Microscopic flow around a diffusing tagged particle: effects of fluctuations on the hydrodynamics description

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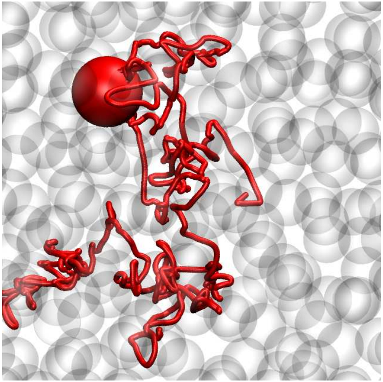
Diffusion in a Lennard-Jones fluid



10000 identical LJ particles
($T^* = 1.5$, $\rho^* = 0.5$)

- Friction from flow around the moving particle
- Relationship between diffusion and viscosity

$$D = \frac{k_B T}{c\pi\eta R}$$

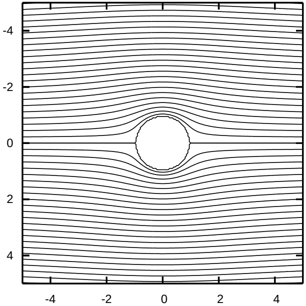
- Flow boundary conditions?
- Direct estimation of the flux?

Stokes'flow

A sphere with a (small) velocity v_1 in an incompressible fluid of viscosity η

- velocity field
  (slip boundary conditions – lab. frame):

$$\vec{v}(\vec{r}) = \frac{f}{4\pi\eta}\left(\frac{1}{r}\cos\theta\,\vec{e}_r - \frac{1}{2r}\sin\theta\,\vec{e}_\theta\right)$$



- drag force f:

$$f = 4\pi\eta R v_1$$

- friction $\xi = 4\pi\eta R$

diffusion $D = \frac{k_B T}{\xi} = \frac{k_B T}{4\pi\eta R}$ (Stokes-Einstein relation)

Velocity field: linear response

Infinitesimal force

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

Averages of observables

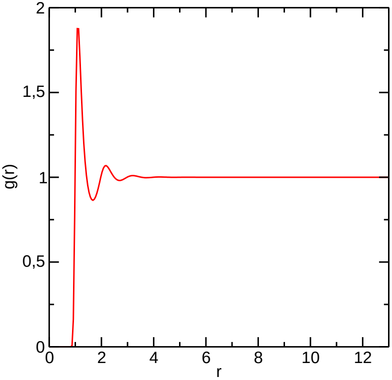
$$\begin{aligned} \langle A \rangle_f &\approx \langle A \rangle_0 + \beta f \int_{-\infty}^{0} dt \langle v_{1,x}(t) A \rangle_0 \\ &\approx \langle A \rangle_0 + f \times \beta \, \langle \Delta r_{1,x} A \rangle_0 \end{aligned}$$

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

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

Lenard-Jones fluid

Above the critical point: $T^* = 1.5$, $\rho^* = 0.5$ ($\sigma = 1$)



10000 identical LJ spheres $\rightarrow$ $L = 27.14\,\sigma$

Velocity field: diffusing particle frame

$$\rho\vec{v}(\vec{r}) = \beta\langle\Delta r_{1,x}\,(\vec{v}_i - \vec{v}_1)\,\delta(\vec{r}-\vec{r}_{1i})\rangle$$

Use of symmetry ?

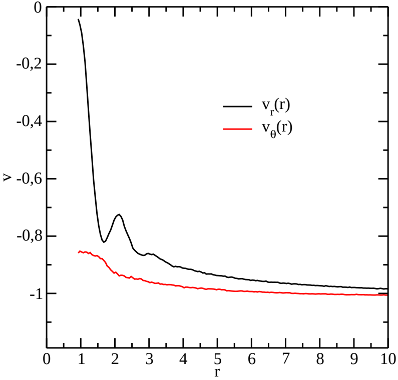
Velocity field: diffusing particle frame

