Virial Coefficients for D-Dimensional Hard Spheres

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Outline

- Hard spheres
- Virial expansion
- Mayer and Ree-Hoover formalism
- Analytical calculation of B_4 in even dimensions
- High dimensional virial coefficients
- High order diagrams
- Monte-Carlo calculation of B_9 and B_{10}
- Geometrically zero diagrams
- Asymptotic behaviour of the virial series

The Hard Sphere System

- The hard sphere system is an idealized classical, continuum model of spherical particles interacting via excluded volume only
- Two body potential for hard spheres with diameter σ is

$$U(\mathbf{r}) = \begin{cases} +\infty & |\mathbf{r}| < \sigma \\ 0 & |\mathbf{r}| > \sigma \end{cases} \tag{1}$$

- Particles may have any dimensionality, but the hard sphere system has been most commonly studied for the cases of hard rods ($D = 1$), hard discs ($D = 2$), and hard spheres ($D = 3$)

Phase Transition

- Hard spheres have a fluid-solid phase transition, as first shown by Alder and Wainright [1] in 1957
- First order transition for $D = 3, 4, 5$
- Either first or second order for discs
- Potential has no attractive component, and hence no first order condensation transition. Different to usual freezing?
- Phase transition entirely driven by entropy - all allowed configurations have zero potential energy
- Appropriate to describe the behaviour of real systems for high P, T, e.g. noble gases
- Hard spheres are “soft matter”, like colloidal suspensions, as the solid phase does not support shear forces

Virial Expansion

- Virial series for the pressure of hard spheres describes the low density, fluid phase

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

- For $D = 2, 3$ all known coefficients are positive, and radius of convergence appears to be greater than the density of the phase transition
- Many proposed equations of state, with leading singularity invariably on the real positive density axis, usually at "random close packing", close packing, or space filling density. Some have the leading singularity at the freezing density
- **Either** the virial expansion breaks down as a description for hard spheres within its radius of convergence **or** the low order terms do not represent the true asymptotic behaviour of the series
- Can the virial expansion provide information about the phase transition?
- What is the asymptotic behaviour of the virial series?

- Gaunt and Joyce [2] caution that low order behaviour can be very different from the asymptotic behaviour, e.g. for hard hexagons

Mayer formalism

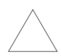
- Mayer and Mayer [3] derived a diagrammatic expansion for B_k in terms of k-point biconnected graphs
- Derivation of cluster expansion in the grand canonical ensemble:

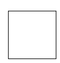
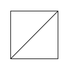
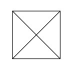
$$\frac{P}{k_B T} = \sum_{k=1}^{\infty} b_k z^k \tag{3}$$

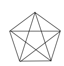
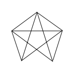
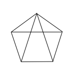
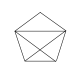
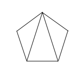
$$\rho = z \frac{d}{dz} \left(\frac{P}{k_B T} \right) = \sum_{k=1}^{\infty} k b_k z^k \tag{4}$$

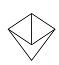
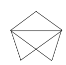
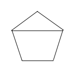
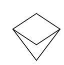
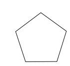
- Low order virial coefficients are:

$B_2 = -1\Big\{\frac{1}{2}$ $\Big\}$

$B_3 = -2\Big\{\frac{1}{6}$  $\Big\}$

$B_4 = -3\Big\{\frac{1}{8}$  $+\frac{1}{4}$  $+\frac{1}{24}$  $\Big\}$

$B_5 = -4\Big\{\frac{1}{120}$  $+\frac{1}{12}$  $+\frac{1}{8}$  $+\frac{1}{4}$  $+\frac{1}{2}$ 

$+\frac{1}{4}$  $+\frac{1}{12}$  $+\frac{1}{2}$  $+\frac{1}{12}$  $+\frac{1}{10}$  $\Big\}$ (5)

- A given point set configuration may contribute to many different diagrams
- Cancellation between positive and negative diagrams means that the final virial coefficient is small compared to each individual diagram
- Massive cancellation $\Rightarrow$ poor numerical results

Ree-Hoover reformulation

- Ree and Hoover [4] reformulated the virial series by substituting $1 = \tilde{f} - f$ in each Mayer graph and expanding

- Star content [4] given as the number of biconnected subgraphs with even number of edges subtract the number of biconnected subgraphs with odd edges

Analytical calculation of B_4 in even dimensions

- B_4 for hard spheres ($D = 3$) calculated by van der Waals, van Laar, and Boltzmann in 19th Century. Confirmed by Nijboer and van Hove in 1953
- B_4 for discs calculated independently in 1964 by Rowlinson, and by Hemmer
- Extended calculation to even dimensions $D = 4, 6, 8, 10, 12$ using Maple
- Ivar Lyberg has recently calculated B_4 for odd dimensions using a different method
- Will be very difficult to extend analytic calculations to B_5 and higher

