The Combinatorics of the Virial Expansion

Combinatorics and Statistical Mechanics Workshop - Warwick University

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Outline

1. Combinatorial Species of Structure - an Overview
2. Mayer's Theory of Cluster and Virial Expansions
3. Graphical Involutions

Brief History of Cluster and Virial Expansions

- Generalise ideal gas Law $PV = NkT$ with power series expansion (1901 - Kamerlingh Onnes)
- Mayer (40) - understood virial coefficients as (weighted) two-connected graphs and cluster coefficients as (weighted) connected graphs
- 60s - Groeneveld (62, 63) Lebowitz and Penrose (64) Ruelle (63, 64, 69) - Kirkwood Salsburg Equations
- Gruber Kunz - Polymer Models (71)

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Brief History of Cluster and Virial Expansions

- Kotecký and Preiss Conditions (86) - also Dobrushin (96) - applied by Poghosyan Ueltschi (09) Combinatorial fixed point equations Faris (10) - further developed by Fernández and Procacci (07, +) - tree operator framework - extended to depth k Temmel (12)
- Graph Tree Identities/Inequalities - Brydges and Federbush (78) Battle (84), Battle and Federbush (84)
- Canonical Ensemble approach - Pulvirenti Tsagkarogiannis (12), Morais Procacci (13)

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Brief History of Combinatorial Species of Structure

- Combinatorial Species - understand bounds better - quick way to recognise virial expansion - Ducharme Labelle Leroux (07) - Faris (10)
- 1981 André Joyal - original paper on Combinatorial Species of Structure - giving a rigorous definition for labelled objects
- Importance is relating generating function with combinatorial structures
- Bergeron Labelle Leroux *Combinatorial Species and Tree-like Structures* - Useful Algebraic Identities (through combinatorics)
- Flajolet and Sedgwick - *Analytic Combinatorics*
- Leroux (04) and Faris (08, 10) - links to Statistical Mechanics

The Combinatorial Identities

Theorem (Bernardi 08)

If $c_{n,k}$:= *the number of* **connected** *graphs with* n *vertices and* k *edges, then:*

$$\sum_{k=n}^{\frac{1}{2}n(n-1)} (-1)^k c_{n,k} = (-1)^{n-1}(n-1)!$$

For the Polytope

$$\Pi_g := \{\mathbf{x}_{[2,n]} \in \mathbb{R}^{n-1} \,|\, |x_i - x_j| < 1 \,\forall \{i,j\} \in g \text{ with } x_1 = 0\}$$

We have the combinatorial equation:

$$\sum_{g \in \mathcal{C}[n]} (-1)^{e(g)} \operatorname{Vol}(\Pi_g) = (-1)^{n-1} n^{n-1}$$

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The Combinatorial Identities

Theorem (T. 14)

If $b_{n,k}$:= *the number of* **two-connected** *graphs with n vertices and k edges, then:*

$$\sum_{k=n}^{\frac{1}{2}n(n-1)} (-1)^k b_{n,k} = -(n-2)!$$

For the Polytope

$$\Pi_g := \{\mathbf{x}_{[2,n]} \in \mathbb{R}^{n-1} \,|\, |x_i - x_j| < 1 \,\forall \{i,j\} \in g \text{ with } x_1 = 0\}$$

We have the combinatorial equation:

$$\sum_{g \in \mathcal{B}[n]} (-1)^{e(g)} \mathrm{Vol}(\Pi_g) = -n(n-2)!$$

Motivation for studying Combinatorial Aspects

- The key paper of Ducharme Labelle and Leroux (07) explains Mayer's first and second theorems through combinatorial species and observes that using the Tonks gas model, which can be solved without using the graphical interpretation, gives the previous theorems, when interpreting the coefficients as weighted graphs
- The challenge is to prove this combinatorially
- This was done for the connected graph case by Bernardi (08) - covering also the one particle hardcore case
- For cluster expansions, these two models represent extremes for the values of the cluster coefficients with positive potentials - Groeneveld
- The combinatorial understanding of the cancellations in the connected graph case gives an alternative to the Penrose construction (67)

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Penrose Construction and Bernardi's Involution

