On the sharp constant in the Lieb–Oxford inequality

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Based on joint work with Mathieu Lewin and Elliott Lieb

Coulomb gases and universality

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Classical Coulomb Systems

Statistical mechanics of N charged particles interacting via Coulomb forces. **Coulomb energy**

$$\mathcal{E}(\mathbb{P}) = \int_{\mathbb{R}^{3N}} \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|} d\mathbb{P}(x_1,\dots,x_N)$$

(Classical) **density functional theory**: minimize over all (probability) distributions $\mathbb{P}$ with given one-particle density ϱ:

$$\mathcal{F}(\varrho) = \min_{\mathbb{P},\, \varrho_{\mathbb{P}}=\varrho} \mathcal{E}(\mathbb{P})$$

where

$$\varrho_{\mathbb{P}}(x) = \sum_{i=1}^{N} \int_{\mathbb{R}^{3(N-1)}} d\mathbb{P}(x_1,\dots,x_{i-1},x,x_{i+1},\dots,x_N)$$

Of particular interest is the difference to the direct (uncorrelated) Coulomb energy,

$$\mathcal{I}(\varrho) = \mathcal{F}(\varrho) - \frac{1}{2}\int_{\mathbb{R}^6} \frac{\varrho(x)\varrho(y)}{|x-y|} dx\, dy$$

Lieb–Oxford Inequality

The **Lieb–Oxford** inequality gives a universal lower bound on $\mathcal{I}$:

THEOREM. For all (non-negative) $\varrho \in L^1(\mathbb{R}^3) \cap L^{4/3}(\mathbb{R}^3)$

$$\mathcal{I}(\varrho) \geq -C_{\rm LO} \int_{\mathbb{R}^3} \varrho(x)^{4/3} dx$$

History:

- [Lieb 1979]: $0.93 \leq C_{\rm LO} \leq 8.52$
- [Lieb–Oxford 1980]: $1.23 \leq C_{\rm LO} \leq 1.68$
- [Chan–Handy 1999]: $C_{\rm LO} \leq 1.64$
- [Lewin–Lieb–S. 2019, 22]: $1.44 \leq C_{\rm LO} \leq 1.58$

The value of $C_{\rm LO}$ is of **practical significance** and used as a constraint in approximate density functionals.

Proof of the LO Inequality (Upper Bound on C_{LO})

For general charge distributions μ and ν, let

$$D(\mu,\nu) = \frac{1}{2}\int \frac{d\mu(x)d\nu(y)}{|x-y|}$$

If μ_x and ν_y are spherically symmetric around x and y, respectively, **Newton's theorem** implies that

$$\frac{1}{|x-y|} \geq 2D(\mu_x,\nu_y)$$

Given $\mathbb{P}$ we choose for fixed spherical μ

$$\mu_x(y) = \varrho_{\mathbb{P}}(x)\mu(\varrho_{\mathbb{P}}(x)^{1/3}(y-x))$$

Positivity of D thus gives **Onsager's Lemma**

$$\sum_{i<j}\frac{1}{|x_i-x_j|} \geq -D(\eta,\eta) + 2\sum_{i=1}^{N} D(\mu_{x_i},\eta) - \sum_{i=1}^{N}\varrho_{\mathbb{P}}(x_i)^{1/3}D(\mu,\mu)$$

Proof of the LO Inequality, part 2

We choose

$$\eta(x) = \int \varrho_{\mathbb{P}}(y) d\nu_x(y)$$

and obtain

$$\mathcal{I}(\varrho) \geq -\int_{\mathbb{R}^6} \varrho(x)\varrho(y) \left(D(\nu_x,\nu_y) + D(\delta_x,\delta_y) - 2D(\mu_x,\nu_y)\right) dxdy - D(\mu,\mu) \int \varrho^{4/3}$$

