Statistical Mechanics and Combinatorics

Stephen Tate
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Supervisor: Daniel Ueltschi
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Background

We work with classical Statistical Mechanics with a pair potential $U(r)$ with Hamiltonian:

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{1 \le i < j \le N} U(r_i - r_j)$$

Background

The Partition function for N particles is:

$$Z_N(\beta) = \frac{1}{N!}\int d^{3N}x \quad d^{3N}p \quad e^{-\beta H}$$

$$= \frac{1}{N!}\int d^{3N}x \quad d^{3N}p \quad e^{-\beta(\sum_{i=1}^{N}\frac{p_i^2}{2m} + \sum_{1\le i<j\le N} U(r_i - r_j))}$$

$$= \frac{(2\pi m/\beta)^{\frac{3N}{2}}}{N!}\int d^{3N}x \quad e^{-\beta \sum_{1\le i<j\le N} U(r_i - r_j)}$$

Background

Grand Canonical Ensemble partition function is

$$Q^{gr}(z) = \sum_{N=0}^{\infty} z^N Z_N(\beta)$$

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

Background

Mayer's Idea is to define:

$$f(r_{i,j}) = f_{i,j} = e^{-U(r_i - r_j)/k_B T} - 1$$

write $\exp\{-\frac{1}{k_B T}\sum_{1\le i<j\le N} U(r_i - r_j)\} = \prod_{1\le i<j\le N}(1+f_{ij})$

and expand the product.

We see that each term can be represented by a simple graph (Mayer Graph).

Where we take a simple graph and give each edge $\{i, j\}$ the weight f_{ij}

Generating Series

We note that the grand canonical partition function is a generating series in z

If we have a set of structures F, where for each n F[n] is the set of F-structures on a set of n points, and a weight function $w: F \mapsto A$

Where A is a subalgebra of power series with complex coefficients in many variables

The weighted exponential generating series is:

$$\sum_{n=0}^{\infty} \frac{z^N}{N!} \sum_{c \in F[n]} w(g)$$

Pressure

The pressure is defined by: $\beta P = \frac{1}{V} \log Z_{gr}(z;V,N,T)$

Where $\beta = \frac{1}{k_B T}$ T is temperature and k_B is Boltzman's constant

As a power series in fugacity we have:

$\beta P(z;V) = \sum_{k=1}^{\infty} z^k b_k(V)$ where $b_k(V) = \frac{1}{k!V} \int_V U_k(r_1,\ldots,r_k) d^D r_1 \ldots d^D r_k$

Where $U_k(r_1 \ldots r_k)$ is the sum of all connected labelled Mayer Graphs on k points

Density

We have that the density is:

$$\rho(z;V) = z\frac{d}{dz}(\beta P(z;V)) = \sum_{k=1}^{\infty} k b_k(V) z^k$$

What are the Combinatorial Structures?

A *combinatorial 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]

Why should we get connected graphs?

If we define the structure SET as being the structure which for any finite set it just gives a single trivial structure on the set, that is the set itself.

This has exponential generating series:

$$\sum_{n=0}^{\infty} \frac{x^n}{n!}$$

Why should we get Connected Graphs?

If we want to compose two structures F(G)

(requiring that there are no G-structures on the empty set)

- We take a partition of the set we have our structure on
- We have a G structure on each subset
- We have an F structure on the points in the partition

Why should we get Connected Graphs?

In the case of connected graphs C, we have G=SET(C)

This is because each simple graph has a unique partition (given by the operation SET and composition) into connected components (which is a C-structure).

Why should we get connected graphs?

It is a theorem that if we have G=SET(C) in terms of structures, we have it for generating series (where the weights are multiplicative on connected components)

So if we consider the weight $w(g) = \sum_{\{i,j\} \in E(g)} f_{ij}$

Then we get the statement for the pressure series, since we take a logarithm.

