

European Research Council
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Computational statistical physics

A numerical microscope

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Labex Bézout PhD Day, May 2024

Molly package in Julia

A bit of chemistry & thermodynamics

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A bit of probability & statistics

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A bit of probability & statistics

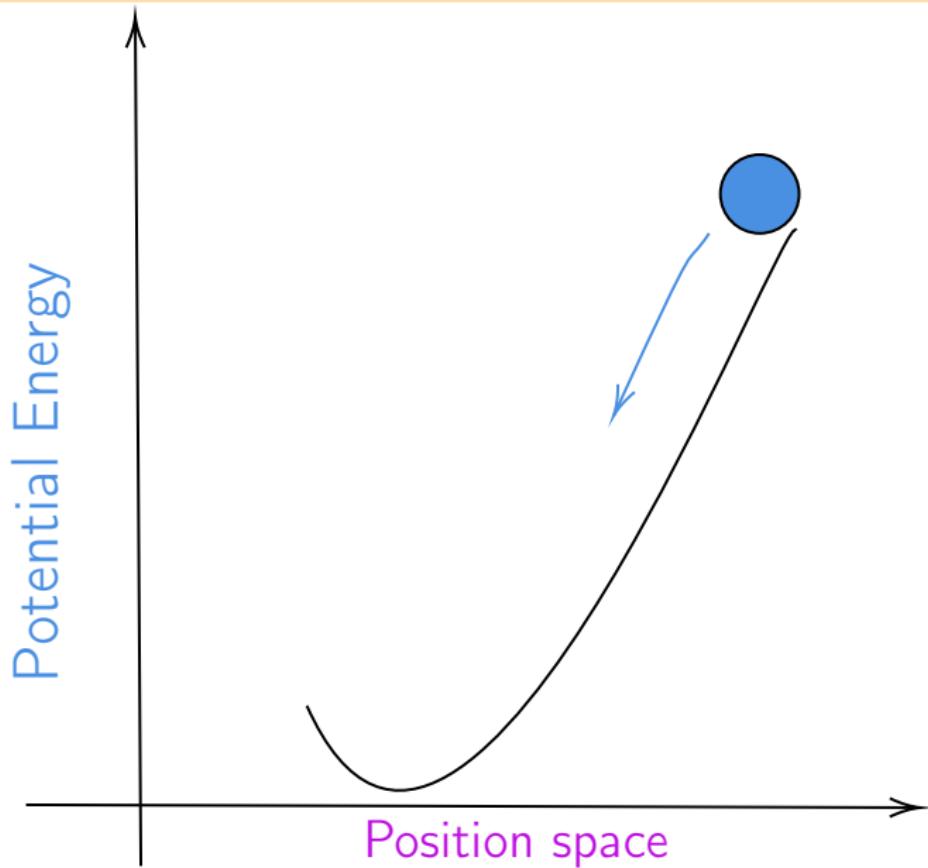
A bit of scientific programming

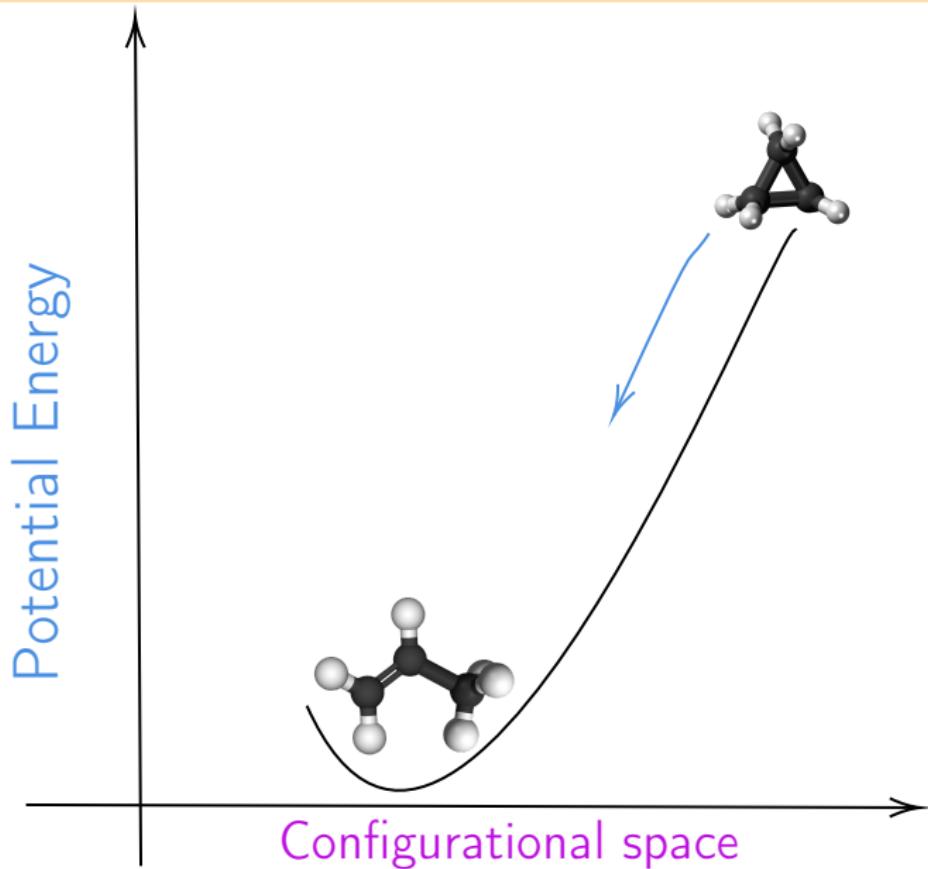
A bit of chemistry & thermodynamics

- Potential wells and exothermic reactions
- Entropy and endothermic processes
- Gibbs & Helmholtz Free Energies

A bit of probability & statistics

A bit of scientific programming





Analogy (?) between mechanics (M) & chemical reactions (CR)

