Coarse graining dynamics using the Mori-Zwanzig formalism: algorithms to reconstruct the projected dynamics

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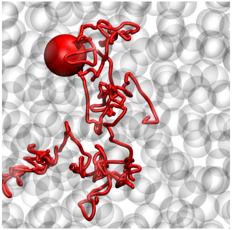
CECAM-Moser discussion meeting

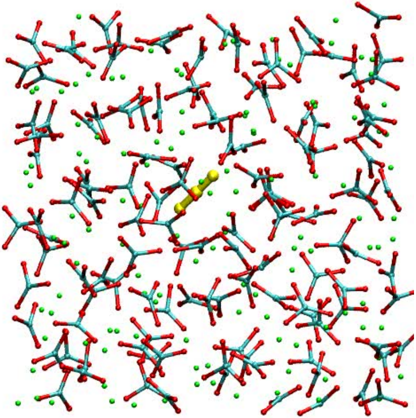
Introduction

- Description of diffusion of a particle in a fluid



- Mechanism, collective variables?
- e.g. proton transport, hops between cages...

Diffusion of CO_2 molecule in molten $CaCO_3$



D. Corradini, F.-X. Coudert, RV, Nature Chemistry **8** (2016): 454-460.

Introduction

- Mori-Zwanzig formalism for projecting on a slow variable
- Application to the diffusion of a particle in a fluid
- Other slow variables: hydrodynamic modes
- Long-time behaviour of the memory kernel?

Mori-Zwanzig formalism for the diffusion of a tagged particle in a fluid

- Here, we will consider the case of diffusion and consider the velocity **v** as relevant variable The projector of any quantity **A** on **v** is defined as

$$\mathcal{P}\mathbf{A} = v\frac{\langle \mathbf{vA} \rangle}{\langle \mathbf{v}^2 \rangle}; \quad \mathcal{Q} = 1 - \mathcal{P}$$

  $\langle \bullet \rangle$ is the average over the canonical distribution function at temperature T
- The microscopic dynamics is decomposed in components othorgonal and along the projection space

$$i\mathcal{L} = i\mathcal{P}\mathcal{L} + i\mathcal{Q}\mathcal{L}$$

Generalized Langevin equation for the tagged particle velocity

- GLE

$$m\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t}(t) = -\int_0^t K(u)\mathbf{v}(t-u)\,\mathrm{d}u + \mathbf{R}(t),$$

- Mori-Zwanzig Memory kernel

$$K(u) = \frac{\langle \mathbf{F}\, e^{i\mathcal{Q}\mathcal{L}u}\mathbf{F}\rangle}{k_B T} = \frac{\langle \mathbf{F}\,\mathbf{R}(u)\rangle}{k_B T}$$

- Random force $\mathbf{R}(t) = e^{i\mathcal{Q}\mathcal{L}t}\mathbf{F}$

- Projection operator $\mathcal{P} = 1 - \mathcal{Q}$: $\mathcal{P}\mathbf{A} = \frac{\langle \mathbf{v}\mathbf{A}\rangle}{\langle \mathbf{v}^2\rangle}\mathbf{v}$

Computation of projected dynamics

We want to compute

$$\mathbf{R}(t) = \exp(i\mathcal{Q}\mathcal{L}t)\mathbf{F}$$

We first note that

$$i\mathcal{Q}\mathcal{L} = i(1-\mathcal{P})\mathcal{L} = i\mathcal{L} + \mathbf{v}\frac{\langle \mathbf{F}\cdot\bullet\rangle}{\langle \mathbf{v}^2\rangle}$$

So that the time evolution of **R** is

$$\frac{d}{dt}\mathbf{R}(t) = i\mathcal{L}\mathbf{R}(t) + \mathbf{v}\frac{\langle \mathbf{F}\cdot\mathbf{R}(t)\rangle}{\langle \mathbf{v}^2\rangle}$$

