Classical density functional theory: Universal bounds and local density approximation

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Outline

The setting

We consider a system of identical classical particles in $\Lambda \subseteq \mathbb{R}^d$, interacting through a pair potential w. The (canonical) free energy at temperature $T \geq 0$ of N particles distributed according to a (symmetric) probability distribution $\mathbb{P}_N$ on Λ^N is given by

$$\mathcal{F}_T(\mathbb{P}_N) = \int_{\Lambda^N} \sum_{j<k}^{N} w(x_j - x_k)\, \mathrm{d}\mathbb{P}_N(x) + T \underbrace{\int_{\Lambda^N} \log(N!\, \mathbb{P}_N(x))\, \mathrm{d}\mathbb{P}_N(x)}_{=:-\mathcal{S}_N(\mathbb{P}_N)}.$$

The minimal free energy at fixed density ρ with $\int \rho = N$ is

$$F_T[\rho] = \inf_{\rho_{\mathbb{P}_N}=\rho} \mathcal{F}_T(\mathbb{P}_N) = \inf_{\rho_{\mathbb{P}_N}=\rho} \left\{ \int_{\Lambda^N} \sum_{j<k}^{N} w(x_j - x_k) + T \log(N!\, \mathbb{P}_N(x))\, \mathrm{d}\mathbb{P}_N(x) \right\}.$$

In the grand-canonical setting, the distribution of the particles is described by a family $\mathbb{P} = (\mathbb{P}_n)_{n\geq 0}$, where each $\mathbb{P}_n$ is a symmetric measure on Λ^n, normalized such that $\sum_{n\geq 0} \mathbb{P}_n(\Lambda^n) = 1$. Minimal grand-canonical free energy at fixed density:

$$G_T[\rho] = \inf_{\rho_{\mathbb{P}}=\rho} \left\{ \sum_{n\geq 0} \int_{\Lambda^n} \sum_{j<k}^{n} w(x_j - x_k) + T \log(n!\, \mathbb{P}_n(x))\, \mathrm{d}\mathbb{P}_n(x) \right\},$$

where

$$\rho_{\mathbb{P}}(x) = \sum_{n\geq 1} \rho_{\mathbb{P}_n}(x) = \sum_{n\geq 1} n \int_{\Lambda^{n-1}} \mathbb{P}_n(x, x_2, \ldots, x_n)\, \mathrm{d}x_2 \cdots \mathrm{d}x_n.$$

For any external potential V, we have the two-step minimization:

$$G_T(V,\Lambda) = \inf_{\mathbb{P}}\left\{\sum_{n\geq 0}\int_{\Lambda^n}\sum_{j=1}^{n}V(x_j) + \sum_{j<k}^{n} w(x_j - x_k) + T\log(n!\,\mathbb{P}_n(x))\,\mathrm{d}\mathbb{P}_n(x)\right\}$$

$$= \inf_{\rho}\left\{\inf_{\rho_{\mathbb{P}}=\rho}\left(\sum_{n\geq 0}\int_{\Lambda^n}\sum_{j<k}^{n} w(x_j - x_k) + T\log(n!\,\mathbb{P}_n(x))\,\mathrm{d}\mathbb{P}_n(x)\right) + \int_{\Lambda} V\rho\right\}$$

$$= \inf_{\rho}\left\{G_T[\rho] + \int_{\Lambda} V\rho\right\}.$$

The inverse problem (Legendre-Fenchel duality): Given a density ρ, if one can find a potential $V(x)$ such that

$$\rho(x_1) = \frac{e^{-\frac{1}{T}V(x_1)}}{Z_{T,V,\mathbb{R}^d}}\sum_{n=1}^{\infty}\frac{n}{n!}\int_{\mathbb{R}^{d(n-1)}} e^{-\frac{1}{T}\left(\sum_{j<k} w(x_j-x_k)+\sum_{j\geq 2} V(x_j)\right)}\,\mathrm{d}x_2\cdots\mathrm{d}x_n,$$

then

$$G_T[\rho] = G_T(V,\mathbb{R}^d) - \int_{\mathbb{R}^d} V\rho.$$

(Chayes and Chayes, 1984; Chayes, Chayes, and Lieb, 1984). Solved explicitly in the 1D hard-core case (Percus, 1976). Uniformly small densities (Jansen, Kuna, and Tsagkarogiannis, 2022).

