Graph weights arising from Mayer’s theory of cluster integrals

par

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In the context of a non-ideal gas with $N$ particles in a vessel $V$, in a $d$-dimensional Euclidian space, the following functions are defined:

**Partition Function:**

$$Z(V, N, T) = \frac{1}{N! \lambda dN} \int_{V^N} \exp \left( -\beta \sum_{i<j} \varphi(|\vec{x}_i - \vec{x}_j|) \right) d\vec{x}_1 \cdots d\vec{x}_N,$$

where $\lambda$ and $\beta$ depend on the temperature $T$ and where the interaction between two particles at distance $r$ is expressed by the potential function $\varphi(r)$.

**Grand-canonical Distribution:**

$$Z_{\text{gr}}(V, T, z) = \sum_{N=0}^{\infty} Z(V, N, T) (\lambda^d z)^N,$$

where the variable $z$ is called the *fugacity* or the *activity*.

**Macroscopic Parameters**

$$\frac{P}{kT} = \frac{1}{V} \log Z_{\text{gr}}(V, T, z),$$

$$\overline{N} = z \frac{\partial}{\partial z} \log Z_{\text{gr}}(V, T, z),$$

$$\rho := \frac{\overline{N}}{V}, \quad \text{etc.}$$
Mayer’s theory of cluster integrals

In order to study these functions, Mayer (1940) sets

\[ 1 + f_{ij} = \exp(-\beta \varphi(|\vec{x}_i - \vec{x}_j|)), \]

where \( f_{ij} = f(|\vec{x}_i - \vec{x}_j|) \).

The general form of Mayer’s function

\[ f(r) = \exp(-\beta \varphi(r)) - 1, \]

compared to the potential function \( \varphi(r) \), is shown in Figure 1.

![Figure 1: a) the function \( \varphi(r) \)  
   b) the function \( f(r) \) ](image)
Since

\[ \prod_{1 \leq i < j \leq N} (1 + f_{ij}) = \sum_{g \in \mathcal{G}[N]} \prod_{\{i,j\} \in g} f_{ij}, \]

where \( \mathcal{G}[N] \) denotes the set of all (simple) graphs over the set of vertices \([N] = \{1, 2, \ldots, N\}\), the partition function \( Z(V, N, T) \) becomes

\[
Z(V, N, T) = \frac{1}{N! \lambda^{3N}} \int_{V^N} \exp \left( -\beta \sum_{i<j} \varphi(|\vec{x}_i - \vec{x}_j|) \right) d\vec{x}_1 \cdots d\vec{x}_N,
\]

\[
= \frac{1}{N! \lambda^{3N}} \int_{V^N} \prod_{1 \leq i < j \leq N} (1 + f_{ij}) d\vec{x}_1 \cdots d\vec{x}_N
\]

\[
= \frac{1}{N! \lambda^{3N}} \sum_{g \in \mathcal{G}[N]} \int_{V^N} \prod_{\{i,j\} \in g} f_{ij} \ d\vec{x}_1 \cdots d\vec{x}_N
\]

\[
= \frac{1}{N! \lambda^{3N}} \sum_{g \in \mathcal{G}[N]} W(g),
\]

where the weight \( W(g) \) of a graph \( g \) is given by the integral

\[
W(g) = \int_{V^N} \prod_{\{i,j\} \in g} f_{ij} d\vec{x}_1 \cdots d\vec{x}_N.
\]

This is the First Mayer weight of a graph \( g \).
For the grand canonical distribution we then have

\[
Z_{gr}(V, T, z) = \sum_{N=0}^{\infty} Z(V, N, T)(\lambda^3 z)^N
\]

\[
= \sum_{N=0}^{\infty} \frac{1}{N!\lambda^{3N}} \sum_{g \in G[N]} W(g)(\lambda^3 z)^N
\]

\[
= \sum_{N=0}^{\infty} \frac{1}{N!} \sum_{g \in G[N]} W(g)z^N
\]

\[
= G_W(z).
\]

Since the first Mayer weight function \(W\) is multiplicative on connected components, the exponential formula can be used:

\[
G_W(z) = \exp(C_W(z)),
\]

where \(C\) denotes the species (class) of connected graphs, so that

\[
\log G_W(z) = C_W(z)
\]

\[
= \sum_{N=1}^{\infty} \frac{1}{N!} \sum_{c \in C[N]} W(c)z^N
\]

and

\[
\frac{P}{kT} = \frac{1}{V} \log Z_{gr}(V, T, z) = \frac{1}{V} C_W(z).
\]
The Thermodynamic Limit

Let \( c \) be a connected graph over \([N]\).