- Minimize potential energy

M - gravity : ball at rest

CR - bond interactions : optimal geometric configuration

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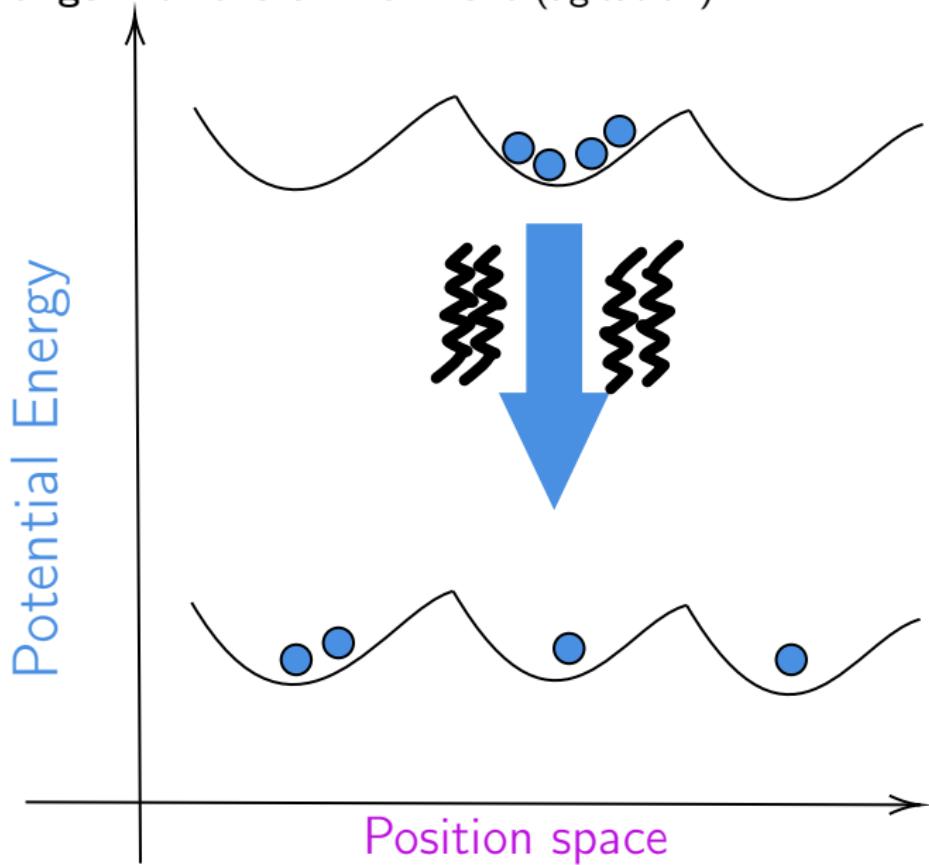
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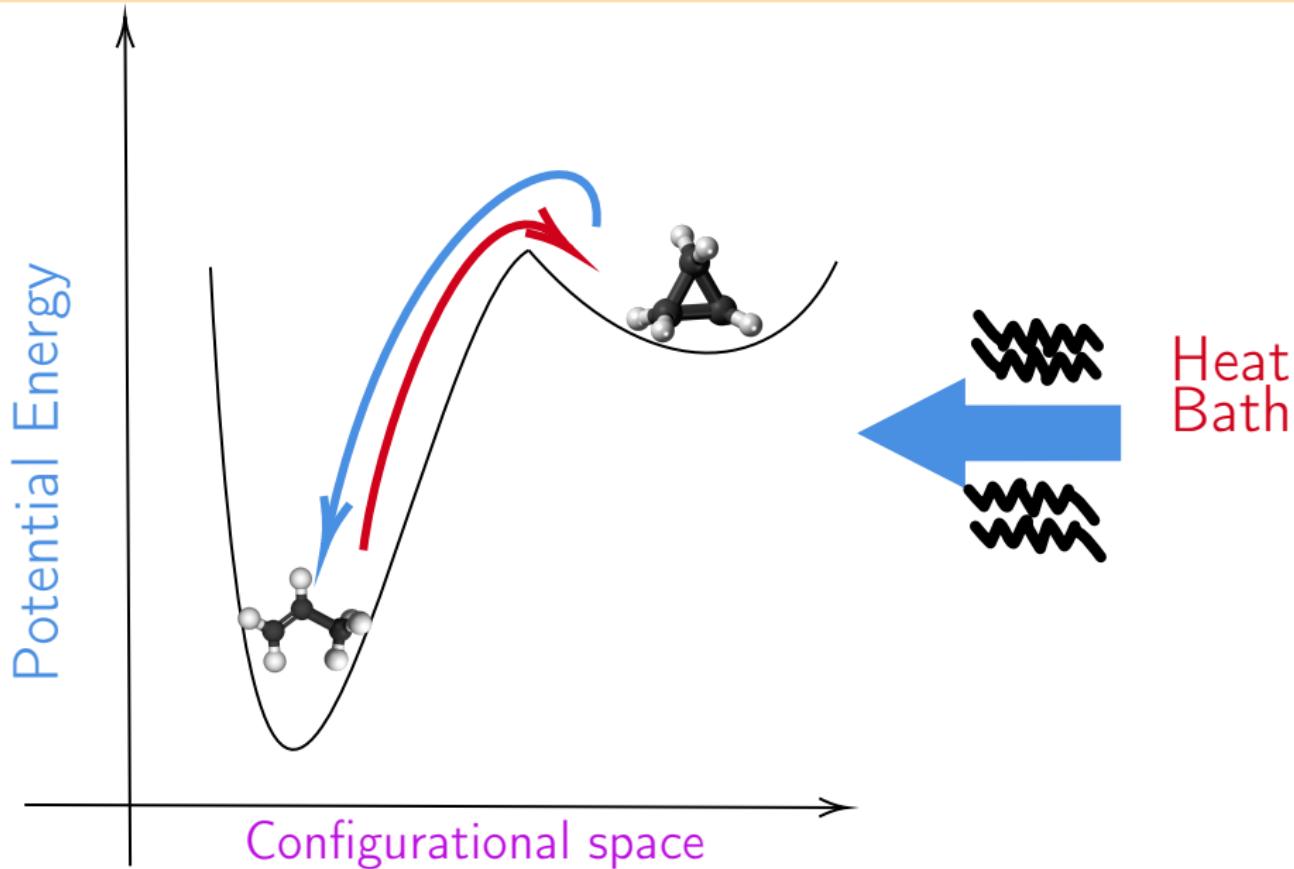
M - ball's kinetic energy increases

