Crystallization in classical particle systems

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– lecture 1 –

Themes

- Understand why atoms / molecules often self-assemble into crystalline order & special shapes
- interplay discrete vs continuum theories / variables

Models

0. Quantum dynamics
I. Molecular dynamics
II. Statistical mech.
III. Potential en. minimization

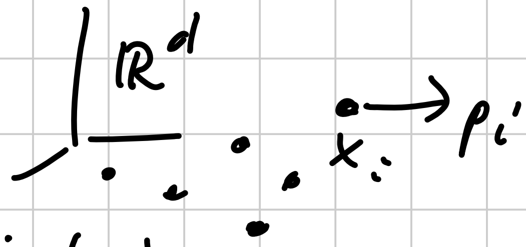
small el./nuclei mass ratio

long time

low temperature

I. Molecular dynamics

a) Hamiltonian eq's.



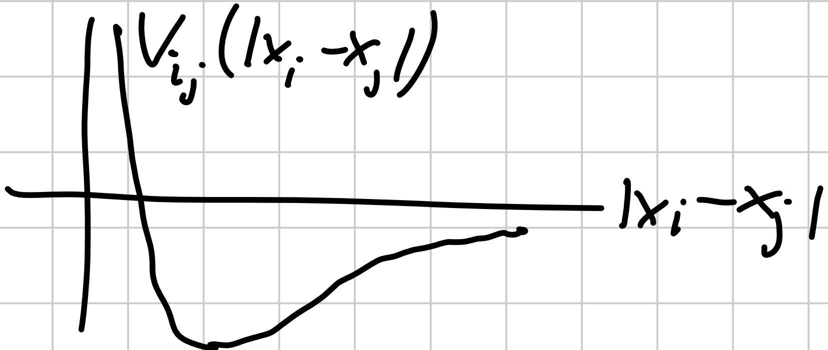
$x_i, p_i \in \mathbb{R}^d$ positions, momenta, $i = 1, \dots, N$

$m_i > 0$ masses

$$H(x, p) = \sum_{i=1}^{N} \frac{|p_i|^2}{2m_i} + V(x_1, \dots, x_N) \quad \text{Hamiltonian}$$

$$\boxed{\begin{aligned} \dot{x}_i &= \frac{1}{m_i} p_i \\ \dot{p}_i &= -\nabla_{x_i} V \end{aligned}}$$

$$\Leftrightarrow \boxed{\begin{aligned} \dot{x}_i &= \nabla_{p_i} H \\ \dot{p}_i &= -\nabla_{x_i} H \end{aligned}}$$



e.g. $V_{ij}(r) = r^{-12} - r^{-6}$
Lennard-Jones

$$V = \sum_{i<j} V_{ij}(|x_i - x_j|)$$

Energy is conserved: $\frac{d}{dt} H(x(t), p(t)) \equiv 0$ along sol'ns

General Q: Conserve energy or minimize energy?

A: closed system → conserve ⇝ Hamilton eqs.
hyperbolic PDE's
transport eq's

Open sys. ⇝ (often) minimize ⇝ finite temp. MD
(parabolic?)

if environment suff'ly complex / "random"

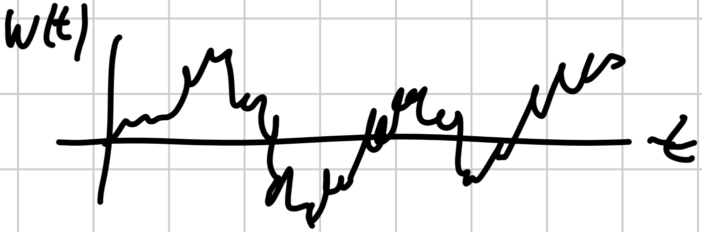
Langevin equation

$$\boxed{\begin{aligned} \dot x_i &= \frac{1}{m_i} p_i \\ \dot p_i &= -\nabla_x V - \underbrace{\gamma \dot x_i}_{\text{damping}} + \underbrace{\sigma \dot W(t)}_{\text{white noise}} \end{aligned}}$$

