A Short Proof of the Reducibility of Hard-Particle Cluster Integrals

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The current article considers Mayer cluster integrals of \( n \)-dimensional hard particles in the \( n > 1 \) dimensional flat Euclidean space. Extending results from Wertheim and Rosenfeld, we prove that the graphs are completely reducible into 1- and 2-point measures, with algebraic rules similar to Feynman diagrams in quantum field theory. The hard-particle partition function reduces then to a perturbatively solvable problem.

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\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{The 4-particle cluster integral splits into two 2- and 3-vertices along the lines \( A, \ldots, E \).}
\end{figure}

Introduction — Hard-particle systems are the simplest example of classical fluids developing a gaseous and solid phase. They are therefore a suitable starting point for understanding realistic fluids, as the asymptotic limit to high packing densities is dominated by their geometry and volume dependence. Understanding the hard-particle free-energy structure is thus an important open problem. Comparing this to the better investigated statistical and quantum field theories, one can identify two differences that are unique to classical particles: their interaction potentials \( V(|r|) \) are strongly singular, i.e., more divergent than \( V(r) \sim r^{n-1} \) in \( n \) dimensions, causing the integral \( \int V(r)r^{n-1}dr \) to be infinite over the particle’s finite domain. Furthermore, the interaction is not local, resulting e.g. in the blocking of particles at high densities. The first problem has been solved by Mayer [1], by expanding the partition function in \( f(r_{ij}) = \exp(-\beta V(r_{ij})) - 1 \) and representing it in cluster integrals. Whereas an approach to the second problem has been found by Rosenfeld [2–7] in splitting the f-function into weight functions or 1-point measures \( f(r_{ij}) \sim \mu(\vec{r}_i) \mu(\vec{r}_j) \). His fundamental measure theory (FMT) of hard spheres has been extended to fluids of convex particles \([8, 9]\) and to the crystalline phase \([10, 11]\), see [12] for a review. The weight functions entering the FMT, were then further investigated by Wertheim [13–16], expanding ring graphs into 2-point measures. Both approaches make use of the observation of Kihara and Ishihara [17, 18] that the second virial coefficient can be understood as the kinematic fundamental formula of integral geometry developed by Blaschke, Santalo and Chern [20, 24]. For further applications and an overview of integral geometry see also [25, 26] and [8, 9] for the discussion of its relation to the 1-point measures in FMT.

In this article we will explain how the intimate relationship between geometry and symmetry leads to the decoupling of arbitrary Mayer clusters into 1- and 2-point measures, extending Wertheim’s result for ring graphs and justifying Rosenfeld’s ansatz for the free-energy. In the first part, we will consider the splitting of the clusters into vertices, using their relation to integral geometry. Whereas the second part focuses onto the process of rejoining the vertices into 2-point measures. As the arguments are not restricted to 3 dimensions, we consider \( n > 1 \) dimensional particles, embedded into the flat Euclidean space \( \mathbb{R}^n \). It will be shown that the 1-point measures have some similarity to the wave functions of bosonic field theory, where the 2-point measure can be interpreted as a propagator and the Mayer cluster as a Feynman diagram, constructed from a finite set of irreducible vertices. Each loop in the diagram introduces constrains that parallels charge and momentum conservation. Our discussion will focus on the mathematical aspects leading to the decoupling. For an extended exposition with applications to 3 dimensions we refer to [27].

