The mean-field approximation of stochastic crystals

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joint work with Éric Cancès & Salma Lahbabi

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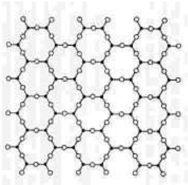
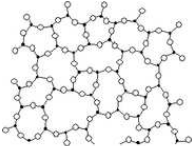
Motivation

- **Goal:** describe a crystal with random defects
  - infinitely many random classical nuclei (e.g. perturbation of a lattice)
  - infinitely many interacting quantum electrons



Crystalline Silica

- **Disordered materials are**
  - present in nature (amorphous materials, impurities, aging solids)
  - industrially made (doped semiconductors, solar cells)



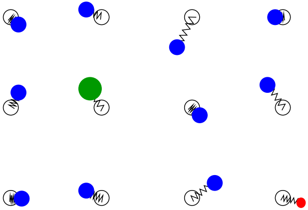
Vitreous Silica

- **What we have done:**
  - appropriate math setting for mean-field (DFT) models
  - construction of electronic state for short range interactions & Coulomb

Many open problems left!

É. Cancès, S. Lahbabi & M. L. Mean-field models for disordered crystals
J. Math. Pure Appl. **100**(2) (2013), 241–274

Nuclei: what you should have in mind



$$\mu(\omega, x) = \sum_{k \in \mathbb{Z}^3} z_k(\omega)\, \nu\big(x - k - \delta_k(\omega)\big), \qquad \nu \geq 0,\ \int_{\mathbb{R}^3} \nu = 1$$

with δ_k and z_k i.i.d. random variables

Example: $\delta_k \sim$ gaussian and $z_k \sim$ Bernouilli

Nuclei: general situation

- measure-preserving action of $\mathbb{Z}^3 \curvearrowright$ probability space $(\Omega, \mathscr{T}, \mathbb{P})$
- ergodicity: $\tau_k A = A$, $\forall k \in \mathbb{Z}^3 \Rightarrow \mathbb{P}(A) = 0$ or 1
- a fn/measure is called **stationary** when $f(\omega, x+k) = f(\tau_k \omega, x)$
- $L^p_s := \{f \in L^p(\Omega, L^p_{\rm loc}(\mathbb{R}^3)) \ : \ f \text{ is stationary}\} \simeq L^p(\Omega \times Q)$ (Q unit cell)

► **Ergodic theorem:** for all $f \in L^1_s$,

$$\lim_{n\to\infty} L^{-3} \int_{LQ} f = \mathbb{E} \int_Q f$$

in $L^1(\Omega)$ and almost-surely

Nuclei

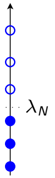
- $0 \leq \mu$ in L^p_s for some $p \geq 1$
- $\mathbb{E} \displaystyle\int_Q \mu =$ average nuclear charge per unit cell

Hartree for finitely many electrons

- N **electrons** $= N$ orthonormal functions $u_1, \dots, u_N$ in $L^2(\mathbb{R}^3) =$ Slater det

Hartree (Kohn-Sham) equation ($\mu \in L^1(\mathbb{R}^3)$)

$$\begin{cases} \left(-\Delta + V + \frac{\partial F_{xc}}{\partial \rho}\right) u_i = \lambda_i\, u_i \\ -\Delta V = 4\pi \left(\sum_{j=1}^N |u_j|^2 - \mu \right) \end{cases}$$



Ground state: $\lambda_1, \dots, \lambda_N = N$ first eigenvals of $-\Delta + V$. Min of energy

$$\sum_{j=1}^N \int_{\mathbb{R}^3} |\nabla u_j|^2 + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\left(\sum_{j=1}^N |u_j|^2 - \mu\right)(x) \left(\sum_{j=1}^N |u_j|^2 - \mu\right)(y)}{|x-y|} dx\, dy + F_{xc}\left(\sum_{j=1}^N |u_j|^2\right)$$

