Cluster and virial expansions for multi-species models

Sabine Jansen
Ruhr-Universität Bochum

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Overview

1. Motivation: dynamic nucleation models
2. Statistical mechanics for mixtures of hard spheres
3. An inversion theorem via Lagrange-Good
4. Application to cluster and virial expansions
5. Explicit solution for Tonks gas in dimension 1

1 A dynamic nucleation model

System of coupled ODEs for variables $\rho_k(t)$, $k \in \mathbb{N}$.
Becker, Döring '35. Version Burton '77, Penrose, Lebowitz '79:

Given: coefficients $a_k, b_k > 0$, $k \in \mathbb{N}$, ODE

$$\begin{cases} \dot\rho_k &= -\big(a_k\rho_k\rho_1 - b_{k+1}\rho_{k+1}\big) + \big(a_{k-1}\rho_{k-1}\rho_1 - b_k\rho_k\big) \quad (k \geq 2) \\ \dot\rho_1 &= -\big(a_1\rho_1^2 - b_2\rho_2\big) - \sum_{k=1}^{\infty}\big(a_k\rho_k\rho_1 - b_{k+1}\rho_{k+1}\big) \end{cases}$$

- Coagulation $(k) + (1) \to (k+1)$ at rate $a_k\rho_k\rho_1$
- Fragmentation $(k+1) \to (k) + (1)$ at rate $b_{k+1}\rho_{k+1}$.
- Choice of $\dot\rho_1$: Total density $\rho = \sum_k k\rho_k(t)$ time-independent.

Question: long time behavior? Ball, Carr, Penrose '86

$$f\big((\rho_k)_{k\in\mathbb{N}}\big) := \sum_{k=1}^{\infty} \rho_k \Big(\log \frac{\rho_k}{Q_k} - 1\Big)$$

$$\frac{Q_{k+1}}{Q_k} = \frac{a_k}{b_{k+1}}, \quad Q_1 = 1.$$

Lyapunov function (decreases along solutions of ODE).
Wanted: minimizer at given density $\rho = \sum_{k=1}^{\infty} k\rho_k$.

Phase transition in Becker-Döring model

Minimizer Assumption: power series $\sum_k z^k Q_k$ has finite radius of convergence R and $\sum_k kR^k Q_k < \infty$. Then

- $\rho < \sum_k kR^k Q_k$: unique minimizer = equilibrium distribution.
- $\rho > \sum_k kR^k Q_k$: no minimizer with $\sum_k k\rho_k = \rho$. Long time behavior:

$$\sum_{k=1}^{\infty} \lim_{t\to\infty} k\rho_k(t) = \sum_{k=1}^{\infty} kR^k Q_k < \rho = \sum_{k=1}^{\infty} k\rho_k(t).$$

Mass escapes to very large droplets.

Interpretation: $\sum_k kR^k Q_k$ = density of saturated vapor.

Problem: What is the physically correct choice of coefficients a_k, b_k?
"Correct" free energy should be a Lyapunov function.

This talk: free energy $f((\rho_k)_{k\in\mathbb{N}})$ via statistical mechanics. Leads to power series in the ρ_k, $k \in \mathbb{N}$: virial expansion.

From here on, no dynamics anymore.

2 Mixture of hard spheres

Spheres of different sizes (radii $k^{1/3}$, $k \in \mathbb{N}$) in $\Lambda \subset \mathbb{R}^3$.
Multi-indices $(N_k) \in \mathbb{N}_0^{\mathbb{N}}$, finitely many non-zero.
Canonical partition function and free energy:

$$Z_\Lambda\Big((N_k)_{k\in\mathbb{N}}\Big) := \frac{1}{\prod_k N_k!} \int_{\Lambda^{N_1}} \mathrm{d}x_{11}\cdots \mathrm{d}x_{1N_1} \int_{\Lambda^{N_2}} \mathrm{d}x_{21}\cdots$$
$$\times \mathbf{1}\Big(\forall k,\ell,i,j: \;\; B(x_{ki},k^{1/3}) \cap B(x_{\ell j},\ell^{1/3}) = \emptyset\Big)$$

$$f\big((\rho_k)_{k\in\mathbb{N}}\big) := -\lim \frac{1}{|\Lambda|} \log Z_\Lambda\Big((N_k)_{k\in\mathbb{N}}\Big)$$

in the limit $|\Lambda| \to \infty$, $N_k \to \infty$ along $N_k/|\Lambda| \to \rho_k$.

