# Langevin dynamics for shear viscosity computations

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# Outline

Context and introduction

Introduction to Statistical Mechanics

Nonequilibrium method for the Shear Viscosity

Numerical illustrations I

Asymptotics for large frictions

Numerical illustrations II

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Numerical illustrations II

# Hydrodynamics in clay nanopores

## Multiscale materials:

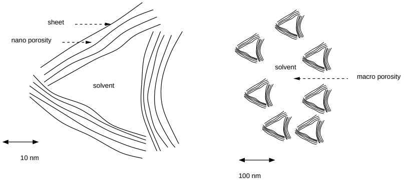


Figure: multiscale structure of clays (courtesy of B. Rotenberg)

- Stack of sheets forming particles of nanometric size;
- Solvent (water) et ions;

A need of numerical simulation to understand the transport properties of the material at the nanoscale

# The Newton law for shear viscosity

- Shear viscosity of a Newtonian fluid $\mathbf{u} = (u_x, u_y)$ velocity field.

$$\eta = -\frac{\sigma_{xy}}{\tau_{xy}}, \qquad \tau_{xy} = \frac{\partial u_x}{\partial y}.$$

- Incompressible Navier-Stokes equation in a periodic channel

$$\rho \partial_t u_x = \eta \frac{\partial^2}{\partial y^2} u_x(y) + \rho F(y) + \text{PBC}$$

Goal: Obtain the shear viscosity from a microscopic description of the fluid.

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# Classical systems

- $N$ particles system

$$(q,p) = (q_1,\dots,q_N,p_1,\dots,p_N) \in \mathcal{D}^N \times \mathbb{R}^{2N}$$

$\mathcal{D} = \mathbb{R}/L_x\mathbb{Z} \times \mathbb{R}/L_y\mathbb{Z}$ for positions and $\mathbb{R}^{2N}$ for momenta.

- The Hamiltonian

$$H(q,p) = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(q_1,\dots,q_N).$$

all the physics is contained in $V$.
Hypothesis: $V$ smooth and given as the sum of pairs interactions.

# Thermodynamical averages

- Macroscopic averages in a thermodynamic ensemble

$$\langle f \rangle_\mu = \int_{\mathcal{D}^N \times \mathbb{R}^{2N}} f(q,p)\mu(dp,dq),$$

  $f$ observable, $\mu$ probability measure ($\mu \geq 0$, $\mu(\mathcal{D}^N \times \mathbb{R}^{2N}) = 1$).

- Example of the canonical measure (NVT)
  macroscopic constraints :
  N (number of particles), V (accsessible volume), T (temperature).

$$\mu_{NVT}(dq,dp) = Z_{\mathrm{NVT}}^{-1} e^{-\beta H(q,p)} dqdp = \psi_0 dqdp,$$

# Sampling an invariant measure

Difficulty : Integrals in high dimension $d = 2N \gg 2$: we have to use stochastic methods.
Idea : Replace the computation of $\langle f \rangle_\mu$ by an ergodic average:

$$\langle f \rangle_\mu = \lim_{\tau \to +\infty} \frac{1}{\tau} \int_0^\tau f(q(t), p(t))dt.$$

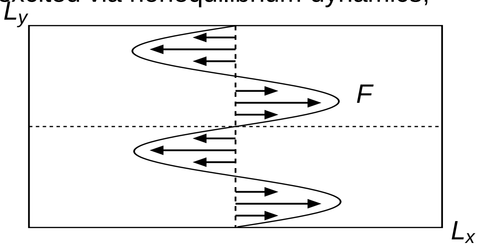
$\longrightarrow$ find a dynamics that samples $\mu$.