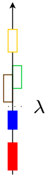
Hartree equation, density matrix $\gamma = \sum_{j=1}^N |u_j\rangle\langle u_j|$

$$\begin{cases} \gamma = \mathbb{1}\left(-\Delta + V \leq \lambda_N\right) \\ -\Delta V = 4\pi \left(\rho_\gamma - \mu\right) \end{cases}$$

with $\rho_\gamma(x) = \gamma(x, x)$

Hartree equation for infinite random crystals

$$\begin{cases} \gamma = \mathbb{1}\left(-\Delta + V \leq \lambda\right) \\ -\Delta V + m^2 V = 4\pi\left(\rho_\gamma(\omega,x) - \mu(\omega,x)\right) \\ \mathbb{E}\int_Q \rho_\gamma = \mathbb{E}\int_Q \mu \end{cases}$$



- **History:**
  - μ periodic: Catto-Le Bris-Lions (2001), Cancès-Deleurence-M.L (2008)
  - μ periodic+local perturbation: Cancès-Deleurence-M.L (2008)
  - μ random: Cancès-Lahbabi-M.L. (2013)
  - μ periodic with gap + global perturb. small in L^∞ ($m > 0$): Lahbabi (2013)

- **Plan:**
  - stationary operators γ_ω with finite local kinetic energy
  - properties of ρ_γ
  - Poisson's equation & the stationary Laplacian
  - existence thms for Coulomb ($m = 0$) and Yukawa ($m > 0$)

Stationary density matrices

- stationary density matrix = operators $(\gamma_\omega)_{\omega\in\Omega}$ with $0 \leq \gamma_\omega \leq 1$ a.s. and $T_k \gamma_\omega T_{-k} = \gamma_{\tau_k \omega}$, $T_v f = f(\cdot + v)$. Spectrum: $\sigma(\gamma) = \Sigma$ a.s.
- If $\mathbb{E}\,\mathrm{tr}(\mathbb{1}_Q \gamma \mathbb{1}_Q) < \infty$ then $\rho_\gamma \in L^1_s$ and

$$\underline{\mathrm{tr}}(\gamma) := \mathbb{E} \int_Q \rho_\gamma = \lim_{L\to\infty} \frac{\mathrm{tr}(\mathbb{1}_{LQ}\gamma\mathbb{1}_{LQ})}{L^3} = \text{average \# electrons per unit vol.}$$

- Similarly, $\underline{\mathrm{tr}}(-\Delta)\gamma$ = average kinetic energy per unit vol.

Theorem (Density)

$$\underline{\mathrm{tr}}(-\Delta)\gamma \geq \begin{cases} C\,\mathbb{E}\int_Q \rho_\gamma^{1+2/d} \geq C\left(\underline{\mathrm{tr}}(\gamma)\right)^{1+2/d} & \text{(Lieb-Thirring)} \\ \mathbb{E}\int_Q |\nabla\sqrt{\rho_\gamma}|^2 & \text{(Hoffmann-Ostenhof)} \end{cases}$$

Proof: truncate, use the known inequalities, pass to the limit using ergodic thm

Spectral projections

Theorem (Spectral projections)

Let $V \in L^2_s$ *with* $V_- \in L^{1+d/2}_s$. *Then the spectral projections*

$$\gamma = \mathbb{1}(-\Delta + V \leq \lambda)$$

are stationary density matrices satisfying

$$C\left(\underline{\mathrm{tr}}(\gamma)\right)^{1+2/d} \leq \underline{\mathrm{tr}}\,(-\Delta)\gamma \leq C\,\left(\mathbb{E}\int_Q (V-\lambda)_-^{1+d/2}\right).$$

Furthermore, the unique stationary solutions to

$$\min_{0\leq\gamma\leq 1}\left(\underline{\mathrm{tr}}(-\Delta-\lambda)\gamma + \mathbb{E}\int_Q V\rho_\gamma\right)$$

are $\gamma = \mathbb{1}(-\Delta + V \leq \lambda) + \delta$, *with* $0 \leq \delta \leq \mathbb{1}(-\Delta + V = \lambda)$.