Virial Expansion

The first order approximation is the ideal gas law

$$P = \rho k_B T$$

Heike Kamerlingh Onnes proposed the idea of a Virial Expansion in 1901, to write pressure as a power series in density to extend this to interacting systems

Virial Expansion

The initial perturbation given by Van der Waals Equation is:

$$(P + a\rho^2)(1 - \rho b) = \rho RT$$

The second Virial coefficient is given by:

$$\frac{P}{k_B T} = \rho - \frac{1}{2}\rho^2 \int d^D x \quad (e^{-u(x)/k_B T} - 1) + O(\rho^3)$$

Methods used to bound further coefficients, bound them in terms of the second coefficient

Virial Expansion

The Virial Expansion is: $\beta P = \rho + \sum_{k=1}^{\infty} \rho^{k+1} B_{k+1}$

where: $B_{k+1} = -\frac{k}{k+1}\beta_k$

$$\beta_k = \frac{1}{k!}\int V_{k+1}(r_1 \ldots r_k)\, d^D r_1 \ldots d^D r_{k+1}$$

Where $V_{k+1}(r_1 \ldots r_{k+1})$ is the sum of the weights of 2-connected graphs on k+1 vertices

Graph Theory

- An articulation point in a connected graph is a vertex, which, when it and all the adjacent edges are removed, renders the graph disconnected
- 2-connected graph is one without articulation points
- A block in a connected graph is a maximal 2-connected subgraph

The Main Identity

- If B represents the species of 2-connected graphs and C the species of connected graphs:

Then we have the identity:

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

We have already encountered the notion of composition, but not pointing (represented by the star).

Pointing

For a species of structure F, the species F^* is the set of F-structures, where an element of the underlying set is identifies or "pointed at".

In terms of generating series if $C(z)=\sum_{n=0}^{\infty}\frac{c_n}{n!}z^n$

then:

$$C^*(z)=\sum_{n=0}^{\infty}\frac{nc_n}{n!}z^n=z\frac{d}{dz}C(z)$$

The Relationship

The relationship means that for each n

$$|C[n]|+|B^*(C^*)[n]| = |C^*[n]|+|B(C^*)[n]|$$

Where $|F[n]|$ is the number of F-structures on n points

Method

To prove this relationship, we realise that we can surject each of the sets onto the set of connected graphs.

What to do for C and C* is straightforward

For B*(C*) and B(C*) structures we consider the connected graph, where from each set in the partition (which is a C*-structure) we take the "pointed vertex" and connect it to the pointed vertices in the other sets in the partition according to the B*-structure.

Method

So we can compare the size of both sides we count how many times we get a particular connected graph from these surjections:

$C \quad \mathbf{1}$

$C^* \quad n$

$B^*(C^*)$

$v(c)+\sum_{A}(B_A-1)$

$B(C^*)$ no of blocks in C

Putting Weights on

Using the weight $$w(c) = \lim_{V \to \infty} \frac{1}{V} \int_V \prod_{\{i,j\} \in E(c)} f_{ij} d^D x$$

We find that: $C = \beta P \qquad C^* = \rho$

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

gives

$$\beta P + \sum_{k=1}^{\infty} \frac{(k+1)\beta_k}{k+1} \rho^{k+1} = \rho + \sum_{k=1}^{\infty} \frac{\beta_k}{k+1} \rho^{k+1}$$

$$\beta P = \rho - \sum_{k=1}^{\infty} \frac{k}{k+1} \beta_k \rho^{k+1}$$

Penrose Partitions

We can partition the set of all connected graphs into a collection of trees and with each tree a collection of edges we can decide to either add or not, such that each connected graph is contained in one of the sets.

This leads to tree bounds on Mayer coefficients

Penrose Partitions for 2-connected graphs?

It is still left open to see if there is an analogue of trees in the realm of 2-connected graphs

Conclusions

- Combinatorics has been useful to understand the deeper connection between the Mayer and Virial Expansion
- It provides a quick and easy way to understand the relationship

Conclusions

- Combinatorial tricks such as the tree bound help in determining the radius of convergence of the series expansions
- The understanding of these expansions relies on interplay between areas of Mathematics such as Analysis, Probability and Combinatorics

Literature

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Thank you for your attention.

Are there any questions?