Crystallization in classical particle systems

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– lecture 2 –

Summary (Mol. dyn.):

Hamiltonian dyn. $\rightsquigarrow$ Liouville eq. $\rightsquigarrow$ all $\rho(x,p) = f(H(x,p))$ invariant

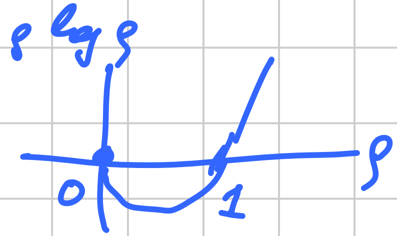
Langevin eq. $\rightsquigarrow$ Fokker-Planck eq. $\rightsquigarrow$ unique invariant $\rho = Z e^{-\beta H}$, global attractor

II. Statistical mech.

Free en. of a system with phase space density $\rho(x,p,t)$, ≥ 0, $\int \rho = 1$

$(x,p) \in \mathbb{R}^d$, $H(x,p)$ Hamiltonian:

$$F[\rho] = \underbrace{\int_{\mathbb{R}^{2d}} H \cdot \rho}_{\text{en.}} + T \underbrace{\int_{\mathbb{R}^{2d}} \rho \log \rho}_{= -\text{entropy} = -\eta}$$



Well defined as fctnal $L^1_+(\mathbb{R}^{2d}) \to \mathbb{R} \cup \{+\infty\}$ if H meas., bdd below

Proposition a) $-\eta$ is not a Lyapunov fctn of Fokker-Planck, i.e. entropy can temporarily decrease, but F is a Lyapunov fctn. *)

b) Unique minimizer of F s/to $\int \rho = 1$ is the Gibbs measure

$$\rho = Z e^{-\beta H}, \quad Z = \left(\int e^{-\beta H}\right)^{-1}$$

*) In my oral presentation of a) I confused $-\eta$ with F. Thanks to the student who corrected me. The fact that $-\eta$ can temporarily increase is in contrast to Boltzmann's equation, where $-\eta$ is a Lyapunov fctn.
I have included a proof of a) below.

<u>Pf of b)</u> $\left.\frac{d}{d\varepsilon}\right|_{\varepsilon=0} F[\rho+\varepsilon\varphi] = \int H\varphi + T\int (\log\rho \cancel{-1})\varphi = 0 \quad \forall \varphi ; \int\varphi = 0$

$=0$

$$\Rightarrow \quad H + T\log\rho = \text{Const}$$

$$\Rightarrow \quad \log\rho = \frac{\text{const} - H}{T}$$

$$\Rightarrow \quad \rho = e^{\frac{c}{T}} \cdot e^{-\frac{1}{T}H} \qquad \Big|\ \beta = \frac{1}{T}$$

$$\int\rho = 1 \Rightarrow e^{\frac{c}{T}} = Z \qquad \checkmark$$

Moral of the tale:

- Free en. minimization is a useful approx. of long time dynamics in the sense that minimizing sequences have the same limit as the dynamics

- Note however that off equilibrium the relationship between free en. & Langevin dynamics is not as simple as the rel'ship between entropy & the diffusion eq. Langevin is <u>not</u> a gradient flow of free en. with respect to a suitable metric (but the diffusion eq. is a grad. flow of entropy w.r.to the Wasserstein metric, cf. Jordan / Kinderlehrer / Otto).

<u>Pf of a)</u>

$$\frac{d}{dt}\frac{1}{\beta}\int \rho\log\rho = \frac{1}{\beta}\int(\log\rho - 1)\rho_t \underset{\uparrow\ \int\rho \text{ conserved}}{=} \frac{1}{\beta}\int \log\rho\,\rho_t$$

$$v = \begin{pmatrix}\partial H/\partial p \\ -\partial H/\partial x\end{pmatrix} \qquad \underset{\uparrow}{=} \frac{1}{\beta}\int \log\rho\cdot\left(-\mathrm{div}(v\rho) + \mathrm{div}_p\left(\gamma M^{-1}p\,\rho + \frac{\sigma^2}{2}\nabla_p\rho\right)\right)$$

$$\underset{\uparrow\ \text{int. by parts}}{=} \frac{1}{\beta}\underbrace{\int \nabla\rho\cdot v}_{=\int \mathrm{div}(\rho v) = 0} - \frac{1}{\beta}\int \nabla_p\rho\cdot\gamma M^{-1}p - \frac{1}{\beta}\int\frac{\sigma^2}{2}\frac{|\nabla_p\rho|^2}{\rho}$$

$$\underset{\uparrow\ \text{int. by parts}}{=} \frac{\gamma}{\beta}\,\mathrm{tr}M^{-1}\int\rho - \frac{\sigma^2}{2\beta}\int\frac{|\nabla_p\rho|^2}{\rho}$$