Natural questions:

- Representability: Given a density $\rho \in L^1(\mathbb{R}^d)$, when are $G_T[\rho]$ and $F_T[\rho]$ finite? Which densities arise as the one-particle density of some many-body state with finite energy?
- Can $G_T[\rho]$ and $F_T[\rho]$ be bounded in terms of ρ? Difficulty: Construction of states with densities exactly equal to a prescribed $\rho \in L^1(\mathbb{R}^d)$.
- How can $G_T[\rho]$ and $F_T[\rho]$ be approximated in practice?

Initial observations:

- Any canonical state is also a grand-canonical state, so

$$G_T[\rho] \leq F_T[\rho]$$

whenever ρ has integer mass.

- If $\int_{\mathbb{R}^d} \rho = N + t$ with $t \in (0,1)$ and $N \in \mathbb{N}$, we can write $\rho = (1-t)\frac{N}{N+t}\rho + t\,\frac{N+1}{N+t}\rho$ and obtain after using the concavity of the entropy

$$G_T[\rho] \leq (1-t)\, F_T\left[\frac{N}{N+t}\rho\right] + t\, F_T\left[\frac{N+1}{N+t}\rho\right].$$

- Weak interactions ($w \in L^1(\mathbb{R}^d)$). Using an uncorrelated state $\mathbb{P} = (\rho/N)^{\otimes N}$ immediately gives

$$\begin{aligned} F_T[\rho] &\leq \frac{1-1/N}{2} \iint_{\mathbb{R}^d \times \mathbb{R}^d} w(x-y)\rho(x)\rho(y)\,\mathrm{d}x\,\mathrm{d}y + T\int_{\mathbb{R}^d} \rho\log\rho \\ &\leq \frac{\|w_+\|_{L^1}}{2}\int_{\mathbb{R}^d}\rho^2 + T\int_{\mathbb{R}^d}\rho\log\rho. \end{aligned}$$

The interaction potential

Assumption (A)

Let $w : \mathbb{R}^d \to \mathbb{R} \cup \{+\infty\}$ be a lower semi-continuous and even function satisfying for some $\kappa > 0$:

- w is *stable*, that is,

$$\sum_{1 \le j < k \le N} w(x_j - x_k) \ge -\kappa N$$

  for all $N \in \mathbb{N}$ and $x_1, \ldots, x_N \in \mathbb{R}^d$;

- w is *upper* and *lower regular*, that is, there exist $0 \le \alpha < \infty$ and $s > d$ such that

$$\frac{\mathbb{1}(|x| < 1)}{\kappa |x|^\alpha} - \frac{\kappa}{1 + |x|^s} \le w(x) \le \frac{\kappa \mathbb{1}(|x| < 1)}{|x|^\alpha} + \frac{\kappa}{1 + |x|^s}.$$

- α determines the repulsive strength of w near the origin. When $\alpha < d$, w is integrable on $\mathbb{R}^d$. When $\alpha \ge d$, w has a non-integrable singularity at the origin. In this case, for any state with finite energy, the particles cannot be too close to each other and must be heavily correlated.
- When $\int \rho |\log \rho| < \infty$, stability of w implies

$$G_T[\rho] \ge -\kappa \int_{\mathbb{R}^d} \rho - T \max_{\rho_{\mathbb{P}} = \rho} \mathcal{S}(\mathbb{P}) = -(\kappa + T) \int_{\mathbb{R}^d} \rho + T \int_{\mathbb{R}^d} \rho \log \rho,$$

  by taking $\mathbb{P}$ to be the Poisson state $\mathbb{P} = \left(\frac{e^{-\int \rho}}{n!} \rho^{\otimes n} \right)_{n \ge 0}$.

Representability and bounds in one dimension

Theorem ($d = 1$)

Suppose $1 \le \alpha < \infty$. Then for any density $0 \le \rho \in L^1(\mathbb{R})$ with $\int_{\mathbb{R}} \rho \in \mathbb{N}$ and $T \int_{\mathbb{R}} \rho |\log \rho| < \infty$,

$$F_T[\rho] \le C\kappa \int_{\mathbb{R}} \rho^2 + CT \int_{\mathbb{R}} \rho + T \int_{\mathbb{R}} \rho \log \rho + \begin{cases} C\kappa \int_{\mathbb{R}} \rho^{1+\alpha} & \text{for } \alpha > 1, \\ C\kappa \left(\int_{\mathbb{R}} \rho^2 + \int_{\mathbb{R}} \rho^2 (\log \rho)_+ \right) & \text{for } \alpha = 1. \end{cases}$$