$\gamma > 0$, $\sigma > 0$, $\boxed{\sigma^2 = \frac{2\gamma}{\beta}}$ fluctuation-dissipation relation

$\beta = \frac{1}{T}$ inverse temperature

$W(t)$ = Brownian motion



This eq. makes rigorous sense without elaborate theories of stochastic processes. $t \mapsto W(t) \in C^{0,\alpha}$ $\forall \alpha < \frac{1}{2}$ (Hölder) $\Rightarrow W \in L^1_{loc} \Rightarrow \dot W$ well-defined as a standard weak derivative.

(Noise additive → don't need Itô calculus)

(If noise multiplicative, e.g. Portfolio models $\dot z = (a + \alpha \dot W) z$ → need Itô)

Rigorous notion of sol'n to $\begin{cases} \dot{Z} = v(Z) + \tilde{\sigma}\dot{\tilde{W}}, & \tilde{\sigma} \in M^{n\times m}, \quad (*) \\ Z(0) = Z_0 \end{cases}$

$\tilde{W}$ m-dim Brownian motion, v smooth VF

$\{Z(t)\}_{t\geq 0}$ collection of random var's in $\mathbb{R}^n$ s.th.

(i) $Z(0) = Z_0$

(ii) $t \to Z(t)$ cts

(iii) $Z(t) - Z(s) = \int_s^t v(Z(\tau))d\tau + \tilde{\sigma}(\tilde{W}(t) - \tilde{W}(s)) \quad \forall t > s.$

Def. (Brownian motion) $\{W(t)\}_{t\geq 0}$ random var's

- $W(0) = 0$
- $t \mapsto W(t)$ cts
- $W(t) - W(s)$ indep of $W(s)$ $\forall t > s$
- $W(t) - W(s)$ normally distr. w/ mean 0 & var. $t-s$, ie

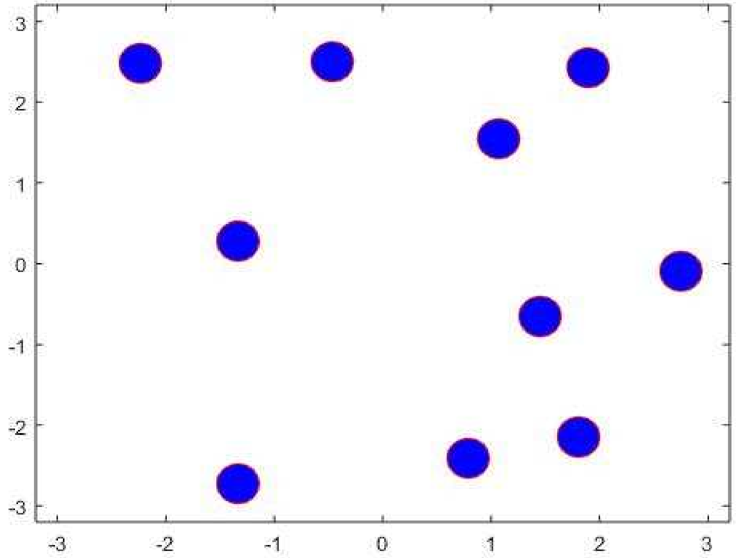
$$\mathbb{P}(W(t) - W(s) \in A) = \int_A \frac{e^{-\frac{x^2}{2(t-s)}}}{(2\pi(t-s))^{m/2}}\,dx$$

Ref: P. Mörters, book
(elementary construction as continuum limit of random walk)