... can be positive or negative!

$$\frac{d}{dt}\int H\rho = \int H\left(-\mathrm{div}(v\rho) + \mathrm{div}_p\left(\gamma M^{-1}p\,\rho + \frac{\sigma^2}{2}\nabla_p\rho\right)\right)$$

int. by parts

$$= \int(\underbrace{\nabla H\cdot v}_{=0})\rho - \int(\nabla_p H)\rho\cdot\gamma M^{-1}p - \frac{\sigma^2}{2}\underbrace{\int \nabla_p H\cdot\nabla_p\rho}_{= -\int \mathrm{div}(\nabla_p H)\cdot\rho}$$

$\nabla_p H = M^{-1}p$

$$= -\gamma\int |M^{-1}p|^2\rho + \frac{\sigma^2}{2}\operatorname{tr}M^{-1}\int\rho$$

Hence the time derivative of free energy is

$$\frac{d}{dt}F[\rho] = \left(\frac{\gamma}{\beta}+\frac{\sigma^2}{2}\right)\operatorname{tr}M^{-1}\int\rho - \gamma\int|M^{-1}p|^2\rho - \frac{\sigma^2}{2\beta}\int\frac{|\nabla_p\rho|^2}{\rho}.$$

This is ≤ 0, by Heisenberg uncertainty: Write $\frac{|\nabla_p\rho|^2}{\rho} = 4|\nabla\sqrt{\rho}|^2$ and use the Heisenb. unc. inequality

$$\int|\sqrt{\rho}|^2 = -2\int(p_j\sqrt{\rho})\left(\frac{\partial}{\partial p_j}\sqrt{\rho}\right) \leq 2\,\|p_j\sqrt{\rho}\|_{L^2}\,\left\|\frac{\partial}{\partial p_j}\sqrt{\rho}\right\|_{L^2}$$

$$\Rightarrow \int\frac{2}{\beta}\cdot\frac{1}{m_j}\int|\sqrt{\rho}|^2 \leq 2\cdot\frac{1}{m_j}\|p_j\sqrt{\rho}\|_{L^2}\cdot\frac{2}{\beta}\left\|\frac{\partial}{\partial p_j}\sqrt{\rho}\right\|_{L^2}$$

$$\underset{2ab\leq a^2+b^2}{\leq} \frac{1}{m_j^2}\int p_j^2\rho + \left(\frac{2}{\beta}\right)^2\int\left|\frac{\partial}{\partial p_j}\sqrt{\rho}\right|^2.$$

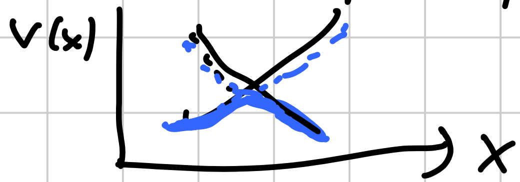
Using the fluctuation-dissipation rel. $\frac{\sigma^2}{2} = \frac{\gamma}{\beta}$ and summing over j shows $\frac{d}{dt}F \leq 0$.

=

Ref's on QM → Liouville: Ambrosio, GF, Giannoulis 2010 Comm. PDE
Ambr., Figalli, GF, Giannoulis, Paul 2011 CPAM

Unique flow on L^1, rigorous limit of Schrödinger eq.

ab-initio ∇V is not Lipschitz, but only BV



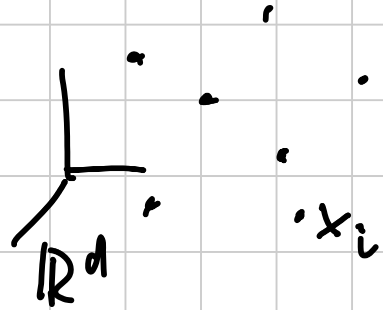
$V(x) = \min \operatorname{spec} H_{ee}(x) \rightsquigarrow$ e-value crossings

No ref. on QED / "open quantum dyn." → Fokker-Planck
(the Langevin thermostat is a semi-empirical atomistic model, just as the thermodynamic parts of continuum models are semi-empir.)