Projected dynamics along the flow

- Force is transported unchanged backward in the phase-space flow:

$$\frac{d}{dt}\mathbf{F}(t) = i\mathcal{L}\mathbf{F}(t)$$
$$\mathbf{F}(q, p; t + \delta t) = \mathbf{F}(q_{\delta t}, p_{\delta t}; t)$$

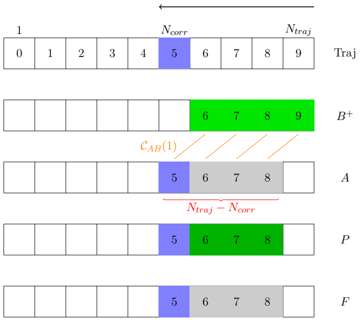
- Total derivative of the random force in the flow is non zero

$$\frac{d}{dt}\mathbf{R}(t) = i\mathcal{L}\mathbf{R}(t) + \mathbf{v}\frac{\langle \mathbf{F} \cdot \mathbf{R}(t)\rangle}{\langle \mathbf{v}^2\rangle}$$

$$\mathbf{R}(q, p; t + \delta t) = \mathbf{R}(q_{\delta t}, p_{\delta t}; t) + \frac{\langle \mathbf{F} \cdot \mathbf{R}(t)\rangle}{\langle \mathbf{v}^2\rangle}\mathbf{v}(q_{\delta t}, p_{\delta t}; t)$$

Going backward

$$\mathbf{R}(q,p;t+\delta t) = \mathbf{R}(q_{\delta t},p_{\delta t};t) + \frac{\langle \mathbf{F}\cdot\mathbf{R}(t)\rangle}{\langle \mathbf{v}^2\rangle}\mathbf{v}(q_{\delta t},p_{\delta t};t)$$



Order 1: Carof, A.; Vuilleumier, R.; Rotenberg, B. *J. Chem. Phys.* 2014, **140**, 124103.

Order 2: Lesnicki, D.; Vuilleumier, R.; Carof, A.; Rotenberg, B. *Phys. Rev. Lett.* 2016, **116**, 147804.

Illustration: double well potential

- Characteristic function for the products and reactants

$$h(x) = \begin{cases} 1 \text{ if } x > 0 \\ 0 \text{ otherwise} \end{cases}$$

- Reaction rate τ^{-1}:

$$\int_0^{+\infty} K(t)\, dt = \int_0^{+\infty} \frac{\langle \dot{h}\, e^{i\mathcal{Q}\mathcal{L}t}\, \dot{h} \rangle}{k_B T}\, dt = \lim_{t\to\infty} \frac{\langle \dot{h}\, e^{i\mathcal{Q}\mathcal{L}t}\, h \rangle}{k_B T} = \tau^{-1}$$

but

$$\int_0^{+\infty} C(t)\, dt = \int_0^{+\infty} \frac{\langle \dot{h}\, \dot{h}(t) \rangle}{k_B T}\, dt = \lim_{t\to\infty} \frac{\langle \dot{h}\, h(t) \rangle}{k_B T} = 0$$

Illustration: double well potential

$$h(x) = \begin{cases} 1 \text{ if } x > 0 \\ 0 \text{ otherwise} \end{cases} \qquad \int_0^T C(t)\,dt = \langle \dot{h}(0) h(T) \rangle = \langle \dot{h}\, e^{i\mathcal{L}T}\, h \rangle$$