- Exact results for B_2, B_3, and B_4. Results for B_4, $D = 4, 6, 8, 10, 12$ are due to Clisby and McCoy [5]

D	B_2	B_3/B_2^2	B_4/B_2^2
1	σ	1	1
2	$\frac{\pi\sigma^2}{2}$	$\frac{4}{3} - \frac{\sqrt{3}}{\pi}$	$2 - \frac{9\sqrt{3}}{2\pi} + \frac{10}{\pi^2}$
3	$\frac{2\pi\sigma^3}{3}$	$\frac{5}{8}$	$\frac{219\sqrt{2}}{2240\pi} - \frac{89}{280} + \frac{4131}{2240\pi}\arctan\sqrt{2}$
4	$\frac{\pi^2\sigma^4}{4}$	$\frac{4}{3} - \frac{\sqrt{3}}{\pi}\frac{3}{2}$	$2 - \frac{27\sqrt{3}}{4\pi} + \frac{832}{45\pi^2}$
5	$\frac{4\pi^2\sigma^5}{15}$	$53/2^7$	
6	$\frac{\pi^3\sigma^6}{12}$	$\frac{4}{3} - \frac{\sqrt{3}}{\pi}\frac{9}{5}$	$2 - \frac{81\sqrt{3}}{10\pi} + \frac{38848}{1575\pi^2}$
7	$\frac{8\pi^3\sigma^7}{105}$	$289/2^{10}$	
8	$\frac{\pi^4\sigma^8}{48}$	$\frac{4}{3} - \frac{\sqrt{3}}{\pi}\frac{279}{140}$	$2 - \frac{2511\sqrt{3}}{280\pi} + \frac{17605024}{606375\pi^2}$
9	$\frac{16\pi^4\sigma^9}{945}$	$6413/2^{15}$	
10	$\frac{\pi^5\sigma^{10}}{240}$	$\frac{4}{3} - \frac{\sqrt{3}}{\pi}\frac{297}{140}$	$2 - \frac{2673\sqrt{3}}{280\pi} + \frac{49048616}{1528065\pi^2}$
11	$\frac{32\pi^5\sigma^{11}}{10395}$	$35995/2^{18}$	
12	$\frac{\pi^6\sigma^{12}}{1440}$	$\frac{4}{3} - \frac{\sqrt{3}}{\pi}\frac{243}{110}$	$2 - \frac{2187\sqrt{3}}{220\pi} + \frac{11565604768}{337702365\pi^2}$

High dimensional virial coefficients

- Transformed integration coordinates in order to calculate B_k with $k = 4, 5, 6$ for $k - 1 \leq D \leq 50$
- Showed that B_6 is negative for $D \geq 6$
- Ree-Hoover ring diagram dominates in the limit of large dimension: even virial coefficients are negative, odd coefficients positive

High order diagrams

- For $D = 2$, the largest diagram up to high order seems to be complete star diagram
- But, ring will become larger than complete star for sufficiently high order, even for $D = 2$ (at about $k = 22$ for $D = 2$)
- Low order coefficients, with anomalously large contribution from positive complete star diagrams, are well away from asymptotic behaviour
- These results from Clisby and McCoy [6]

Virial coefficients B_9 and B_{10}

- Key problem: calculate the star content of graphs either before the Monte-Carlo integration procedure, or quickly as graphs are generated
- Up to $2^{k(k-1)/2}$ labeled subgraphs - hard problem!
- Calculate star content for all biconnected graphs, using fact that the number of subgraphs of G can be obtained from the subgraphs of G with one edge less
- Extensively used the program “nauty” (no automorphisms yes?) due to McKay [7] for canonically labeling graphs. Necessary for Monte-Carlo calculation as well as star content
- Problem: number of graphs grows extremely rapidly, and hence this method will become very difficult for $k > 11$

- Used standard hit or miss Monte-Carlo integration procedure
- Generate graph randomly, if it can be identified as a biconnected graph with non-zero star content then increment the number of hits for that graph. Repeat until enough configurations have been generated (up to 1.5×10^{12} for B_{10} with $D = 3$)
- Require a set of spanning trees that can generate all of the biconnected graphs with non-zero star content

Results

- Systematic Monte-Carlo calculation for B_k, $k = 5, \ldots, 10$, in dimensions $D = 2, \ldots, 8$
- B_9 and B_{10} new, likewise B_7 for $D \geq 6$ and B_8 for $D \geq 5$
- Find negative coefficients for $D \geq 5$
- We analyse virial coefficient behaviour using ratio analysis, plot $\frac{B_k}{B_{k-1}\rho_{cp}}$ versus $\frac{1}{k}$.
- Fit series using differential approximants

Geometrically zero diagrams

- In general the number of biconnected graphs grows asymptotically as

$$N(k) \sim \frac{2^{k(k-1)/2}}{k!} \tag{6}$$

- For $D = 1$ only one diagram contributes
- Many diagrams with non-zero star content do not contribute for $D = 2$
- Expect that for $k >> D$ most diagrams will not contribute (due to forbidden subgraphs)
- Question: how does the number of contributing diagrams grow asymptotically for fixed D?