III. Energy minimization

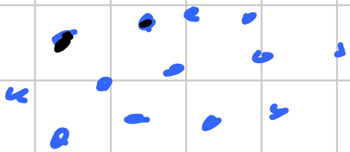
Minimize $E(x_1, \dots, x_N)$

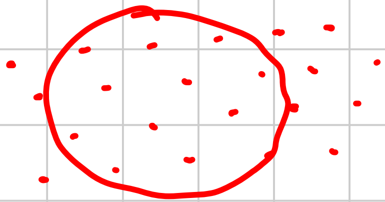
$\mathcal{S}_N = \{x_1, \dots, x_N\} \subset \mathbb{R}^d$



1) Understand why minimizers often exhibit crystalline order

(*) $\mathcal{S}_N \approx$ subset of $\mathcal{L} + a$, $\mathcal{L} = A\mathbb{Z}^d$, $A \in M^{d\times d}$, $a \in \mathbb{R}^d$





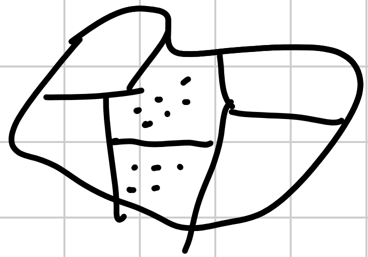
2) Understand why "region occupied by atoms" approaches special shapes as $N \to \infty$

a) Most basic math. form of (*): smooth subsets of lattice have same en. per particle as $N \to \infty$

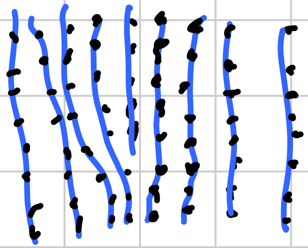
$$\lim_{N\to\infty} \overbrace{\frac{\inf_{\mathcal{S}_N} E}{\#\mathcal{S}_N}}^{e_N} = \lim_{R\to\infty} \frac{E(\mathcal{L} \cap B_R)}{\# \mathcal{L} \cap B_R} \qquad (**)$$

- doesn't give "rigidity"

fracture

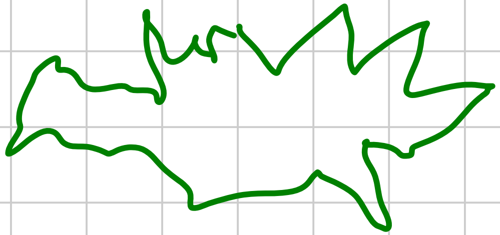


polycrystal



dislocation

- doesn't give shape :



heuristics

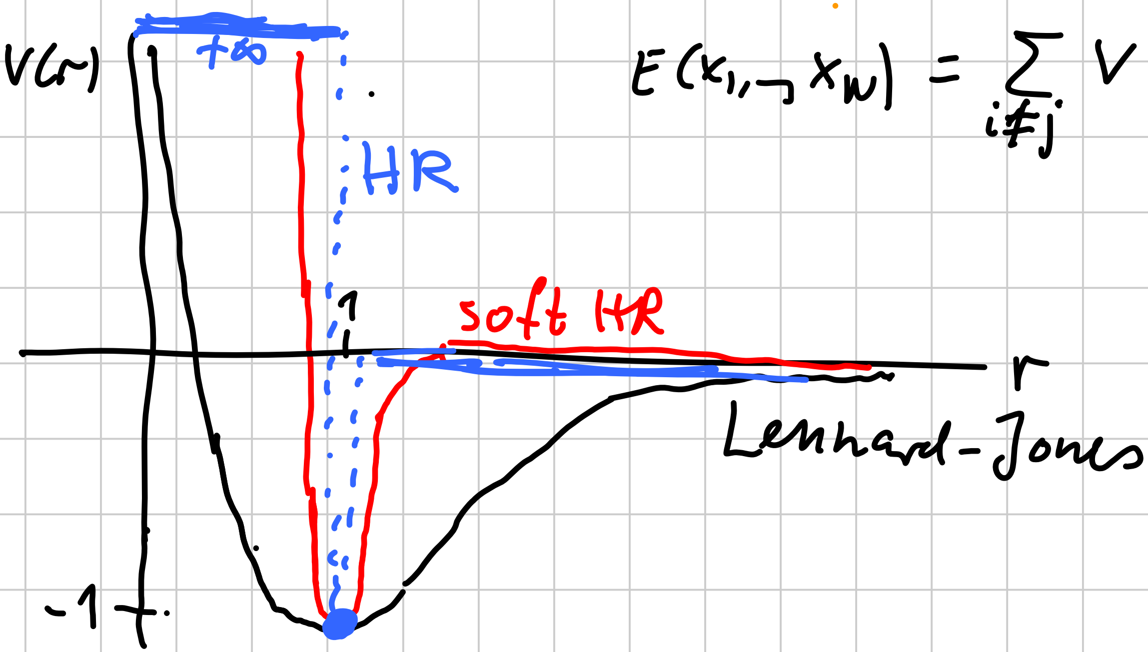
$$E(x_1,\dots,x_N) \approx \underbrace{\int_\Omega \text{en. properties}}_{N\cdot \lim_{N\to\infty} e_N} + \underbrace{\int_{\partial\Omega} \text{surface en}}_{O(N^{\frac{d-1}{d}})} + \dots$$