Splitting the Cluster — Mayer clusters \([1]\) are graphical representations of cluster integrals over the flat Euclidean space \( \mathbb{R}^n \) with bonds as f-functions and black circles representing space points of overlapping particles. In the following we will call a black circle with \( k \) outgoing lines a \( k \)-vertex, corresponding to \( k \) intersecting particles \( D_1 \cap \ldots \cap D_k \neq \emptyset \). FIG. 1 gives an example for a star graph with 2- and 3-vertices. Each diagram is then integrated over all positions and orientations of its particles in \( \mathbb{R}^n \). From an active point of view, this is identical to an integration over all translations and rotations in space, generated by the \( k \)-fold tensor product of the \( n(n+1)/2 \) dimensional Lie group \( \text{ISO}(n) \simeq \mathbb{R}^n \times \text{SO}(n) \). Now, let \( \Sigma \) be a smooth, orientable Riemannian manifold of \( n-1 \) dimensions, embedded into the flat Euclidean space \( D : \Sigma \leftrightarrow \mathbb{R}^n \). Each point in the domain \( p \in D \) belongs to a local, orthonormal coordinate frame \((p, e_n, \ldots, e_1)\) of the tangential space. The elements of the dual space
then derive from Cartan’s defining equations $dp = e_i \theta^i$ and $de^i = \omega^i_j e^j$ for $i, j = 1, \ldots, n$. The vielbeins $\theta^i$ and spin connections $\omega^i_j$ are the elements of the Lie algebra iso($n$) with the Maurer-Cartan equations following from the vanishing torsion $T^i = \partial^0 + \omega^i_j \land \theta_j = D^{(n)} \theta = 0$ and the curvature of the flat Euclidean space $\Omega^{(n)}_{ij} = d\omega_{ij} + \omega_k \land \omega_{kj}$ is zero. Here, $D^{(n)}$ is the covariant derivative in $n$ dimensions. Let $e_n$ be the outward normal vector of the surface $\Sigma = \partial D$. The curvature form $\Omega^{(n)}_{ij}$ splits then into the two contributions

\begin{align}
\Omega^{(n-1)}_{\alpha \beta} &= \omega_{\alpha n} \land \omega_{\beta n} \\
D^{(n-1)} \omega_{\alpha n} &= 0 \quad \text{for } \alpha, \beta = 1, \ldots, n-1.
\end{align}

Now, the first part of the proof will show, by explicit calculation, that the integral density of the kinematic fundamental formula factorizes into an infinite set of 1-point measures, analogous to the known integrated form of Minkowski functionals.

As already noted before, the vertex of order $k$ corresponds to $k$ intersecting domains $D_1 \cap \ldots \cap D_k \neq 0$ integrated over all translations and rotations. With $dD_m$ as the reduced kinematic measure of particle $m$, the vertex contribution to the cluster can be rewritten

\begin{align}
dD_1 \land \ldots \land dD_k \mid_{D_1 \cap \ldots \cap D_k \neq 0} &= \gamma_{n,k} K(\partial(D_1 \cap \ldots \cap D_k)) \land dD_2 \land \ldots \land dD_k
\end{align}

generalizing (3). From this we will now derive two characteristic properties of the vertices, leading to the splitting of diagrams into 1-point measures.

Observe, that the Euler form of (4) depends only on the boundary of the intersecting particles. As follows from homology theory, the boundary operator is a derivation $\partial \{\text{point}\} = 0$, $\partial^2 = 0$ acting on homology elements. Its operation on two domains

\begin{align}
\partial(D_1 \cap D_2) &= \partial D_1 \cap D_2 + D_1 \cap \partial D_2 + \partial D_1 \cap \partial D_2
\end{align}

can then be extended in an obvious way to an arbitrary set of intersecting particles. But as each operation of $\partial$ decreases the space dimension by one, the intersection of $n+1$ surfaces is identically zero. This proofs the first result that the number of irreducible terms of a vertex is at most $n$, reducing the problem to intersections of the form $\Sigma_1 \cap \ldots \cap \Sigma_k \cap D_{k+1} \cap \ldots \cap D_m$ for $k \leq n$. This can be further simplified, as the coordinate frames of intersecting domains $D_{k+1}, \ldots, D_m$ are unrelated and decouple as volume forms from (5). The case of $\Sigma_k \cap D_{k+1}$ is similar but introduces the constrain $e_n^{(k)} = \pm e_n^{(k+1)}$ among the normal vectors. Again, the integral measure of the domain factorizes from (5) as a volume form, with a sign absorbed in $\gamma_{n,k+1}$. It remains to determine the kinematic measure for $\Sigma_1 \cap \ldots \cap \Sigma_k$, generalizing the explicit calculation of Chern. The case of $\Sigma_k \cap D_{k+1}$ is similar but introduces the constrain $e_n^{(a)} = \pm e_n^{(b)}$ for $a = 1, \ldots, k$, particles related by the $(k-1)/2$ intersection angles