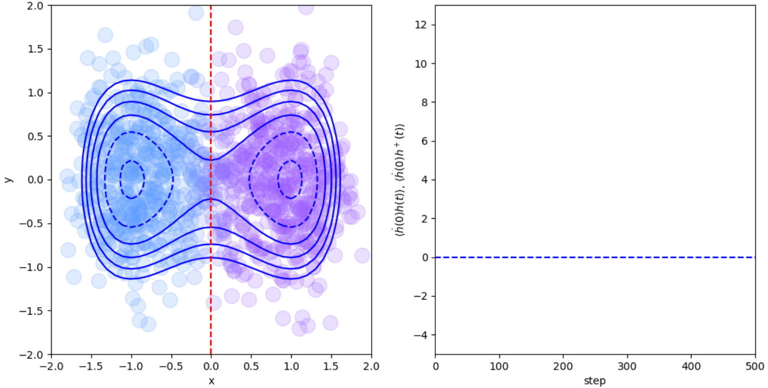
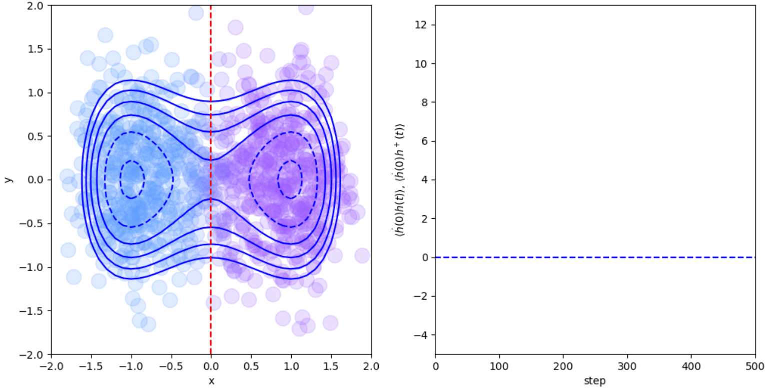


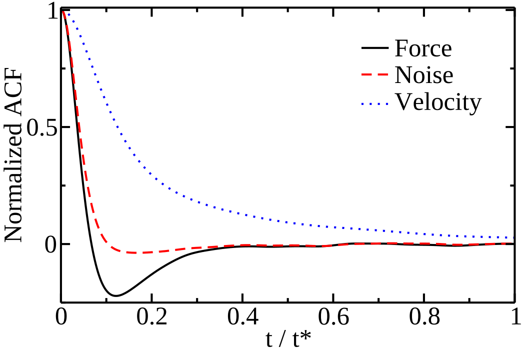
Illustration: double well potential – projection

$$h(x) = \begin{cases} 1 \text{ if } x > 0 \\ 0 \text{ otherwise} \end{cases} \qquad \int_0^T K(t)\, dt = \langle \dot{h}\, e^{i\mathcal{QL}T} h \rangle \qquad \mathcal{P}\mathbf{A} = \frac{\langle h\mathbf{A} \rangle}{\langle h^2 \rangle} h$$

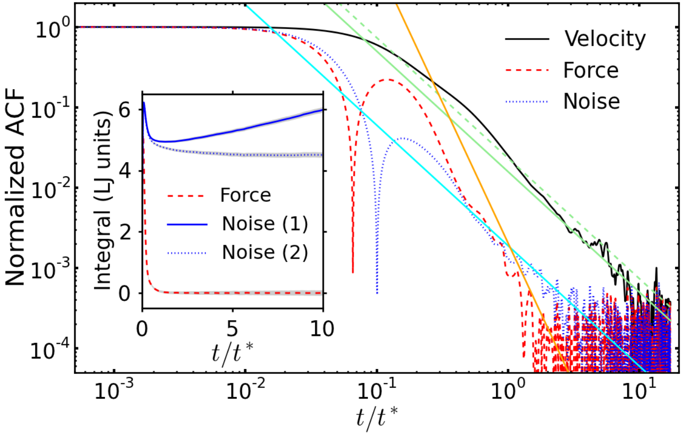


Diffusion in a Lennard-Jones fluid – correlation function

MD simulations of liquid Argon at $T^* = 1.5$, $\rho^* = 0.5$ (10000 particles)



Asymptotic behaviour: MD results



Lesnicki, D.; Vuilleumier, R.; Carof, A.; Rotenberg, B. *Phys. Rev. Lett.* 2016, **116**, 147804.

