_1i_2} \tilde{\Lambda}_{2,1} + \sum_{n \geq 2} \sum_{i_3 \ldots l_n} \int K(\gamma_{i_3} \ldots \gamma_{i_n} \gamma_{j_3} \ldots \gamma_{l_n} e_{i_1i_2}) \rho_{i_3} \ldots \rho_{i_n} d\gamma_{i_3} \ldots d\gamma_{i_n}
\]

\[
= e_{i_1i_2} \tilde{\Lambda}_{2,1} + \sum_{n \geq 2} \sum_{i_3 \ldots l_n} \mathcal{P}_{a} \mathcal{P}_{b} \int w_{a}^{i_3} \ldots w_{a}^{i_n} w_{b}^{j_3} \ldots w_{b}^{l_n} \rho_{i_3} \ldots \rho_{i_n} d\gamma_{i_3} \ldots d\gamma_{i_n}
\]

\[
= e_{i_1i_2} \tilde{\Lambda}_{2,1} + \mathcal{P}_{a} \mathcal{P}_{b} w_{a}^{i_3} \ldots w_{a}^{i_n} w_{b}^{j_3} \ldots w_{b}^{l_n} \sum_{n \geq 2} x_{a_1 \ldots a_p}
\]

where we introduced the $x$-variable

\[
x_{a_1 \ldots a_p} = \int w_{0}^{i_3}(r_{a_1}) \ldots w_{0}^{i_n}(r_{a_p}) \rho_{i} d\gamma
\]
from [12] and used the property of [16] that the intersection probability for a single particle is zero $g_{aa}w_{a}^{i} = 0$. The final correlation functional has then the analytic form

$$g_{iiz}|_{2}(r_{i_{1}}, r_{i_{2}} | r_{a}, r_{b}) = e_{iizi} \left( \delta(r_{ai_{1}}) \delta(r_{bi_{2}}) + D_{a}D_{b} \frac{w_{a}^{i_{1}} w_{b}^{i_{2}}}{1 + x_{ab}} \right).$$ (38)

This result is exact up to the third virial order, but significantly improved by the additional pole at $x_{ab} = 1$. To illustrate this effect of the resummation process, let us derive the leading order of the contact probability $g_{iiz}(|r_{i_{1}} - r_{i_{2}}| = D^{+})$ for spheres of radius $R$ and diameter $D = 2R$. The polynomial expansion of the numerator of (38) up to first order in $\rho$ yields three terms

$$g_{iiz}|_{2}(r_{i_{1}}, r_{i_{2}}) = e_{iizi} \int \left( \delta_{ii} + D_{a}D_{b} \frac{w_{a}^{i_{1}} w_{b}^{i_{2}}}{1 + x_{ab}} \right) d\gamma_{a} d\gamma_{b}$$

$$= e_{iizi} \left( \int \left( \delta_{ii} + D_{a}D_{b} \frac{w_{a}^{i_{1}}}{1 + x_{ab}} \right) d\gamma_{a} d\gamma_{b} \right)$$

$$= \int e_{iizi} \left( \delta_{ii}(1 - 2x_{ab}) + \int (D_{a}w_{a}^{i_{1}})(D_{b}w_{b}^{i_{2}}) \rho_{ii_{1}, i_{2}} d\gamma_{i_{1}} d\gamma_{i_{2}} \right),$$ (39)

of which two correspond to the second and third virial orders, whereas $-2x_{ab}$ originates from resummation. Their respective integrals determine the lens-like volumes of overlapping spheres

$$V_{R}(r) = \frac{4\pi}{3} R^{3} \left[ 1 - \frac{r}{2R} + \frac{3}{16} \frac{r^{3}}{R^{3}} \right], \quad V_{D}(r) = \frac{4\pi}{3} D^{3} \left[ 1 - \frac{r}{4D} + \frac{3}{16D} \frac{r^{3}}{D^{3}} \right]$$ (40)

and can be readily evaluated for $|r_{i_{1}} - r_{i_{2}}| = D$. Observing that the last term corresponds to the third virial integral

