A novel inversion theorem with applications to density functionals

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New directions in classical density functional theory
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Context:
Equilibrium statistical mechanics of inhomogeneous fluids, polydisperse mixtures, liquid crystals (Onsager functionals?)...

Wanted:

- Density functionals for Helmholtz free energy

$$\mathcal{F}[\rho] = k_{\mathrm{B}} T \int \rho(x)(\log \rho(x) - 1)\, \mathrm{d}x + \text{power series in } \rho.$$

  Rigorous mathematical convergence theory for well known graphical expansions Stell; Hiroike, Morita...?

- Inversion of the relation between an activity profile $z(x) = z_0 \exp(-V_{\mathrm{ext}}(x)/k_{\mathrm{B}} T)$ and density profile $\rho(x)$?

Outline

1. Equilibrium statistical mechanics: mathematical setup
2. Mathematical difficulty:
   why not use an inversion theorem in Banach spaces?
   $\hookrightarrow$ Problematic for polydisperse mixtures with unbounded object size.
3. (Abstract inversion theorem)
4. Back to statistical mechanics

Grand-canonical partition function in finite box $\Lambda_L = [0,L]^d$

$$\Xi_L[z] = 1 + \sum_{n=1}^{\infty} \frac{1}{n!} \int_{\mathbb{X}_L^n} \exp\Big(-\beta \sum_{1\le i<j\le n} v(q_i,q_j)\Big) \prod_{i=1}^n z(q_i)\,\mathrm{d}q_i,$$

Landau grand potential $\Omega_L = -\beta^{-1} \log \Xi_L$.

- $\mathbb{X}_L$ configuration space for single particle, reference measure $\mathrm{d}q$
  - $\mathbb{X}_L = [0,L]^d$ pointlike particles
  - $\mathbb{X}_L = [0,L]^d \times \mathbb{S}^{d-1}$ thin rods with orientation $\boldsymbol{n} \in \mathbb{S}^{d-1}$
  - $\mathbb{X}_L = [0,L]^d \times \mathbb{N}$ hard spheres with radii R_k, $k \in \mathbb{N}$.
- $\beta = 1/(k_{\mathrm{B}} T)$ inverse temperature
- pair potential $v : \mathbb{X}_L \times \mathbb{X}_L \to \mathbb{R} \cup \{\infty\}$, $v(x,y) = v(y,x)$
- activity profile $z(q)$, for example $z(q) = z_0 \exp(-\beta V_{\mathrm{ext}}(q))$.

Density profile

$$\rho(q;z) = z(q)\frac{\delta}{\delta z(q)}\log \Xi_L[z] = \Big\langle \sum_{i=1}^n \delta(q-q_i)\Big\rangle_{L,z}$$
$$= z(q)\Big\langle \exp\Big(-\beta\sum_{i=1}^n v(q,q_i)\Big)\Big\rangle_{L,z},$$

expected value of a function $f:\sqcup_{n\in\mathbb{N}_0}\mathbb{X}_L^n\to\mathbb{R}$

$$\langle f\rangle_{L,z} = \frac{1}{\Xi_L[z]}\left(f(\varnothing)+\sum_{n=1}^\infty \frac{1}{n!}\int_{\mathbb{X}_L^n} f(q_1,\dots,q_n)\mathrm{e}^{-\beta\sum_{i<j}v(q_i,q_j)}\prod_{i=1}^n z(q_i)\mathrm{d}\boldsymbol{q}\right)$$

Free energy

$$\mathcal{F}[\rho] = \beta^{-1}\sup_z\Big(\int_{\mathbb{X}_L}\rho(q)\log z(q)\,\mathrm{d}q - \log \Xi_L[z]\Big)$$

Mayer expansion (sufficient convergence conditions are known)

$$\log \Xi_L[z] = \sum_{n=1}^{\infty} \frac{1}{n!} \int_{\mathbb{X}_L^n} \varphi_n^{\mathsf{T}}(q_1,\dots,q_n) \prod_{i=1}^n z(q_i) \mathrm{d}\boldsymbol{q}$$

Ursell function = a sum over connected graphs G with vertices $1,\dots,n$, edge set $E(G)$

$$\varphi_n^{\mathsf{T}}(q_1,\dots,q_n) = \sum_{G\in\mathcal{C}_n} \prod_{\{i,j\}\in E(G)} \left(\mathrm{e}^{-\beta v(q_i,q_j)} - 1\right)$$

Expansion of the density

$$\boxed{\rho(q;z) = z(q)\Big(1 + \sum_{n=1}^{\infty} \frac{1}{n!} \int_{\mathbb{X}_L^n} \varphi_n^{\mathsf{T}}(q_1,\dots,q_n) \prod_{i=1}^n z(q_i) \mathrm{d}\boldsymbol{q}\Big).}$$

Functional $z \mapsto \rho[z]$, $\rho[z](q) = \rho(q;z)$ is a power series! Can we invert it?

