Connections between graph theory and the virial expansion

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This is an abbreviated version of the full talk: some material was presented on whiteboard which is only briefly described here.

Big picture version. There are two really nice problems that are ripe for study:

- A new graph polynomial which is a generalisation of the Tutte polynomial that arises naturally from the definition of the virial expansion. (For wont of time to work on this problem, I don't have a proper definition of the polynomial yet.)
- Open questions regarding the kind of geometric graphs which can arise from configurations of points.

Please contact me if the glossed over details are sufficiently interesting to you that you would like a deeper explanation!

- The hard sphere model.
- Cluster and virial coefficients.
- Why is the virial expansion boring?
- $\cdots$ and interesting?
- Connection with the chromatic polynomial.
- A generalization of the chromatic polynomial?
- Progress in evaluating B_5 for hard discs.
- Future prospects.

Hard spheres

- "Billiard ball" model of a gas - the simplest continuum system imaginable.
- Has been studied for over 100 years, important model in statistical mechanics.
- For particles of diameter σ, two body potential is

$$U(\mathbf{r}) = \begin{cases} +\infty & |\mathbf{r}| < \sigma \\ 0 & |\mathbf{r}| > \sigma \end{cases}$$

  Repulsion infinite whenever particles overlap.
- Interaction purely entropic - temperature plays a trivial role.
- Hard problem; little prospect for exact solution.

Phase transition

- Surprising result: system has a fluid-solid phase transition, despite absence of attractive forces.
- Discovered for $d = 3$ in 1957 by Alder and Wainright via molecular dynamics, and Wood and Jacobson through Monte Carlo.
- Discovered for $d = 2$ via molecular dynamics in 1962 by Alder and Wainright.
- First order for $d \geq 3$.
- Controversial for $d = 2$, most likely KTHNY scenario: second order transition from fluid phase to hexatic phase with short range positional and quasi long range orientational order, then another second order transition to the solid phase which has quasi long range positional and orientational order.

Cluster coefficients

- Cluster expansion: pressure and density in terms of the activity.

$$\frac{P}{k_B T} = \sum_{k=1}^{\infty} b_k z^k$$

$$\rho = \sum_{k=1}^{\infty} k b_k z^k$$

- Mayer formulation: cluster coefficients b_k are given as the sum of integrals which may be represented by connected graphs of k points.

Virial coefficients

- Virial expansion: series expansion for pressure in terms of density valid for low density. For hard spheres, coefficients are independent of temperature:

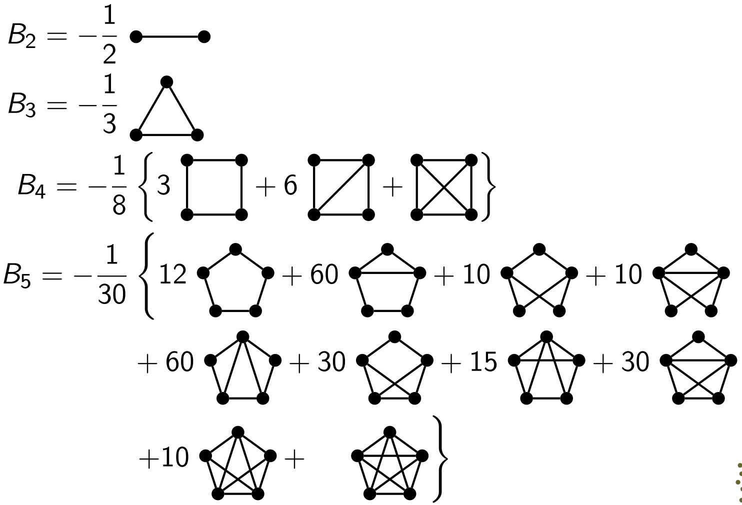
$$\frac{P}{k_B T} = \rho + \sum_{k=2}^{\infty} B_k \rho^k$$

- Known to converge for sufficiently small density.
- Mayer formulation: virial coefficients B_k are given as the sum of integrals which may be represented by (vertex) biconnected graphs of k points.
- Biconnected $\equiv$ there are no vertices whose removal would result in a disconnected graph.

