Statistical mechanics and graph generating functions

Uniqueness methods in statistical mechanics: recent developments and algorithmic applications

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Abstract

In 1940 Joseph Edward and Maria Goeppert Mayer published their influential book "Statistical Mechanics" which included beautiful theorems about corrections to the ideal gas law ($PV \propto T$) in terms of generating functions for three classes of graphs. Furthermore they found surprising simple functional relations between these generating functions. I will review this background and some of the later development to set the stage for the new progress to be presented by other speakers.

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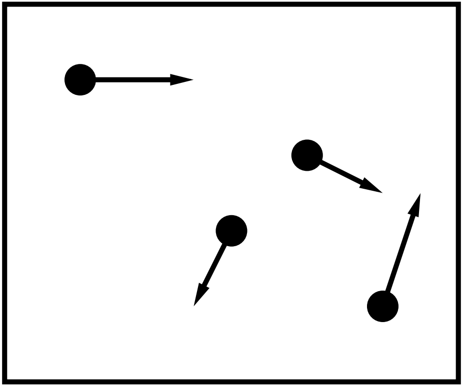
- Pressure $P =$ expected rate of change of momentum per unit area of $\partial\Lambda$

Pressure



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$$\text{Partition function} \qquad Z_{\text{ideal}} := \sum_{n=0}^{\infty} \frac{z^n}{n!} \int_{\Lambda^n} d^n x = e^{z|\Lambda|}$$

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$$Z = \sum_{n=0}^{\infty} \frac{z^n}{n!} \int_{x \in \Lambda^n} \mathbb{1}_{\text{no spheres overlap}} \, d^n x$$

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Goal: for hard spheres compute the pressure via $\log Z$.

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Oliver Penrose reduced the sum over $\mathcal{C}$ to a sum over the set $\mathcal{T}$ of tree graphs = minimally connected graphs.

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Complete graph on $n = 5$ vertices

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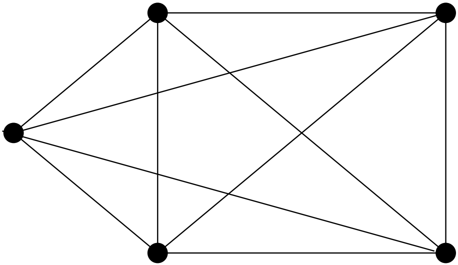

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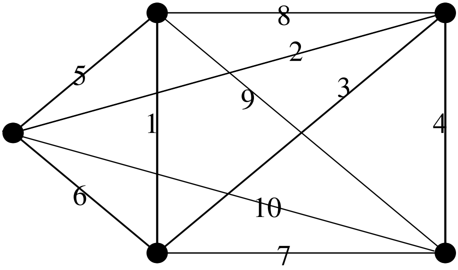

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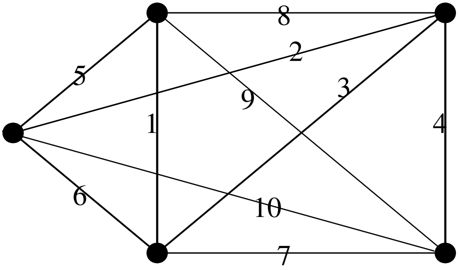

Ordered edges for $n = 5$

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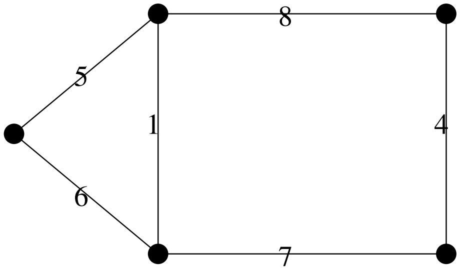

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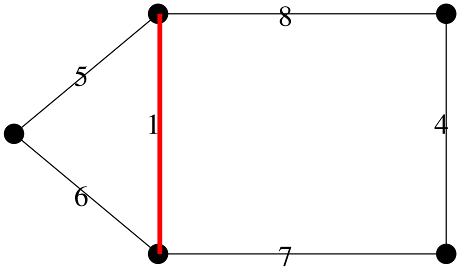

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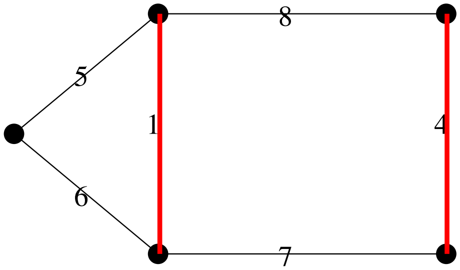

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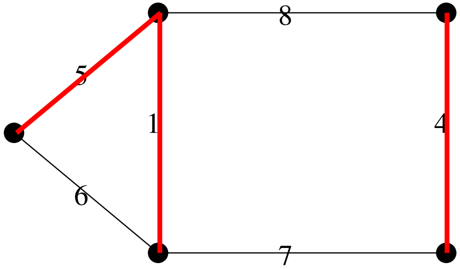

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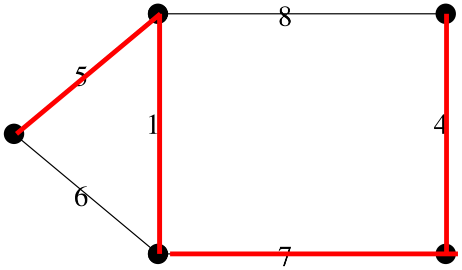

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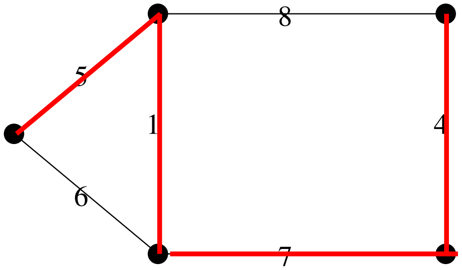

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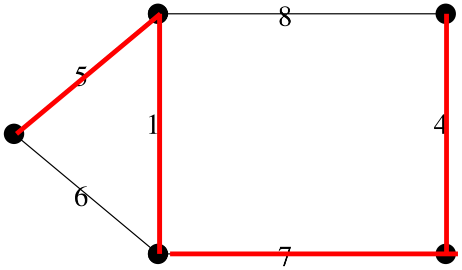

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All graphs G such that $k(G) = T$ satisfy $T \subset G \subset M$.