⇝ crystalline order ⇝ shape

5) Best possible form of (*): Minimizers φ_N are subsets of some $\mathcal{L}+a$.

1. Soft version of Heitmann-Radin model 2D

2. Original — // — 2D, 3D



$$E(x_1, \dots, x_N) = \sum_{i \neq j} V(|x_i - x_j|)$$

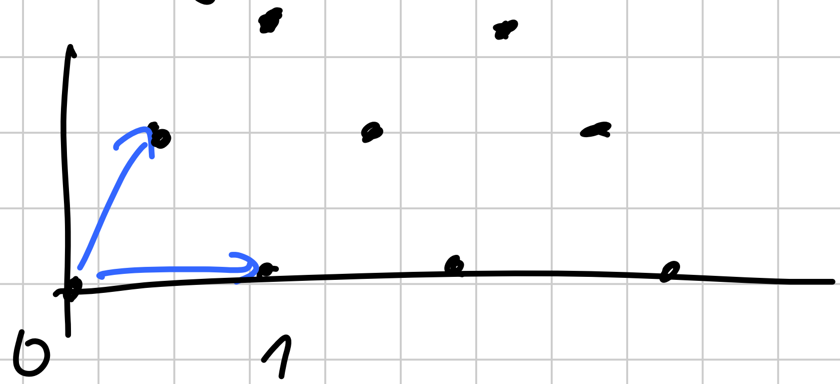
Soft HR pot.: $V \begin{cases} = +\infty, & r \leq 1-\varepsilon \\ = 0, & r \geq 1+\varepsilon \\ \text{cts}, & r \in (1-\varepsilon, 1+\varepsilon) \\ \text{unique min. at } r=1, & V(1) = -1 \end{cases}$

HR pot.: $V = \begin{cases} +\infty, & r < 1 \\ -1, & r = 1 \\ 0, & r > 1 \end{cases}$

Joint work with Au Yeung, GF, B. Schmidt Calc Var PDE ~2011

<u>Proposition:</u> ε suff'ly small $\Rightarrow$ (**) holds with

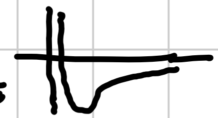
$$\mathcal{L} = \text{triangular lattice } \left\{ i\begin{pmatrix}1\\0\end{pmatrix} + j\begin{pmatrix}1/2\\ \sqrt{3}/2\end{pmatrix} : i,j\in\mathbb{Z}\right\}$$



Pf:
$$-6N \leq E(x_1, \ldots, x_N) \leq -6N + O(N^{1/2})$$

$\uparrow$ 2D: a point has maximally 6 nbrs of distance 1 if all mutual distances ≥ 1 "kissing no"

$\uparrow$ trial state: ball intersected with triangular lattice

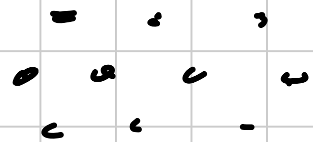
Theil, 2005: (**) also holds for potentials which are allowed to be finite in $(0,1)$, and <0 in $(1,\infty)$, with $\mathcal{L}$ = triang. lattice with <u>renormalized</u> lattice constant 