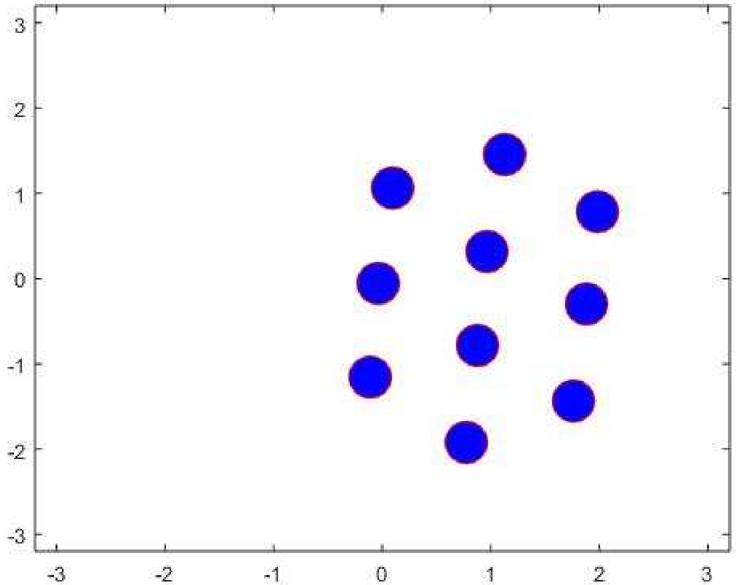
Simulation

Langevin equation, $V(r)=r^{-12} - r^{-6}$, $\beta=10^5$, $\gamma=0.06$

initial state (random)



crystallized state



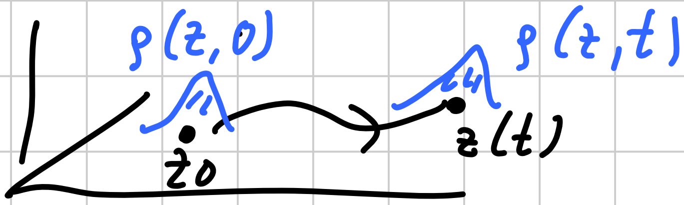
How to understand this?

$\to$ move to "densities", but no coarse-graining

$\updownarrow$

"ensembles of initial cdn's"

Ham. $\rightsquigarrow$ Liouville eq.



$\rho(z,t)$ = push-forward of $\rho(z,0)$ under flow $\Phi(z_0,t)$ = sol'n to (Ham.) $\dot z = v(z),\ z(0)=z_0$

$= \rho(\Phi^{-1}(z,t), 0)$

$\Leftrightarrow\ \rho(\Phi(z,t),t) = \rho(z,0)$

$\Rightarrow\ 0 = \frac{d}{dt}\rho(\Phi(z,t),t) = \nabla\rho\cdot\underbrace{\frac{d}{dt}\Phi(z,t)}_{=v(z)} + \frac{\partial\rho}{\partial t}$

$\Rightarrow\ \boxed{\frac{\partial\rho}{\partial t} = -v\cdot\nabla\rho}$ Liouville eq. $\quad v=\begin{pmatrix}\frac{\partial H}{\partial p}\\ -\frac{\partial H}{\partial x}\end{pmatrix}$

$\Leftrightarrow$ $\boxed{\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho v) = 0}$ $\operatorname{div}_{x,p} v = \operatorname{tr} \frac{\partial^2 H}{\partial x \partial p} - \operatorname{tr} \frac{\partial^2 H}{\partial p \partial x} = 0.$

Liouville eq., divergence form.

Energy conservation for Hamilton's eq's $\rightsquigarrow$ all densities $\rho(x,p) = f(H(x,p))$ are invariant under Liouville eq.

Langevin $\rightsquigarrow$ Fokker-Planck eq.