CR - heat dissipation

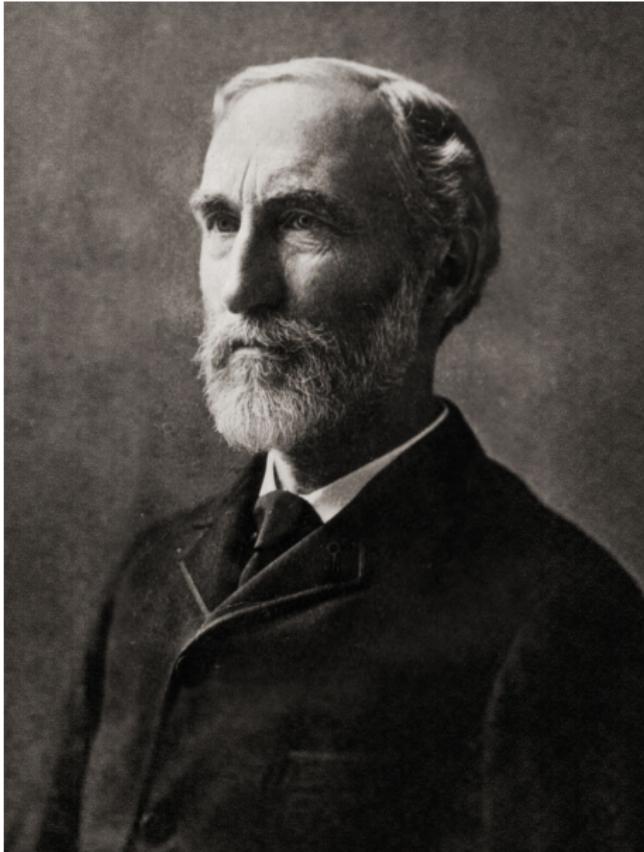
We should only see exothermic reactions...right ?

Heat exchange with the environment (agitation)





A chemical reaction happens if the Free Energy decreases



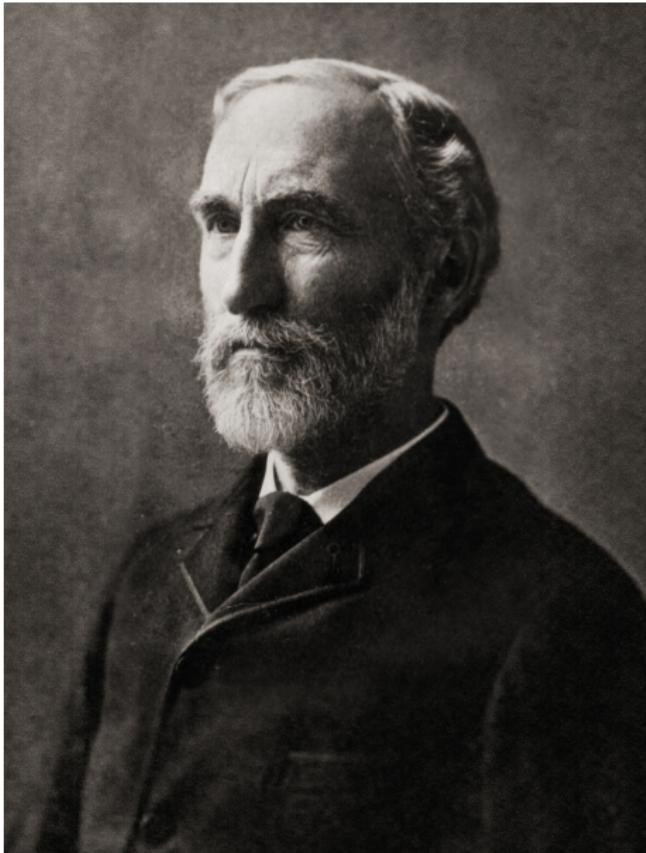
Josiah Willard Gibbs (1839-1903)