- Explicit expression:

$$B_k = \frac{1-k}{k!} \sum_{G \epsilon \mathscr{B}_k^L} S(G)$$
$$= \frac{1-k}{k!} \sum_{G \epsilon \mathscr{B}_k^U} C(G) S(G)$$

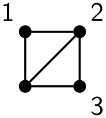
where $S(G)$ is the value of the integral represented by G, $\mathscr{B}_k^L$ is set of all labeled, biconnected graphs, $\mathscr{B}_k^U$ is set of all unlabeled biconnected graphs. $C(G)$ is total number of distinguishable labelings of a graph.


$B_2 = -\frac{1}{2}$
$B_3 = -\frac{1}{3}$
$B_4 = -\frac{1}{8}\{3 + 6 + \}$
$B_5 = -\frac{1}{30}\{12 + 60 + 10 + 10$
$+ 60 + 30 + 15 + 30$
$+10 + \}$

Each edge in a graph represents function

$$
\begin{aligned}
f(\mathbf{r}) &= \exp\left(-U(\mathbf{r})/k_B T\right) - 1 \\
&= \begin{cases} -1 & |\mathbf{r}| < \sigma \\ 0 & |\mathbf{r}| > \sigma \end{cases}
\end{aligned}
$$

Evaluate integral by fixing one vertex at the origin, and integrating other vertices over $\mathbb{R}^d$, e.g.



$$= \int d\mathbf{r_1} d\mathbf{r_2} d\mathbf{r_3} f(\mathbf{r_1}) f(\mathbf{r_2}) f(\mathbf{r_3}) f(\mathbf{r_1} - \mathbf{r_2}) f(\mathbf{r_3} - \mathbf{r_2})$$

The virial expansion is boring because $\cdots$

- In statistical mechanics, interested in collective behaviour (phase transitions).
- Virial expansion has not (so far) shed any light on this.
- C.f. exact solutions, numerical simulation (MC, MD), renormalization group, field theory.

and interesting because $\cdots$

- Useful for modeling fluids.
- Can get exact results, even for continuum models.
- Nice connections with graph theory and geometry.
- For some models (hard spheres) it is the only rigorous analytic approach.
- May be able to extract information about phase transition via analytic continuation?

Mayer representation

- Advantages:
  - Many diagrams can be evaluated exactly (those with few f-bonds).
  - Independence of vertices can be exploited to reduce dimensionality of some integrals to allow fast numerical evaluation.
- Disadvantages:
  - Massive cancellation between positive and negative terms.
  - Cumbersome to evaluate integrals because large number of geometric sub-cases to consider.
  - Some diagrams, such as "complete star", are hard to evaluate, numerically or analytically.

Ree-Hoover re-summation

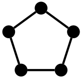
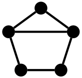
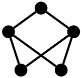
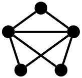
- In 1964, Ree and Hoover re-summed expansion by substituting $1 = \tilde{f} - f$ for pairs of vertices not connected by f bonds, with

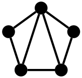
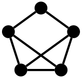
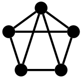
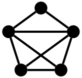
$$\tilde{f}(\mathbf{r}) = 1 + f(\mathbf{r}) = \exp\left(-U(\mathbf{r})/k_B T\right)$$

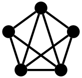
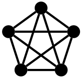
$$= \begin{cases} 0 & |\mathbf{r}| < \sigma \\ +1 & |\mathbf{r}| > \sigma \end{cases} \qquad \text{for hard spheres}$$

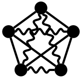
- f bonds force vertices to be close together; $\tilde{f}$ bonds force vertices apart.
- Competing conditions mean that for some graphs there are no point configurations $\Rightarrow$ corresponding integral is zero for geometric reasons.
- Any configuration of points contributes to at most one Ree-Hoover diagram, in contrast to Mayer diagrams.