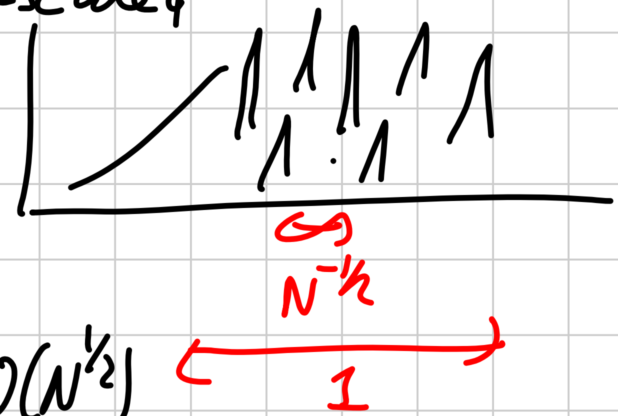
Theorems on shape

Au Yeung, GF, Schmidt

Eulerian viewpt

$\{x_1, \dots, x_N\}$. $\leftrightarrow$ empirical measure μ_N, rescaled





1) Existence of shape

Spse $E(\{x_1^{(N)}, \dots, x_N^{(N)}\}) \leq N \cdot e_\infty + O(N^{1/2})$

$e_\infty = \lim_{N\to\infty} e_N$ asymptotic en. per particle. Spse $\{x_1^{(N)}, \dots, x_N^{(N)}\}$ connected.

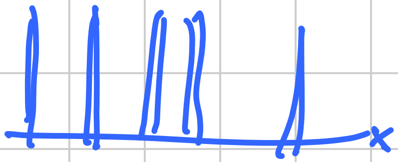
automatic for minimisers

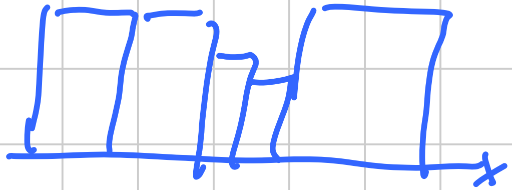
Then (up to transl.)

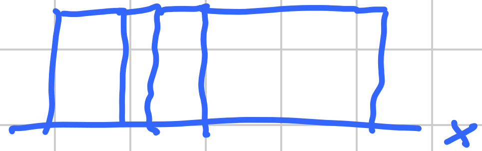
$$\mu_N = \frac{1}{N} \sum \delta_{\frac{x_i^{(N)}}{\sqrt{N}}} \xrightarrow[\text{subs.}]{*} c_0 \chi_\Omega$$

for some set Ω of finite perimeter, & $c_0 = \frac{2}{\sqrt{3}}$ = dens. of particles in triang. lattice.

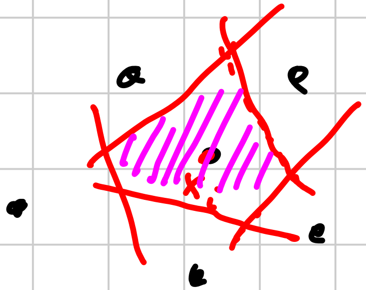
Pf $\quad \frac{1}{N}\sum_i \delta_{\frac{x_i}{\sqrt{N}}} \underset{\text{weak}*}{\approx} \frac{1}{N}\sum_i \frac{\chi_{\frac{V(x_i)}{\sqrt{N}}}}{\mathrm{vol}\left(\frac{V(x_i)}{\sqrt{N}}\right)} \underset{L^1}{\approx} \frac{1}{N}\sum_i \frac{\chi_{\frac{V(x_i)}{\sqrt{N}}}}{\mathrm{vol}\left(\frac{h(x_i)}{\sqrt{N}}\right)}$



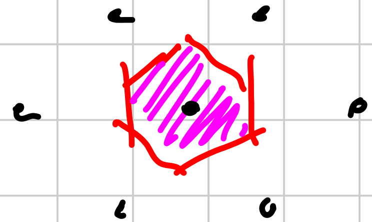




$V(x_i)$ Voronoi cell of x_i $= \{ y \in \mathbb{R}^2 : |y - x_i| \leq |y - x_j| \ \forall j \neq i \}$



$V(x_i)$



$h(x_i)$ Voronoi cell of pt in lattice

error $= \cancel{\frac{1}{N}} \sum_i \chi_{\frac{V(x_i)}{\sqrt{N}}} \underbrace{\left(\frac{1}{\mathrm{vol}\left(\frac{V(x_i)}{\sqrt{N}}\right)} - \frac{1}{\mathrm{vol}\left(\frac{h(x_i)}{\sqrt{N}}\right)} \right)}_{= \cancel{N} \underbrace{\left(\frac{1}{\mathrm{vol}\, V(x_i)} - \frac{1}{\mathrm{vol}\, h} \right)}_{=: \Phi(x_i) \text{ volume excess function}}}$