Hydrodynamic limit ($L \to +\infty$ then $t \to +\infty$):
Asta, A. J.; Levesque, M.; Vuilleumier, R.; Rotenberg, B. *Phys. Rev. E* 2017, **95** (6).

Asymptotic behaviour: theory

- Velocity autocorrelation function (Bedeaux and Mazur)

$$Z(t) = \frac{1}{3}\langle \mathbf{v} \cdot \mathbf{v}(t) \rangle \sim \frac{2k_B T}{3\rho m}[4\pi(D+\nu)t]^{-\frac{3}{2}}$$

- Force autocorrelation function

$$\langle F(t)F(0) \rangle = \frac{\mathrm{d}^2}{\mathrm{d}t^2} Z(t) \sim t^{-\frac{7}{2}}$$

- Random force autocorrelation function: Corngold (PRA 1972)

$$K(t) \sim -\frac{\xi^2}{k_B T} Z(t) \sim -\frac{2\xi^2}{3\rho m}[4\pi(D+\nu)t]^{-\frac{3}{2}}$$

Retrieving the hydrodynamic solution: Basset-Boussinesq force

- Integrating by parts the GLE (for long times t)

$$m\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t}(t) = -\int_0^t K(u)\mathbf{v}(t-u)\,\mathrm{d}u + \mathbf{R}(t)$$
$$= -\xi\mathbf{v}(t) - \int_0^t L(u)\dot{\mathbf{v}}(t-u)\,\mathrm{d}u$$

with

$$L(u) = \int_u^{+\infty} K(\tau)\,\mathrm{d}\tau$$

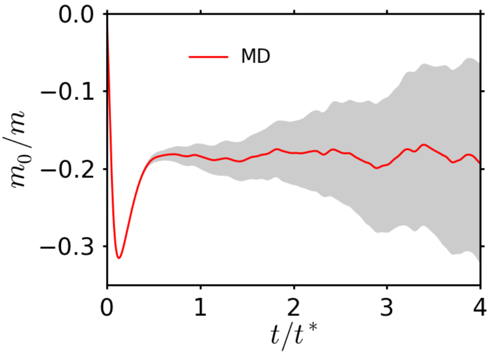
- Generalized friction force

$$m\dot{\bar{v}}(t) = f_\epsilon(t) - \xi\bar{v}(t) - m_0\dot{\bar{v}}(t) - \alpha\pi^{-1/2}\int_0^t (t-u)^{-\frac{1}{2}}\dot{\bar{v}}(u)\,\mathrm{d}u$$

- Hydrodynamic added mass $m_0^{BB} = \frac{2}{3}\pi R^3\rho_0$

Added mass

$$m_0 \equiv -\int_0^{+\infty} \left(K(t) + \frac{1}{2}\alpha\pi^{-1/2} t^{-3/2} \right) t \,\mathrm{d}t$$



$m_0 = -0.18$

Interpretation of the negative contribution to the added mass

- Retardated force

$$m\dot{\bar{v}}(t) = f_\epsilon(t) - \xi_E \bar{v}(t-\tau_0) = f_\epsilon(t) - \xi_E \bar{v}(t) + \xi_E \times \tau_0 \times \dot{\bar{v}}(t)$$

- Short-time decay of the memory kernel

$$K(t) = \frac{\xi_E}{\tau_0} e^{-t/\tau_0}$$

- Enskog contribution to the added mass

$$m_0^E = -\xi_E \tau_0 \approx -0.29\ m,$$

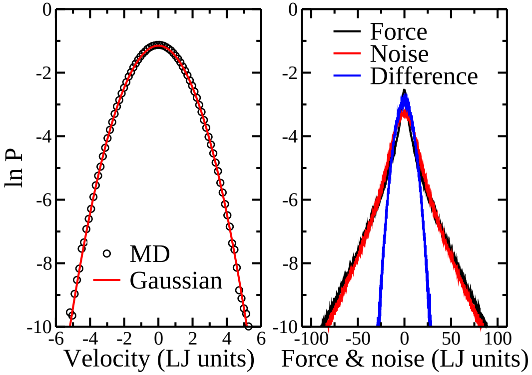
with $\tau_0 \sim 0.05\ t^*$ and $\xi_E \approx 5.8$