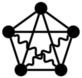
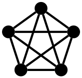
Mayer and Ree-Hoover expressions for B_5; note some RH diagrams have coefficient 0.

$B_5 = -\frac{1}{30}\Big\{$ 12  + 60  + 10  + 10 

+ 60  + 30  + 15  + 30 

+10  +  $\Big\}$

$B_5 = -\frac{1}{30}\Big\{$ 12  + 10  − 60 

+45  − 6  $\Big\}$

Exact results for virial coefficients

- Hard problem - not much progress in 100 years.
- B_2 and B_3 elementary to compute.
- B_4 in $d = 3$ by Boltzmann and van Laar at end of 19^{th} century.
- B_4 in $d = 2$ independently by Rowlinson and Hemmer in 1964.
- "Recently" B_4 in $d = 4, 6, 8, 10, 12$ by Clisby and McCoy, $d = 5, 7, 9, 11$ by Lyberg.
- B_4 for $d > 3$ more tedious, but not intrinsically harder.
- For B_5, some diagrams known exactly, but integrals such as complete star diagram are difficult.

- The second virial coefficient is

$$B_2 = \frac{\sigma^d \pi^{d/2}}{2\,\Gamma(1+d/2)}$$

- B_3 for abitrary d:

$$B_3/B_2^2 = \frac{4\,\Gamma(1+\frac{d}{2})}{\pi^{1/2}\Gamma(\frac{1}{2}+\frac{d}{2})} \int_0^{\pi/3} d\phi\,(\sin\phi)^d$$

d	B_2	B_3/B_2^2
1	σ	1
2	$\pi\sigma^2/2$	$\frac{4}{3} - \frac{\sqrt{3}}{\pi}$
3	$2\pi\sigma^3/3$	$5/8$
4	$\pi^2\sigma^4/4$	$\frac{4}{3} - \frac{\sqrt{3}}{\pi}\frac{3}{2}$
5	$4\pi^2\sigma^5/15$	$53/2^7$
6	$\pi^3\sigma^6/12$	$\frac{4}{3} - \frac{\sqrt{3}}{\pi}\frac{9}{5}$
7	$8\pi^3\sigma^7/105$	$289/2^{10}$
8	$\pi^4\sigma^8/48$	$\frac{4}{3} - \frac{\sqrt{3}}{\pi}\frac{279}{140}$
9	$16\pi^4\sigma^9/945$	$6413/2^{15}$
10	$\pi^5\sigma^{10}/240$	$\frac{4}{3} - \frac{\sqrt{3}}{\pi}\frac{297}{140}$
11	$32\pi^5\sigma^{11}/10395$	$35995/2^{18}$
12	$\pi^6\sigma^{12}/1440$	$\frac{4}{3} - \frac{\sqrt{3}}{\pi}\frac{243}{110}$