$$\Delta G = \Delta H - T\Delta S$$

Enthalpy $H = U + PV$

Entropy S

A chemical reaction happens if the Free Energy decreases



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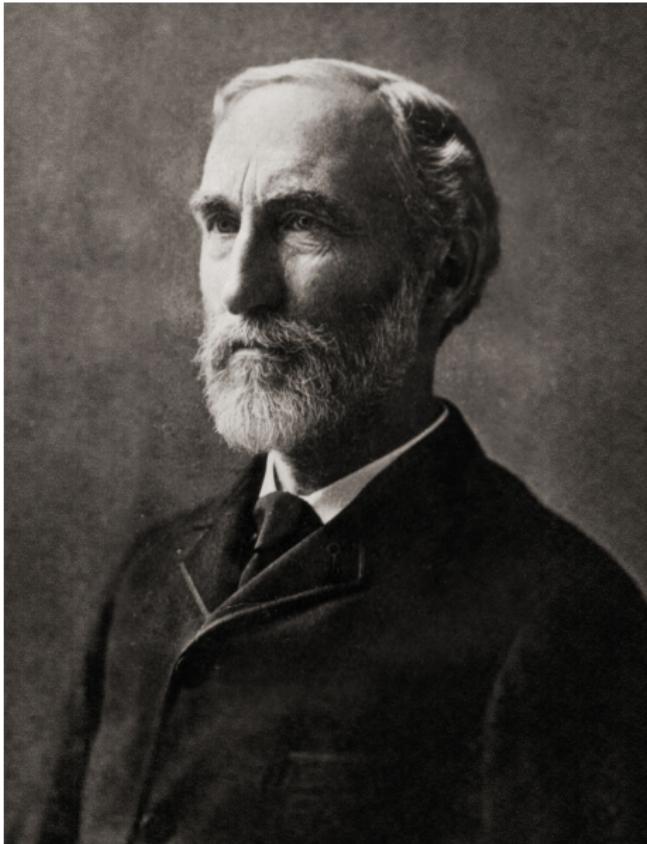
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$\Delta G \leq 0 \implies$ Favorable reaction

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Useful for systems with constant pressure and temperature

A chemical reaction happens if the Free Energy decreases

Hermann von Helmholtz (1821-1894)



$$\Delta F = \Delta U - T\Delta S$$

Potential energy U

Entropy S

Useful for systems with constant temperature

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- Boltzmann approach: maximize the entropy
- Assigning probabilities to microscopic states
- Computing thermodynamic quantities of interest

A bit of scientific programming

A system is at thermal equilibrium if the entropy is maximal



Ludwig Eduard Boltzmann
(1844-1906)

$$S = k_B \log W$$

Entropy S

Boltzmann constant k_B

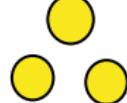
$$k_B = 1.38 \times 10^{-23} \text{ J/K}$$

Number of microscopic states W

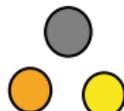
0 ε 2ε 3ε

$$U = 3\varepsilon, \quad N = 3$$

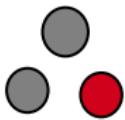
$$W = \frac{N!}{N_0!N_1!N_2!N_3!}$$



$$\begin{aligned}N_0 &= 0 \\N_1 &= 3 \\N_2 &= 0 \\N_3 &= 0 \\W &= 1\end{aligned}$$



$$\begin{aligned}N_0 &= 1 \\N_1 &= 1 \\N_2 &= 1 \\N_3 &= 0 \\W &= 6\end{aligned}$$



$$\begin{aligned}N_0 &= 2 \\N_1 &= 0 \\N_2 &= 0 \\N_3 &= 1 \\W &= 3\end{aligned}$$