Ideal mixture: neglect overlap of spheres.

$$Z_\Lambda^{\mathrm{ideal}}\Big((N_k)_{k\in\mathbb{N}}\Big) = \prod_k \frac{|\Lambda|^{N_k}}{N_k!} \approx \prod_k \Big(\frac{|\Lambda|}{N_k/e}\Big)^{N_k}$$
$$f^{\mathrm{ideal}}\big((\rho_k)_{k\in\mathbb{N}}\big) = \sum_k \rho_k(\log \rho_k - 1).$$

Recognize Lyapunov function of Ball, Carr, Penrose.

Goal: $f = f^{\mathrm{ideal}} +$ convergent power series.

Pressure and grand-canonical ensemble

Given: parameters $z_k > 0$ *activities*.

Grand-canonical partition function and pressure:

$$\Xi_\Lambda\big((z_k)_{k\in\mathbb{N}}\big) := 1 + \sum_{\boldsymbol{N}\in\mathcal{I}} \Big(\prod_k \frac{z_k^{N_k}}{N_k!}\Big) \int_{\Lambda^{n_1}} \mathrm{d}x_{11}\cdots\mathrm{d}x_{1,n_1} \int_{\Lambda^{n_2}} \mathrm{d}x_{n_1,1}\cdots$$

$$\times\, \mathbf{1}\Big(\forall k,\ell,i,j:\ B(x_{ki},k^{!/3})\cap B(x_{\ell j},\ell^{1/3}) = \emptyset\Big),$$

$$p(\boldsymbol{z}) := \lim_{|\Lambda|\to\infty} \frac{1}{|\Lambda|}\log \Xi_\Lambda(\boldsymbol{z}), \quad \boldsymbol{z} = (z_k)_{k\in\mathbb{N}}.$$

Remark: associated Gibbs measure= "Poisson exclusion process".

Ideal mixture = independent Poisson point processes

$$\Xi_\Lambda^{\mathrm{ideal}} = 1 + \sum_{\boldsymbol{N}}\prod_k \Big(\frac{z_k|\Lambda|^{N_k}}{N_k!}\Big) = \exp(|\Lambda|\sum_k z_k), \quad p^{\mathrm{ideal}} = \sum_k z_k.$$

Equivalence of ensembles: free energy $\leftrightarrow$ pressure via Legendre transformation

$$f\big((\rho_k)_{k\in\mathbb{N}}\big) = \sup_{(z_k)}\Big(\sum_k \rho_k \log z_k - p\big((z_k)_{k\in\mathbb{N}}\big)\Big).$$

Density vs. activity:

$$\rho_k(\boldsymbol{z}) = z_k \frac{\partial p}{\partial z_k}(\boldsymbol{z}).$$

Cluster expansion

Overlap rare enough $\Rightarrow$ small perturbation.

Known: suppose there is an $a > 0$ such that

$$\forall \ell \in \mathbb{N}: \sum_{k=1}^{\infty} |z_k| \, |B(0, \ell^{1/3} + k^{1/3})| \exp(ak) < a\ell.$$

Poghosyan, Ueltschi '09. Sufficient: $\sum_k k|z_k| \exp(ak) < \mathrm{const} a$. Then

$$p(\boldsymbol{z}) = \sum_{\boldsymbol{m}} b(\boldsymbol{m}) \prod_k z_k^{m_k} = \sum_k z_k + \text{higher order terms},$$

absolutely convergent series. Also convergent: series $\rho_k(\boldsymbol{z})$

$$\rho_k(\boldsymbol{z}) := z_k \frac{\partial p}{\partial z_k}(\boldsymbol{z}) = z_k + \text{higher order terms}.$$

Question: Inverse map $\boldsymbol{z} = \boldsymbol{z}(\boldsymbol{\rho})$? If exists, then

$$f(\boldsymbol{\rho}) = \sum_k \rho_k \log z_k(\boldsymbol{\rho}) - p(\boldsymbol{z}(\boldsymbol{\rho})).$$

Finitely many variables: inverse function theorem! $(\mathrm{D}_{\boldsymbol{z}} \boldsymbol{\rho})(\boldsymbol{0}) = \mathrm{id}$ invertible.
Infinitely many: bounds not good enough to prove Fréchet differentiability between natural Banach spaces.