d	B_4/B_2^3
2	$2-\frac{9}{2}\frac{\sqrt{3}}{\pi}+10\frac{1}{\pi^2}$
3	$\frac{2707}{4480}+\frac{219}{2240}\frac{\sqrt{2}}{\pi}-\frac{4131}{4480}\frac{\arccos(1/3)}{\pi}$
4	$2-\frac{27}{4}\frac{\sqrt{3}}{\pi}+\frac{832}{45}\frac{1}{\pi^2}$
5	$\frac{25315393}{32800768}+\frac{3888425}{16400384}\frac{\sqrt{2}}{\pi}-\frac{67183425}{32800768}\frac{\arccos(1/3)}{\pi}$
6	$2-\frac{81}{10}\frac{\sqrt{3}}{\pi}+\frac{38848}{1575}\frac{1}{\pi^2}$
7	$\frac{299189248759}{290596061184}+\frac{159966456685}{435894091776}\frac{\sqrt{2}}{\pi}-\frac{292926667005}{96865353728}\frac{\arccos(1/3)}{\pi}$
8	$2-\frac{2511}{280}\frac{\sqrt{3}}{\pi}+\frac{17605024}{606375}\frac{1}{\pi^2}$
9	$\frac{2886207717678787}{2281372811001856}+\frac{2698457589952103}{5703432027504640}\frac{\sqrt{2}}{\pi}-\frac{8656066770083523}{2281372811001856}\frac{\arccos(1/3)}{\pi}$
10	$2-\frac{2673}{280}\frac{\sqrt{3}}{\pi}+\frac{49048616}{1528065}\frac{1}{\pi^2}$
11	$\frac{17357449486516274011}{11932824186709344256}+\frac{16554115383300832799}{29832060466773360640}\frac{\sqrt{2}}{\pi}-\frac{52251492946866520923}{11932824186709344256}\frac{\arccos(1/3)}{\pi}$
12	$2-\frac{2187}{220}\frac{\sqrt{3}}{\pi}+\frac{11565604768}{337702365}\frac{1}{\pi^2}$

- Virial coefficients for hard spheres have been calculated via Monte Carlo up to B_{10}.
- Hard to push this further due to difficulty in calculating combinatorial factors of diagrams, and cancellation between diagrams makes problem increasingly numerically challenging even for Ree-Hoover representation.
- (Still, more can be done).

Some important questions regarding virial expansion for hard spheres.

- Do virial coefficients contain information about phase transition? Or is there a crossover to high density phase via Maxwell construction in which case low density phase contains no information about high density phase?
- What is the asymptotic behaviour of the virial series (where are the leading singularities in the complex density plane)?
- Can virial coefficients be expressed, to all orders, in terms of well-known mathematical functions?
  - If yes, for fixed d is the set of functions required to express B_k bounded?

Connections with the chromatic polynomial

- Note: I haven't written this up carefully, and there may be well be an overall sign error for definitions below.
- Ree-Hoover transformation results in an additional factor for each graph, the 'Star Content'. By definition, for a graph G we obtain the star content by the weighted sum of all biconnected spanning subgraphs (these subgraphs include all vertices and a subset of edges).

$$\mathrm{SC}(G) = \sum_{V=V_G, E \subseteq E_G, (V,E) \text{ biconnected}} (-1)^{|E|}$$

- If we transform the cluster expansion in the same way (the cluster expansion expresses the pressure of a gas as a sum of connected graphs), we end up with a different quantity (unpublished, but here I'll call it CC for connected content).

$$\mathrm{CC}(G) = \sum_{V=V_G, E \subseteq E_G, (V,E) \text{ connected}} (-1)^{|E|}$$

- But this is equivalent to a standard expression for the Tutte polynomial!

$$
\begin{aligned}
\mathrm{CC}(G) &= \sum_{V=V_G,E\subseteq E_G,(V,E)\text{ connected}} (-1)^{|E|} \\
&\equiv T_G(1,0) \qquad \text{(Tutte polynomial)} \\
&\equiv P(G,0) \qquad \text{(Chromatic polynomial)} \\
&= \text{Number of acyclic orientations with a single fixed source}
\end{aligned}
$$

- The star content has some interesting properties: the star content is zero if there is a clique separator (in comparison the Tutte polynomial factors).
- May be regarded as a generalisation of Tutte polynomial which preserves vertex biconnectivity instead of connectivity (for the Tutte polynomial, connectivity is preserved by the delete-contract operation).

There are many interesting open questions regarding geometric 'Ree-Hoover' graphs.