# Transport coefficients computations

- Transports coefficients (shear viscosity, thermal conductivity, diffusion) describe dynamics properties of fluids;
- Calculation are possible via Green-Kubo type formula, for the shear viscosity:

$$\eta := \beta \left|\mathcal{D}\right| \left\langle \int_0^{+\infty} \sigma_{xy}(0)\sigma_{xy}(t)dt \right\rangle_{\text{eq}} .$$

  $\sigma_{xy}$ being an off-diagonal term of the microscopic Cauchy stress tensor;
- They can be "measured" in a system where thermodynamics fluxes are excited via nonequilibrium dynamics;



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Context and introduction

Introduction to Statistical Mechanics

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Numerical illustrations I

Asymptotics for large frictions

Numerical illustrations II

# Nonequilibrium Langevin Dynamics I

Hamiltonian + Ornstein-Uhlenbeck + linear nongradient perturbation:

$$\begin{cases} dq_t = \dfrac{p_t}{m}\,dt, \\ dp_{x,t} = -\nabla_{q_x} V(q_t)\,dt + \xi F(q_{y,t})\,dt - \gamma_x \dfrac{p_{x,t}}{m}\,dt + \sqrt{\dfrac{2\gamma_x}{\beta}}\,dW_t^x, \\ dp_{y,t} = -\nabla_{q_y} V(q_t)\,dt - \gamma_y \dfrac{p_{y,t}}{m}\,dt + \sqrt{\dfrac{2\gamma_y}{\beta}}\,dW_t^y, \end{cases} \tag{1}$$

$\xi \in \mathbb{R}$, $\gamma_x, \gamma_y > 0$ (frictions coefficients), $(W_t^x, W_t^y)_{t \geq 0}$ standard brownian motions on $\mathbb{R}^{2N}$.

# Nonequilibrium Langevin Dynamics II

Motivations:

- Artificial dissipation mechanism that allows steady states;
- Rigorous mathematical arguments (ergodicity, linear response);

Theoretical questions:

- Existence and uniqueness of an invariant measure (Rey-Bellet [4], Pavliotis-Stuart [3] ('04));
- Analysis of the Shear Viscosity : Irving Kirkwood identification process ('54) [1];
- Asymptotics for large frictions.

# Infinitesimals generators

- Generators for the Nonequilibrium dynamics:

$$\mathcal{A}_\xi = \mathcal{A}_0 + \xi \mathcal{B};$$
$$\mathcal{A}_0 = \mathcal{A}_{\text{ham}} + \mathcal{A}_{\text{thm}};$$
$$\mathcal{B} = \sum_{i=1}^{N} F(q_{yi}) \partial_{p_{xi}};$$

- Adjoints defined on $L^2(\psi_0)$ : $\mathcal{L}_\xi = A_\xi^*$;
- Fokker-Planck equation for the law of the process $(q_t, p_t)_{t \geq 0}$:

$$\partial_t \psi = \mathcal{L}_\xi \psi,$$

# Structure of the invariant measure

Theorem The dynamics (1) has a unique invariant measure with density $\psi_\xi \in C^\infty(\mathcal{D}^N \times \mathbb{R}^{2N})$ et

$$\psi_\xi = f_\xi \psi_0, \qquad f_\xi = 1 + \sum_{k \geq 1} \xi^k \mathrm{f}_k, \tag{2}$$

and $\mathrm{f}_k \in L^2(\psi_0)$.

Average w.r.t the nonequilibrium invariant measure $\psi_\xi$:

$$\langle h \rangle_\xi = \int_{\mathcal{D}^N \times \mathbb{R}^{2N}} h(q,p)\, \psi_\xi(q,p)\, dq\, dp = \langle h, f_\xi \rangle_{L^2(\psi_0)}.$$

Linear response:

$$\lim_{\xi \to 0} \frac{\langle \mathcal{A}_0 h \rangle_\xi}{\xi} = -\frac{\beta}{m} \left\langle h, \sum_{i=1}^N p_{xi} F(q_{yi}) \right\rangle_{L^2(\psi_0)}. \tag{3}$$

# Localization

Longitudinal momenta

$$U_x^\varepsilon(Y,q,p) = \frac{L_y}{Nm} \sum_{i=1}^N p_{xi} \chi_\varepsilon(q_{yi} - Y),$$

Off-diagonal stress tensor term:

$$\Sigma_{xy}^\varepsilon(Y,q,p) = \frac{1}{L_x} \sum_{i=1}^N \frac{p_{xi} p_{yi}}{m} \chi_\varepsilon(q_{yi} - Y) \tag{4}$$

$$- \frac{1}{L_x} \sum_{1 \le i < j \le N} \mathcal{V}'(|q_i - q_j|) \left( \frac{q_{xi} - q_{xj}}{|q_i - q_j|} \right) \int_{q_{yi}}^{q_{yj}} \chi_\varepsilon(s - Y)\, ds. \tag{5}$$