The Second Mayer weight \( w(c) \) is defined as the limit

\[
    w(c) = \lim_{V \to \infty} \frac{1}{V} W(c)
    = \lim_{V \to \infty} \frac{1}{V} \int_{V^N} \prod_{\{i,j\} \in c} f_{ij} \, d\vec{x}_1 \ldots d\vec{x}_N.
\]

**Proposition 1.** If the function \( f : [0, \infty) \to \mathbb{R} \) is integrable and bounded and if

\[
    \int_0^\infty r^{d+\epsilon-1} |f(r)| \, dr < \infty,
\]

(for example if \( |f(r)| = O\left(\frac{1}{r^{d+2\epsilon}}\right) \), \( r \to \infty \)), then for any fixed \( \vec{x}_N \in \mathbb{R}^d \), the function \( F_{\vec{x}_N} : \mathbb{R}^{d \cdot (N-1)} \to \mathbb{R} \), defined by

\[
    F_{\vec{x}_N}(\vec{x}_1, \ldots, \vec{x}_{N-1}) = \prod_{\{i,j\} \in c} f(|\vec{x}_i - \vec{x}_j|) = \prod_{\{i,j\} \in c} f_{ij}
\]

is integrable over \((\mathbb{R}^d)^{N-1}\) and its integral is independent of \( \vec{x}_N \). Moreover the above limit \( w(c) \) exists and is equal to

\[
    w(c) = \int_{(\mathbb{R}^d)^{N-1}} \prod_{\{i,j\} \in c; \vec{x}_N=0} f_{ij} \, d\vec{x}_1 \ldots d\vec{x}_{N-1}.
\]
In this Thermodynamic limit, the pressure is given by

\[
\frac{P}{kT} = \lim_{V \to \infty} \frac{1}{V} \log Z_{gr}(V, T, z)
\]

\[
= \lim_{V \to \infty} \frac{1}{V} C_W(z)
\]

\[
= \sum_{N=1}^{\infty} \frac{1}{N!} \sum_{c \in \mathcal{C}[N]} \lim_{V \to \infty} \frac{1}{V} W(c) z^N
\]

\[
= \sum_{N=1}^{\infty} \frac{1}{N!} \sum_{c \in \mathcal{C}[N]} w(c) z^N
\]

\[
= C_w(z).
\]

**Proposition 2.** The weight function

\[
w(c) = \int_{(\mathbb{R}^d)^{N-1}} \prod_{\{i,j\} \in c; \: \vec{x}_{N} = \vec{0}} f_{ij} \, d\vec{x}_1 \ldots d\vec{x}_{N-1}
\]

is multiplicative with respect to 2-connected components.

See Figure 2
Figure 2: A connected graph with blocks $b_1, b_2, b_3, b_4$

For example, for the graph $c$ shown in Figure 2, we have

$$w(c)$$

$$= \int_{\mathbb{R}^{d-7}} f_{12}f_{13}f_{23}f_{34}f_{56}f_{37}f_{36}f_{67}f_{68}f_{78} \, d\vec{x}_1d\vec{x}_2 \cdots d\vec{x}_7$$

$$= \int f_{12}f_{13}f_{23}d\vec{x}_1d\vec{x}_2 \, f_{34}d\vec{x}_4 \, f_{56}d\vec{x}_5 \, f_{37}f_{36}f_{67}f_{68}f_{78} \, d\vec{x}_3d\vec{x}_6d\vec{x}_7$$

$$= w(b_1)w(b_2)w(b_3)w(b_4).$$

**Corollary.** Let $\mathcal{B}$ denote the species of 2-connected graphs. Then

$$\mathcal{C}^\bullet_w(z) = z \exp(\mathcal{B}_w'(\mathcal{C}^\bullet_w(z))),$$

where $\mathcal{C}^\bullet_w(z) = z \frac{d}{dz} \mathcal{C}_w(\bar{z})$. 

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**Proof.** As Figure 3 shows, we have the isomorphism of species

\[ C' = E(B'(C^\bullet)). \]

Since \( C^\bullet = X \cdot C' \), multiplication by X gives

\[ C^\bullet = X E(B'(C^\bullet)). \]

The fact that \( w \) is multiplicative over 2-connected components implies that the above relation will carry over to the weighted generating functions, i.e.

\[ C_w^\bullet(x) = x \exp(B'_w(C_w^\bullet(x))). \]

Figure 3: \( C' = E(B'(C^\bullet)) \)
An example: the Gaussian Model.

Let
\[ f(r) = -\exp(-\alpha r^2), \quad \alpha > 0, \]
which corresponds to a soft repulsive potential, at constant temperature. In this case, all cluster integrals can be explicitly computed (see Uhlenbeck and Ford, 1963): In dimension \( d \), the weight \( w(c) \) of a connected graph \( c \) with \( N \) vertices, has value
\[
w(c) = (-1)^{e(c)} \left( \frac{\pi}{\alpha} \right)^{\frac{d}{2}(N-1)} \gamma(c)^{-\frac{d}{2}},
\]
where \( e(c) \) is the number of edges of \( c \) and \( \gamma(c) \) is the graph complexity of \( c \), that is, the number of spanning subtrees of \( c \).
The hard-core continuum gas in one dimension.

Consider $N$ hard particles of diameter 1 on a line segment, of the form $[-D, D]$.