Use general fact from stochastic analysis ($\rightsquigarrow$ lecture notes, G. Pavliotis):

$$\dot{z} = V(z) + \tilde{\sigma}\, \dot{W}, \qquad \mathbb{P}(z(t) \in A) = \int_A \rho(z,t)\, dz$$

$$\Rightarrow \quad \frac{\partial \rho}{\partial t} + \operatorname{div}(\rho v) = \frac{1}{2} \tilde{\sigma}\tilde{\sigma}^T \bullet D^2 \rho$$

Ex. 1 $\quad v = 0, \; \tilde{\sigma} = \sigma I \Rightarrow \frac{\partial \rho}{\partial t} = \frac{1}{2}\sigma^2 \Delta \rho \quad$ heat eq.

Ex. 2 $\quad v = \begin{pmatrix} \partial H / \partial p \\ -\partial H / \partial x \end{pmatrix} - \begin{pmatrix} 0 \\ \gamma M^{-1} p \end{pmatrix} \qquad M = \begin{pmatrix} m_1 & & \\ & \ddots & \\ & & m_N \end{pmatrix}$

$$\tilde{\sigma} = \begin{pmatrix} 0_{d\times d} & 0_{d\times d} \\ 0_{d\times d} & \sigma I_{d\times d} \end{pmatrix} \qquad z = \begin{pmatrix} x \\ p \end{pmatrix}$$

$$\Rightarrow \quad \boxed{\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho v) = \operatorname{div}_p\left(\gamma M^{-1} p \, \rho\right) + \frac{1}{2}\sigma^2 \Delta_p \rho}$$

Fokker-Planck eq. (forward Kolmogorov eq.)

- positivity-preserving
- cons. of total prob. (because $\frac{\partial \rho}{\partial t}$ = divergence)

<u>Thm</u> (Hérau, Nier 2004)

ρ sol'n to Fokker-Planck (suitable conds on V & ρ_0)

$$\Rightarrow \quad \rho(\cdot, t) \xrightarrow[t \to \infty]{} \left(\int_{\mathbb{R}^{2d}} \rho(\cdot, 0)\right) \rho_\beta \quad \text{exp'ly fast}$$

$$\rho_\beta(x,p) = Z e^{-\beta H(x,p)}, \qquad Z = \left(\int e^{-\beta H}\right)^{-1}$$

Gibbs measure at inverse temperature β.

More elementary pf. (convergence, but no rate)

$$\partial_t \rho = (A+B)\rho, \qquad A\rho = -v\cdot\nabla\rho = -\mathrm{div}(v\rho)$$

Liouville operator

$$B\rho = \mathrm{div}_p(\gamma M^{-1}p\,\rho) + \frac{\sigma^2}{2}\Delta_p \rho$$

dissip./noise operator

<u>Lemma 1</u> ρ solves (FP), $\rho = u\,e^{-\beta H}$ (ie $u := \frac{\rho}{e^{-\beta H}}$)

$$\Rightarrow \partial_t u = (A + B^*)u, \qquad B^* = L^2\text{-adjoint of } B$$
$$= -\gamma M^{-1}p\cdot\nabla_p + \frac{\sigma^2}{2}\Delta_p$$

<u>Pf</u> $\partial_t u = \partial_t(e^{\beta H}\rho) = e^{\beta H}(A+B)\rho = \underbrace{e^{\beta H}(A+B)e^{-\beta H}}_{\text{"Witten Fokker Planck op."}}u$

Rest: elementary calculation (Homework).

Lemma 2 (Lyapunov fcn)

$$\frac{d}{dt}\int_{\mathbb{R}^{2d}} \frac{1}{2}u^2 e^{-\beta H}\, dz = -\frac{\sigma^2}{2}\int_{\mathbb{R}^{2d}} |\nabla_p u|^2 e^{-\beta H}$$

Pf: see Appendix.