Regularization with mollifiers: $\chi_\varepsilon$ with $\lim_{\varepsilon \to 0} \chi_\varepsilon(\cdot - y) = \delta_y$

# Conservation equation

## Proposition (G. Stoltz, RJ '11): Conservation of the longitudinal momenta [2]

The following limits hold true

$$u_x(Y) = \lim_{\varepsilon \to 0} \lim_{\xi \to 0} \frac{\langle U_x^\varepsilon(Y, \cdot) \rangle_\xi}{\xi}$$

and

$$\sigma_{xy}(Y) = \lim_{\varepsilon \to 0} \lim_{\xi \to 0} \frac{\left\langle \Sigma_{xy}^\varepsilon(Y, \cdot) \right\rangle_\xi}{\xi}$$

and

$$\frac{d\sigma_{xy}(Y)}{dY} + \frac{\rho}{m} \gamma_x u_x(Y) = \frac{\rho}{m} F(Y). \tag{6}$$

in the classical sense.

# Discretization of the SDE

Splitting between the Hamiltonian and fluctuation/dissipation part:

- Verlet scheme for the Hamiltonian equations;
- Exact integration of the drifted Ornstein-Uhlenbeck process:

$$\begin{cases} p^{n+1/4} = p^n - \dfrac{\Delta t}{2} \nabla V(q^n), \\ q^{n+1} = q^n + \Delta t \, p^{n+1/4}, \\ p^{n+1/2} = p^{n+1/4} - \dfrac{\Delta t}{2} \nabla V(q^{n+1}), \\ p_x^{n+1} = \alpha_x p_x^{n+1/2} + \sqrt{\dfrac{1}{\beta}(1-\alpha_x^2)}\, G_x^n + (1-\alpha_x) \dfrac{\xi}{\gamma_x} F\left(q_y^{n+1}\right), \\ p_y^{n+1} = \alpha_y p_y^{n+1/2} + \sqrt{\dfrac{1}{\beta}(1-\alpha_y^2)} G_y^n, \end{cases} \tag{7}$$

where $\alpha_{x,y} = \exp(-\gamma_{x,y}\Delta t)$, and $G_x^n, G_y^n$ are i.i.d standard Gaussian random variables.

# Closure relation and practical computations

- Closure relation (postulate)

$$\sigma_{xy}(Y) = -\eta \frac{du_x(Y)}{dY}.$$

- Fourier representation of the solution of (6) thanks to PBC:

$$U_k = \frac{2}{L_y} \int_0^{L_y} u_x(y) \exp\left(\frac{2ik\pi y}{L_y}\right) dy.$$

The coefficients $U_k$ can be approximated numerically using trajectory averages as

$$U_k^{N_{\rm iter}} = \frac{2}{N_{\rm iter}\xi N} \sum_{n=1}^{N_{\rm iter}} \sum_{i=1}^{N} \frac{p_{xi}^n}{m} \exp\left(\frac{2ik\pi q_{yi}^m}{L_y}\right).$$

- Practical computations of the shear viscosity by using the closure relation:

$$\eta = \overline{\rho}\left(\frac{F_k}{Uk} - \gamma_x\right)\left(\frac{L_y}{2k\pi}\right)^2.$$

with $F_k$ the fourier coefficients of the nongradient force.

# Outline

Context and introduction

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Asymptotics for large frictions

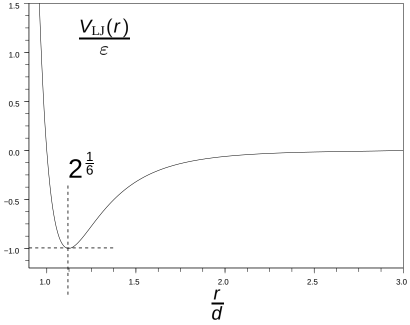
Numerical illustrations II

# Lennard-Jones system

Lennard-Jones potential:

$$V_{\mathrm{LJ}}(r) = 4\varepsilon\left(\left(\frac{d}{r}\right)^{12} - \left(\frac{d}{r}\right)^{6}\right).$$

Thermodynamic state: $(\rho, T) = (0.7, 2.5)$.
Truncated interaction at $r_{\mathrm{cut}} = 3d$.