Previously known

- Inversion on the level of formal power series: Stell, Hiroike, Morita...
  Problem: no convergence results on expansions.
- Rich mathematical literature on convergence of activity expansions:
  Penrose, Groeneveld, Ruelle, Dobrushin, Kotecký, Preiss, Minlos, Poghosyan, Brydges, Ueltschi, Fernández, Procacci... (random order, non-exhaustive)
  Based on tree-graph inequalities, induction, Kirkwood-Salsburg equations.
- Density expansions for homogeneous systems:
  Lebowitz, Penrose '64, Groeneveld '67 & more recent works
- Mixtures for finitely many types of objects, translationally invariant densities:
  Baer, Lebowitz '64
- Mixtures with countably many types of objects:
  Jansen, Tate, Tsagkarogiannis, Ueltschi 2014

Results on density expansions **do not cover truly inhomogeneous systems**, and they **do not work** for objects **with continuous internal degrees of freedom** (e.g. orientation of a thin rod).

Mathematical difficulty: hard-sphere mixtures

- Space $\mathbb{X}_L = [0, L]^3 \times \mathbb{N}$
- Element (x, k) = sphere $B(x, R_k)$ of radius $R_k = k^{1/3}$ centered at x.
- Hard-core interaction

$$v\big((x,k);(y,\ell)\big) = \begin{cases} \infty, & B(x,R_k) \cap B(y,R_\ell) \neq \varnothing, \\ 0, & \text{else.} \end{cases}$$

- Average density of k-spheres at point x satisfies

$$\rho(x,k) = z(x,k) \Big\langle \mathbf{1}_{\{\text{no sphere intersects } B(x,R_k)\}} \Big\rangle_{L,z}$$

can be shown to be exponentially small in sphere volume, $\exp(-\mathrm{const}(z)\,|B(x,R_k)|)$.

Toy model inspired by hard spheres

Mapping $(z_k)_{k\in\mathbb{N}} \mapsto (\rho_k)_{k\in\mathbb{N}}$ given by

$$\rho_1 = z_1, \quad \rho_k = z_k \exp(-kz_1).$$

Clearly, invertible. Derivative at origin:

$$\frac{\partial \rho_k}{\partial z_j}(\mathbf{0}) = \delta_{j,k} \quad \text{identity matrix.}$$

Banach space inversion theorem? If $z \in \ell^\infty(\mathbb{N})$, then image of every open ball $\{z : ||z||_\infty < \varepsilon\}$ includes sequence ρ_k with $\rho_k \geq \frac{1}{2}\varepsilon \exp(\varepsilon k/2) \to \infty$ (pick $z_1 = -\varepsilon/2$). Target Banach space needs to allow for exponential growth of (ρ_k).

$\Rightarrow$ Derivative at zero is not identity map, but embeds one Banach space into a bigger space. Embedding has no bounded inverse.
Banach inversion theorem not applicable.

Abstract inversion theorem

Switch notation $z(q)\mathrm{d}q \to z(\mathrm{d}q)$. Space $\mathbb{X}_L \to \mathbb{X}$ (could be $\mathbb{R}^d$).

Given: functional $z \mapsto \rho[z]$,

$$\boxed{\rho[z](\mathrm{d}q) = z(\mathrm{d}q)\exp\big(-A(q;z)\big),}$$

power series

$$A(q;z) = \sum_{n=1}^{\infty} \frac{1}{n!} \int_{\mathbb{X}^n} A_n(q;x_1,\dots,x_n) z^n(\mathrm{d}\boldsymbol{x}).$$

domain $\mathcal{D}(A) = \sigma$-finite measures z for which

$$\forall q \in \mathbb{X}: \ \sum_{n=1}^{\infty} \frac{1}{n!} \int_{\mathbb{X}^n} \big|A_n(q;x_1,\dots,x_n)\big| z^n(\mathrm{d}\boldsymbol{x}) < \infty.$$

Wanted: inverse map $\rho \mapsto z[\rho]$.