Proof: Draw a one dimensional chess board. □

Using the same approach in any dimension $d \ge 1$, cutting $\mathbb{R}^d$ into slices $L_j \times \mathbb{R}^{d-1}$, gives the following:

Corollary (Representability in any dimension)

For any density $\rho \in L^1(\mathbb{R}^d)$ with $T \int \rho |\log \rho| < \infty$, we have $G_T[\rho] < \infty$, and when $\int \rho \in \mathbb{N}$, we have $F_T[\rho] < \infty$.

If w is a hard-core potential, the question of representability is highly non-trivial, and classifying the set of representable densities in this case is an open problem.

Grand canonical bounds

Theorem (Jex-Lewin-M. 2023)

Suppose that $d \le \alpha < \infty$, *and assume that* $0 \le \rho \in L^1(\mathbb{R}^d)$ *satisfies* $T \int_{\mathbb{R}^d} \rho |\log \rho| < \infty$. *Then*

$$G_T[\rho] \le C\kappa \int_{\mathbb{R}^d} \rho^2 + CT \int_{\mathbb{R}^d} \rho + T \int_{\mathbb{R}^d} \rho \log \rho$$

$$+ \begin{cases} C\kappa \int_{\mathbb{R}^d} \rho^{1+\frac{\alpha}{d}} & \text{for } \alpha > d, \\ C\kappa \left(\int_{\mathbb{R}^d} \rho^2 + \int_{\mathbb{R}^d} \rho^2 \big(\log \rho \big)_+ \right) & \text{for } \alpha = d. \end{cases}$$

Here the constant C *depends only on the dimension* d *and the powers* α, s.

Outline of proof:

- If $\int \rho \le 1$, we take $\mathbb{P} = (\mathbb{P}_n)$ defined by $\mathbb{P}_0 = 1 - \int \rho$, $\mathbb{P}_1 = \rho$, $\mathbb{P}_n = 0$ for $n \ge 2$.
- Suppose ρ is compactly supported with $\int \rho > 1$, and fix $c > 0$ sufficiently small. For each $x \in \operatorname{supp} \rho$, define $\ell(x)$ to be the largest number such that

$$\int_{x+\ell(x)\mathcal{C}} \rho(y)\, \mathrm{d}y = c,$$

  where $\mathcal{C} = (-1/2; 1/2)^d$ is the unit cube.

Lemma (Besicovitch covering with minimal distance (Frank, Laptev, and Weidl, 2022; Guzmán, 1975))

There exists a set of points $x_j^{(k)}$ *with* $1 \leq k \leq K \leq 3^d(4^d+1)$ *and* $1 \leq j \leq J_k < \infty$ *such that*

- *the cubes* $\mathcal{C}(x_j^{(k)}) := x_j^{(k)} + \ell(x_j^{(k)})\mathcal{C}$ *cover the support of* ρ *and each* $x \in \mathbb{R}^d$ *is in at most* 2^d *such cubes,*
- *for every* k*, the cubes* $(\mathcal{C}(x_j^{(k)}))_{1\leq j\leq J_k}$ *in the* k*th collection satisfy*

$$\mathrm{d}\left(\mathcal{C}(x_j^{(k)}), \mathcal{C}(x_\ell^{(k)})\right) \geq \frac{1}{2}\min\left\{\ell(x_j^{(k)}), \ell(x_\ell^{(k)})\right\}.$$

- We obtain the following partition of unity:

$$\mathbb{1}_{\operatorname{supp}\rho} = \sum_{k=1}^{K}\sum_{j=1}^{J_k} \frac{\mathbb{1}_{\mathcal{C}(x_j^{(k)})\cap \operatorname{supp}\rho}}{\eta}, \qquad \mathbb{1}_{\operatorname{supp}\rho} \leq \eta := \sum_{k=1}^{K}\sum_{j=1}^{J_k} \mathbb{1}_{\mathcal{C}(x_j^{(k)})} \leq 2^d.$$