\begin{align}
< e_n^{(a)} | e_n^{(b)} > &= \cos(\phi_{ab})
\end{align}

These additional constrains generalize the coset space of one particle to the $kn$ dimensional, reduced kinematic measure of $k$ intersecting surfaces $SO(n) \times SO(k)/SO(n-k)$. In order to calculate the new $n-k$ form $K(\Sigma_1 \cap \ldots \cap \Sigma_k)$, define the orthonormal frame

\begin{align}
(e_1, \ldots, e_{n-k}, v_{n-k+1}, \ldots, v_n) &= S(e_1, \ldots, e_{n-k}, e_n^{(k)}, \ldots, e_n^{(1)}),
\end{align}

where $S \in GL(k)$ is a linear, invertible transformation, most easily constructed by the Gram-Schmidt process. To parameterize the change of angular phase at the intersection, introduce the additional 1-point measures, analogous to the known integrated form of Minkowski functionals. From this we will now derive two characteristic properties of the vertices, leading to the splitting of diagrams into 1-point measures.
\( \sigma_{ab} \), one obtains a polynomial in the principal curvatures \( |K(\{\kappa_\alpha\}, \{\phi_{ab}\})| \), depending only on the intersection angles and the form \( \kappa_{n-k}^{(1)} \). To get a symmetric result, we still have to incorporate the intersection constraints into the remaining integral measure \( dD_2 \wedge \ldots \wedge dD_k \). As explained in more detail in [27], a suitable coordinate system for the domain \( D_\alpha \) follows from the above transformation \((e_1^{(n)},\ldots,e_n^{(n)},S_1^{(n)},\ldots,S_n^{(1)})\), corresponding to the decomposition \( SO(k) = SO(k)/SO(k-1) \times \ldots \times SO(3)/SO(2) \times SO(2) \). Taking into account the additional constrains \( \theta_\alpha^{(n)} = 0 \) at \( \Sigma_\alpha \), the integral measure for the \( k \)-vertex obtains the final form

\[
dD_1 \wedge \ldots \wedge dD_k |_{\Sigma_1 \cap \ldots \cap \Sigma_k \neq 0} = \hat{\gamma}_{n,k}|K(\{\kappa_\alpha^{(n)}\}, \{\phi_{ab}\})|dG \wedge d\Sigma_1 \wedge \ldots \wedge d\Sigma_k, \tag{10}\]

factorizing into the reduced kinematic measures of individual particles \( d\Sigma_m \), the group measure \( dG \) and the determinant \( |K| \).

Equation (10) generalizes Wertheim’s decoupling of the second virial diagram [13] into 1-point measures \( \mu^{j}(D_{\alpha}) \) by expanding the \( \phi_{ab} \) dependent function \( |K|dG \) into tensor products of its vectors. Formally, this splitting parallels the known generalization of the integrated form of the kinematic fundamental equation of integral geometry [29]. But the Minkowski functionals [21] are now replaced by the infinite set of 1-point measures

\[
\mu^{A}_{\beta}(D) = p_{\sigma}(\{\kappa_\alpha\}) \prod_{i=0}^{\infty} (e_i) \otimes M_i \otimes \pi \tag{11}
\]

for the f-function \( A \) at a fixed root point (see FIG. 1), where the multi-index \( k \) = \( (\sigma, \hat{M}) \) carries further information about the polynomial \( p_\sigma \) of principal curvatures \( \kappa_\alpha \), classified by the Young diagram \( \sigma \) of the symmetric group and the tensorial exponents \( M_i \in \mathbb{N}^* \) of the vectors. The additional variable \( \pi \) indicates the parity of the tensor valued function under axial rotations, defined later.