- The Penrose construction gives a specific mapping $R : \mathcal{T} \to \mathcal{C}$ such that the sets:

$$[\tau, R(\tau)] = \{g \in \mathcal{C} | \, E(\tau) \subset E(g) \subset E(R(\tau))\}$$

  form a partition of all connected graphs.
- This can give an explanation in the one particle hardcore case
- The approach of Bernardi is to define an involution $\Psi : \mathcal{C} \to \mathcal{C}$ - effectively pairs all but a subset of graphs, differing by an edge to give cancellations
- There is a link between defining the involution and defining the partition

Penrose Construction and Bernardi's Involution

- Take the lexicographical order on the edges
- For the Penrose construction, we consider graph distance from the vertex labelled 1, defined as function of vertex labels d_1
- For a graph g, a pair $\{i, j\}$ (may not be an edge of graph) is called *g-active* if $d_1(i) = d_1(j)$ or $d_1(i) = d_1(j) + 1$ and there is a neighbour i' of i with $d_1(i') = d_1(j)$ and $i' > j$
- The involution adds/removes the largest g-active edge for each graph
- Fixed graphs are the linear trees rooted at 1.

Penrose Construction and Bernardi's Involution

- We can form a partition from Bernardi's involution by the map:

$$R(\tau) = (V(\tau), E(\tau) \cup \{\{\{i,j\} \subset V(\tau) | \{i,j\} \text{ is } \tau\text{-active } \}$$

- In the case of Bernardi, an edge $\{i,j\}$ is τ-active, if the subgraph of τ consisting only of edges strictly larger than $\{i,j\}$ contains a cycle including the edge $\{i,j\}$ if it is added.
- Indeed we see this notion of being active links both to the involution and the partition
- If we find an involution for two-connected graphs, could it lead to an analogue of the Penrose construction?

Overview

1. Combinatorial Species of Structure - an Overview

2. Mayer's Theory of Cluster and Virial Expansions

3. Graphical Involutions

Combinatorial Species of Structure - Definition

Definition

A Combinatorial Species of Structure is a rule F, which

i. for every finite set U gives a finite set of structures $F[U]$
ii. for every bijection $\sigma : U \to V$ gives a bijection $F[\sigma] : F[U] \to F[V]$

Furthermore, the bijections $F[\sigma]$ are required to satisfy the functorial properties:

i. If $\sigma : U \to V$ and $\tau : V \to W$, then $F[\tau \circ \sigma] = F[\tau] \circ F[\sigma]$
ii. For the identity bijection: $Id_U : U \to U$, $F[Id_U] = Id_{F[U]}$

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Interpretation of the Definition

- The structures have labels (the elements of the set U)
- The structures are characterised by sets $\{1, \cdots, n\} = [n]$, so characterisation by size of set
- Our collection of structures must be finite
- Relabelling the elements in the structure must behave well (functorial property)

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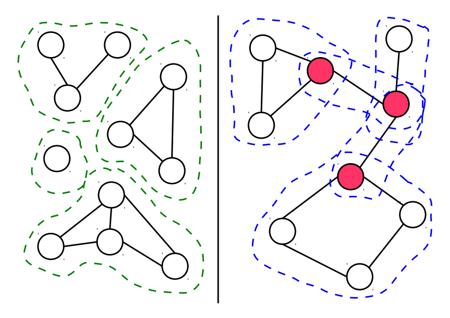
Examples of Species of Structure

Example

The important examples of this talk are (simple) graphs $\mathcal{G}$, connected graphs $\mathcal{C}$ two-connected graphs $\mathcal{B}$ and trees $\mathcal{T}$

Example (An Example of a Graph and a Connected Graph)



Two-connected Graphs

Articulation Points

An articulation point in a connected graph $\mathcal{C}$ is a vertex such that its removal and the removal of all incident edges renders the graph disconnected.

Two-connected Graph

A Two-connected graph is a connected graph with no articulation points.

Blocks in Connected Graphs

A maximal Two-connected subgraph of a connected graph is called a *Block*.

Exponential Generating Functions

We use the notation $[n]$ for the set $\{1, \cdots, n\}$

Exponential Generating Function

The (Exponential) Generating function of a species of structure F is:

$$F(z) = \sum_{n=1}^{\infty} f_n \frac{z^n}{n!} \tag{1}$$

where $f_n = \#F[n]$

Weighted Exponential Generating Functions

We may also add weights to our objects and we have the corresponding generating function: If each structure $s \in F[U]$ is given a weight, $w(s)$, we have the weighted generating function:

Weighted Generating Function

If $f_{n,w} = \sum_{s \in F[n]} w(s)$, then the weighted generating function is:

$$F_w(z) = \sum_{n=0}^{\infty} f_{n,w} \frac{z^n}{n!} \qquad (2)$$

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Operations on Species of Structure

For (formal) power series we have useful operations such as:

- Addition $(F + G)(z) = F(z) + G(z)$
- Multiplication $(F \star G)(z) = F(z) \times G(z)$
- Substitution $(F(G))(z) = F \circ G(z)$
- Differentiation $F'(z)$
- Euler Derivative (rooting) $F^{\bullet}(z) = z\frac{d}{dz}F(z)$

There is a corresponding operation on the level of species for each of the above.