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

Same symmetry as the Stokes flow around a sphere

Velocity field: diffusing particle frame

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



Velocity field: diffusing particle frame

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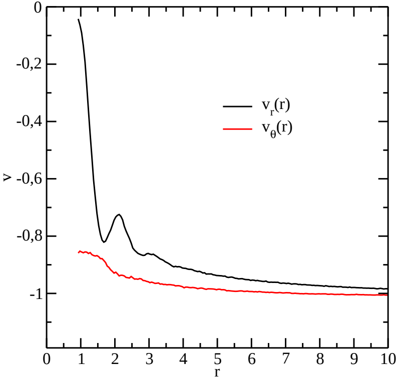
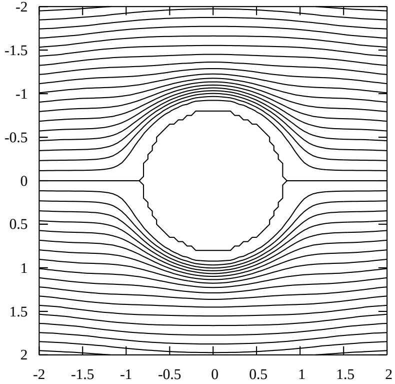
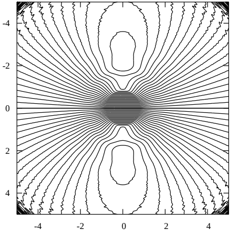
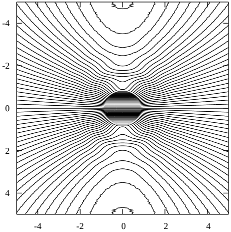




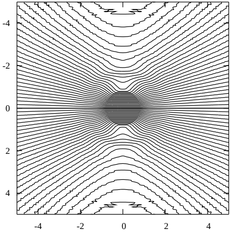
Laboratory frame: *backflow*



$t = 1$



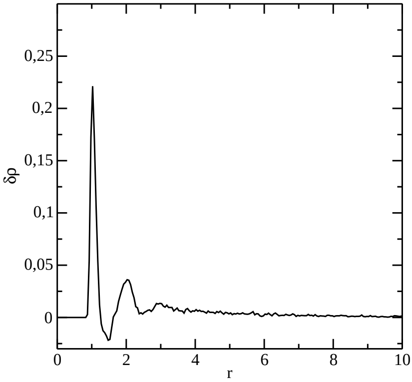
$t = 10$

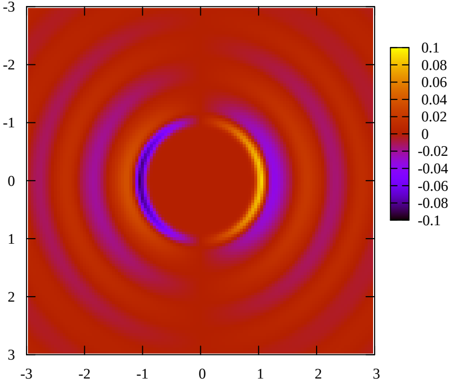


$t = 100$

Density map

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

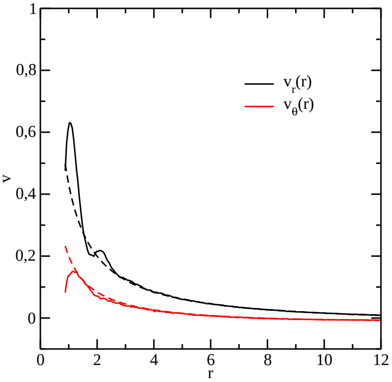




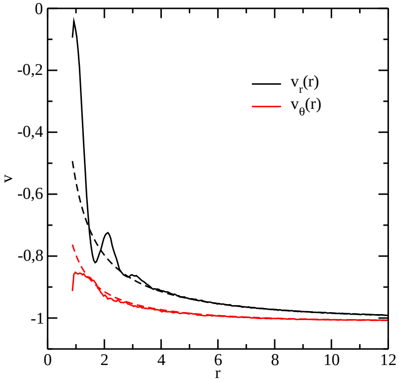
Force felt by the particle = applied force

Hydrodynamic flow – Boundary conditions

Fit of an hydrodynamic flow with slip boundary conditions



Labo. frame

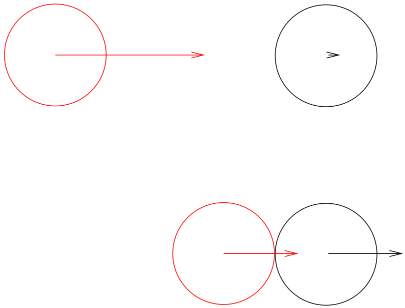


Part. frame

The normal velocity is non zero at contact!