$\|\text{error}\|_{L^1} \leq \frac{1}{N} \cdot \sum_i \phi(x_i) = O\left(\frac{1}{\sqrt{N}}\right).$

$\sum_i |\phi(x_i)| \leq O(\sqrt{N})$ controlled by energy

2) Unique and explicit asymptotic ("Wulff") shape

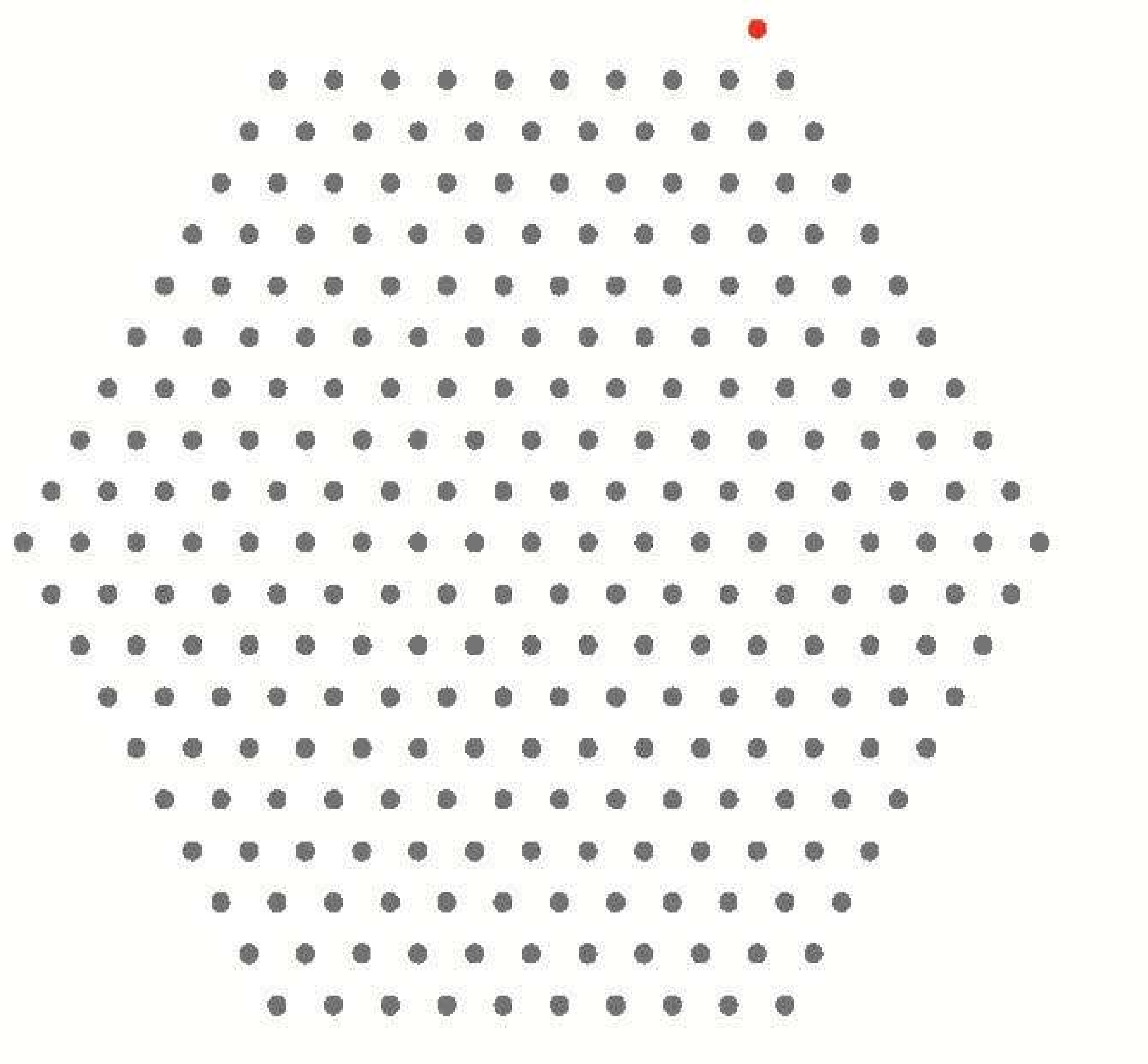
If $\{x_1^{(N)}, \dots, x_N^{(N)}\}$ seq. of minimizers, and V = HR model, then up to translation