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Classical Gas Background

- We have the Canonical Ensemble partition function:

$$Z_N := \sum_{(p_i, q_i) \in \mathbb{R}^N \times V^N} \exp\left(-\beta H_N(\{p_i, q_i\})\right)$$

  β is inverse temperature; H_N is the N-particle Hamiltonian; q_i are generalised coordinates and p_i are the conjugate momenta.

- The Grand Canonical Partition Function:

$$\Xi(z) := \sum_{N=0}^{\infty} \frac{z^N}{N!} Z_N$$

  where $z = e^{\beta\mu}$ is the fugacity parameter and μ is the chemical potential.

The Cluster Expansion and Virial Expansion

- The Grand Canonical Partition function:

$$\Xi(z) = \sum_{N \geq 0} \frac{z^N}{N!} Z_N$$

- In the thermodynamic limit $|\Lambda| \to \infty$, we have the pressure $\beta P = \lim_{|\Lambda| \to \infty} \frac{1}{|\Lambda|} \log \Xi(z)$
- We assume the existence of such a limit
- Expansion for pressure P in terms of fugacity z is the *cluster expansion*
- We have $\rho = z \frac{\partial}{\partial z} \beta P$, the density
- We may invert this equation and substitute for z to obtain a power series in ρ
- The virial development of the Equation of State is the power series $\beta P = \sum_{n=1}^{\infty} c_n \rho^n$ called the *virial expansion*.

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The Classical Gas

With pair potential interactions, we have the Hamiltonian

$$H_N = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j} \varphi(x_i, x_j)$$

If we use Mayer's trick of setting $f_{i,j} = \exp(-\beta\varphi(x_1, x_j)) - 1$, we may express the interaction as:

$$\prod_{i<j} \exp(-\beta\varphi(x_i, x_j)) = \prod_{i<j} (f_{i,j} + 1)$$

$$= \sum_{g \in \mathcal{G}[N]} \prod_{\{i,j\} \in E(g)} f_{i,j}$$

It thus makes sense to define our weights on a graph as:

$$w(g) := \prod_{e \in E(g)} f_e$$

which is edge multiplicative.

The Classical Gas

If we define $\tilde{w}(g) = \int\limits_V \cdots \int\limits_V w(g)\,\mathrm{d}x_1 \cdots \mathrm{d}x_N$, then we have that the grand canonical partition function can be identified as the generating function of weighted graphs in the parameter z.

Grand Canonical Partition Function as Graph Generating Function

$$\Xi(z) = \mathcal{G}_{\tilde{w}}(z)$$

Obtaining the Pressure

From the relationship $\mathcal{G} = \mathcal{E}(\mathcal{C})$ and noting that the generating function for $\mathcal{E}$ is the exponential function, we have that:

$$\log \Xi(z) = \mathcal{C}_{\tilde{w}}(z)$$

We recognise that $\beta P = \log \Xi(z)$, so that:

The Pressure as Connected Graph Generating Function

$$\beta P = \mathcal{C}_{\tilde{w}}(z)$$

The Density

We use the relationship for the density: $\rho = z\frac{d}{dz}\beta P$, to get the combinatorial interpretation:

Generating Function for Density

$$\rho(z) = \mathcal{C}^{\bullet}_{\tilde{w}}(z)$$

The Dissymmetry Theorem

The Dissymmetry Theorem

If we let $\mathcal{C}$ represent the species of connected graphs and $\mathcal{B}$ the species of two-connected graphs, then we have the combinatorial relationship:

$$\mathcal{C} + \mathcal{B}^{\bullet}(\mathcal{C}^{\bullet}) = \mathcal{C}^{\bullet} + \mathcal{B}(\mathcal{C}^{\bullet})$$