3 An inversion theorem

Given: Power series $\rho_k(\boldsymbol{z}) = z_k(1 + \text{higher order terms})$, $k \in \mathbb{N}$. Other power series $\Phi(\boldsymbol{z})$, e.g. $\Phi(\boldsymbol{z}) = z_k$.
Lemma: inversion $z_k = z_k(\boldsymbol{\rho})$ well defined as formal power series.
Question: convergence?

Theorem (J., Tate, Tsagkarogiannis, Ueltschi '14)

Let D be a polydisk $D = \{\boldsymbol{z} \in \mathbb{C}^{\mathbb{N}} \mid \forall k : \ |z_k| < R_k\}$. Assume:

1. *The series $\rho_k(\boldsymbol{z})$, $\Phi(\boldsymbol{z})$ are abs. conv. and uniformly bounded in D.*
2. *$\rho_k(\boldsymbol{z}) = z_k \exp(A_k(\boldsymbol{z}))$ with $a_k := \sup_{\boldsymbol{z} \in D} |A_k(\boldsymbol{z})| < \infty$.*

Choose $0 < r_k < R_k$ so that $\sum_k \sqrt{r_k/R_k} < \infty$, $\sum_k r_k a_k^2/R_k < \infty$. Then:

$$\exists C > 0 \ \forall \boldsymbol{n} : \ \Big|[\boldsymbol{\rho}^{\boldsymbol{n}}]\Phi\big(\boldsymbol{z}(\boldsymbol{\rho})\big)\Big| \leq C \sup_{\boldsymbol{z} \in D} |\Phi(\boldsymbol{z})| \prod_k \Big(\frac{\exp(a_k)}{r_k}\Big)^{n_k}.$$

Consequence: sufficient for convergence of $\Phi(\boldsymbol{z}(\boldsymbol{\rho}))$ as series of $\boldsymbol{\rho}$:

$$\forall k : \ |\rho_k| < r_k \exp(-a_k), \quad \sum_k |\rho_k| \exp(a_k)/r_k < \infty.$$

Typical situation: $|z_k| \leq R_k \approx \exp(-ak)$, $|A_k(\boldsymbol{z})| \leq ak$, $|\rho_k| < \exp(-2ak)/k^p$.

Proof idea: Lagrange-Good inversion

$$
\begin{aligned}
[\boldsymbol{\rho}^{\boldsymbol{n}}]\Phi(\boldsymbol{z}(\boldsymbol{\rho})) &= \Big(\prod_k \frac{1}{2\pi \mathrm{i}} \oint \frac{\mathrm{d}\rho_k}{\rho_k^{n_k+1}}\Big)\Phi(\boldsymbol{z}(\boldsymbol{\rho})) \\
&= \Big(\prod_k \frac{1}{2\pi \mathrm{i}} \oint \frac{\mathrm{d}z_k}{\rho_k(\boldsymbol{z})^{n_k+1}}\Big)\Phi(\boldsymbol{z}) \det\Big[\Big(\frac{\partial \rho_\ell}{\partial z_j}(\boldsymbol{z})\Big)_{j,\ell}\Big], \quad \rho_\ell = z_\ell \exp(A_\ell(\boldsymbol{z})) \\
&= \Big(\prod_k \frac{1}{2\pi \mathrm{i}} \oint \frac{\mathrm{d}z_k}{z_k^{n_{k+1}}}\Big)\Phi(\boldsymbol{z}) e^{-\sum_\ell n_\ell A_\ell(\boldsymbol{z})} \det\Big[\Big(\delta_{\ell j} + z_\ell \frac{\partial A_\ell}{\partial z_j}(\boldsymbol{z})\Big)_{j,\ell}\Big].
\end{aligned}
$$

$$
\boxed{[\boldsymbol{\rho}^{\boldsymbol{n}}]\Phi(\boldsymbol{z}(\boldsymbol{\rho})) = [\boldsymbol{z}^{\boldsymbol{n}}]\Phi(\boldsymbol{z}) e^{-\sum_\ell n_\ell A_\ell(\boldsymbol{z})} \det\Big[\Big(\delta_{\ell j} + z_\ell \frac{\partial A_\ell}{\partial z_j}(\boldsymbol{z})\Big)_{j,\ell \in \mathrm{supp}\ \boldsymbol{n}}\Big].}
$$

- Analytic proof (convergent series, finitely many variables):
  GOOD '60: *Generalization to several variables of Lagrange's expansion, with applications to stochastic processes.*
- Combinatorial proof (formal series, finitely many variables):
  GESSEL '87: *A combinatorial proof of the multivariable Lagrange inversion formula.*
- Combinatorial proof for infinitely many variables:
  EHRENBORG, MÉNDEZ '94: *A bijective proof of infinite variated Good's inversion.*

4 Application to cluster and virial expansions

... for non-overlapping spheres of radii $k^{1/3}$, $k \in \mathbb{N}$ in $\mathbb{R}^3$.