If $V \in L^\infty_s$, *then* $\delta = 0$ *a.s.* (Bourgain-Klein '13).

Think of matrices: $\begin{cases} \min_{0\leq M\leq 1}\mathrm{tr}(AM) = -\,\mathrm{tr}\,A_- \\ \mathrm{argmin}_{0\leq M\leq 1}\mathrm{tr}(AM) = \{\mathbb{1}(A<0)+D\}_{0\leq D\leq \mathbb{1}_{\ker(A)}} \end{cases}$

Small digression: representability

Fundamental question in Density Functional Theory: what is the set of all the ρ's arising from stationary γ's with $\underline{\mathrm{tr}}(-\Delta)\gamma < \infty$?

Theorem (3D Representability)

Let $\rho \in L^3_s$ with $\nabla\sqrt{\rho} \in L^2_s$. Then there exists a stationary $0 \le \gamma \le 1$ such that $\underline{\mathrm{tr}}\,(1-\Delta)\gamma < \infty$ and $\rho = \rho_\gamma$.

Proof follows the method of Lieb (1983)

Open problem

Is $\nabla\sqrt{\rho} \in L^2_s$ and $\rho \in L^{5/3}_s$ sufficient?

Electrostatics

Open problem

For which stationary $\rho \in L^p_s$ can one solve Poisson's equation

$$-\Delta V = 4\pi\rho$$

with $V \in L^q_s$? and with finite electrostatic energy, $\mathbb{E}\int_Q |\nabla V|^2 < \infty$?

- **Necessary condition:** $\mathbb{E}\int_Q \rho = 0$ (neutral)
- It is easier to find electric field $E = -\nabla V \in L^2_s$ than V itself
  But we need to define $-\Delta + V$...

Lemma (Yukawa)

For all $\rho \in L^p_s$ and $m > 0$, there exists a unique $V \in L^p_s$ such that $(-\Delta + m^2)V = 4\pi\rho$.

Reason: $V(x) = \int_{\mathbb{R}^3} \underbrace{\frac{e^{-m|x-y|}}{|x-y|}}_{\in \ell^1(L^1)} \rho(\omega, y)\, dy$

Stationary Laplacian

Let $(-\Delta)_s$ be the Friedrichs extension in L^2_s of the operator

$$\begin{cases} D(A) = L^2_s \cap L^2(\Omega, C^2(\mathbb{R}^3)) \subset L^2_s \\ Af = -\Delta f, \quad \forall f \in D(A). \end{cases}$$

Laplacian in x on $\Omega \times Q$ with "stationary boundary conditions" , e.g. $f(\tau_1\omega, 0) = f(\omega, 1)\ \forall\omega$, in 1D

- **Simple properties/examples:**
  - 0 is a simple eigenvalue with eigenfn $f \equiv 1$ (ergodicity);
  - $\sigma(-\Delta)_s$ contains $\sigma(-\Delta)_{\rm per}$;
  - If Ω is finite, then $\sigma(-\Delta)_s$ is discrete;
  - If $\Omega = S^{\mathbb{Z}}$ and τ_k is the shift, then $\sigma(-\Delta)_s = [0, \infty)$
  - If $\Omega = [0, 1]$ and $\tau_k(\omega) = \omega + ak \pmod 1$, $a \in \mathbb{R} \setminus \mathbb{Q}$, then $\sigma_p(-\Delta_s)$ is dense in [0,1]

$\rightsquigarrow$ difficulty to solve $-\Delta_s V = 4\pi\rho$. $V \in L^2_s$ requires $\rho \in D(-\Delta)_s$

Open problem

Understand better the spectral properties of $(-\Delta)_s$

Energy: existence theorem

For $\rho \in L^1_s$, we define the Yukawa/Coulomb interaction energy per unit vol. as

$$D_m(\rho) := \frac{1}{8\pi}\mathbb{E}\int_Q |\nabla V_m|^2 \quad \text{with} \quad (-\Delta + m^2)V_m = 4\pi\rho$$

$$D_0(\rho) := \lim_{m\to 0} D_m(\rho)$$

and the total energy per unit vol. as

$$\mathcal{E}_m(\gamma) := \underline{\mathrm{tr}}(-\Delta)\gamma + D_m(\rho_\gamma - \mu)$$