Furthermore, the combinatorial relationship gives it as a generating function relationship:

$$C(z) + B^{\bullet}(C^{\bullet}(z)) = C^{\bullet}(z) + B(C^{\bullet}(z))$$

We can also add appropriate weights to get a weighted identity:

$$C_w(z) + B_w^{\bullet}(C_w^{\bullet}(z)) = C_w^{\bullet}(z) + B_w(C_w^{\bullet}(z))$$

The Dissymmetry Theorem and Virial Expansion

We have the density $\rho = \mathcal{C}_w^\bullet(z)$ and $\beta P = \mathcal{C}_w(z)$ and so, using the dissymmetry theorem, we get:

$$\begin{aligned}\beta P &= \rho + \sum_{n=2}^{\infty} \frac{\beta_{n,\tilde{w}}}{n!}\rho^n - \sum_{n=2}^{\infty} \frac{n\beta_{n,\tilde{w}}}{n!}\rho^n \\ &= \rho - \sum_{n=2}^{\infty} \frac{(n-1)\beta_{n,\tilde{w}}}{n!}\rho^n\end{aligned}$$

where $\beta_{n,\tilde{w}} = \sum_{g \in \mathcal{B}[n]} \tilde{w}(g)$

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The one particle hard-core model

For a one-particle hard-core model, we have that the potential is always ∞, that is the factor $e^{-\beta\varphi(x_i,x_j)} = 0$ and hence the edge factor is $f_{i,j} = -1$ for all i, j. This gives the grand canonical partition function as:

$$\Xi(z) = 1 + z$$

giving the pressure as:

$$\beta P = \log(1+z) = \sum_{n\geq 1} \frac{(-1)^{n+1} z^n}{n}$$

upon comparison with the combinatorial version (in terms of weighted connected graphs) we have:

$$\sum_{k=n-1}^{\frac{1}{2}n(n-1)} (-1)^k c_{n,k} = (-1)^{n-1}(n-1)!$$

The one-particle hard-core model

Furthermore, we may take the Euler derivative and obtain density:

$$\rho = \frac{z}{1+z}$$

which may be inverted

$$z = \frac{\rho}{1-\rho}$$

and then substituted to obtain pressure in terms of density:

$$\beta P = -\log(1-\rho) = \sum_{n \geq 1} \frac{\rho^n}{n}$$

Upon comparison with the combinatorial version (in terms of weighted two-connected graphs) we have:

$$\sum_{k=n}^{\frac{1}{2}n(n-1)} (-1)^k b_{n,k} = -(n-2)!$$

Combinatorial Puzzle from Mayer's Theory of Cluster Integrals

- Bernardi(08) proved the connected case through an involution $\Phi : \mathcal{C} \to \mathcal{C}$
- Involution involves adding or removing edges to a graph
- Created a pairing of graphs G with $\Psi(G)$ for those which aren't fixed
- The fixed graphs ($\Psi(G) = G$) are increasing trees - only graphs which are not cancelled
- Generalised to the case of the Tonks Gas

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One Particle Hardcore Interaction

- The cancellations for the one particle hardcore gas can also be described through an involution $\Psi : \mathcal{B} \to \mathcal{B}$
- This time the fixed graphs are those formed from an increasing tree on the indices $[n-1]$ with vertex n adjacent to all the other vertices.
- All the fixed graphs have precisely $2n-3$ edges, giving the definite sign for the coefficients.
- This can be generalised towards the Tonks gas

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The Tonks Gas

For the Tonks gas which is the hardcore gas in one dimension, we have that the pair potential is given by (for diameter 1)

$$\varphi(x_i, x_j) = \begin{cases} \infty & \text{if } |x_i - x_j| < 1 \\ 0 & \text{otherwise} \end{cases}$$

This gives the exponential and pair potential as

$$\exp(-\beta\varphi(x_i, x_j)) = \begin{cases} 0 & \text{if } |x_i - x_j| < 1 \\ 1 & \text{otherwise} \end{cases}$$

$$f_{i,j} = \begin{cases} -1 & \text{if } |x_i - x_j| < 1 \\ 0 & \text{otherwise} \end{cases} = -\mathbb{1}_{|x_i - x_j| < 1}$$

The Tonks Gas

One can derive the expression of pressure in terms of density directly from the Canonical Ensemble and achieve from this also the cluster expansion. These are:

$$\beta P = \sum_{n=1}^{\infty} \rho^n = \frac{\rho}{1-\rho}$$

$$\beta P = \sum_{n=1}^{\infty} \frac{n^{n-1}}{n!}(-1)^{n-1} z^n = W(z)$$

where $W(z)$ is the Lambert W-function.
The weight is the product of the indicator functions and we understand that we have one arbitrary x_i, since they depend only on differences of the variables, but we divide by volume and so we can fix $x_1 = 0$ and integrate over the other variables to achieve the weight.