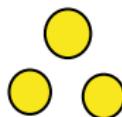
$\Delta F \leqslant 0 ?$

$$\Delta F = \Delta U - T\Delta S = -T k_B \Delta \ln W = -T k_B \ln \frac{6}{1} = -T k_B \ln 6 < 0$$



$$N = 3$$

$$W = \frac{N!}{N_0! N_1! N_2! N_3!}$$



$$N_0 = 0$$

$$N_1 = 3$$

$$N_2 = 0$$

$$N_3 = 0$$

$$U_0 = 3\epsilon, W_0 = 1$$

$$\Delta F \leqslant 0 ?$$



$$N_0 = 1$$

$$N_1 = 0$$

$$N_2 = 1$$

$$N_3 = 1$$

$$U_1 = 5\epsilon, W_1 = 6$$

$$\Delta F = \Delta U - T\Delta S = 2\epsilon - T k_B \ln 6 \leqslant 0 \quad \text{if } \frac{1}{6} \leqslant \exp\left(-\frac{2\epsilon}{k_B T}\right)$$

More generally if $\frac{W_0}{W_1} \leqslant \exp\left(-\frac{U_1 - U_0}{k_B T}\right)$

If the system is only interacting with a heat bath of fixed temperature T

$$\mathbb{P}(\text{microstate}) \propto \exp\left(-\frac{U(q)}{k_B T}\right)$$

Potential energy U : bond interactions

Microstate: all positions $q = (q_x^1, q_y^1, q_z^1, q_x^1, \dots, q_z^N) \in \mathbb{R}^{3N}$

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Gibbs distribution ($\beta = (k_B T)^{-1}$)

$$\pi(dq) = Z^{-1} \exp(-\beta U(q)) dq, \quad Z = \int_{\mathbb{R}^{3N}} \exp(-\beta U(q)) dq$$

- The physicist wants to know the **average pressure P**
- He tells me that, **for a given microstate $q \in \mathbb{R}^{3N}$,**

$$P(q) = -q \cdot \nabla U(q)$$

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$$\mathbb{E}_\pi[P] = \int_{\mathbb{R}^{3N}} -q \cdot \nabla U(q) \pi(dq) = \int_{\mathbb{R}^{3N}} -q \cdot \nabla U(q) Z^{-1} e^{-\beta U(q)} dq$$

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Another example: **specific heat**

$$C \propto \mathbb{E}_\pi[U^2] - \mathbb{E}_\pi[U]^2$$

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- Simulate Langevin dynamics
- A Markov Chain Monte Carlo method
- Can I improve this ?

Aim: compute averages with respect to the Gibbs distribution π

Method: Use **overdamped Langevin dynamics**: $q_t \in \mathbb{R}^{3N}$

$$dq_t = -\nabla V(q_t) dt + \sqrt{2\beta^{-1}} dW_t \quad (1)$$

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This is simply a **stochastic perturbation** of gradient dynamics

Aim: compute averages with respect to the Gibbs distribution π

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$$\boxed{\mathrm{d}q_t = -\nabla V(q_t) \, \mathrm{d}t + \sqrt{2\beta^{-1}} \, \mathrm{d}W_t} \quad (1)$$

This is simply a **stochastic perturbation** of gradient dynamics

Ergodic averages:

$$\mathbb{E}_\pi[P] \approx \frac{1}{N} \sum_{i=1}^N P(q^i)$$

where (q^i) are samples from a trajectory solving (1)

Discretization using the Euler–Maruyama method

Choose a time step $\Delta t > 0$ and update the positions:

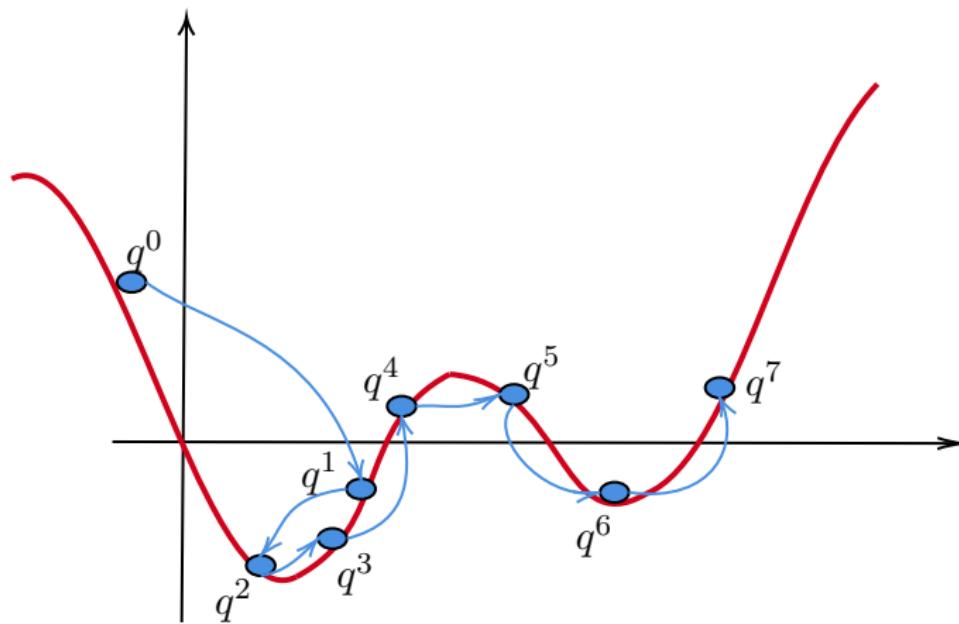
$$q^{n+1} = q^n - \nabla V(q^n) \Delta t + \sqrt{2\beta^{-1}\Delta t} G^{n+1}, \quad G \sim \mathcal{N}(0, I_{3N})$$

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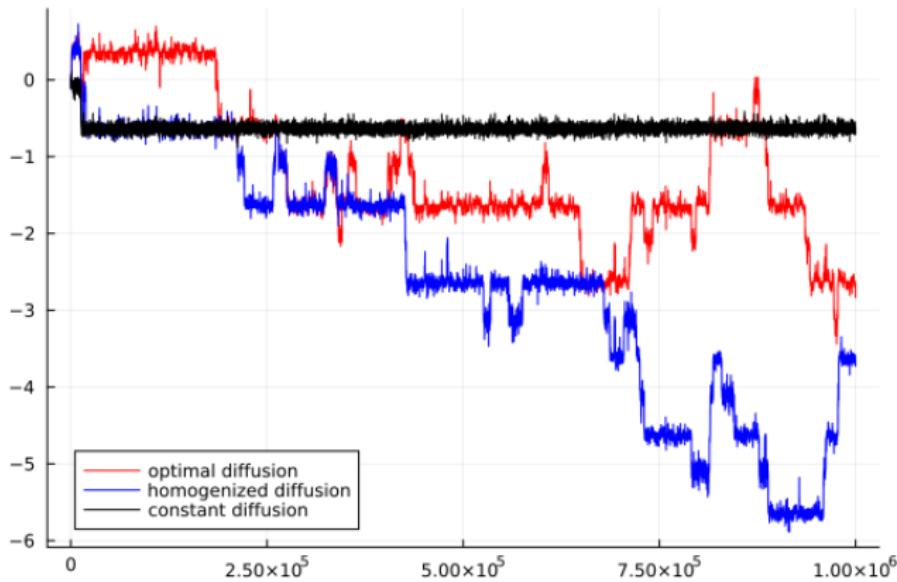
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Technical point: this update needs to be corrected using a Metropolis procedure



Can I improve this ?

21/21



Part of my PhD subjectIntroduce a nonconstant diffusion coefficient $D(q) \in \mathcal{S}_{3N}^{++}(\mathbb{R})$ **Generalized overdamped Langevin dynamics**

$$dq_t = (-D(q_t)\nabla V(q_t) + \beta^{-1}\operatorname{div} D(q_t)) dt + \sqrt{2\beta^{-1}} D(q_t)^{1/2} dW_t$$