Theorem (Existence of minimizers)

For $\mu \in L^1_s$ and $m \geq 0$, the energy has at least one minimizer γ on the set

$$\left\{0 \leq \gamma \leq 1 \text{ stationary } : \ \underline{\mathrm{tr}}(-\Delta)\gamma < \infty,\ D_m(\rho_\gamma - \mu) < \infty,\ \underline{\mathrm{tr}}(\gamma) = \mathbb{E}\int_Q \mu\right\}$$

(when not empty!). All the minimizers share the same density ρ_γ.

Proof: convexity + weak topology

Equation: existence theorem

- **Main questions:**
  - have we solved the original Hartree equation?
  - are we able to define the (one-particle) mean-field Hamiltonian $-\Delta + V$?

Theorem (Hartree equation, Yukawa case)

Let $\mu \in L^2_s \cap L^{5/2}_s(L^1)$ and $m > 0$. Then $V_m \in L^2_s$, $(V_m)_- \in L^{5/2}_s$ and $-\Delta + V$ is a.s. essentially self-adjoint.

There exists $\lambda \in \mathbb{R}$ such that the minimizers are all of the form

$$\gamma = \mathbb{1}(-\Delta + V \leq \lambda) + \delta, \qquad \text{with} \quad 0 \leq \delta \leq \mathbb{1}(-\Delta + V = \lambda).$$

If furthermore $\mu \in L^\infty_s$, then $\rho_\gamma, V \in L^\infty_s$, $\delta \equiv 0$ and the minimizer is unique.

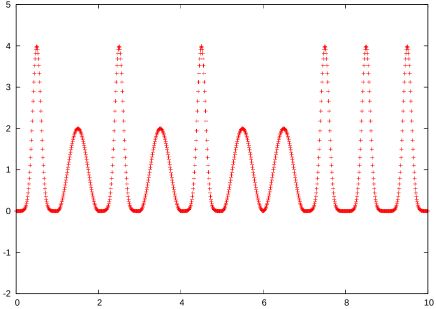
Open questions:

- Is there enough screening in the Coulomb case? $\rightsquigarrow V$
- What are the properties of $-\Delta + V$ (even in short range case)?

Anderson Localization? Numerics

1D with Bernouilli ($p = 0.5$):

$$\mu = \sum_{k\in\mathbb{Z}} q_k(\omega)\frac{1}{\sqrt{0.02\pi}}e^{-\frac{(x-k-1/2)^2}{0.02}} + (1-q_k(\omega))(1-\cos(2\pi(x-k)))$$

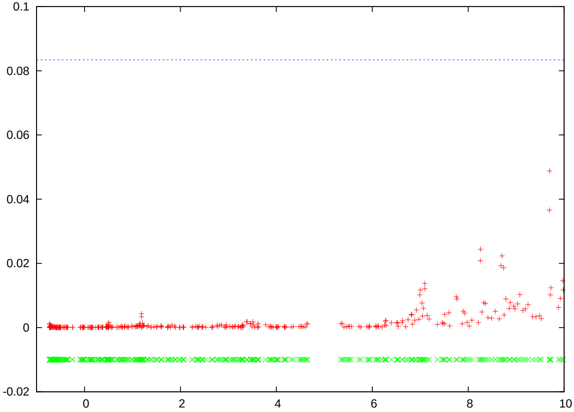


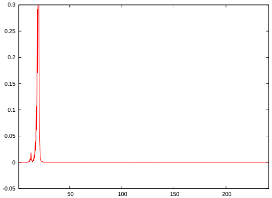
One realization for μ

S. Lahbabi, *PhD thesis*, Univ. Cergy-Pontoise, 2013.

Anderson Localization? Linear case

Box of size $L = 240$ with periodic b.c., 30×240 Fourier modes, Yukawa ($m = 1$)
Drop interaction: $V = -e^{-|x|} * \mu$