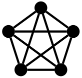
- Although number of graphs grows super-exponentially, the number of non-zero integrals in fixed dimension d grows exponentially.
- For an integral to be zero this means that there is no configuration of points which satisfies the conditions imposed for particles to be at distances less than or equal to 1 for f-bonds or greater than or equal to 1 for $\tilde{f}$-bonds.
- For $d = 2$ one of the 5 point graphs is zero.
- For $d = 3$ the first zero graph has 6 points.
- Any graph which includes a vertex induced subgraph which is geometrically forbidden must also be zero.
- Is there a nice way to characterize the class of non-zero graphs? Does the set of forbidden subgraphs close?
- Simpler problem which has similar structure is the model of parallel hard hypercubes. All virial coefficients / cluster coefficients end up being rational in this case.

Exact result for B_5? Accurate integration for low-dimensional integrals via tanh-sinh quadrature.

Final B_5 should have 50+ decimal places, c.f.

$$\frac{B_5}{B_2^4} = 0.33355604(4) \qquad \text{(Kratky, 1982)}$$

Monte Carlo might be able to get 1 or two additional decimal places on current computer hardware.

$\frac{1}{5}$  $/\, B_2^4 =$

$$\begin{aligned}&0.3618130485552536592783583517585812340367344424\\&\quad 7741453653871964270240015655613927701332741411\\&\quad 7284337887831580823679687361469016399373651229\\&\quad 8015882457642610598205969040359358145737614003\\&\quad 6259974180408551789905303600235516914478795836\\&\quad 9988609165365540090361308285954314217840776110\\&\quad 2442417832871015973699634660896689756807890895\\&\quad 9178099815395519920803192088122432109383943700\\&\quad 5539722655892427092859530654861064179470593281\\&\quad 2703322348680124921883242900163164036786440849\\&\quad 94292579356688316039904200322\cdots\end{aligned}$$

- PLSQ: integer relation detection algorithm - put in high precision floating point numbers, attempt to detect integer relations between them.
- Given floating point numbers $f_1, f_2, \cdots, f_N$, try to solve

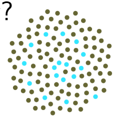
$$i_1 f_1 + i_2 f_2 + \cdots + i_N f_N = 0$$

  to within numerical precision for the integers $i_1, i_2, \cdots, i_N$, where the integers are constrained in size.
- Higher precision, more information $\Rightarrow$ fit more constants with larger integer factors.
- Need insight into which constants to choose. No luck / inspiration yet!

- Gaussian model: Mayer f functions become (unphysical) Gaussian functions, i.e. $f(r) = \exp(-r^2/\sigma^2)$.
- For this model, value of integrals just given by the number of spanning trees of the corresponding graph, $= \mathrm{const}(-1)^k \lambda(G)^{-d/2}$.
- For hard parallel hypercubes, the integrals are integers, and effect of dimensionality is trivial. May be similar to hard spheres, but more tractable.
- For fixed d, large k, almost all graphs must be zero! Can only be exponentially many non-zero graphs, but number of labeled graphs $\sim 2^{k(k-1)/2}$.
- Can we characterise non-zero graphs (e.g. forbidden subgraphs)? Can we re-sum series so that it is more computationally tractable?

Conclusion

- “Solving” the hard sphere model seems a remote prospect.
- Nonetheless, opportunities for progress:
  - ‘Exact’ B_5 for hard discs, then B_6 for hard discs, B_5 for hard spheres?
  - Possible to extend series for B_k using Monte Carlo, gaining insight into asymptotic behaviour of series.
  - Any useful insights into chromatic polynomial for geometric graphs? (algorithms, identities, computational complexity)
  - Is the generalisation to biconnectivity useful more broadly?
  - Can we characterise geometric graphs in, say, $d = 2$? (either Ree-Hoover, or cluster)
  - How does the number of these graphs grow asymptotically?



Acknowledgements

- Thanks to Barry McCoy for useful discussions.
- Thanks to Brendan McKay for insight into connection between cluster series and chromatic polynomial.
- Thanks to MASCOS and the ARC for funding.