Revisiting Groeneveld's approach to the virial expansion

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Uniqueness methods in statistical mechanics: recent developments and algorithmic applications

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Mayer's first theorem: Logarithm of partition function $\leftrightarrow$ exponential generating function of weighted, labelled, connected graphs.

$$\log \Xi_\Lambda(z) = \sum_{n=1}^{\infty} \frac{z^n}{n!} \int_{\Lambda^n} \sum_{G \in \mathcal{C}_n} w(G; x_1, \ldots, x_n) \mathrm{d}\boldsymbol{x}$$

Convergence of the expansion, uniformly in the volume, with tree-graph inequalities.

Mayer's second theorem brings in 2-connected graphs.

Question: Convergence?

Problem: There is no tree-graph inequality for 2-connected graphs.

Today:

- Groeneveld's proof of convergence (1967) revisited. Different from Lebowitz-Penrose '64—not based on inversion of density-activity relation!
- (Relation with Kirkwood-Salsburg equations). Bogolyubov, Petrina, Khatset '69
- New bounds for inhomogeneous systems.

Outline

1. Setting: inhomogeneous systems
2. Expansions with 2-connected graphs
3. Recursive bounds & recursive structure of graphs
4. Main theorem
5. Recovering Groeneveld's bound for homogeneous systems

Partition function for inhomogeneous systems

$\mathbb{X} = \mathbb{R}^d$ or other measurable space ($\mathbb{Z}^d$, $\mathbb{R}^d \times \mathbb{S}^1 \dots$).

Activity $z(\mathrm{d}x) = z(x)\mathrm{d}x$ with position-dependent $z(x)$.

Pair interaction $v(x,y) = v(y,x)$, Mayer's f-function

$$f(x,y) = \mathrm{e}^{-v(x,y)} - 1.$$

Example: hard spheres of radius r,

$$v(x,y) = \infty \cdot \mathbb{1}_{\{|x-y| \leq 2r\}}, \qquad f(x,y) = -\mathbb{1}_{\{|x-y| \leq 2r\}}.$$

Energy

$$U_n(x_1,\dots,x_n) = \sum_{1 \leq i < j \leq n} v(x_i,x_j), \quad U_0 = U_1 = 0.$$

Partition function

$$\Xi(z) = 1 + \sum_{n=1}^{\infty} \frac{1}{n!} \int_{\mathbb{X}^n} \exp\Big(-U_n(x_1,\dots,x_n)\Big) z(\mathrm{d}x_1) \cdots z(\mathrm{d}x_n).$$

Legendre transform and density

Free energy of a density profile $\rho(\mathrm{d}x) = \rho(x)\mathrm{d}x$:

$$\mathcal{F}(\rho) = \sup_h \Big(\int h(q)\rho(\mathrm{d}q) - \log \Xi(z\mathrm{e}^h) \Big),$$

supremum over functions $\mathbb{X} \ni x \mapsto h(x)$. Supremum attained at μ solving

$$\rho(q) = \frac{\delta}{\delta h(q)} \log \Xi(z\mathrm{e}^h)$$

(variational derivative). At $h = 0$, gives

$$\rho(q) = z(q) \times \frac{1}{\Xi(z)} \left(1 + \sum_{n=1}^{\infty} \frac{1}{n!} \int_{\mathbb{X}^n} \exp\Big(-U_{n+1}(q, x_1, \dots, x_n) \Big) z^n(\mathrm{d}\boldsymbol{x}) \right)$$

Statistical mechanics interpretation: $\rho(\mathrm{d}q) = \rho(q)\mathrm{d}q$ represents average number of points per unit volume in small neighborhood of q = density at q.

($\simeq$ probability to find a point at q.)

Expansion with 2-connected graphs

A graph G is 2-connected if it is connected and if it stays connected after removal of a vertex = if it has no cutpoints (a.k.a. articulation points).