This infinite tensor space is an example of an explicit manipulation of (11). But there is another alternative approach that might hint at connections to index theory [28]. From the Gauss-Codazzi equation (2) we see, that \( \kappa_\alpha, e_a \) and \( e_n \) are covariantly constant and lie in the kernel of the eigenvalue equation \( D^{(n-1)} \Phi = \lambda \Phi \). Therefore, we can characterize the set of 1-point measures as the tensor valued space

\[
\mathcal{M}(\Sigma, \mathbb{R}^n) = \{ \Phi(\kappa_\alpha, e_i) | D^{(n-1)} \Phi = 0 \} \tag{12}
\]

leading to the second result that the irreducible elements of \( k \)-vertices decompose into the infinite dimensional tensor space of 1-point measures \( \mathcal{M}(\Sigma, \mathbb{R}^n) \) with multiplicative structure defined by the kinematic equation (11).

Comparing this to the Hilbert space of quantum mechanics, one might interpret the 1-point measures as the wave functions \( \phi \) of a massless bosonic particle with vertex interactions up to order \( \phi^3 \).

There are many open questions concerning this space, of which some will be discussed in [27]. Let us here only mention the case of Riemannian surfaces \( T_g \) of genus \( g \) and Euler characteristic \( \chi(T_g) = 2 - 2g \). For \( g \geq 1 \) the volume dependent part of the second virial \( \chi(D_1)vol(D_2) \) is either zero or negative, contradicting experience. This inconsistency follows from the representation in Mayer functions and can be mended by including further homotopic invariants as the Euler linking number [29]. As these forms are again decomposable into 1-point measures, the above result remains unchanged even for homotopically nontrivial manifolds.

**Rebuilding the Cluster** — With the decoupling of the cluster integrals into vertices, diagrams as that of FIG. 1 reduce to expressions of the form

\[
C_{i_1i_1}^{\alpha(EF)} C_{j_1j_1}^{\beta(ED)} C_{j_2j_2}^{\gamma(AB)} C_{\gamma \beta}^{\gamma(AB)} C_{j_3j_3}^{\gamma(ED)} C_{j_4j_4}^{\gamma(ED)}
\times (\mu^{A}_{i_1} \mu^{A}_{j_1})(\mu^{B}_{i_2} \mu^{B}_{j_2})(\mu^{C}_{i_3} \mu^{C}_{j_3})(\mu^{D}_{i_4} \mu^{D}_{j_4})(\mu^{E}_{i_5} \mu^{E}_{j_5}) \tag{13}
\]

where the angular brackets between the coefficients \( C_{ij}^{kl} \) indicate the symmetric permutation of f-labels. Calculating the angular products of 1-point products \( (\mu^{A}_{i_1} \mu^{A}_{j_1}) \) for the rigid particle \( \Sigma_A \). But both measures have been derived at independent points in the embedding space, here denoted by \( \vec{r}_1 \) and \( \vec{r}_2 \). It is therefore necessary to merge these two coordinate systems into the one of the rigid body, denoted by \( (e_1, \ldots, e_n) \), with the axial direction \( e_n \vec{r} = \vec{r}_1 - \vec{r}_2 \). Generalizing Wertheim’s discussion to \( n \) dimensions, the tensorial part of (11) can be reduced by integral averaging over axial rotations, resulting in breaking up the symmetry group \( SO(n) \) into \( SO(n)/SO(n-1) \times SO(n-1) = SO^{n-1} \times SO(n-1) \). But the two Lie groups \( SO(2l+1) = B_l \) and \( SO(2l) = D_l \) belong to different Dynkin diagrams, where \( D_l \) carries an additional \( Z_2 \) automorphism [28] that induces possible sign changes under axial rotations. This is an additional degree of freedom, we have taken care of by including the parity symbol \( \pi \) in (11). The existence of such odd and even parity tensors might have a significant influence on the solid phase structure, with a special focus on \( n = 8 \) and its \( Z_2 \) automorphism group of \( D_4 \).