- Sum of contributions

$$m_0 = m_0^E + m_0^{BB} \approx -0.16\ m$$

Random force distribution

MD simulations of liquid Argon at $T^* = 1.5$, $\rho^* = 0.5$ (10000 particles)



Eigenfunctions of $i\mathcal{QL}$ for the double well potential

- $i\mathcal{QL}$ has a non-trivial eigenfunction with zero eigenvalue
- On the left:

$$h(i\mathcal{QL}) = 0$$

since $\mathcal{Q}h = 0$

- On the right:

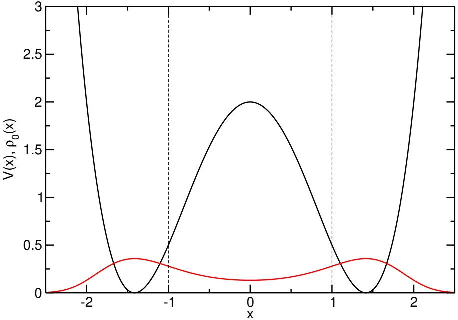
$$i\mathcal{QL}\tau_h = 0 \quad \Rightarrow \quad i\mathcal{L}\tau_h \propto h$$

Formally,

$$\tau_h = \frac{1}{i\mathcal{L}} h = \int_0^\infty e^{i\mathcal{L}t} h \, dt = \int_0^\infty h(t) \, dt$$

Committor time

1D model

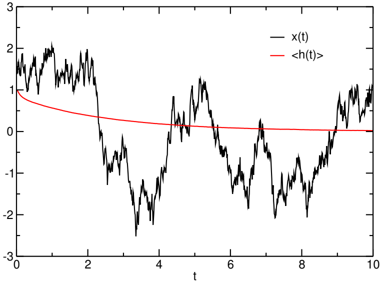


Overdamped dynamics: $i\mathcal{L} = -\frac{D}{kT}\frac{\partial V}{\partial x}\frac{\partial}{\partial x} + D\frac{\partial^2}{\partial x^2}$

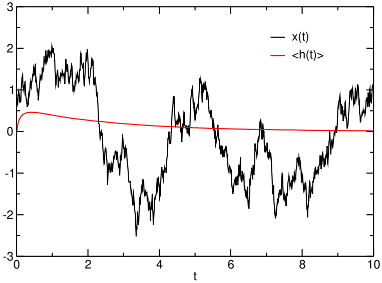
$$D = 1,\ kT = 2$$

$\tau_h = t_A - t_B$: committor time

1D model



x(0)=1.5

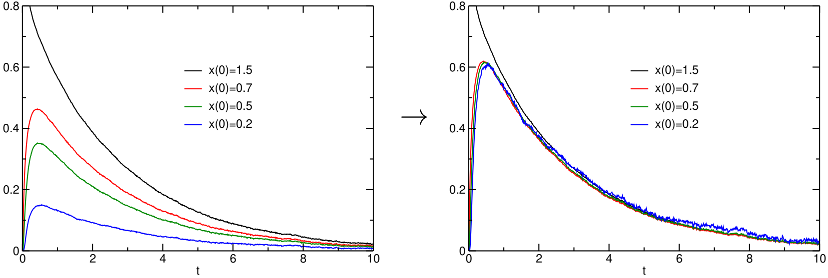


x(0)=0.7

Relation between τ_h and p_c

Committor p_c

Rescaling $\langle h(t) \rangle$ by p_c:



$\tau_h \approx \tau_0 \times p_c$, with τ_0 the reaction time

Equation for τ_h and p_c

- τ_h satisfies

$$\left(-\frac{D}{kT}\frac{\partial V}{\partial x}\frac{\partial}{\partial x} + D\frac{\partial^2}{\partial x^2}\right)\tau_h = -h$$

  A: source, B: sink; $\tau_h \rho_0$ stationary state

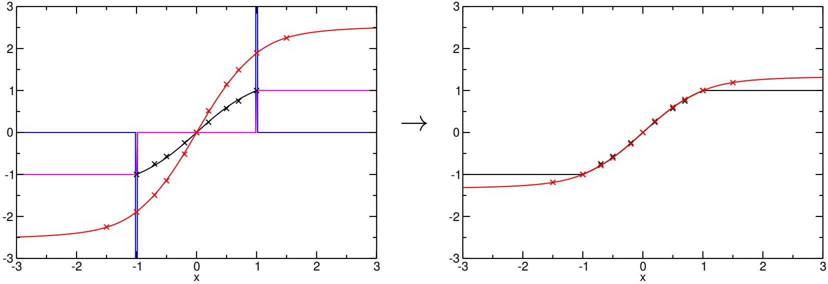
- p_c satisfies

$$\left(-\frac{D}{kT}\frac{\partial V}{\partial x}\frac{\partial}{\partial x} + D\frac{\partial^2}{\partial x^2}\right)p_c = 0; \quad p_c(\partial A) = 1, \quad p_c(\partial B) = -1$$

  Can be solved using Lagrange multipliers

$$\left(-\frac{D}{kT}\frac{\partial V}{\partial x}\frac{\partial}{\partial x} + D\frac{\partial^2}{\partial x^2}\right)p_c = \lambda(x)$$

1D model



in 1D: $\tau_h = \tau_0 \times p_c$ outside A and B

Inspection of $\lim_{T\to\infty} e^{i\mathcal{QL}T} v$

- Taking limits in the GLE
- It can be shown with some algebra that

$$\int_{-\infty}^{0} \langle \mathbf{v}(t)\mathbf{B}\rangle \,\mathrm{d}t = \frac{\int_0^{+\infty} \langle \mathbf{v}\mathbf{v}(t)\rangle \,\mathrm{d}t}{\langle \mathbf{v}^2\rangle} \times \lim_{T\to+\infty} \langle \mathbf{B} e^{-i\mathcal{QL}T}\mathbf{v}\rangle$$

- in the sense of a density, we can say that

$$\lim_{T\to+\infty} e^{-i\mathcal{QL}T}\mathbf{v} = \int_{-\infty}^{0} \mathbf{v}(t) = \lim_{T\to+\infty} (\mathbf{r}(0) - \mathbf{r}(-T))$$

Comparison with linear response

Infinitesimal force

force f applied on particle 1 since $t = -\infty$ along x

Averages of observables

$$\begin{aligned} \langle A \rangle_f &\approx \langle A \rangle_0 + \beta f \int_{-\infty}^{0} dt \langle v_{1,x}(t) A \rangle_0 \\ &\approx \langle A \rangle_0 + f \times \beta \left\langle \Delta r_{1,x} A \right\rangle_0 \end{aligned}$$

$\Delta r_{1,x}$: displacement along x of particle 1 from $t = -\infty$ to $t = 0$

$A \equiv v_1$: $\beta \left\langle \Delta r_{1,x} v_1 \right\rangle_0$ is the mobility

Observables B

Induced local structure

- Particle density:

$$\rho(\mathbf{r}) = \sum_i m_i \delta^3 (\mathbf{r} - \mathbf{r}_i)$$

Induced flow around the diffusing particle

- Momentum density:

$$\rho\mathbf{v}(\mathbf{r}) = \sum_i m_i (\mathbf{v}_i - \mathbf{v}_1) \delta^3 (\mathbf{r} - \mathbf{r}_i)$$

$$\mathbf{v}(\mathbf{r}) = \frac{\rho\mathbf{v}(\mathbf{r})}{\rho(\mathbf{r})\mathcal{U}}$$