- Write ρ as a convex combination

$$\rho = \frac{1}{K}\sum_{k=1}^{K}\left(\sum_j \rho_j^{(k)}\right), \qquad \rho_j^{(k)} := \frac{K\rho\mathbb{1}_{\mathcal{C}(x_j^{(k)})}}{\eta},$$

where for c small,

$$\int \rho_j^{(k)} \leq 3^d(4^d+1)\int_{\mathcal{C}(x_j^{(k)})} \rho = 3^d(4^d+1)c \leq 1.$$

- Define a trial state by $\mathbb{P} := \frac{1}{K}\sum_{k=1}^{K}\mathbb{P}^{(k)}$, where

$$\mathbb{P}^{(k)} = \bigotimes_{j=1}^{J_k}\left(\left(1-\int_{\mathbb{R}^d}\rho_j^{(k)}\right)\oplus\rho_j^{(k)}\oplus 0\oplus\cdots\right).$$

- Calculate the free energy, using $\frac{1}{\ell(x)^\alpha} \leq c^{-\frac{\alpha+d}{d}}\int_{\mathcal{C}(x)}\rho^{1+\frac{\alpha}{d}}$ for all $x\in\mathbb{R}^d$ (exercise). □

It is very difficult to control the mass contained in each collection $\left(\mathcal{C}(x_j^{(k)})\right)_{1\leq j\leq J_k}$, making the approach unsuitable to use in the canonical case.

Canonical bounds

Theorem (Jex-Lewin-M. '23)

Suppose $d \leq \alpha < \infty$. *Let* $0 \leq \rho \in L^1(\mathbb{R}^d)$ *with* $2 \leq \int_{\mathbb{R}^d} \rho \in \mathbb{N}$, *and* $T \int_{\mathbb{R}^d} \rho |\log \rho| < \infty$. *Then we have*

$$F_T[\rho] \leq C(\kappa + T) \int_{\mathbb{R}^d} \rho^2 + CT \int_{\mathbb{R}^d} \rho + T \int_{\mathbb{R}^d} \rho \log \rho + T \int_{\mathbb{R}^d} \rho \log R^d$$
$$+ \begin{cases} C\kappa \int_{\mathbb{R}^d} \rho^{1+\frac{\alpha}{d}} & \text{for } \alpha > d, \\ C\kappa \left(\int_{\mathbb{R}^d} \rho^2 + \int_{\mathbb{R}^d} \rho^2 \left(\log \rho \right)_+ \right) & \text{for } \alpha = d, \end{cases}$$

where the constant C *only depends on the dimension* d *and the powers* α, s.

When $\int_{\mathbb{R}^d} \rho(y)\,\mathrm{d}y > 1$, we define the local radius $R(x)$, $x \in \mathbb{R}^d$ to be the largest number satisfying

$$\int_{B(x,R(x))} \rho(y)\,\mathrm{d}y = 1.$$

We conjecture that the bound holds without the non-local term $\int \rho \log R^d$.

The local radius and optimal transport

- The function R is 1-Lipschitz continuous with $\min_{x\in\mathbb{R}^d} R(x) > 0$, and $R(x) \sim |x|$ as $|x| \to \infty$.
- Connection to the Hardy-Littlewood maximal function:

$$\frac{1}{|B_1|R(x)^d} = \frac{1}{|B_{R(x)}|}\int_{B(x,R(x))} \rho(y)\,\mathrm{d}y \leq \sup_{r>0} \frac{1}{|B_r|}\int_{B(x,r)} \rho(y)\,\mathrm{d}y =: M_\rho(x).$$

- Recall the Hardy-Littlewood maximal inequality: $\|M_\rho\|_p \leq C_{d,p}\|\rho\|_p$ for $p > 1$.

Theorem (Optimal transport state (Colombo, Di Marino, and Stra, 2019))

Let $0 \leq \rho \in L^1(\mathbb{R}^d)$ with $N = \int_{\mathbb{R}^d} \rho \in \mathbb{N}$. There exists an N-particle state $\mathbb{P}_{OT}$ with density $\rho_{\mathbb{P}_{OT}} = \rho$ such that

$$|x_i - x_j| \geq \max\left(\min_{x\in\mathbb{R}^d} R(x), \tfrac{R(x_i)+R(x_j)}{3}\right) \quad \text{for } 1 \leq i \neq j \leq N$$

$\mathbb{P}_{OT}$–almost everywhere.

The state $\mathbb{P}_{OT}$ emerges as the optimizer for a multi-marginal optimal transport problem. The proof is non-constructive and relies on Kantorovich duality. $\mathbb{P}_{OT}$ is usually singular with respect to the Lebesgue measure.