The first term can be written as

$$\frac{1}{2}\int_{\mathbb{R}^6} \frac{\Psi_{\mu\nu}(|x-y|\varrho(x)^{1/3}, |x-y|\varrho(y)^{1/3})}{|x-y|^7} dxdy$$

with $\Psi_{\mu\nu} = \Phi_{\mu\nu} + \Phi_{\nu\mu} - \Phi_{\nu\nu}$ and

$$\Phi_{\mu\nu}(a,b) = a^3 b^3 \left(1 - 2D(\mu_{0,a}, \nu_{e_1,b})\right) \quad , \quad \mu_{x,a} = a^3 \mu(a(\cdot - x))$$

Now if we can find an f such that $\Psi_{\mu\nu}(a,b) \leq f(a) + f(b)$ we obtain **Lieb–Oxford** with

Proof of the LO Inequality, part 3

$$C_{\mathrm{LO}} \leq \int_{\mathbb{R}^3} \frac{f(y)}{|y|^7} dy + D(\mu, \mu)$$

We have numerically optimized this bound over μ and ν, yielding $C_{\mathrm{LO}} \leq 1.58$.

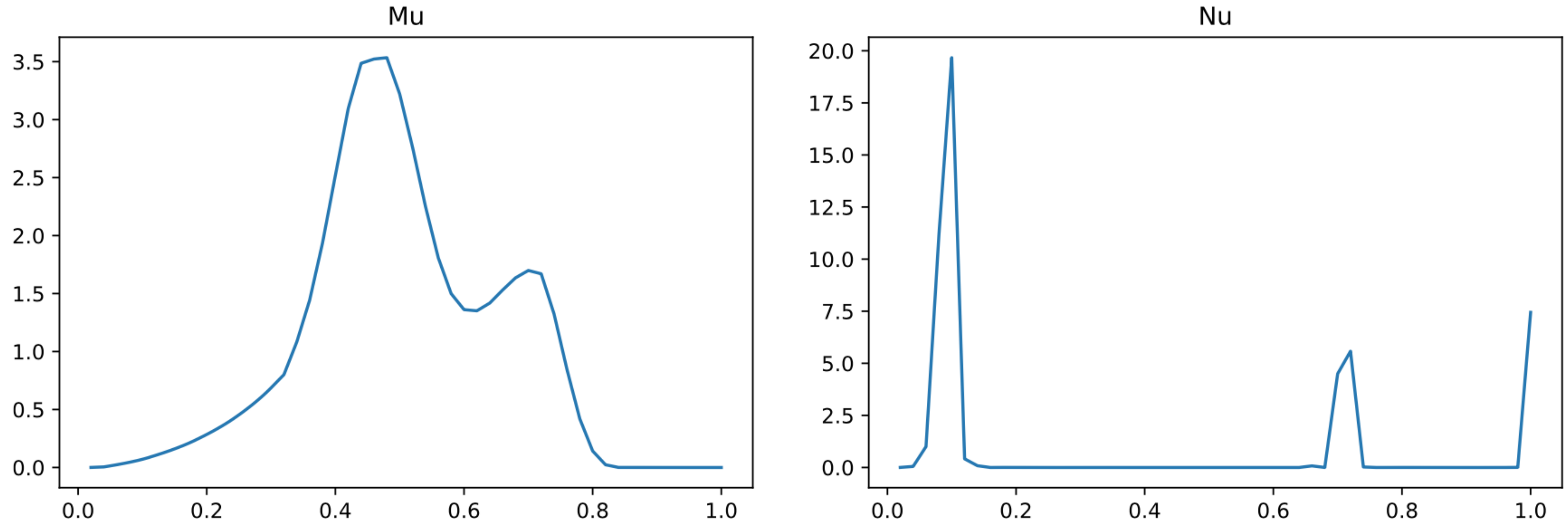
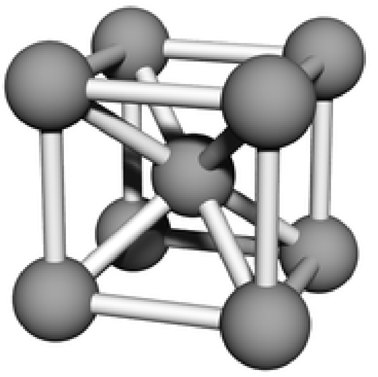