The hard core constraint translates into the interaction potential $\chi(|x_i - x_j| \geq 1)$ and the Mayer function $f_{ij}$ is defined by

\[
1 + f_{ij} = \chi(|x_i - x_j| \geq 1)
\]

\[
\Leftrightarrow f_{ij} = -\chi(|x_i - x_j| < 1).
\]

The weight function $w(c)$ of a connected graph $c$ is then

\[
w(c) = (-1)^{|E(c)|} \int_{\mathbb{R}^{N-1}} \prod_{\{i,j\} \in c; x_N=0} \chi(|x_i - x_j| < 1) \, dx_1 \ldots dx_{N-1}.
\]

**Classical result.** The pressure of this system is given by

\[
\frac{P}{kT} = C_w(z) = L(z),
\]

where $L(z)$ is the Lambert function defined by the functional equation $L(z) \exp(L(z)) = z$. In fact, $L(z) = -T(-z)$, where $T(z)$ is the exponential generating function of rooted trees.

In other words, we have

\[
\sum_{c \in \mathcal{C}[N]} w(c) = (-N)^{N-1}.
\]
In other words, we have

\[
\sum_{c \in \mathcal{C}[N]} w(c) = (-N)^{N-1}.
\]

In virtue of the functional equation

\[
\mathcal{C}_w(z) = z \exp(\mathcal{B}'_w(\mathcal{C}_w(z))),
\]

the formula \( \mathcal{C}_w(z) = L(z) \) is equivalent to

\[
\mathcal{B}_w(z) = z \log(1 - z)
\]

or, equivalently,

\[
\sum_{c \in \mathcal{B}[N]} w(c) = -N(N - 2)!. 
\]

**Question 1.** Is there a combinatorial interpretation – proof – of these formulas?

**Question 2.** Can we compute the individual weights \( w(c) \) of given connected graphs \( c \) and interpret them in terms of other graph invariants?
**Observation.** Except for the sign, the weight

\[ w(c) = (-1)^{|E(c)|} \int_{\mathbb{R}^{N-1}} \prod_{\{i,j\} \in c; x_N=0} \chi(|x_i-x_j| < 1) \, dx_1 \ldots dx_{N-1} \]

can be seen as the volume of a convex polytope \( \mathcal{P}(c) \) in \( \mathbb{R}^{N-1} \) bounded by the constraints \(|x_i - x_j| < 1\), for \( \{i,j\} \in c \), with \( x_N = 0 \). We can compute this volume using Ehrhart polynomials.

**Theorem (Ehrhart).** Let \( \mathcal{P} \) be a convex polytope of dimension \( d \) in \( \mathbb{R}^m \), with vertices having integer coordinates. Let \( n\mathcal{P} = \{n\alpha : \alpha \in \mathcal{P}\} \) denote the \( n \)-fold expansion of \( \mathcal{P} \), and \( i(\mathcal{P}, n) \), the number of points with integer coordinates which lie inside \( n\mathcal{P} \). Then \( i(\mathcal{P}, n) \) is a polynomial function of \( n \) of degree \( d \) whose leading coefficient is the volume \( \text{Vol}(\mathcal{P}) \) of \( \mathcal{P} \).

**Proposition 3.** The vertices of \( \mathcal{P}(c) \) have integer coordinates.

**Proof.** The vertices will occur as intersections of faces defined by equations of the form \( x_i - x_j = 1 \), for \( \{i,j\} \in c \). Now the matrix of such a system will be invertible if and only if the edges of the selected equations form a spanning subtree of \( c \). Since \( x_N = 0 \), each \( x_i \) will be an integer.
Hence the volume of the polytope $\mathcal{P}(c)$ and the weight

$$w(c) = (-1)^{|E(c)|} \text{Vol}(\mathcal{P}(c))$$

can be deduced by computing the Ehrhart polynomial function of $n, i(\mathcal{P}(c), n)$. We have carried out this computation for all 2-connected graphs having $N$ vertices, for $N \leq 6$. The weight of any connected graph $c$ whose blocks have size at most 6 can then be deduced by multiplicativity.

**Numerical results.**
The numerical results have led us to conjecture and then prove the following two results, for the cycle and the complete graph of size $N$:

**Proposition 4.** For the complete graph $K_N$, we have

$$w(K_N) = (-1)^{\binom{N}{2}}N.$$  

**Proof (Idea of Frédéric Chapoton).** Revert to the original definition of $w(c)$ and use the symmetry of the polytope $\mathcal{P}_N$ in $\mathbb{R}^N$ to compute its volume.

$$w(K_N) = \lim_{D \to \infty} \frac{1}{2D} W(K_N)$$

$$= \lim_{D \to \infty} \frac{1}{2D} (-1)^{\binom{N}{2}} \int_{[-D,D]^N} \prod_{\{i,j\}} \chi(|x_i - x_j| < 1) \, dx_1 \ldots dx_N.$$ 

**Proposition 5.** For the (unoriented) cycle $C_N$ with $N$ vertices, we have

$$w(C_N) = \frac{(-1)^N}{(N - 1)!} \sum_{i=0}^{\left\lfloor \frac{N-1}{2} \right\rfloor} (-1)^i \binom{N}{i} (N - 2i)^{N-1}.$$  

**Proof.** Uses the iterated convolution products of the $\chi$ function.
References