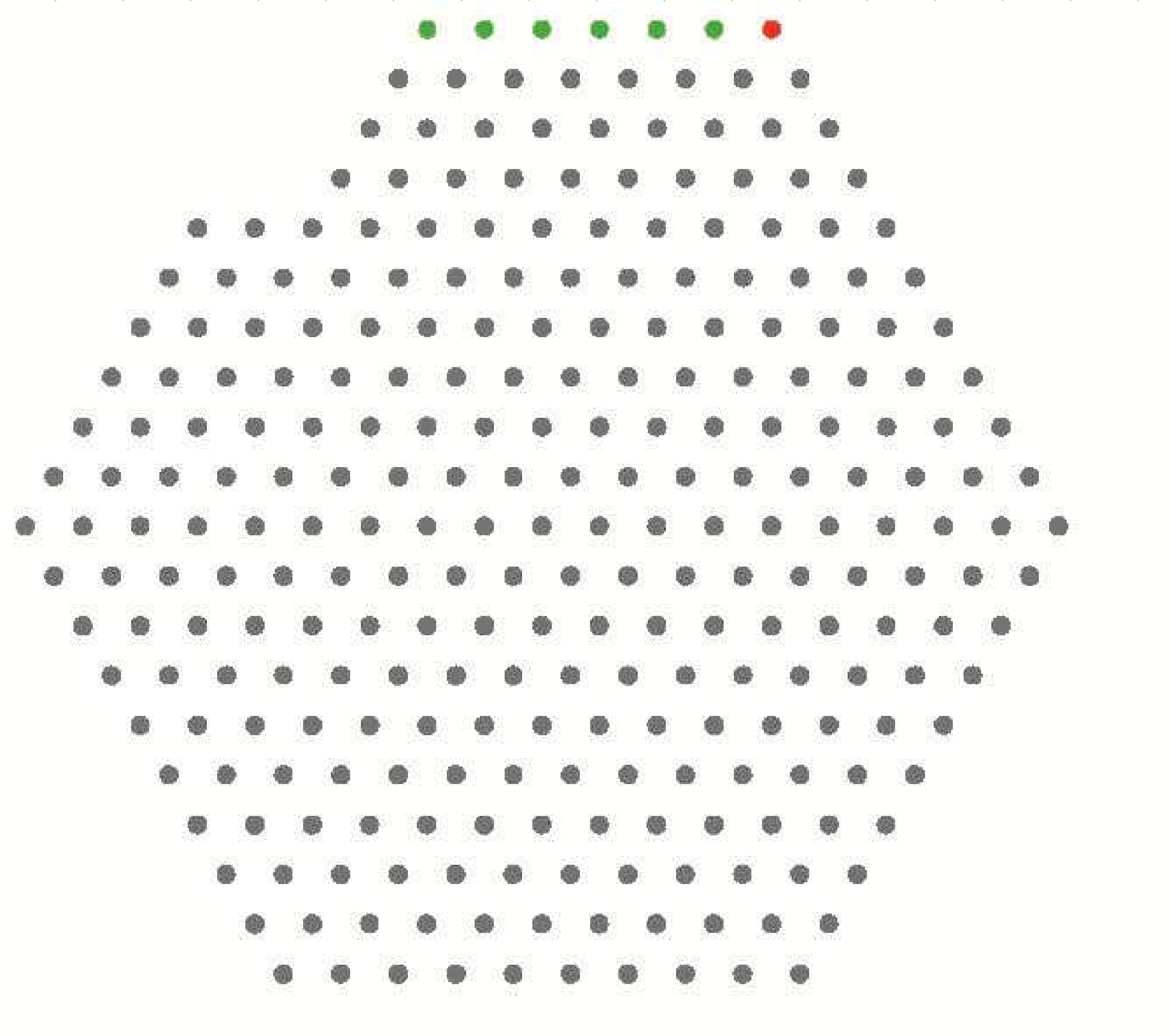
$$\frac{1}{N}\sum_i \delta_{\frac{x_i}{\sqrt{N}}} \xrightarrow{*} c_0 \chi_\Omega$$