Boundary conditions – normal velocity

Correlation between the particle velocity and the presence of a particle at contact

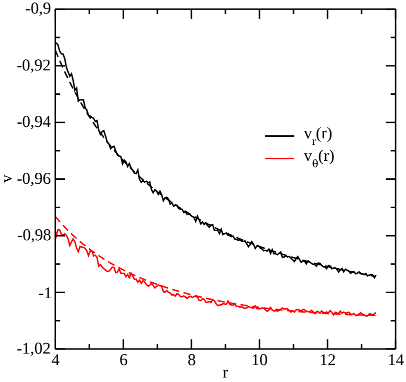


- velocity lower than the average tagged particle velocity
- apparent normal velocity at contact

Hynes, J. T., Kapral, R. et Weinberg, M., *JCP* **70**, 1456 (1979).

Dissipation through viscosity

Velocity field in the long range part



- Momentum flux due to viscosity corresponds to only a force $f = 0.76$ injected in the fluid
- Is there a dissipation term other than viscosity?

Equation of motion for the velocity field

At long times (laboratory frame):

$$\nabla_\beta \langle v_{i,\alpha} \cdot v_{i,\beta} \rangle_1(\vec{r}) - \sum_{j \neq 1} \langle f_{j \to i,\alpha} \rangle_1(\vec{r}) - \nabla_\beta \langle v_{i,\alpha} \cdot v_{1,\beta} \rangle_1(\vec{r}) = \langle f_{1 \to i,\alpha} \rangle_1(\vec{r})$$

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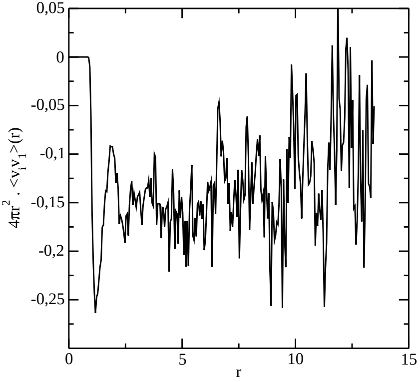
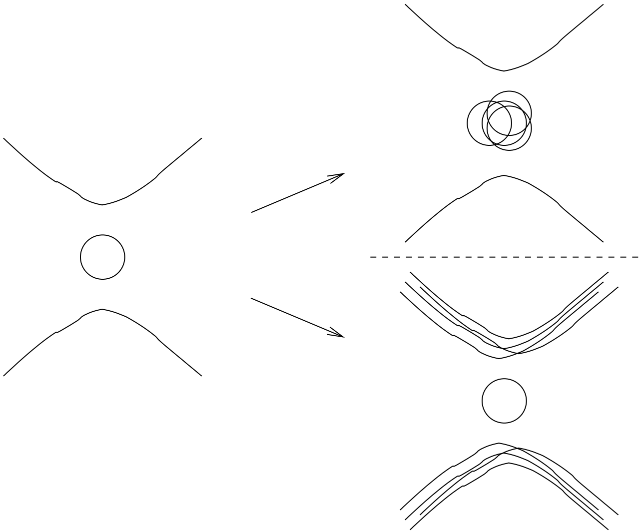


- Momentum flux through a sphere of radius r
- Contribution from the term $\langle v_{i,\alpha} \cdot v_{1,\beta} \rangle_1(\vec{r})$