Asymptotic behaviour of the virial series

- $D \geq 5$: the radius of convergence limited by singularity below freezing density. Singularity is not on the positive real axis
- $D = 4$: very likely the same scenario
- $D = 3$: see non-convex behaviour. Suggestive that singularity is not on the real axis. Naively extrapolating ratio plot gives singularity at $\eta \simeq 0.93$
- $D = 2$: completely smooth. Singularity which determines radius of convergence at $\eta = 1$.

Summary

- Negative coefficients for $D \geq 5$
- There will be negative coefficients for $D = 4$, and likely also for $D = 3$
- More coefficients (B_{11}, B_{12}) could confirm this result for $D = 3$
- Unlikely to be able to find out anything about phase transition without a dramatically different approach

Open Questions

- What is the asymptotic behaviour of the virial series for $D = 2$?
- Can we obtain enough coefficients with sufficient accuracy to determine the leading singularities for $D = 3, 4, 5, \cdots$?
- Can we find a fast algorithm for calculating the star content of a randomly generated graph?
- How many graphs contribute to B_k for fixed D as $k \to \infty$?

- Packing fraction of the phase transition compared to the estimated radius of convergence, the lower bounds on the radius of convergence of Lebowitz and Penrose [8], and the packing fraction of the densest lattice packing

D	η_f	η_s	η_R	η_{LP}	η_{cp}
1	–	–	1	0.07238	1
2	~ 0.71	~ 0.71	~ 1	0.03619	$0.90689\cdots$
3	0.49	0.56	~ 0.93	0.01810	$0.74048\cdots$
4	0.31	0.42	$\cdots$	0.00905	$0.61685\cdots$
5	0.19	0.29	~ 0.116	0.00452	$0.46525\cdots$
6	$\cdots$	$\cdots$	~ 0.055	0.00226	$0.37294\cdots$
7	$\cdots$	$\cdots$	~ 0.035	0.00113	$0.29529\cdots$
8	$\cdots$	$\cdots$	~ 0.025	0.00057	$0.25366\cdots$

References

[1] B. J. Alder and T. E. Wainwright. Phase transition for a hard sphere system. *J. Chem. Phys.*, 27:1208–1209, 1957.

[2] D. S. Gaunt and G. S. Joyce. Virial expansions for hard-core fluids. *J. Phys. A*, 13:L211–L216, 1980.

[3] J. E. Mayer and M. G. Mayer. *Statistical Mechanics*. Wiley, 1940.

[4] F. H. Ree and W. G. Hoover. Reformulation of the Virial Series for Classical Fluids. *J. Chem. Phys.*, 41:1635–1645, 1964.

[5] N. Clisby and B. M. McCoy. Analytical calculation of B_4 for hard spheres in even dimensions. *J. Stat. Phys.*, 114:1343–1361, 2004.

[6] N. Clisby and B. M. McCoy. Negative virial coefficients and the dominance of loose packed diagrams for D–dimensional hard spheres. *J. Stat. Phys.*, 114:1361–1392, 2004.

[7] B. D. McKay. Practical Graph Isomorphism. *Congressus Numerantium*, 30:45–87, 1981.

[8] J. L. Lebowitz and O. Penrose. Convergence of virial expansion. *J. Math. Phys.*, 5:841, 1964.

Table 1: Number of batches of 10^7 configurations used in virial coefficient calculations, as a function of order and dimension

D	B_4/B_2^3	B_5/B_2^4	B_6/B_2^5	B_7/B_2^6	B_8/B_2^7	B_9/B_2^8	B_{10}/B_2^9
2	1000	9625	9000	9000	15384	19553	6149
3	1000	52573	53463	63751	64675	87609	151349
4	1000	8454	9400	10299	21400	31903	38699
5	23199	8436	8618	8597	15607	21042	15398
6	1000	8423	8600	8542	5899	6300	1229
7	23010	8213	8600	8500	5898	6300	1300
8	1000	8209	8500	8493	5763	6265	1300

Table 2: Number of Mayer and Ree-Hoover diagrams

	Order						
	4	5	6	7	8	9	10
Mayer	3	10	56	468	7123	194066	9743542
RH	2	5	23	171	2606	81564	4980756
RH/Mayer	0.667	0.500	0.410	0.365	0.366	0.420	0.511
RH, $D = 1$	1	1	1	1	1	1	1
RH, $D = 2$	2	4	15	73	647	8417	110529
RH, $D = 3$	2	5	22	161	>2334	>60902	
RH, $D = 4$	2	5	23	169	>2556	>76318	