Combinatorial Species and the Virial Expansion

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Combinatorial Species

Definition 1

A *Species of Structure* is a rule F which

i) *Produces* for each finite set U, a finite set F[U]

ii) *Produces* for each bijection σ: U→V, a function

F[σ]: F[u]→F[V]

The functions $F[\sigma]$ should satisfy the following **Functorial Properties**:

a) For all bijections $\sigma: U \rightarrow V$ and $\tau: V \rightarrow W$

$$F[\tau \cdot \sigma] = F[\tau] \cdot F[\sigma]$$

b) For the identity map $Id_U : U \rightarrow U$

$$F[Id_U] = Id_{F[U]}$$

An element s ε F[U] is called an **F-structure** on U

The function F[σ] is called the **transport** of F-structures along σ

F[σ] is necessarily a bijection

Examples

- Set Species $\mathscr{S}$ where:

  $\mathscr{S}$[U]= {U} for all sets U

- Species of Simple Graphs $\mathscr{G}$

  Where s ε $\mathscr{G}$[U] iff s is a graph on the points in U

Associated Power Series

Exponential Generating Series

The formal power series for species of structure F is

$$F(x) = \sum_{n=0}^{\infty} f_n \frac{x^n}{n!}$$

where f_n is the cardinality of the set F[n]=F[{1 ... n}]

Operations on Species of Structure

Sum of species of structure

Let F and G be two species of structure.

An (F+G)-structure on U is an F-structure on U or (exclusive) a G-structure on U.

$(F+G)[U] = F[U]\times\{\dagger\} \cup G[U]\times\{\ddagger\}$

i.e. a DISJOINT union

$$(F+G)[\sigma](s)=\begin{cases} F[\sigma](s) \text{ if } s \in F[U] \\ G[\sigma](s) \text{ if } s \in G[U] \end{cases}$$

Product of a species of structure

Let F and G be two species of structures.

The species FG called the *product* of F and G is defined as follows:

An FG structure on U is an ordered pair s=(f,g)

- f is an F structure on U_1
- g is a G structure on U_2
- (U_1,U_2) is a decomposition of U

Substitution of Species of Structures

Let F and G be two species of structures such that $G[\phi]=\phi$.

The species F(G) called the *partitional composite* of G in F

An (F(G))-structure on U is a triplet $s=(\pi,\psi,\gamma)$

- π is a partition of U
- ψ is an F-structure on the set of classes of π
- $\gamma = (\gamma_p)_{p \varepsilon \pi}$, where for each class p of π, γ_p is a G-structure on p

The Derivative of a Species of Structures

Let F be a species of structures.

The species F', called the *derivative* of F, is defined as follows:

An F'-structure on U is an F-structure on

$U^+ = U \cup \{\#\}$, where $\# = \#_U$ is an element chosen outside of U

How the operations effect the Power Series

SUM

$$(F+G)(x) = F(x) + G(x)$$

PRODUCT

$$(FG)(x) = F(x)G(x)$$

SUBSTITUTION

$$(F(G))(x) = F(G(x))$$

DERIVATIVE

$$(F')(x) = \frac{d}{dx}F(x)$$

Weighted Species

Let **K** ≤ **C** be an integral domain and **A** a ring of formal power series in an arbitrary number of variables with coefficients in **K**

Definition

An **A**-*weighted set* is a pair (A,w), where A is a set and:

$$w: A \rightarrow \mathbf{A}$$

Is a function which associates a *weight* w(a) ε **A** for each element a ε A

SUM

The *sum* (A,w) + (B,v) is the **A**-weighted set (A+B, μ), where A+B denotes the *disjoint* union of A and B and μ is the weight function:

$$\mu(x)= \begin{cases} w(x) \text{ if } x \in A \\ v(x) \text{ if } x \in B \end{cases}$$

PRODUCT

The *product* (A,w) X (B,v) is the **A**-weighted set (AxB, ρ) where ρ is the weight function defined by: $\rho(x,y)=w(x)v(y)$

Definition

An **A**-*weighted species* is a rule F, which

- *produces*, for each finite set U, a finite or summable **A**-weighted set

$$(F[U],w_U)$$

- *produces*, for each bijection $\sigma:U \rightarrow V$, a function

$$F[\sigma] : (F[U],w_U) \rightarrow (F[V],w_V)$$

preserving the weights

Main Result from Combinatorics

Definition

The operation F → F* of pointing F-structures at an element of the underlying set is defined by:

$$F^* = X\,F'$$

Theorem

Let $\mathscr{C}$ be the species of connected graphs and $\mathscr{B}$ the species of 2-connected graphs. Then:

$$\mathscr{C}' = \mathscr{S}(\mathscr{B}'(\mathscr{C}^*))$$

Where $\mathscr{S}$ is the set species from before.