Use of symmetries

- Density

$$\delta\rho(\mathbf{r}) = \gamma_1(r)\cos\theta$$

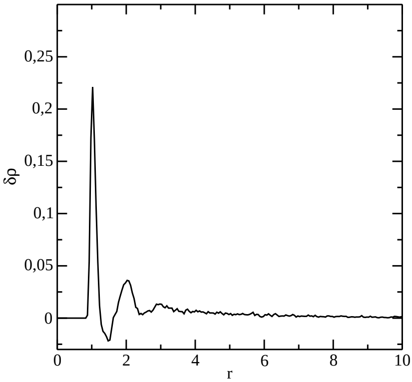
- Momentum density

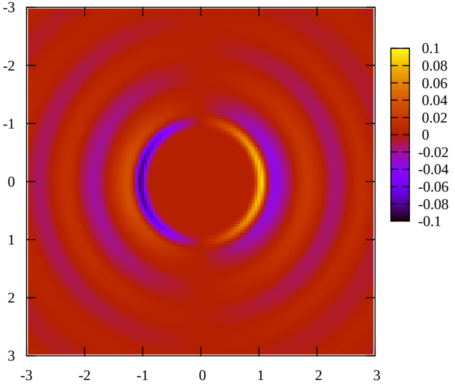
$$\rho\mathbf{v}(\mathbf{r}) = \Theta_L(r)\cos\theta\,\mathbf{u}_r + \Theta_T(r)\sin\theta\,\mathbf{u}_\theta$$

Same symmetries as Stokes flow!

Density map

$$\delta\rho(\mathbf{r}) = \beta\langle\Delta r_{1,x}\,\delta(\mathbf{r} - \mathbf{r}_{1i})\rangle = h(r)\cos\theta$$

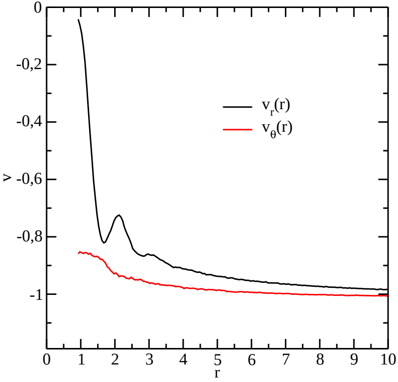


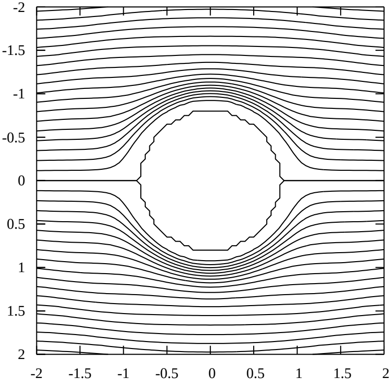


Force felt by the particle = applied force

Velocity field: diffusing particle frame

$$\rho \mathbf{v}(\mathbf{r}) = \beta \langle \Delta r_{1,x} \, (\mathbf{v}_i - \mathbf{v}_1) \, \delta(\mathbf{r} - \mathbf{r}_{1i}) \rangle = f(r) \cos\theta \cdot \mathbf{e}_r + g(r) \sin\theta \cdot \mathbf{e}_\theta$$





Lesnicki, D.; Vuilleumier, R. *J. Chem. Phys.* 2017, **147**, 094502.

Summary

- An algorithm to compute accurately projected correlation function and random noise from equilibrium MD simulations
- We found the expected long-time behaviour of the projected correlation function
- Extraction of an added mass
- Determination of molecular flow
- Extension to collective variables to describe diffusion mechanism of diffusion?
- Proton transport,...

Acknowledgements

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