Fig. 3 Plot of the two radial measures $r \mapsto r^2\mu(r)$ (left) and $r \mapsto r^2\nu(r)$ (right) found by the BFGS algorithm for $K = 50$, $M = 100$, $R = 10$. We obtain the upper bound $c_{\mathrm{LO}} \leq 1.5765$ claimed in (79)

The Uniform Electron Gas

One can show that the limit $e_{\text{UEG}} = \lim_{\ell\to\infty} |\ell\Omega|^{-1}\mathcal{I}(\mathbb{1}_{\ell\Omega})$ exists and is independent of Ω. Clearly $C_{\text{LO}} \geq -e_{\text{UEG}}$.

It is claimed in the physics and chemistry literature that



$$e_{\text{UEG}} = \zeta_{\text{BCC}}(1) \approx -1.4442$$

where $\zeta_{\mathcal{L}}$ denotes the **Epstein Zeta Function**

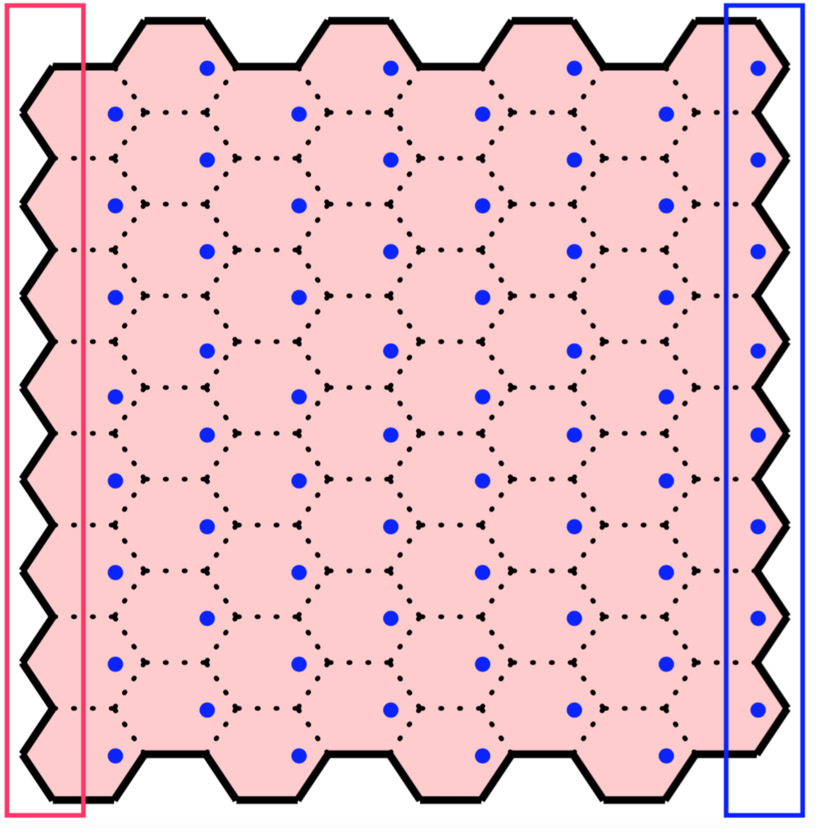
$$\zeta_{\mathcal{L}}(s) = \frac{1}{2}\sum_{x\in\mathcal{L}\setminus\{0\}} \frac{1}{|x|^s} \quad \text{for } s > 3$$

This emerges from the picture of a **Wigner crystal** in a uniformly charged background ("jellium"):

$$\min_{x_1,\dots,x_N}\left\{\sum_{1\leq i<j\leq N}\frac{1}{|x_i-x_j|} - \sum_{i=1}^{N}\int_\Omega \frac{1}{|x_i-y|}dy + \frac{1}{2}\int_{\Omega\times\Omega}\frac{1}{|x-y|}dx\,dy\right\}$$

A Floating Crystal

To obtain a **uniform density**, one can average the crystal over a unit cell:



This does **not** work, however!

