Combinatorics and Statistical Mechanics

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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 Combinatorial Species of Structure

- 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

Brief History of Cluster and Virial Expansions

- Generalise Ideal gas Law $PV = NkT$ with power series Expansion (1901 - Kamerlingh Onnes)
- Mayer (40) - understood coefficients as (weighted) 2-connected graphs (algebraic/complicated method)
- Reawakened 60s Groeneveld (62, 63) Lebowitz and Penrose (64) Ruelle (63, 64, 69) - Kirkwood Salsburg Equations
- Gruber Kunz - Polymer Models (71)
- Kotecký and Preiss Conditions (86) - developed by Dobrushin (96) and applied in other ways by Poghosyan Ueltschi (09) - further developed by Fernández and Procacci (07) - Combinatorial fixed point equations
- Graph Tree Identities/Inequalities - Brydges and Federbush (78) Battle (84), Battle and Federbush (84)
- Combinatorial Species - understand bounds better - quick way to recognise virial expansion

Overview

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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: $Id_U : U \to U$, $F[Id_U] = Id_{F[U]}$

Interpretation of the Definition

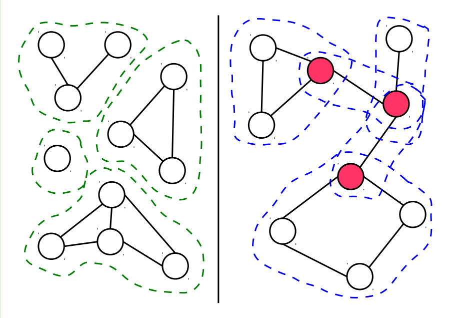
- The structures have labels (the elements of the set U)
- The structures are characterised by sets $\{1, \cdots, n\} = [n]$, so characterisation by size of set
- Our collection of structures must be finite
- Relabelling the elements in the structure must behave well (functorial property)

Examples of Species of Structure

Example

The important examples I will be using are those of graphs $\mathcal{G}$, connected graphs $\mathcal{C}$ 2-connected graphs $\mathcal{B}$ and trees $\mathcal{T}$

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



2-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.

2-connected Graph

A 2-connected graph is a connected graph with no articulation points.

Blocks in Connected Graphs

A maximal 2-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:

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

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.

Overview

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*.

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:

$$\prod_{i<j} \exp(-\beta\varphi(x_i, x_j)) = \prod_{i<j} (f_{i,j} + 1) \tag{3}$$

$$= \sum_{g \in \mathcal{G}[N]} \prod_{\{i,j\} \in E(g)} f_{i,j} \tag{4}$$

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

$$w(g) := \prod_{e \in E(g)} f_e \tag{5}$$

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

$$\Xi(z) = \mathcal{G}_{\tilde{w}}(z) \tag{6}$$

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:

$$\log \Xi(z) = \mathcal{C}_{\tilde{w}}(z) \tag{7}$$

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

The Pressure as Connected Graph Generating Function

$$\beta P = \mathcal{C}_{\tilde{w}}(z) \tag{8}$$

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

$$\rho(z) = \mathcal{C}^{\bullet}_{\tilde{w}}(z) \tag{9}$$

The Dissymmetry Theorem

The Dissymmetry Theorem

If we let $\mathcal{C}$ represent the species of connected graphs and $\mathcal{B}$ the species of 2-connected graphs, then we have the combinatorial relationship:

$$\mathcal{C} + \mathcal{B}^{\bullet}(\mathcal{C}^{\bullet}) = \mathcal{C}^{\bullet} + \mathcal{B}(\mathcal{C}^{\bullet}) \tag{10}$$

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

$$C(z) + B^{\bullet}(C^{\bullet}(z)) = C^{\bullet}(z) + B(C^{\bullet}(z)) \tag{11}$$

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

$$C_w(z) + B_w^{\bullet}(C_w^{\bullet}(z)) = C_w^{\bullet}(z) + B_w(C_w^{\bullet}(z)) \tag{12}$$

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:

$$\beta P = \rho + \sum_{n=2}^{\infty} \frac{\beta_{n,\tilde{w}}}{n!}\rho^n - \sum_{n=2}^{\infty} \frac{n\beta_{n,\tilde{w}}}{n!}\rho^n \tag{13}$$

$$= \rho - \sum_{n=2}^{\infty} \frac{(n-1)\beta_{n,\tilde{w}}}{n!}\rho^n \tag{14}$$

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 2-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

Theorem (Bernardi 08)

Let $c_{n,k}$ denote the number of **connected graphs** *with n vertices and k edges, then*

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

The cancellations coming from a graph involution $\Psi : \mathcal{C} \to \mathcal{C}$, fixing only increasing trees.

- Involution involves adding or removing edges to a graph
- Created a pairing of graphs G with $\Psi(G)$ for those which aren't fixed
- May be generalised to the case of the Tonks Gas

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One particle hard core interaction

We have from the virial expansion:

Theorem (T. - In preparation)

If $b_{n,k}$ = number of **2-connected graphs** with n vertices and k edges, then:

$$\sum_{k=n}^{\frac{1}{2}n(n-1)} (-1)^k b_{n,k} = -(n-2)! \tag{15}$$

The cancellations coming from a graph involution $\Psi : \mathcal{B} \to \mathcal{B}$ fixing only the 2-connected graphs which are formed from an increasing tree on the indices $[1, n-1]$ and has vertex n connected to all the other vertices.

This method can also be generalised to the Tonks Gas

The Tonks Gas

The appropriate weight for this model is:

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

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 key technique in proving both of these is a splitting of each polytope into subpolytopes of equal volume. This first appeared in the paper by Ducharme, Labelle and Leroux, but is attributed to Lass.

The Tonks Gas

One may consider an integer-valued vector $\mathbf{h} \in \mathbb{Z}^{n-1}$ and a permutation $\sigma[2, n] \to [2, n]$, which indicates order on the indices, giving a unique $n-1$-dimensional simplex with origin at the integer point. These all have volume $\frac{1}{(n-1)!}$ and one can determine a relation on the pair $(\mathbf{h}, \sigma)$, which allows it to be 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.

The Tonks Gas

- The key difference in this case is to consider the vector $\bar{\mathbf{h}} = (h_i + \frac{\sigma(i)-1}{n})_{i\in[2,n]}$ providing an order to the edges in the graph which may be different from the usual lexicographical ordering provided by the labels on the graph.
- For the two-connected version it is necessary to first order the edges by the differences $|\bar{h}_i - \bar{h}_j|$
- We achieve a suitable modification of the one particle hard-core case, which gives a different involution for each pair $(\mathbf{h}, \sigma)$ providing all cancellations.
- In the connected graph case, we end up with an identification with the rooted connected graphs.
- 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.

Conclusions

The Main Conclusions are:

- We have the combinatorial identities which provide us with a simple way of recognising the virial coefficients
- The virial expansion is understood in a broader context from a combinatorial viewpoint
- Statistical Mechanics provides motivation for combinatorial identities
- Langrange Inversion and the Dissymmetry Theorem run in parallel to provide in the former case a method of computing coefficients exactly and in the latter case an interpretation of the coefficients in terms of combinatorial structures
- There is an interpretation of the combinatorial identities provided by simple models in statistical mechanics

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?
- What are the general properties of convergence of functions related by Lagrange Inversion?