Weight of a graph G with vertices $1, \dots, n$

$$w(G; x_1, \dots, x_n) = \prod_{\{i,j\} \in E(G)} f(x_i, x_j).$$

Notation: $\mathcal{D}_n$ = 2-connected graphs with vertex set $\{1, \dots, n\}$,

$$D_n(x_1, \dots, x_n) = \sum_{G \in \mathcal{D}_n} w(G; x_1, \dots, x_n).$$

Known: Expansion of the partition function in powers of the density is

$$\log \Xi(z) = \int_{\mathbb{X}} \rho(\mathrm{d}x) - \sum_{n=1}^{\infty} \frac{1}{n!} \int_{\mathbb{X}^n} (n-1) D_n(x_1, \dots, x_n) \rho^n(\mathrm{d}\boldsymbol{x}).$$

Convergence?

Generating function for rooted 2-connected graphs:

$$d(q;\rho) = \sum_{n=1}^{\infty} \frac{1}{n!} \int_{\mathbb{X}^n} D_{n+1}(q, x_1, \dots, x_n) \rho(\mathrm{d}x_1) \cdots \rho(\mathrm{d}x_n).$$

Theorem (J., Kuna, Tsagkarogiannis '19)

Suppose $v(x,y) \geq 0$. If there exists a function $a: \mathbb{X} \to \mathbb{R}_+$ such that

$$\int_{\mathbb{X}} |f(x,y)| \mathrm{e}^{2a(y)} \rho(\mathrm{d}y) \leq a(x)$$

for all $x \in \mathbb{X}$, then $d(q;\rho)$ is absolutely convergent, $\leq a(q)$.

Improves result for countable sets $\mathbb{X}$ [J., Tate, Tsagkarogiannis, Ueltschi '14].

Hard spheres with $|B(0,2r)| = 1$, homogeneous density $\rho(\mathrm{d}x) = \rho\, \mathrm{d}x$: radius of convergence at least

$$\sup_{a>0} a \exp(-2a) = \frac{1}{2\mathrm{e}} \approx 0.18.$$

How to prove convergence

Standard procedure Lebowitz-Penrose '64:

1. Start from convergence results for activity expansions (powers of z).
2. Express ρ as a series in z.
3. Invert density-activity relation with help of some inverse function theorem, expand z in powers of ρ.
4. Compose expansions $z(\rho)$ and $\log \Xi(z)$
   $\to$ expansion of $\log \Xi(z(\rho))$ in powers of ρ.
5. Bounds on radius of convergence aided by Lagrange(-Good) inversion
   J., Kuna, Tsagkarogiannis: instead, inversion with trees.

Problem: bounds inherit limitations from activity expansions.
Other approaches?

- Expansion in the canonical ensemble
  E. Pulvirenti, Tsagkarogiannis
- Recursive properties of graphs weights upon removal of a point:
  Groeneveld
- Kirkwood-Salsburg equation in the canonical ensemble
  Bogolyubov, Hacet, Petrinas

Recursive bounds

Variant of classical idea:

e.g. Minlos-Poghosyan '75, Ueltschi '04, Poghosyan-Ueltschi '09

Bound

$$\sum_{n=1}^{N} \frac{1}{n!} \int_{\mathbb{X}^n} \big|D_{n+1}(q, x_1, \dots, x_n)\big| \rho^n(\mathrm{d}\boldsymbol{x})$$

by induction over N. This corresponds to an induction over number of vertices $N+1$ in generating function of 2-connected graphs.

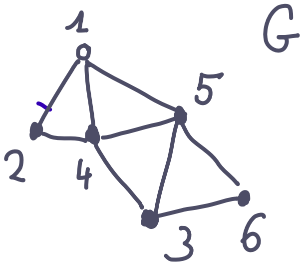
Investigate what happens to a 2-connected graph when one vertex is removed.

Hope that this leads to recurrence relation between D_n and D_k, $k \leq n-1$, that help the inductive derivation of bounds.

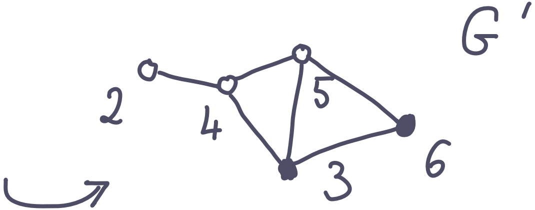
(Actually, things are more complicated—need to introduce additional classes of graphs. Correspond to expansions of correlation functions.)