Charge fluctuations at the boundary lead to a macroscopic energy shift

$$\zeta_{\mathcal{L}}(1) + \frac{2\pi}{3} \int_Q |x|^2 dx$$

where Q is the unit cell of $\mathcal{L}$. [Lewin, Lieb, 2015]

Hence it remains unclear whether $e_{\mathrm{UEG}} = e_{\mathrm{Jellium}}$ or $e_{\mathrm{UEG}} > e_{\mathrm{Jellium}}$.

Floating Crystal with Melted Surface

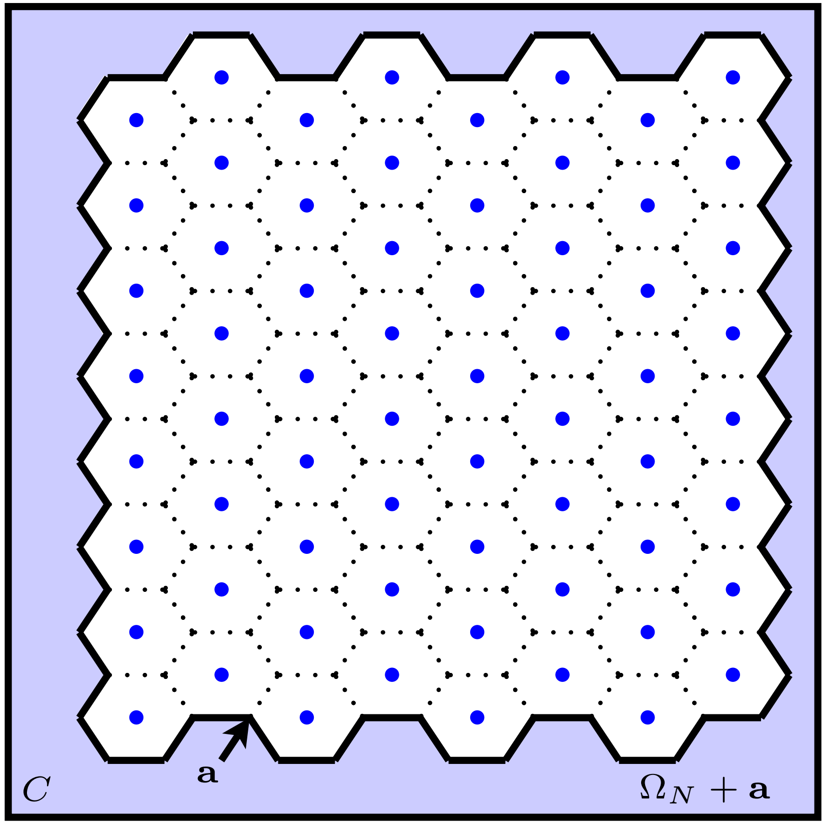
To avoid the boundary charge fluctuations, one can immerse the crystal in a **thin layer of fluid**, which fills the space close to the boundary. This leads to:

THEOREM:

$$e_{\mathrm{UEG}} = e_{\mathrm{Jellium}}$$

It remains an open problem to show that $e_{\mathrm{Jellium}} = \zeta_{\mathrm{BCC}}(1)$.

Crystallization has only been proved to occur in dimensions 1, 8 and 24.



Summary and Open Problems

- We investigate the value of the sharp constant in the **Lieb–Oxford Inequality**

$$\int_{\mathbb{R}^{3N}} \sum_{1\leq i<j\leq N} \frac{1}{|x_i - x_j|} d\mathbb{P}(x_1,\ldots,x_N) \geq D(\varrho_{\mathbb{P}},\varrho_{\mathbb{P}}) - C_{\mathrm{LO}} \int \varrho_{\mathbb{P}}^{4/3}$$

- With the aid of numerical optimization, we prove the upper bound $C_{\mathrm{LO}} \leq 1.58$
- Via the construction of a trial state for a **uniform electron gas**, we show that $C_{\mathrm{LO}} \geq -e_{\mathrm{UEG}} \geq 1.44$

Many **open problems** remain:

- What is the exact value of C_{LO}? (It has been conjectured to equal $-\zeta_{\mathrm{BCC}}(1) \approx 1.4442$.)
- (Non-)existence of optimizers?
- Improved bounds in the quantum case?