Theorem (J., Tate, Tsagkarogiannis, Ueltschi '14)

We have

$$f\big((\rho_k)_{k\in\mathbb{N}}\big) = \sum_k \rho_k(\log \rho_k - 1) + \sum_{\boldsymbol{n}:\sum_k n_k \geq 2} d(\boldsymbol{m}) \prod_k \rho_k^{m_k}$$

Sufficient for absolute convergence:

$$\boxed{\forall k \in \mathbb{N}: \quad |\rho_k| < \varepsilon(a) k^{-7} \exp(-2ak)}$$

$a > 0$ *arbitrary,* $\varepsilon(a) > 0$ *sufficiently small.*

Proof: Theory of cluster expansions $\Rightarrow$ conditions of inversion theorem are fulfilled.

Similar results for more general models:

- different shapes
- different interactions – not only hard core.

More difficult: object with internal degrees of freedom, "flexible" shapes.

Discussion

Previously known:

1. Bounds for convergence of single-species virial expansion PENROSE, LEBOWITZ '60S: proof via Lagrange inversion.
2. Formulas for expansion coefficients $d(\boldsymbol{m})$ as sums over doubly connected graphs – formal expansion for several variables (without convergence) MAYER 40'S.
3. Polymers ("lattice animals") on lattices: expansion in monomer density ρ_1 without control of the individual ρ_k's GRUBER, KUNZ '75.

New:
Existence of a non-trivial convergence domain for infinitely many variables.

Observation:
our theorems works only for exponentially decaying densities
$\rho_k \leq \exp(-2ak) \to 0$.

Open:
Convergence without exponential decay?

5 Explicit solution in dimension 1

Non-overlapping rods of lengths ℓ_k, $k \in \mathbb{N}$ on the real line (Tonks gas).

Theorem (J.' 15)

$$p(\boldsymbol{z}) = \sum_{\boldsymbol{n}} \frac{\boldsymbol{z}^{\boldsymbol{n}}}{\boldsymbol{n}!} \Big(- \sum_k \ell_k n_k \Big)^{\sum_k n_k - 1}$$

Absolutely convergent if and only if

$$\exists a > 0 : \ \sum_k |z_k| \exp(a \ell_k) \leq a.$$

Remark: generating function of colored labelled weighted trees. Generalizes well-known single-species result.

Theorem (J. '15)

$$f(\boldsymbol{\rho}) = \sum_k \rho_k \Big(\log \frac{\rho_k}{1 - \sum_j \ell_j \rho_j} - 1 \Big)$$

$$z_k(\boldsymbol{\rho}) = \frac{\rho_k}{1 - \sum_j \ell_j \rho_j} \exp\Big(\frac{\ell_k \rho_k}{1 - \sum_j \ell_j \rho_j} \Big).$$

Virial expansion converges $\Leftrightarrow \sum_k \ell_k \rho_k < 1$.

Virial expansion converges in domain bigger than activity expansion.

Summary

Existence of a non-trivial domain of convergence for many-species virial expansion.

Proof ingredients:
Lagrange-Good inversion – contour integrals – cluster expansions.
Condition

$$\exp(-ak) \leq |\rho_k(\boldsymbol{z})/z_k| \leq \exp(ak)$$

instead of invertibility of $\mathrm{D}_{\boldsymbol{z}}\boldsymbol{\rho}$ in neighborhood of $\mathbf{0}$.

References:

- S. Jansen, S. J. Tate, D. Tsagkarogiannis, D. Ueltschi:
  Multispecies virial expansions.
  Comm. Math. Phys. 330, 801–817 (2014).
- S. Jansen:
  Cluster and virial expansions for the multi-species Tonks gas.
  J. Stat. Phys. 161, 1299–1323 (2015).