The Tonks Gas

The weight for this model is:

$$w(g) = (-1)^{e(g)}\mathsf{Vol}(\Pi_g)$$

Where Π_g is the polytope of the graph g, which is defined by:

$$\Pi_g := \{\mathbf{x}_{[2,n]} \in \mathbb{R}^{n-1} | |x_i - x_j| \leq 1 \forall (i,j) \in g \; x_1 = 0\}$$

The identities arising from this are:

$$\sum_{g \in \mathcal{C}[n]} (-1)^{e(g)} \, \mathrm{Vol}(\Pi_g) = (-1)^{n-1}(n)^{n-1}$$

$$\sum_{g \in \mathcal{B}[n]} (-1)^{e(g)} \, \mathrm{Vol}(\Pi_g) = -n(n-2)!$$

The approach is to split each polytope into simplices of equal volume. This first appeared in the paper by Ducharme, Labelle and Leroux (07) and is attributed to Lass.

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Splitting Polytope into Simplices

- Consider the pair $(\mathbf{h}, \sigma)$ comprising of an integer-valued vector $\mathbf{h} \in \mathbb{Z}^{n-1}$ and a permutation $\sigma : [2, n] \to [2, n]$
- The permutation indicates order on the indices
- The pair $(\mathbf{h}, \sigma)$ represents a unique $n-1$-dimensional simplex with origin at the integer point.
- The simplices all have volume $\frac{1}{(n-1)!}$
- A simple relation on the pair $(\mathbf{h}, \sigma)$ indicates when it is contained in the polytope Π_g.
- The important thing to realise is that either such a simplex is contained in the polytope or it only intersects on the boundary.
- One can reorder the sum over these graphs in a canonical way to ensure that we represent the collection of simplices by $\mathbf{h}$ and have a specific condition for it to be counted in the sum for Π_g

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The Tonks Gas

- Instead of the lexicographic order, we use the vector $\bar{\mathbf{h}} = (h_i + \frac{\sigma(i)-1}{n})_{i\in[2,n]}$ to give an order to the edges in the graph
- For the two-connected version it is necessary to first order the edges by the differences $|\bar{h}_i - \bar{h}_j|$
- Within edges with the same difference, we take as an order, the natural order on the $\bar{\mathbf{h}}$ entries

The Tonks Gas

- We achieve a suitable modification of the one particle hard-core case, which gives a different involution for each $\mathbf{h}$ providing all cancellations.
- In the connected graph case, we end up with an identification with the rooted connected graphs - Bernardi (08)
- In the two-connected case, we actually obtain more cancellations and have only fixed graphs for $\mathbf{h} = (0, \cdots, 0, -1, \cdots, -1)$. We have n such vectors and have the same interpretation for the fixed graphs, except we have the ordering on the labelled vertices dictated by the ordering of the entries of $\bar{\mathbf{h}}$.

Difficulty in Obtaining the Penrose Construction Analogue

- The fixed graphs are no longer the minimal two-connected graphs - more complex than a partition determined by a function R from a set containing the fixed graphs to $\mathcal{B}$
- Matroid extension of tree graph inequality - Faris (12) - hasn't been modified to work in this case
- Possibly useful are the notions of internally and externally active edges used in Arithmetic Matroid structures present in Potts Model - Sokal (01, 05)
- Some useful generalisation of the Fundamental Theorem of Calculus towards more general partially ordered sets (developed from Abdesselam Rivasseau(94) Faris (12))

Conclusions

The Main Conclusions are:

- We have the combinatorial identities which provide us with a simple way of recognising the virial coefficients
- Statistical Mechanics provides motivation for combinatorial identities
- There is an interpretation of the combinatorial identities provided by simple models in statistical mechanics
- These cancellations can be extended to an understanding of a reorganisation of the sums in the connected case

Open Questions

- Other physical models/problems to apply combinatorial species of structure - renormalisation in QFT?
- Can the cancellations be understood in a larger framework/context?
- How can we use this knowledge and understanding of combinatorics to make effective cancellations in inequalities for our expansions?