Role of the central particle fluctuations

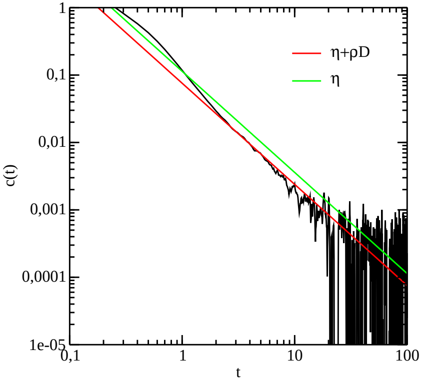


Asymptotic behavior of the velocity autocorrelation function

$c(t) \approx a_0 t^{-3/2}$ with

- $a_0 = \dfrac{2k_B T \rho^{1/2}}{4\pi\eta^{3/2}}$: viscosity only
- $a_0 = \dfrac{2k_B T \rho^{1/2}}{4\pi(\eta + \rho D)^{3/2}}$:

  including fluctuations



Evolution equations

The evolution equations are modified

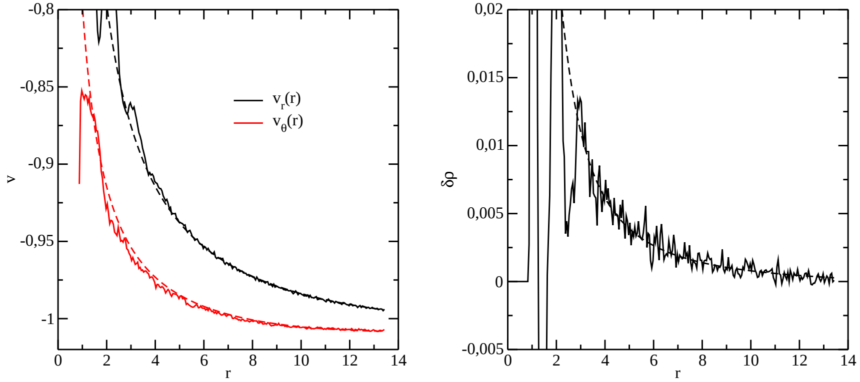
$$\rho\frac{d\vec{v}}{dt} = -\vec{\nabla}P + \eta\nabla^2\vec{v} + \rho D\nabla^2\vec{v}$$

$$\frac{d\delta\rho}{dt} = D\nabla^2\delta\rho - \vec{\nabla}\rho\vec{v}(\vec{r})$$

In regions where $\rho \approx$ cte., the solution still satisfies $\vec{\nabla}\vec{v} = 0$

Renormalisation of viscosity

Hydrodynamique avec $f = 1$ et $\eta \to \eta + \rho D$



$$D = D_0 + \frac{k_B T}{4\pi(\eta + \rho D)} \frac{1}{R}$$

Bedeaux, D. et Mazur, P, *Physica* **73**, 431 (1974).

Diffusion mechanism

Most mobile configurations

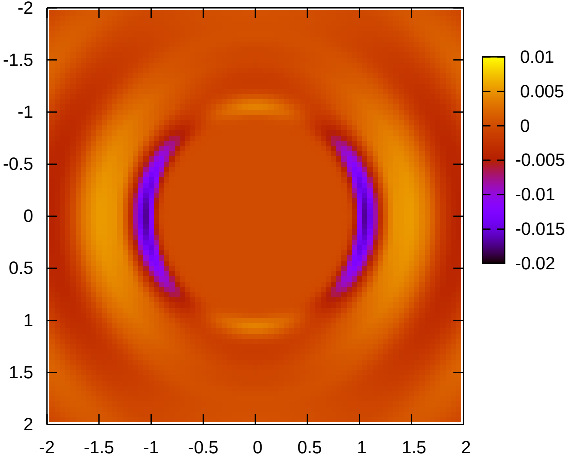
- Diffusion constant is the average of $\Delta r_{1,x} \cdot v_{1,x}$
- How variations of this quantity correlate with the local structure ?