The interaction energy of $\mathbb{P}_{OT}$

- Fix $x = (x_1, \dots, x_N)$ in the support of $\mathbb{P}_{OT}$ with $R(x_1) \leq R(x_2) \leq \cdots \leq R(x_N)$. Then

$$\sum_{j=i+1}^{N} \frac{1}{|x_i - x_j|^\alpha} \leq \frac{1}{|B(0, \frac{1}{6} R(x_i))|} \int_{B(0, \frac{1}{3} R(x_i))^c} \frac{1}{|y|^\alpha} \, \mathrm{d}y = C \frac{1}{R(x_i)^\alpha}.$$

- Calculating the interaction energy in the state $\mathbb{P}_{OT}$, one finds (for $\alpha > d$)

$$\begin{aligned} F_0[\rho] &\leq \kappa \int_{\mathbb{R}^{dN}} \sum_{i=1}^{N} \sum_{j=i+1}^{N} \left(\frac{1}{|x_i - x_j|^\alpha} + \frac{1}{1 + |x_i - x_j|^s} \right) \mathrm{d}\mathbb{P}_{OT}(x) \\ &\leq C\kappa \int_{\mathbb{R}^{dN}} \sum_{i=1}^{N} \frac{1}{R(x_i)^\alpha} + \frac{1}{R(x_i)^d} \, \mathrm{d}\mathbb{P}_{OT}(x) \\ &= C\kappa \int_{\mathbb{R}^d} \frac{\rho(x)}{R(x)^\alpha} + \frac{\rho(x)}{R(x)^d} \, \mathrm{d}x \\ &\leq \widetilde{C}\kappa \int_{\mathbb{R}^d} \rho(x)^{1+\frac{\alpha}{d}} + \rho(x)^2 \, \mathrm{d}x. \end{aligned}$$

- To handle positive temperature, $\mathbb{P}_{OT}$ needs to be regularized. This can be done using the Besicovitch covering lemma and the block approximation (Carlier et al., 2017), which locally replaces $\mathbb{P}_{OT}$ with a pure tensor, while keeping the density fixed.

The (grand-canonical) local density approximation

The minimal free energy $G_T[\rho]$ at density ρ is approximated using a local functional,

$$G_T[\rho] \approx \int_{\mathbb{R}^d} f(\rho(x))\,\mathrm{d}x.$$

The function $f(\rho_0)$ is typically the free energy per unit volume of an infinite homogeneous system at density ρ_0.

Previous results:

- Classical uniform electron gas with Coulomb interaction in 3D (Lewin, Lieb, and Seiringer, 2018).
- Quantum systems with Coulomb interactions in 3D (Lewin, Lieb, and Seiringer, 2020).
- Extension of the quantum case to a class of smooth short-range interactions (Mietzsch, 2020).

All previous results rely on the Graf-Schenker inequality/screening properties of the Coulomb potential. All exclusively 3D and grand-canonical.

Thermodynamic limits

Usual thermodynamic limit: For any $\rho_0 > 0$ and reasonable sequence of domains $\Lambda_n \subseteq \mathbb{R}^d$ with $\Lambda_n \nearrow \mathbb{R}^d$, the thermodynamic limit exists,

$$f_T(\rho_0) := \lim_{\substack{n\to\infty \\ n|\Lambda_n|^{-1}\to\rho_0}} \frac{F_T(n,\Lambda_n)}{|\Lambda_n|},$$

and is independent of the sequence Λ_n. Here, $F_T(n,\Lambda_n)$ is the minimal *canonical* free energy of an n-particle system in Λ_n, *without* restrictions on the density. The limit function f_T is known to be convex and C^1 (Ruelle, 1970, 1999).

Proposition (Jex-Lewin-M. 202?)

Let $\rho_0 > 0$. Suppose that $\Lambda_n \subseteq \mathbb{R}^d$ is a sequence of bounded connected domains with sufficiently regular boundaries, and such that $|\Lambda_n| \to \infty$. Then we have

$$\lim_{n\to\infty} \frac{G_T[\rho_0 \mathbb{1}_{\Lambda_n}]}{|\Lambda_n|} = f_T(\rho_0).$$

Futhermore, if $\rho_0|\Lambda_n| \in \mathbb{N}$ for all n, then

$$\lim_{n\to\infty} \frac{F_T[\rho_0 \mathbb{1}_{\Lambda_n}]}{|\Lambda_n|} = f_T(\rho_0).$$

Clearly, $F_T[\rho_0 \mathbb{1}_{\Lambda_n}] \geq F_T(\rho_0|\Lambda_n|,\Lambda_n)$. The lower bound on $G_T[\rho_0 \mathbb{1}_{\Lambda_n}]$ follows from Legendre duality (equivalence of ensembles). The upper bounds are proved by construction of a trial state in the spirit of the floating Wigner crystal.