Recursive properties of 2-connected graphs

A 2-connected graph:



After removal of the vertex 1.



○ white vertices 2, 4, 5 · adjacent to 1 in G

● black vertices 3, 6 : not adj. to 1 in G

G' is not 2-connected, but ...

Recursive properties of 2-connected graphs

Observation:
Starting from a 2-connected graph G with vertices $1, \ldots, n$

1. Color the vertex 1 and all vertices adjacent to 1 white, other vertices black.
2. Remove the vertex 1.
3. Remaining graph G' has vertices $\{2, \ldots, n\}$, some white, some black. It is not necessarily 2-connected, but: it is connected, and in addition
   (i) Every black vertex is connected to a white vertex by a path in G'.
   (ii) Property (i) survives the removal of any vertex (black or white).

Groeneveld removes edges incident to vertex 1 one by one.
We remove vertex 1 and incident edges in one go.

Given W, B disjoint finite sets of white and black vertices, define $\mathcal{D}(W, B) :=$ graphs with vertex set $W \cup B$ that satisfy properties (i) and (ii).

Associated generating functions:
Generalize D_n-weights to white/black graphs

$$\psi\big((x_i)_{i\in W};(x_j)_{j\in B}\big) := \sum_{G\in\mathcal{D}(W,B)} w\big(G;(x_i)_{i\in W\cup B}\big),$$

generating function for s white vertices, variable number of black vertices

$$g_s(x_1,\dots,x_s) := \psi(x_1,\dots,x_s;\varnothing) + \sum_{n=1}^{\infty}\frac{1}{n!}\int_{\mathbb{X}^n}\psi(x_1,\dots,x_s;x_{s+1},\dots,x_{s+n})\rho(\mathrm{d}x_{s+1})\cdots\rho(\mathrm{d}x_{s+n}).$$

We pin white vertices.
We sum / integrate over black vertices.

Known: $g_s(x_1,\dots,x_s)$ related to s-point correlation functions by

$$g_s(x_1,\dots,x_s) = \frac{\rho_s(x_1,\dots,x_s)}{\rho(x_1)\cdots\rho(x_s)}.$$

Stell '64

Main theorem

An integral operator

Given a function $m : \sqcup_{s\in\mathbb{N}}\mathbb{X}^s \to \mathbb{R}_+$, define

1. An auxiliary function $R_\rho m : \mathbb{X} \to \mathbb{R}_+$ by

$$(R_\rho m)(x_1) = \sum_{k=1}^{\infty} \frac{1}{k!} \int_{\mathbb{X}^j} \prod_{i=1}^{k} |f(x_1, y_i)| m(y_1, \dots, y_k) \rho^k(\mathrm{d}\boldsymbol{y}).$$

2. A new function $\mathbf{K}_\rho m : \sqcup_{s\in\mathbb{N}}\mathbb{X}^s \to \mathbb{R}_+ \cup \{\infty\}$ by

$$(\mathbf{K}_\rho m)(x_1) = 1$$

and for $s \geq 2$,

$$(\mathbf{K}_\rho m)(x_1, \dots, x_s) = \prod_{i=2}^{s} \big(1 + f(x_1, x_i)\big) \Bigg(m(x_2, \dots, x_s) + \sum_{k=1}^{\infty} \frac{1}{k!} \int_{\mathbb{X}^k} \prod_{i=1}^{k} |f(x_1, y_i)| m(x_2, \dots, x_s, y_1, \dots, y_j) \rho^j(\mathrm{d}\boldsymbol{y}) \Bigg) \times \left(\sum_{k=0}^{\infty} \Big((R_\rho m)(x_1) \Big)^k \right).$$

$\overline{g}_s$, $\overline{d}$: same definition as g_s, d, but with absolute values around D_n and ψ.