Assuming this lemma and sufficient "compactness", $u(\cdot,t)$ approaches the set of states with $\nabla_p u \equiv 0$ as $t \to \infty$. But the only such state is the Gibbs measure:

$$\nabla_p u \equiv 0 \Rightarrow \underset{\text{in (FP)}}{u = u(x) \Rightarrow} \underbrace{M^{-1}}_{\neq 0 \text{ a.e.}} p \cdot \nabla_x u = 0 \Rightarrow \underset{\substack{\text{connected}\\ x\text{-domain}}}{u \equiv \text{const}}$$

$$\Rightarrow \rho = u e^{-\beta H} = \text{const}\, e^{-\beta H}$$

Rigorous for $u(\cdot,0) \in L^2(\mathbb{R}^{2d}; e^{-\beta H} dp\,dx)$

Appendix: Pf of lemma 2.

$$\frac{d}{dt}\int \frac{u^2}{2} e^{-\beta H} = \int \underbrace{(u\, \partial_t u)}_{= u\cdot Au \;+\; u\cdot B^* u} e^{-\beta H} \qquad (A1)$$

Properties of $u\cdot Au$:

(i) $u\cdot Au = u\cdot(-v\cdot\nabla u) = -v\cdot\nabla\left(\frac{1}{2}u^2\right) = A\left(\frac{1}{2}u^2\right)$

(ii) L^2-adjoint of A: $A^* = -A$, because

$$\int Af\cdot g = \int \big(\underbrace{(-v\cdot\nabla)f}_{= -\operatorname{div}(vf),\ \text{since } \operatorname{div} v = 0}\big) g = \int f\cdot(v\cdot\nabla) g = -\int f\cdot Ag$$

(iii) $Ae^{-\beta H} = 0$

(Gibbs measure, like any fctn of the Hamiltonian, invariant under Liouville eq.)

$$\Rightarrow \int u\cdot Au\, e^{-\beta H} \underset{(i)}{=} \int \left(A\frac{u^2}{2}\right) e^{-\beta H} \underset{(ii)}{=} -\int \frac{1}{2}u^2 A e^{-\beta H} \underset{(iii)}{=} 0 \qquad (A2)$$

Properties of $u\cdot B^* u$:

(i) By the product rule of the Laplacian, $\Delta(fg) = \Delta f\cdot g + 2\nabla f\cdot\nabla g + f\Delta g$,

$$\Delta \frac{u^2}{2} = u\,\Delta u + |\nabla u|^2$$

$$\Rightarrow \quad u\cdot B^* u = u\cdot\left(-\gamma M_p^{-1}\cdot\nabla_p + \frac{\sigma^2}{2}\Delta_p\right)u$$
$$= -\gamma M^{-1}p\cdot\nabla_p \frac{u^2}{2} + \frac{\sigma^2}{2}\left(\Delta_p \frac{u^2}{2} - |\nabla_p u|^2\right)$$
$$= B^* \frac{u^2}{2} - \frac{\sigma^2}{2}|\nabla_p u|^2$$

(ii) L^2-adjoint of B^* is $B = \mathrm{div}_p(\gamma M^{-1}p\,\bullet) + \frac{\sigma^2}{2}\Delta_p$

(iii) $B e^{-\beta H} = 0$ (Gibbs measure invariant under Fokker-Planck eq.), since

$$B e^{-\beta H} = \mathrm{div}_p\left[\left(\underbrace{\gamma M^{-1}p + \frac{\sigma^2}{2}\cdot(-\beta M^{-1}p)}_{=0 \text{ by fluctuation-dissipation rel. } \frac{\gamma}{\beta}=\frac{\sigma^2}{2}}\right) e^{-\beta H}\right]$$

$$\Rightarrow \int (u\cdot B^* u)\, e^{-\beta H} \underset{(i)}{=} \int\left(B^*\frac{u^2}{2} - \frac{\sigma^2}{2}|\nabla_p u|^2\right)e^{-\beta H} \underset{(ii)}{=} \int \frac{u^2}{2} \underbrace{B e^{-\beta H}}_{\underset{(iii)}{=}0} - \frac{\sigma^2}{2}\int |\nabla_p u|^2 e^{-\beta H} \qquad (A3)$$

Combining (A1), (A2), (A3) gives the assertion of the lemma.