Computation of

$$\langle \Delta r_{1,x} \cdot v_{1,x} \, \delta(\vec{r} - \vec{r}_{1i}) \rangle$$

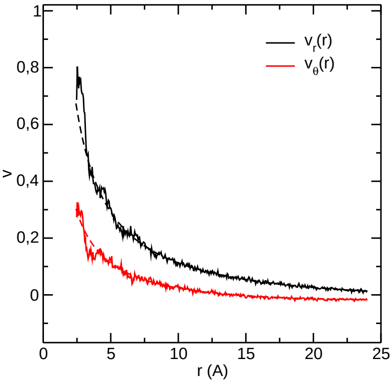
Most mobile configurations in a high density LJ fluid

$T^* = 0.785$, $\rho^* = 0.8$

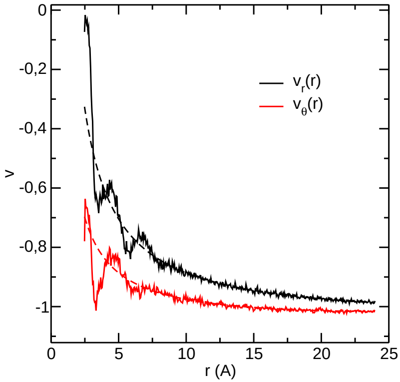


Elongated (de-structured) and squeezed solvation shell

Water self diffusion at ambient conditions



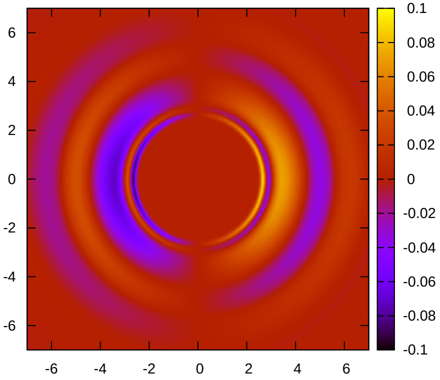
Labo. frame

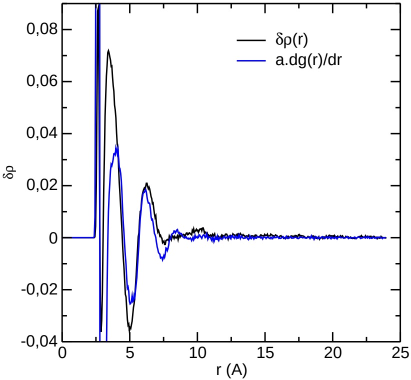


Part. frame

Slip boundary conditions even for hydrogen bonded system!

Displacement inside the cage

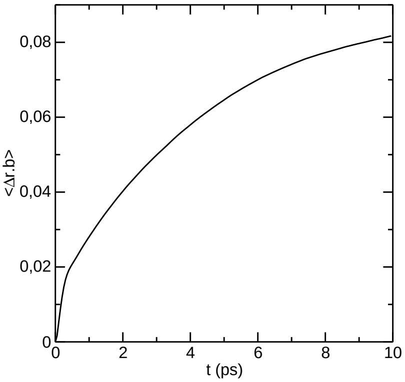


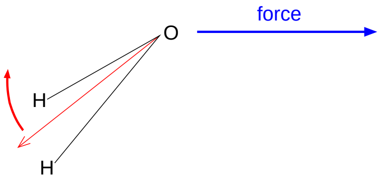


- The water molecule seems displaced in its cage.
- Except in its close vicinity
- The first shell is also destructured
- Characteristic retardation time $\tau_{ret} = 350$ fs

Rotation of the water molecule coupled to diffusion

Computation of $\langle \Delta \vec{r}_1 \cdot \vec{b}_1 \rangle$





In liquid water, $\text{meanfreepath} = 0.04$ Å

Conclusions

Summary

- Hydrodynamic is valid already for $r = 4$ with slip boundary conditions
- Effects of the central particle fluctuations:
  - Boundary conditions with non-zero normal velocity
  - An additional dissipation term

Some perspectives

- Ions in water, hydrophilic and hydrophobic interactions
- Solute-solvent coupling in transport phenomena
- Glasses, silver halides, gaussian core particles, ionic liquids. . .
- Diffusion mechanism of an excess proton in water, in membranes

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