# Validation of the Newton law

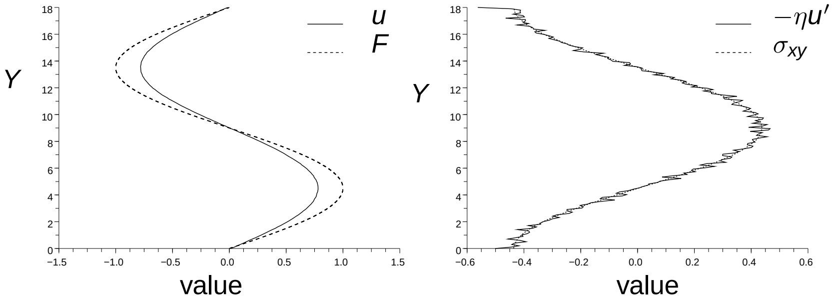



Figure: Velocity profile / pressure term $\sigma_{xy}$ evaluated with binning methods, sinusoidal perturbation.

# Validation of the Newton law

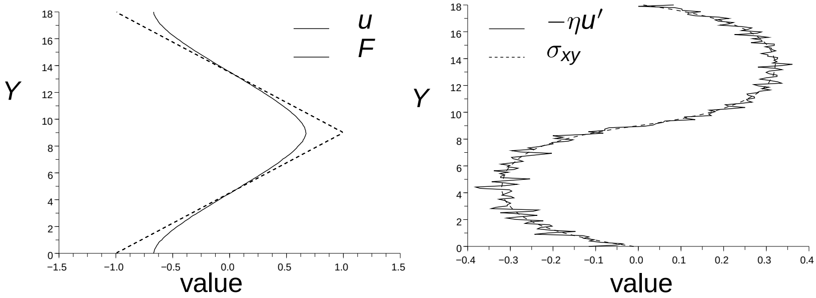



Figure: Velocity profile / stress tensor term $\sigma_{xy}$ evaluated with binning methods, piecewise linear perturbation.

# Validation of the Newton law

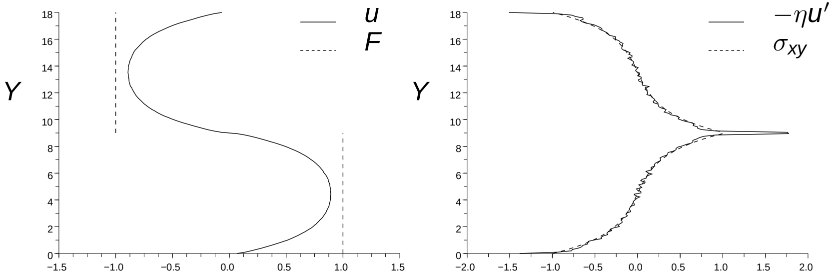



Figure: Velocity profile / pressure term $\sigma_{xy}$ evaluated with binning methods, piecewise constant constant perturbation (discontinuous).

# Linear response

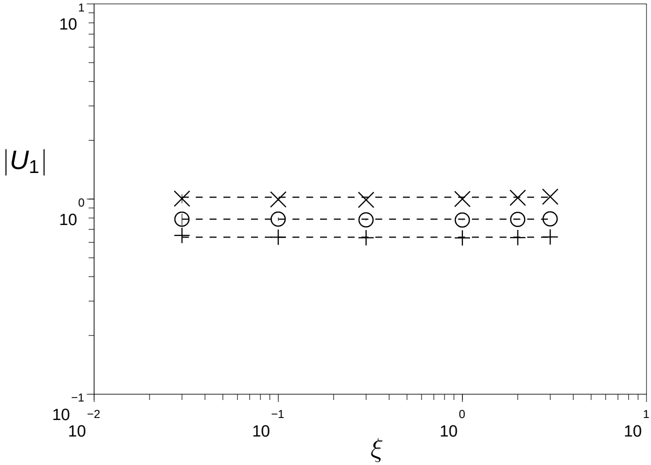



Figure: $|U_1|$ as a function of $\xi$; 3 shape of forces. Left: $\gamma_x = 0$ and $\gamma_y = 1$. Right:$\gamma_x = 1$ and $\gamma_y = 1$