In terms of exponential generating functions:

$$C'(x) = \exp(B' (C^*(x)))$$

Multiplying by x on both sides gives:

$$C^*(x) = x \exp (B' (C^*(x)))$$

Further Theorems from Combinatorics

Definition

A weight function w on the species $\mathscr{G}$ of graphs is said to be *multiplicative on the connected components* if for any graph g ε $\mathscr{G}$[U] whose connected components are c_1 c_2 ... c_k we have

$$w(g) = w(c_1)w(c_2)...w(c_k)$$

Definition

The generating function of a weighted species of structure F_w is:

$$F_w(x) = \sum_{n=0}^{\infty} |F[n]|_w \frac{x^n}{n!} = \sum_{n=0}^{\infty} \frac{x^n}{n!} \sum_{s \in F[n]} w(s)$$

Theorem

For weighted exponential generating functions G_w of graphs and C_w of connected graphs, where w is multiplicative on connected components, we have:

$$G_w(x) = \exp(C_w(x))$$

Definition

A *block* is a maximally two connected subgraph of a connected graph.

Definition

A weight function on connected graphs is said to be *block-multiplicative* if for any connected graph c, whose blocks are b_1 b_2 ... b_k , we have:

$$w(c) = w(b_1)\ w(b_2)\ \ldots\ w(b_k)$$

Theorem

Let w be a block multiplicative weight function on connected graphs. Then we have:

$$C^*_w(x) = x \exp(B'_w(C^*_w(x)))$$

Statistical Mechanics

Non-ideal gas of N particles interacting in vessel V of volume V with positions $\mathbf{x}_1$ $\mathbf{x}_2$ ... $\mathbf{x}_N$.

HAMILTONIAN

$$H = \sum_{i=1}^{N} \left(\frac{\overrightarrow{p_i}^2}{2m} + U(\overrightarrow{x_i})\right) + \sum_{1 \leq i < j \leq N} \varphi(|\overrightarrow{x_i} - \overrightarrow{x_j}|)$$

Canonical Partition Function

$$Z(V,N,T) = \frac{1}{N!\,h^{3N}}\int \exp(-\beta H)\,d\gamma$$

where h is Planck's constant, $\beta = \frac{1}{kT}$, T is the absolute temperature and K is Boltzmann's constant, and γ represents the state space of positions and momenta of dimension 6N.

- Assume Potential Energy $U(x_i)$ is negligible
- Evaluate Gaussian integrals over momenta

The final expression for the partition function is:

$$Z(V,N,T) = \frac{1}{N!\,\mu^{3N}} \int_V \cdots \int_V \exp\left(-\beta \sum_{i<j} \varphi(|\vec{x_i} - \vec{x_j}|)\right) d\vec{x_1} \ldots d\vec{x_N}$$

Where $\mu = h(2\pi mkT)^{-\frac{1}{2}}$

The *grand-canonical distribution* is the generating function for canonical partition functions, defined by

$$Z_{gr}(V,T,z) = \sum_{N=0}^{\infty} Z(V,N,T)(\mu^3 z)^N$$

Definitions

Variable z is called the *fugacity* or *activity*

P is *pressure*

$\bar{N}$ is *average number of particles*

ρ is the *density*

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

$$\rho := \frac{\bar{N}}{V}$$

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

The Virial Expansion

Kamerlingh Onnes proposed a series expansion:

$$\frac{P}{kT} = \frac{\bar{N}}{V} + \gamma_2(T)\left(\frac{\bar{N}}{V}\right)^2 + \gamma_3(T)\left(\frac{\bar{N}}{V}\right)^3 + \ \dots$$

Called the **VIRIAL EXPANSION**

Mayer's idea consisted of setting:

$$1 + f_{ij} = \exp\left(-\beta\varphi\left(\left|\vec{x_i} - \vec{x_j}\right|\right)\right)$$

We can rewrite the partition function by noticing that the product $\prod_{1 \leq i < j \leq N} (1 + f_{ij})$

Can be rewritten as the sum of terms, which can be represented by simple graphs, where the vertices are the particles and the edges are the chosen factors f_{ij}

$$Z(V,N,T) = \frac{1}{N!\,\mu^{3N}} \sum_{g \in G[N]} W(g)$$

where $W(g) = \int_V \dots \int_V \prod_{\{ij\} \in g} f_{ij}\, d\overrightarrow{x_1} \dots d\overrightarrow{x_N}$

Theorem

The weight function W is multiplicative on the connected components.