$$\int (D_{a}w_{a}^{i_{1}})(D_{b}w_{b}^{i_{2}}) \rho_{ii_{1}, i_{2}} d\gamma_{i_{1}} d\gamma_{i_{2}} = \delta_{ii} \int f_{iizi}(x_{ab}, x_{ab}) d\gamma_{i_{1}} d\gamma_{i_{2}} = \delta_{ii} \rho V_{D}(r_{i1i2} = D)$$ (41)

and that the intersection coordinates can be chosen to coincide

$$\int x_{ab} \delta(r_{ai_{1}}) \delta(r_{bi_{2}}) d\gamma_{a} d\gamma_{b} = \rho V_{R}(r_{ab} = 0) = \eta,$$ (42)

the integral (39) yields the contact probability as a function of the packing fraction $\eta$:

$$g_{iizi}(r_{i1i2} = D^{+}) = \frac{1}{(1 - \eta)^{2}} (1 - 2\eta + \frac{5}{2} \eta) + \frac{\eta^{2}}{(1 - \eta)^{2}} \left( \frac{\eta^{2}}{(1 - \eta)^{3}} \right)$$

$$= 1 + \frac{1 + \frac{1}{2} \eta}{(1 - \eta)^{2}} + \frac{\eta^{2}}{(1 - \eta)^{3}},$$ (43)

which agrees with the Carnahan-Starling polynomial to first order in the numerator as well as the Wetherill-Thiele, Baxter solution of the Ornstein-Zernike equation [17 33 35 36]. The latter observation is especially interesting because its closing condition $c_{2}(r > D) = 0$ corresponds to the 1-center approximation of the functional expansion, whereas (43) reflects the 2-center representation of $g_{2}$. To obtain the same accuracy for the distribution functional therefore requires a larger number of intersections centers than for its dual direct correlation.
Deriving higher order functionals is now a matter of simple algebra. Here we list the leading orders of the 2-particle correlations with up to four intersection centers. The corresponding intersection diagrams for the RH-classes in the notation of Fig. 1b) are obtained by successive contraction of pair-wise intersection centers

\[ \tilde{\Lambda}^{(2)}_{2,1} : e_{i_1i_2} + e_{i_1i_2} \frac{y^{(1)}_i}{b_i} \]

\[ \tilde{\Lambda}^{(2)}_{2,1} + \tilde{\Lambda}^{(2)}_{4,1} : e_{i_1i_2} + e_{i_1i_2} \frac{y^{(1)}_i}{b_i} + e_{i_3i_4} \frac{y^{(1)}_i}{b_i} + e_{i_3i_4} \frac{y^{(1)}_i}{b_i} \]

\[ \tilde{\Lambda}^{(2)}_{2,1} + \tilde{\Lambda}^{(2)}_{4,1} + \tilde{\Lambda}^{(2)}_{4,1} : e_{i_1i_2} + e_{i_1i_2} \frac{y^{(1)}_i}{b_i} + e_{i_3i_4} \frac{y^{(1)}_i}{b_i} + e_{i_3i_4} \frac{y^{(1)}_i}{b_i} \]

\[ + e_{i_1i_2} e_{i_3i_4} \frac{y^{(1)}_i}{b_i} + e_{i_1i_2} e_{i_3i_4} \frac{y^{(1)}_i}{b_i} \]

with the corresponding 2-particle correlation functionals

\[ g_{i_1i_2} = e_{i_1i_2} \left( \delta_M + \mathcal{D}_a \mathcal{D}_b \frac{w^i_i w^j_j}{1-x_{ab}} \right) \]

\[ g_{i_1i_2} = e_{i_1i_2} \left( \delta_M + \mathcal{D}_a \mathcal{D}_b \mathcal{D}_c \frac{w^i_i w^j_j x_{abc}}{1-x_{abc}} \right) \]

\[ g_{i_1i_2} = e_{i_1i_2} \left( \delta_M + \mathcal{D}_a \mathcal{D}_b \mathcal{D}_c \frac{w^i_i w^j_j x_{abc}}{1-x_{abc}} \right) \]

where we introduced the Boltzmann weighted densities

\[ y^{(1)}_{abc} = \sum_{i,j,k} e_{i_1i_2} e_{i_1i_3} e_{i_1i_4} \rho_i w^c \rho_j d \gamma_i d \gamma_j \]

\[ y_{a_1a_2b_1b_2} = \sum_{i,j,k} e_{i_1i_2} w^i_i \rho_i w^j_j \rho_j d \gamma_i d \gamma_j \]