Bounds on f_T

Proposition

Let w satisfy Assumption (A). There are constants $C, c > 0$ depending only on w and the dimension d, such that for any $\rho \geq 0$, we have

$$f_T(\rho) \leq \begin{cases} C\rho^{\max(2,1+\alpha/d)} + C(1+T)\rho + T\rho\log\rho, & \alpha \neq d, \\ C\rho^2(\log\rho)_+ + C(1+T)\rho + T\rho\log\rho, & \alpha = d, \end{cases}$$

and

$$f_T(\rho) \geq \begin{cases} c\rho^{\max(2,1+\alpha/d)} - (C+T)\rho + T\rho\log\rho, & \alpha \neq d, \\ c\rho^2\left(\log c\rho\right)_+ - (C+T)\rho + T\rho\log\rho, & \alpha = d. \end{cases}$$

- Let $M > 0$, and consider $G_T[\rho]$ for the class of densities $0 \leq \rho \in (L^1 \cap L^\infty)(\mathbb{R}^d)$ with $\|\rho\|_\infty \leq M$. The universal upper bound simplifies

$$G_T[\rho] \leq C(M, T, w, d) \int_{\mathbb{R}^d} \rho + T \int_{\mathbb{R}^d} \rho \log \rho.$$

- For any density $\rho \in L^1(\mathbb{R}^d)$ and $\ell > 0$, we denote $C_\ell := [-\ell/2, \ell/2]^d$ is the cube of side length ℓ, and

$$\delta\rho_\ell(z) := \operatorname*{ess\,sup}_{x,y \in z + C_\ell} \frac{|\rho(x) - \rho(y)|}{\ell}.$$

  When $\rho = \rho_0 \mathbb{1}_\Lambda$, then $\delta\rho_\ell = 0$ everywhere, except at distance of order ℓ to the boundary $\partial\Lambda$, where it is bounded by ρ_0/ℓ.

The local density approximation

Theorem (Jex-Lewin-M. 202?)

Let $M > 0$, $T \geq 0$, $p \geq 1$, and $b > \begin{cases} 2 - \frac{1}{2p} & \text{if } p \geq 2, \\ \frac{3}{2} + \frac{1}{2p} & \text{if } 1 \leq p < 2. \end{cases}$
Let w be a short-range interaction satisfying Assumption (A) with $s > d+1$. There exists a constant $C > 0$ depending on M, T, w, d, p, b, such that

$$\left| G_T[\rho] - \int_{\mathbb{R}^d} f_T(\rho(x))\,\mathrm{d}x \right| \leq \frac{C}{\sqrt{\ell}} \left(\int_{\mathbb{R}^d} \sqrt{\rho} + \ell^{bp} \int_{\mathbb{R}^d} \delta\rho_\ell(z)^p\,\mathrm{d}z \right),$$

for any $\ell > 0$, and any density $\rho \geq 0$ such that $\sqrt{\rho} \in (L^1 \cap L^\infty)(\mathbb{R}^d)$ with $\|\rho\|_\infty \leq M$.

- Bounds on G_T and f_T ensure that the left hand side is finite. Note that $\int \rho|\log\rho| \leq \|\sqrt{\rho}\log\rho\|_\infty \int \sqrt{\rho}$.
- Valid for all densities satisfying the conditions, but only useful for slowly varying densities.
- The constant C increases exponentially with M, and with the growth rate α of w near the origin.
- One could expect a similar estimate to hold without the constraint on $\|\rho\|_\infty$, where $\sqrt{\rho}$ is replaced by

$$\int_{\mathbb{R}^d} \rho + \rho^{\max(2,1+\alpha/d)} + T\rho(\log\rho)_-.$$

When ρ has additional regularity, we have:

Corollary

Suppose, in addition to the assumptions from before, that $p > d$ and $\nabla\rho \in L^p(\mathbb{R}^d)$. Then we have

$$\left| G_T[\rho] - \int_{\mathbb{R}^d} f_T(\rho(x))\,\mathrm{d}x \right| \leq C\varepsilon \left(\int_{\mathbb{R}^d} \sqrt{\rho} + \frac{1}{\varepsilon^{2bp}} \int_{\mathbb{R}^d} |\nabla\rho|^p \right)$$

for any $\varepsilon > 0$.