Theorem (J. '20)

Suppose there exists a measurable function $m : \sqcup_{s\in\mathbb{N}}\mathbb{X}^s \to \mathbb{R}^+$ *with* $(R_\rho m)(x_1) < 1$ *for all* $x_1 \in \mathbb{X}$ *and*

$$(\mathbf{K}_\rho m)(x_1,\dots,x_s) \le m(x_1,\dots,x_s) \tag{1}$$

for all $s \in \mathbb{N}$ *and* $(x_1,\dots,x_s) \in \mathbb{X}^s$. *Then*

$$\bar{g}_s(x_1,\dots,x_s;\rho) \le m(x_1,\dots,x_s) < \infty \tag{2}$$

for all $s \in \mathbb{N}$ *and* $(x_1,\dots,x_s) \in \mathbb{X}^s$ *and*

$$\bar{d}(q;\rho) \le -\log\Big(1-(R_\rho m)(q)\Big) < \infty \tag{3}$$

for all $q \in \mathbb{X}$.

Proof uses recursive properties of graphs in $\mathcal{D}(W;B)$ upon removal of a white vertex and a Möbius inversion on the lattice of set partitions. Builds on a related convergence condition for activity expansions J., Kolesnikov '20.

$\mathbb{R}^d$, translationally invariant pair potential $v(x-y)$, $C := \int_{\mathbb{R}^d} |\mathrm{e}^{-v(y)} - 1| \mathrm{d}y$.

Theorem (Groeneveld recovered)

Let v be a stable translationally invariant pair potential in $\mathbb{R}^d$ with stability constant $B > 0$ and $\rho > 0$ (constant density). Set $u := \mathrm{e}^{2B}$. Assume there exists $\kappa \geq 0$ such that

$$(1+u)\mathrm{e}^{C\rho\kappa} - 1 \leq \kappa.$$

Then for all $s \geq 2$ and $x_1, \ldots, x_s \in \mathbb{R}^d$,

$$\bar{g}(x_1, \ldots, x_s; \rho) \leq \kappa^{s-1}$$

and

$$\bar{d}(x_1; \rho) \leq -\log\Big(1 - \frac{1}{\kappa}\big(\mathrm{e}^{C\rho\kappa} - 1\big)\Big) < \infty.$$

For non-negative pair potentials: $v \geq 0$, $B = 0$, $u = 1$, convergence condition equivalent to radius of convergence at least (think $\mu = C\rho\kappa$)

$$C\rho \leq \sup_{\mu > 0} \frac{\mu}{2\exp(\mu) - 1} \simeq 0.23196.$$

Groeneveld's criterion is proven by applying our theorem with the choice

$$m(x_1, \dots, x_s) = \kappa^{s-1}.$$

Other choices lead to other criteria, for example:

$$m(x_1, \dots, x_s) = \kappa^{s-1} \mathrm{e}^{-U_s(x_1,\dots,x_s)}$$

leads to sufficient convergence condition

$$\rho \le \sup_{\mu>0} \frac{\mu}{2\Psi(\mu) - 1}$$

where

$$\Psi(\mu) := 1 + \sum_{k=1}^{\infty} \frac{\mu^k}{k!} \int_{(\mathbb{R}^d)^k} \prod_{i=1}^{k} |f(0, y_i)| \prod_{1 \le i < j \le k} \big(1 + f(y_i, y_j)\big) \mathrm{d}\boldsymbol{y}.$$

Due to Nguyen, Fernández '20, who deduced for hard spheres in $d = 2$: bound $\simeq 0.30$ instead of 0.23196.

Conclusion

Summary

- Proof of a convergence condition for the density expansion that is not based on an inversion of the density-activity relation.
- Instead, uses recursive properties of graphs.
- Recursive properties of graphs yield integral equations for generating functions of graphs with several roots / white vertices.
- Integral equations related to Kirkwood-Salsburg equations for correlation functions.
- Results apply to homogeneous and inhomogeneous systems.

Main contribution:
A new look at Groeneveld's somewhat forgotten proof.

Still missing:
Does the criterion help us understand why density expansions are sometimes better than activity expansions?