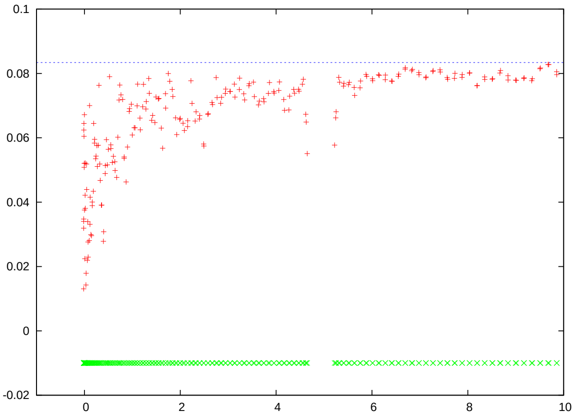


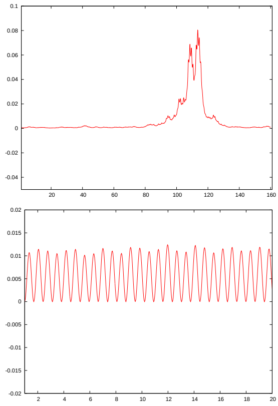
1st eigenfn

Variance: $\frac{1}{L^2} \inf_{0 \le \ell \le L} \int_\ell^{\ell+L} x^2 |u(x)|^2 \, dx - \left(\int_\ell^{\ell+L} x |u(x)|^2 \, dx \right)^2 \in [0, \frac{1}{12}]$

Anderson Localization? Nonlinear case

Box of size $L = 160$ with periodic b.c., 30×160 Fourier modes, Yukawa ($m = 1$)
Self-consistent potential: $V = e^{-|x|} * (\rho_\gamma - \mu)$, 1 e^- per unit cell





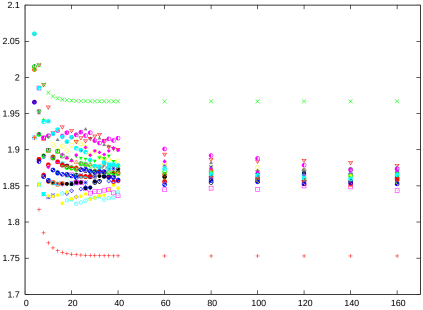
1st and last eigenfns

Variance: $\frac{1}{L^2} \inf_{0 \le \ell \le L} \int_\ell^{\ell+L} x^2 |u(x)|^2\, dx - \left(\int_\ell^{\ell+L} x |u(x)|^2\, dx \right)^2 \in [0, \frac{1}{12}]$

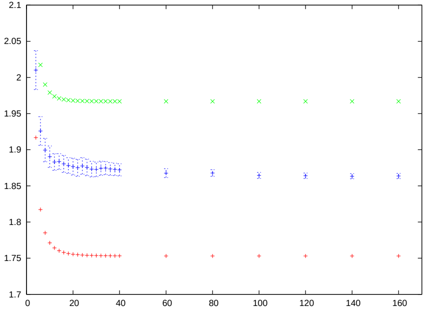
Thermodynamic limit in the short range case

Theorem (Thermodynamic limit, Yukawa)

The Yukawa model ($m > 0$) is the thermodynamic limit, in $L^1(\Omega)$, of the corresponding supercell Hartree problem.



a.s. convergence



$L^1(\Omega)$ convergence

Summary

- A nonlinear model for an infinite system of interacting quantum particles
- Simple enough to investigate the effect of interactions
- For Coulomb, screening is crucial, but not well understood yet
- Localization need further investigation, even in short range case

▶ **I have not talked about**

- the true N-body Schrödinger problem: existence of thermodynamic limit known for random nuclei (Blanc & M.L. '12), but no info on limit
- the small p expansion of the Bernouilli nonlinear Hartree model, in gapped case (Klopp '95, Lahbabi '13)