Calculating the axial average of products of \( SO(n) \) invariant tensors \( |\lambda, m_1, \ldots, m_l| \), reduces now to determining their \( SO(n-1) \) invariant subspaces

\[
< \lambda, m' | B | \lambda, m > = \text{const. for } B \in SO(n-1) \Rightarrow \Lambda(m', m) = 0 \tag{14}
\]

represented by linear constrains between their weight vectors \( \Lambda(m', m) = 0 \). A general solution of this problem has
been given by Cartan \[28\] and extended to a complete classification of Riemannian symmetric spaces. We can therefore assume the constrains \( \Lambda = 0 \) to be known and indicate axially symmetric tensors of rank \( \lambda \) and weight vector \( \vec{m} \) by \(|\lambda, \vec{m}, \epsilon| >_{\Lambda=0}\), where the third component indicates either the coordinate system of the vertex \( \epsilon \), the rigid body \( \epsilon \) or that of the embedding space \( E \). Following the notation of \[13–16\], the 2-point measures are tensor products of the form

\[
\mu(\vec{r}_i) \otimes \mu(\vec{r}_j) = f(r_{ij}, \lambda_i, \lambda_j, \vec{M}_i, \vec{M}_j)e_i > \otimes |\lambda_j, \vec{M}_j, e_j > ,
\]

(15)

whose tensorial part will also be written as \( |e_i > \otimes |e_j > \) if no further reference to the representation space is required. Joining the two coordinate systems \( e_i, e_j \) into that of the rigid body \( \epsilon \), corresponds to an integration

\[
\int <\epsilon|e_i > < \epsilon|e_j > d\omega_i d\omega_j |\epsilon > \otimes |\epsilon >
\]

(16)

over the Haar measure \( d\omega \) of \( SO(n-1) \), reducing the space by \((n-1)(n-2)/2\) dimensions. The resulting 2-point measures

\[
f(r)|\epsilon > \otimes |\epsilon > |_{\Lambda=0}
\]

(17)

are now irreducible tensors in the coordinates \((\epsilon, r) \in S^{n-1} \times \mathbb{R}\) of the particle \( \Sigma \).

The 2-point measures and the expansion coefficient of the vertex \[3\] carry the local properties of the particle \( \Sigma \). But the cluster diagrams also carry global informations, as can be seen from FIG. 1. Consider the star graphs of the free-energy. With the exception of the second virial, all such diagrams are build from closed subdiagrams or loops, introducing a set of constrains \( \vec{r}_2 + \ldots + \vec{r}_{m_1} = 0 \) between the coordinates of the \( m \) root points of one loop. These constrains also couple particles that otherwise do not intersect. This problem occurs first for ring graphs and has been solved by Wertheim in \[13–16\] by introducing the Radon transformation \[31\] to replace the particle fixed coordinate system \((\epsilon, r)\) by that of the embedding space \((E, R)\). This approach can be extended in a straightforward way to arbitrary diagrams in \( n \) dimensions. The Radon transformed 2-point function

\[
F(R, E) = \int <E|\epsilon > < E|\epsilon > |_{\Lambda=0} f(r) \delta(\epsilon E - R) d^n \epsilon
\]

(18)

can then be seen as the propagator of a state vector \(|E >\) along a line of distance \( R \). With \(|E > F(R, E) < E |\) interpreted as the Green’s function, the Mayer cluster can be seen as the analog of Feynman diagrams, with the constrain

\[(r_{12}+12^1 + \ldots + r_{m_1}1_m^1) E = 0, \quad \Lambda = 0 \quad (19)\]

as the conservation laws for each loop. Calculating the virial coefficient reduces now to an integration over the embedding space coordinates \((R, E)\), completing the argument that arbitrary hard-particle clusters in \( n > 1 \) dimensions decouple into 2-point measures. The advantage of this approach is not an efficient calculational tool but the detailed connection between the 1-point measures and their occurrence in the free-energy, opening up a path to better understanding the phase structure of hard-particle fluids by the particle geometry and relative orientations.

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