This is a straightforward application of Morrey's inequality, which states for $p > d$ that

$$|\rho(x) - \rho(y)| \leq K^{\frac{1}{p}} |x-y|^{1-\frac{d}{p}} \left(\int_Q |\nabla\rho|^p \right)^{\frac{1}{p}}, \qquad x, y \in Q,$$

for any cube Q. □

Taking a smooth ρ and rescaling $\rho_N(x) := \rho(N^{-1/d}x)$ yields

$$G_T[\rho_N] = N \int_{\mathbb{R}^d} f_T(\rho(x))\,\mathrm{d}x + O\left(N^{1-\frac{1}{2bd}}\right)$$

for all $b > 7/4$.

Elements of the proof (lower bound)

- Recall the equivalence of ensembles for the usual thermodynamic limit,

$$f_T(\rho_0) = \sup_{\mu\in\mathbb{R}} \big(g_T(\mu) + \mu\rho_0\big),$$

  where $g_T(\mu)$ is the grand canonical energy per unit volume at chemical potential $\mu \in \mathbb{R}$ for an infinite system.

- Introduce an external potential $V(x) = -\sum_{k\in\mathbb{Z}^d} \mu_k(x)\mathbb{1}_{C_k}(x)$. Then

$$G_T[\rho] + \int V\rho \geq \inf_{\mathbb{P}=(\mathbb{P}_n)} \Big\{\mathcal{G}_T(\mathbb{P}) + \sum_{n\geq 1}\int_{\mathbb{R}^{dn}} \sum_{i=1}^{n} V(x_i)\,\mathrm{d}\mathbb{P}_n(x)\Big\} = G_T(V,\mathbb{R}^d).$$

  The minimizer for the right hand side is a Gibbs state $\mathbb{P}_V$.

- Localize into cubes,

$$G_T(V,\mathbb{R}^d) \geq \sum_{k\in\mathbb{Z}^d} G_T(-\mu_k, C_k) + \sum_{\substack{k,m\in\mathbb{Z}^d\\ k\neq m}} \langle I_{k,m}\rangle_{\mathbb{P}_V},$$

  where $\langle I_{k,m}\rangle_{\mathbb{P}_V} = \frac{1}{2}\iint_{C_k\times C_m} w(x-y)\rho^{(2)}_{\mathbb{P}_V}(x,y)\,\mathrm{d}x\,\mathrm{d}y$.

- If μ_k is constant in C_k, then $G_T(-\mu_k, C_k) \approx \ell^d g_T(\mu_k)$. Choose μ_k to satisfy $g_T(\mu_k) + \rho_k\mu_k = f_T(\rho_k)$ for some appropriate ρ_k.
- To control error terms $\langle I_{k,m}\rangle_{\mathbb{P}_V}$ from the interaction, we use uniform bounds on 2-body correlation functions for usual Gibbs states (Ruelle, 1970).

Ruelle bounds

- A family of bounds due to (Ruelle, 1970) which allows one to uniformly control the local average (square) number of particles $\langle n_Q^2 \rangle_{T,\mu,\Omega}$ in a cube Q of side length L, for a Gibbs state in the set $\Omega \subseteq \mathbb{R}^d$. Unfortunately not quantitative in the original paper.
- One version of the bound takes the form

$$\langle n_Q^2 \rangle_{T,\mu,\Omega} \leq |Q|^2 C_T e^{\frac{\mu}{T}} \left(1 + e^{\frac{d\mu}{T\varepsilon}}\right),$$

  for all sufficiently large cubes Q, where $\varepsilon = \min(1, s-d)/2$, and C_T depends only on T and the interaction w.
- Alternatively, in the presence of an external potential V, which is bounded from below by a constant $-\mu_0$,

$$\langle n_Q^2 \rangle_{T,V} \leq C_T |Q| \int_Q e^{-\frac{1}{T}V(x)} \,\mathrm{d}x \left(1 + e^{\frac{d\mu_0}{\varepsilon T}}\right).$$

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