As a last example, we present the leading term of the 3-particle correlation functional with 3 intersection centers. Its intersection diagram has the form

\[ \tilde{\Lambda}^{(3)}_{3,1} : e_{i_1i_2} e_{i_1i_3} e_{i_1i_4} \]

\[ g_{i_1i_2i_3} = e_{i_1i_2} e_{i_1i_3} e_{i_1i_4} \left( \delta_M + \mathcal{D}_a \mathcal{D}_b \mathcal{D}_c \frac{w^i_i w^j_j w^k_k}{1-x_{abc}} \right) \]

The contact probability is therefore to leading order \( g_3 \sim (1-\eta)^{-3} \), which shows that the Kirkwood approximation \( g_{i_1i_2i_3} \approx g_{i_1i_2} g_{i_1i_3} g_{i_1i_4} = |g_2|^3 \sim (1-\eta)^{-6} \) is not applicable when all three particles are close together, in accordance with results obtained
from computer simulations [32]. It is not difficult to generalize this result to an arbitrary r-particle correlation function, whose leading term is $g_r \sim (1 - \eta)^{-r}$, whereas the Kirkwood approximation suggests $[g_2]^r (r-1)/2 \sim (1 - \eta)^{-r(r-1)}$. This excludes the superposition approximation as a construction principle for any distribution functional.

4. Discussion and Conclusion

The current derivation of the distribution functionals completes our investigation of the hard-particle correlations, which started with the analysis of Rosenfeld’s fundamental measure theory. Together with this previous result, it is now possible to calculate all direct and distribution functionals in an expansion of intersection kernels, highlighting the hard-particle interaction as the only known potential whose correlations can be derived by analytic methods instead of molecular dynamic or Monte Carlo simulations.

Despite their complex structure it is possible to derive several characteristic properties from these functionals. For example, we have shown that the Wertheim, Thiele, Baxter solution only includes the third virial integral, whereas the 2-center approximation also contains contributions from the 4-particle diagram. The expansion of the pair correlation to leading order in the intersection kernels therefore applies not only to more general particle geometries than Wertheim’s solution, but also includes approximations of higher virial terms. We also tested the Kirkwood superposition approximation, proving that it fails for any distribution functional, a result that has been previously shown numerically only for the 3-particle correlations.

These examples demonstrate the difficulties to find appropriate methods to evaluate the non-local correlation functionals. A possible approach is, e.g., to generalize Wertheim’s ansatz of expanding the intersection kernels in convolutes of r-point densities. But the integrals soon become intractable to solve. The only alternative, which also applies to concave geometries, is the triangulation of the surfaces and to calculate the functionals numerically. The intersection configurations of the particles can then be generated either by discretization of the imbedding space or by Monte Carlo sampling as has been done by Ree and Hoover. But the time-consuming step remains the determination of the intersection domains and their Euler densities. Both problems have been solved in the framework of discrete geometry and implemented in software libraries for 3-dimensional image manipulation. But the vast number of intersection configurations that have to be evaluated while minimizing the grand potential requires further approximations to reduce the calculational costs in order to be competitive to molecular dynamic and Monte Carlo methods.

The only particle geometry for which the functionals can be evaluated by algebraic relations are spheres. Instead of looking for approximations of the functionals, it is therefore more appropriate to replace the geometry of molecules by sets of overlapping balls. This approach will be discussed in a forthcoming article, where the grand potential for realistic molecules of hard and soft interactions will be derived [13].

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