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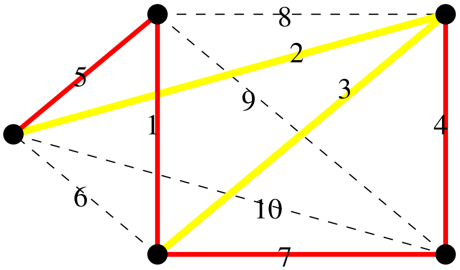

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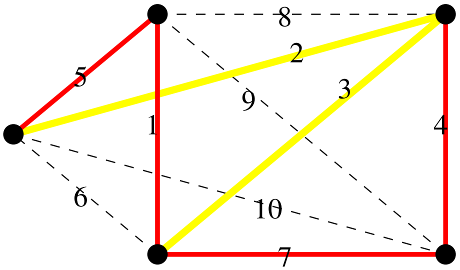

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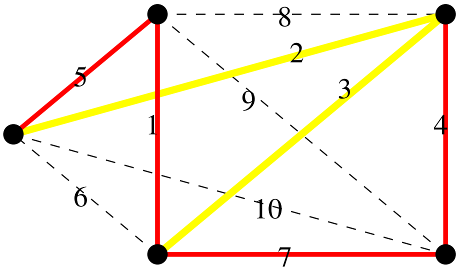

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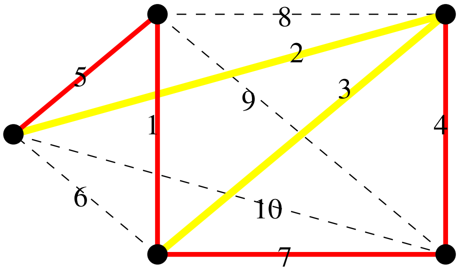

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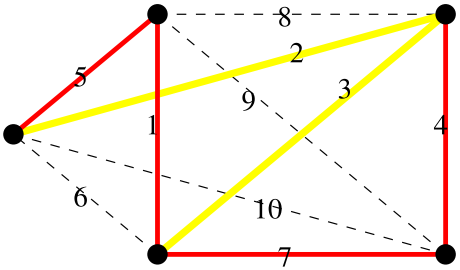

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M is all dotted and red edges.

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Corollary

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$$P = \frac{T}{V}\log Z = \frac{T}{V}\sum_{G\in\mathcal{C}} \frac{z^n}{n!}\int_{\Lambda^n} (-f)^G \; d^n x$$

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is absolutely convergent for $|z| \times 2^d \times$ *volume of sphere* $< \dfrac{1}{e}$ *uniformly in* V*. It converges in disk limited by singularity on the negative* z *axis.*

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Blocks

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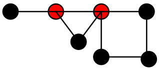
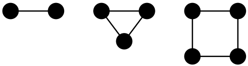


is built from the blocks



linked at the red cutpoints. By definition blocks have no cutpoints.

Legendre Transform

Theorem (Equivalent to Mayer's second theorem)

As formal power series the Legendre transform

$$F(\rho) := \sup_{\mu}(\mu\rho - \frac{1}{V}\log Z(e^{\mu}))$$

of the generating function of connected graphs (AKA Mayer expansion) is given by

$$F(\rho) = F_{ideal}(\rho) - \mathcal{B}(\rho)$$

where

$$\mathcal{B}(\rho) := \frac{1}{V}\sum_{G\in\mathcal{B}}\frac{\rho^n}{n!}\int_{\Lambda^n}(-f)^G \; d^n x$$

is the generating function of blocks (connected graphs without cutpoints).

Equation of state and virial expansion

$$\frac{1}{T}P(e^{\mu}) = \sup_{\rho}\left(\mu\rho - F(\rho)\right)$$
$$= F'(\rho)\rho - F(\rho)$$

By theorem $F(\rho) = F_{\mathrm{ideal}}(\rho) - \mathcal{B}(\rho) = \rho\log\rho - \rho - \mathcal{B}(\rho)$

$$\frac{1}{T}P(e^{\mu}) = -\rho\mathcal{B}'(\rho) + \rho + \mathcal{B}(\rho)$$

Insert $\mathcal{B}(\rho) = \sum_{n\geq 2}\frac{\rho^n}{n!}\underbrace{\int_{\Lambda^n}(-f)^G\ d^n x}_{b_n}$

$$\frac{1}{T}P(e^{\mu}) = \rho + \sum_{n}\frac{1}{n!}(-n+1)b_n\rho^n$$

Problems

- Theory of generating functions for n-irreducible diagrams and Legendre transform wrt n-body potentials?
- Direct proof of convergence of $\mathcal{B}(\rho)$
- Edge irreducible versus cutpoints

Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two points. The third time you go through it, you know you don't understand it, but by that time you are so used to the subject, it doesn't bother you anymore.
Arnold Sommerfeld