Given weight function $b : \mathbb{X} \to \mathbb{R}_+$, define $\mathcal{V}_b$ by

$$\rho \in \mathcal{V}_b \ :\Leftrightarrow \ \forall q \in \mathbb{X} : \ \sum_{n=1}^{\infty} \frac{1}{n!} \int_{\mathbb{X}^n} \big|A_n(q; x_1, \dots, x_n)\big| \mathrm{e}^{b(x_1)+\dots+b(x_n)} \rho^n(\mathrm{d}\boldsymbol{x}) \leq b(q).$$

Theorem (Jansen, Kuna, Tsagkarogiannis 2019)

For every non-negative weight function b, there is a set $\mathcal{U}_b \subset \mathcal{D}(A)$ *such that* $z \mapsto \rho[z]$ *is a bijection from* $\mathcal{U}_b$ *onto* $\mathcal{V}_b$*. The inverse map* $\rho \mapsto z[\rho]$ *is of the form*

$$z[\rho](\mathrm{d}q) = \rho(\mathrm{d}q)\Big(1 + \sum_{n=1}^{\infty} \frac{1}{n!} \int t_n(q; x_1, \dots, x_n) \rho^n(\mathrm{d}\boldsymbol{x})\Big)$$

with uniquely defined coefficients t_n *and*

$$1 + \sum_{n=1}^{\infty} \frac{1}{n!} \int \big|t_n(q; x_1, \dots, x_n)\big| \rho^n(\mathrm{d}\boldsymbol{x}) \leq \mathrm{e}^{b(q)} \qquad (\rho \in \mathcal{V}_b).$$

No need for scales of Banach spaces or Nash-Moser theory.

Back to statistical mechanics

- Single-particle space $\mathbb{X}_L$, repulsive pair potential $v(x,y) \geq 0$.
- 2-connected graphs $\mathcal{D}_n$ = graphs with vertices $1, \ldots, n$ that are connected and stay connected after removal of a vertex. Function D_n

$$D_n(x_1, \ldots, x_n) := \sum_{G \in \mathcal{D}_n} \prod_{\{i,j\} \in E(G)} \left(\mathrm{e}^{-\beta v(x_i, x_j)} - 1\right).$$

- For weight function $a : \mathbb{X}_L \to \mathbb{R}_+$, define a domain of density profiles

$$\boxed{\rho \in \mathcal{R}_a :\Leftrightarrow \ \forall x : \ \int \left(1 - \mathrm{e}^{-\beta v(x,y)}\right) \rho(y) \mathrm{e}^{2a(y)} \mathrm{d}y \leq a(x).}$$

Theorem (Jansen, Kuna, Tsagkarogiannis 2019)

Mapping $z \mapsto \rho[z]$ is bijection from some activity domain onto $\mathcal{R}_a$, inverse given by

$$z(q) = \rho(q) \exp\left(- \sum_{n=1}^{\infty} \frac{1}{n!} \int D_{n+1}(q, x_1, \ldots, x_n) \prod_{i=1}^{n} \rho(x_i) \mathrm{d}\boldsymbol{x} \right).$$

About the convergence condition:

$$\rho \in \mathcal{R}_a \;\Leftrightarrow\; \forall x: \;\int \big(1-\mathrm{e}^{-\beta v(x,y)}\big)\rho(y)\mathrm{e}^{2a(y)}\mathrm{d}y \le a(x).$$

For constant $a(x) \equiv a$, easier sufficient condition reads

$$||\rho||_\infty \sup_x \int \big(1-\mathrm{e}^{-\beta v(x,y)}\big)\mathrm{d}y \le a \exp(-2a).$$

Right side is largest for $a = 1/2$. For **hard spheres of radius** R, criterion reads

$$\boxed{||\rho||_\infty |B(0,2R)| \le \frac{1}{2\mathrm{e}} \simeq 0.18.}$$

(Better than Lebowitz, Penrose '64 but worse than Groeneveld '67.)

$$\rho \in \mathcal{R}_a \;\Leftrightarrow\; \forall x: \; \int \big(1 - \mathrm{e}^{-\beta v(x,y)}\big)\rho(y)\mathrm{e}^{2a(y)}\mathrm{d}y \leq a(x).$$

Theorem (Jansen, Kuna, Tsagkarogiannis 2019)

$v \geq 0$, $\rho \in \mathcal{R}_a$ with $\int_{\mathbb{X}_L} \exp(a(q))\rho(q)\mathrm{d}q < \infty$: the free energy is

$$\boxed{\mathcal{F}[\rho] = \int \rho(q)\big(\log \rho(q) - 1\big)\mathrm{d}q - \sum_{n=2}^{\infty} \frac{1}{n!} \int D_n(q_1, \dots, q_n) \prod_{i=1}^{n} \rho(q_i)\mathrm{d}\boldsymbol{q},}$$

expansion is absolutely convergent.

Theorems proven by combining abstract inversion theorem with known results on activity expansions.

To the best of our knowledge, **first mathematical result on convergence of the density expansion applicable to inhomogeneous polydisperse mixtures with objects of unbounded size**.

Summary:
The inversion of the density-activity relation for inhomogeneous systems and polydisperse mixtures is highly non-trivial, but it can be done.

Yields sufficient convergence conditions for well-known expansions with 2-connected graphs.

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