# Outline

Context and introduction

Introduction to Statistical Mechanics

Nonequilibrium method for the Shear Viscosity

Numerical illustrations I

Asymptotics for large frictions

Numerical illustrations II

# Asymptotics for large frictions I

### Theorem (G. Stoltz, RJ '11): Infinite transverse friction [2]

Let $f_{\gamma_y}$ the unique solution of the Poisson equation:

$$-\mathcal{A}_0 f_{\gamma_y} = \sum_{i=1}^{N} p_{xi} G(q_{yi}),$$

there is $f^0, f^1$ and $C > 0$ such that for all $\gamma_y \geq \gamma_x > 0$

$$\left\| f_{\gamma_y} - f^0 - \gamma_y^{-1} f^1 \right\|_{H^1(\psi_0)} \leq \frac{C}{\gamma_y}.$$

$\longrightarrow$ asymptotic velocity profile $u_x^{\gamma_y} \sim \overline{u}_x^{\infty}$

# Asymptotics for large frictions II

## Theorem (G. Stoltz, RJ '11): Infinite longitudinale friction [2]

Let $f_{\gamma_x}$ the unique solution of the Poisson equation:

$$-\mathcal{A}_0 f_{\gamma_x} = \sum_{i=1}^{N} p_{xi} G(q_{yi}),$$

there is $f^1, f^2$ and $C > 0$ such that for all $\gamma_y \geq \gamma_x > 0$

$$\left\| f_{\gamma_x} - \gamma_x^{-1} f^1 - \gamma_x^{-2} f^2 \right\|_{H^1(\psi_0)} \leq \frac{C}{\gamma_x^2}.$$

$\longrightarrow$ asymptotic velocity profile $u_x^{\gamma_x} \sim \dfrac{F}{\gamma_x}$

# Outline

Context and introduction

Introduction to Statistical Mechanics

Nonequilibrium method for the Shear Viscosity

Numerical illustrations I

Asymptotics for large frictions

Numerical illustrations II

# Parametric exploration: $\gamma_x \to \infty$

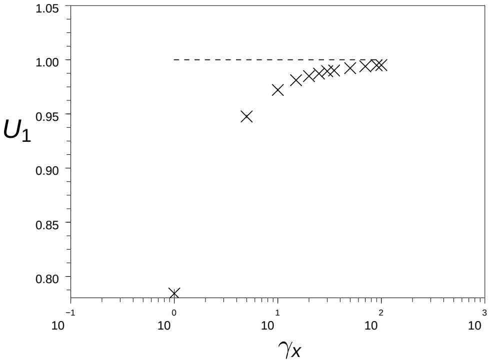



Figure: Fourier coefficient $U_1$ as function of $\gamma_x$, $\gamma_y = 1$ (sinusoidal perturbation).

# Parametric exploration: $\gamma_y \to \infty$

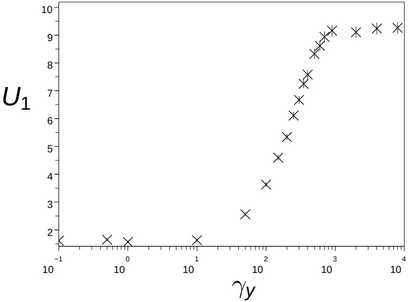



Figure: Shear viscosity $\eta$ as function of $\gamma_y$, $\gamma_x = 1$ (sinusoidal perturbation).

# Conclusions and perspective

What has been done:

- Mathematical understanding of the Method;
- Choice of the friction parameters;
- Robust method and simple to implement in a MD code $\longrightarrow$ test in LAMMPS are running!;

What is left to do:

- Variance reduction method in the case of positive frictions;
- Comparison with other thermostat (Nose-Hoover, DPD) $\longrightarrow$ ongoing work;
- Application to real system (clay, ionic liquids).

**Thank you for your attention!**

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