We have $G_W(z) = \exp(\, C_W(z)\,)$

and $Z_{gr}(V, T, z) = G_w(z)$

These give

$$\frac{P}{kT} = \frac{1}{V} C_W(z)$$

Theorem

For large V, the weight function $w(c) = \frac{1}{V} W(c)$

Is block multiplicative.

Hence we have

$$C^*_w(z) = z \exp(B'_w(C^*_w(z)))$$

Now, for the density $\rho(z)$

$$\rho(z) = z\frac{\partial}{\partial z}\frac{1}{V}\log Z_{gr}(V,T,z)$$

$$= z\frac{\partial}{\partial z}C_w(z) = C^*{}_w(z)$$

This satisfies the recurrence relation:

$$\rho(z) = z\exp\left(B'{}_w\big(\rho(z)\big)\right)$$

Then using the expression for pressure:

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

$$= \int_0^z C'{}_w(t)dt = \int_0^z \frac{\rho(t)}{t}dt$$

Make change of variable: $t(r) = r\exp(-B'_w(r))$

Which is the inverse function of $r = \rho(t)$

$$dt = [\exp\left(-B'_w(r)\right) - r\exp\left(-B'_w(r)\right)B''_w(r)]dr$$

Following the computation of the integral using this substitution

$$\frac{P}{kT} = \int_0^\rho 1 - rB''_w(r))dr$$

$$= \rho - \int_0^\rho rB''_w(r)dr$$

$$= \rho - \int_0^\rho \sum_{n\geq 1} n\beta_{n+1}\frac{r^n}{n!}dr$$

$$= \rho - \sum_{n\geq 2}(n-1)\beta_n\frac{\rho^n}{n!}$$

The Virial Coefficients

This gives Virial Coefficients

$$\gamma_n(T) = -\frac{(n-1)}{n!}\beta_n = -\frac{(n-1)}{n!}|B[n]|_w$$

The Dissymmetry Theorem

We have the Combinatorial Equality:

$$C^* + B(C^*) = B^*(C^*) + C$$

In terms of weighted functions with the weight defined as before, we get:

$$\rho + \sum_{n=1}^{\infty} \frac{\beta_n}{n!} \rho^n = \sum_{n=1}^{\infty} \frac{n\beta_n}{n!} \rho^n + \beta P$$

Dissymmetry Theorem

This then gives the final formula for the Virial Expansion as obtained earlier

$$\beta P = \rho - \sum_{n=2}^{\infty} \frac{\rho^{n}}{n!} \beta_{n} (n-1)$$

An Interesting Result

As an interesting application of the Virial Expansion, we have for a hard-core one-particle interaction, where we have weight function: $(-1)^{e(g)}$, where e(g) is the number of edges in the graph g. Applying this to the Virial Expansion we get:

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

Where $b_{n,k}$ is the number of two-connected graphs on n vertices with k edges

An Interesting Result

If we look at the expressions of pressure and density expanded in terms of fugacity:

$$\beta P = \log(1 + z)$$

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

If we then write z in terms of ρ and substitute this into the first equation, we get:

$$\beta P = -\log(1 - \rho) = \rho + \sum_{n \geq 2} \frac{\rho^n}{n}$$

An Interesting Result

If we compare the two expansions we then get:

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

Future Directions

- There is the Penrose partition of connected graphs related to Penrose trees
- Fernandez and Procacci obtained new results on the convergence of the cluster expansion using this
- I am considering trying to find a similar partition of 2-connected graphs to obtain similar methods of understanding convergence of the virial expansion

References

Bergeron, Labelle, Leroux Combinatorial Species and Tree-like Structuress

Faris, W. G. Combinatorics and cluster expansions

Fernandez, R. Procacci, A. Cluster expansion for abstract polymer models, new bounds

Leroux, P. Enumerative problems inspired by Mayer's theory of cluster integrals

Poghosyan, S. Ueltschi, D. Abstract cluster expansion with applications to statistical mechanical systems

Thank you for listening to my presentation. Do you have any questions?