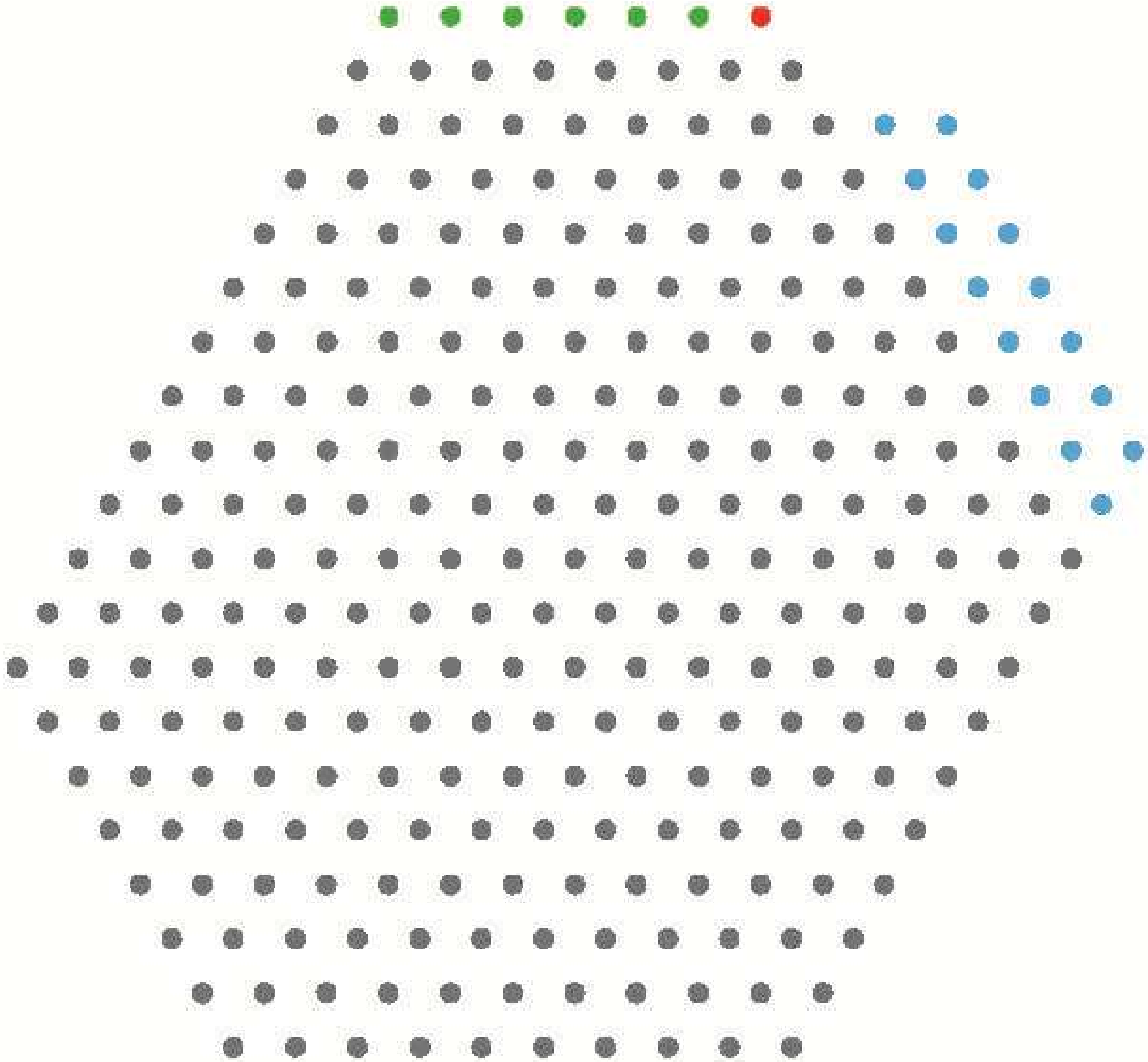
Ω = regular hexagon, $c_0 = \frac{2}{\sqrt{3}}$.

Remark: The uniqueness of the shape is far from true on the atomistic level. Here are 3 examples of exact minimizers of the HR energy with 272 particles.

(pictures by Au Yeung & GF)







Recent work of B. Schmidt shows that the amount of nonuniqueness grows at the sharp rate $O(N^{3/4})$ as $N \to \infty$, as opposed to the naïvely expected $O(N^{1/2})$.