Nanoscale hydrodynamics near solids

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July 2019

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Motivation

- Great interest in the study of fluids in contact with solids in the nanoscale.
- Density layering $\rightarrow$ DFT for equilibrium situations $\rightarrow$ DDFT for the study of the dynamic behaviour of the fluid.
- Slip boundary condition

$$\delta \frac{\partial v}{\partial z} = v_{\text{slip}}, \qquad \delta = \frac{\eta}{\gamma}$$

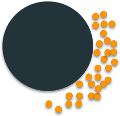
- Bocquet and Barrat [**Bocquet1993**]

$$\gamma = \frac{1}{S k_B T} \int_0^{\tau} dt \left\langle \hat{F}^x(t) \hat{F}^x \right\rangle$$

- Petravic and Harrowell [**Petravic2007**] disagree with the expression obtained by Bocquet and Barrat.
- The expression for γ suffers from the plateau problem.

BEHAVIOUR
FLUID - SOLID
IN THE **NANOSCALE**

KAWASAKI-GUNTON PROJECTION OPERATOR + MARKOVIAN APPROXIMATION

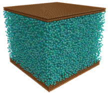


$$\begin{aligned}
\partial_t \rho(\mathbf{r}) &= -\boldsymbol{\nabla}\cdot\mathbf{g}(\mathbf{r})\\
\partial_t \mathbf{g}(\mathbf{r}) &= -\boldsymbol{\nabla}\cdot(\mathbf{g}(\mathbf{r})\mathbf{v}(\mathbf{r})) - \rho(\mathbf{r})\boldsymbol{\nabla}\frac{\delta\mathcal{F}}{\delta\rho(\mathbf{r})}[\rho,\mathbf{R}]\\
&\quad + \boldsymbol{\nabla}\cdot\boldsymbol{\Sigma}(\mathbf{r}) + \boldsymbol{\mathcal{S}}(\mathbf{r})\\
\dot{\mathbf{R}} &= \frac{\mathbf{P}}{M}\\
\dot{\mathbf{P}} &= -\frac{\partial\mathcal{F}}{\partial\mathbf{R}} - \int d\mathbf{r}\,\boldsymbol{\mathcal{S}}(\mathbf{r})
\end{aligned}$$

MORI THEORY

$$C(t) = \exp\{-\Lambda^* t\}\cdot C(0)$$

MD SIMULATIONS



SLIP BOUNDARY CONDITION

Hydrodynamics theory for liquids near solids

The system and the relevant variables

- We study a fluid with N particles in contact with a solid sphere of N' particles.
- $z = (\mathbf{q}_i, \mathbf{p}_i)$ and $z' = (\mathbf{q}_{i'}, \mathbf{p}_{i'})$
- The relevant variables

$$\hat{\rho}_{\mathbf{r}}(z) = \sum_i^N m\delta(\mathbf{r} - \mathbf{q}_i) \qquad \hat{\mathbf{R}}(z) = \frac{1}{N'}\sum_{i'}^{N'} \mathbf{q}_{i'}$$

$$\hat{\mathbf{g}}_{\mathbf{r}}(z) = \sum_i^N \mathbf{p}_i\delta(\mathbf{r} - \mathbf{q}_i) \qquad \hat{\mathbf{P}}(z) = \sum_{i'}^{N'} \mathbf{p}_{i'}$$

- The derivatives of the relevant variables

$$i\mathcal{L}\hat{\rho}_{\mathbf{r}}(z) = -\boldsymbol{\nabla}\cdot\hat{\mathbf{g}}_{\mathbf{r}}(z) \qquad i\mathcal{L}\hat{\mathbf{R}}(z) = \frac{\hat{\mathbf{P}}(z)}{M}$$

$$i\mathcal{L}\hat{\mathbf{g}}_{\mathbf{r}}(z) = -\boldsymbol{\nabla}\cdot\hat{\boldsymbol{\sigma}}_{\mathbf{r}}(z) + \hat{\mathbf{F}}^{\mathrm{s}\to\mathrm{l}}_{\mathbf{r}}(z) \qquad i\mathcal{L}\hat{\mathbf{P}}(z) = -\int d\mathbf{r}\hat{\mathbf{F}}^{\mathrm{s}\to\mathrm{l}}_{\mathbf{r}}(z)$$

Kawasaki-Gunton projection operator

- Clear separation of timescales between the evolution of the averages and the decay of the memory kernel

$$\frac{\partial}{\partial t} a_i(t) = v_i(t) + \sum_j D_{ij}(t)\lambda_j(t)$$

- Reversible term: $v_i = \mathrm{Tr}[\overline{\rho}_t i\mathcal{L}\hat{A}_i]$
- The relevant ensemble:

$$\overline{\rho}(z) = \frac{1}{Z[\lambda]}\rho_0 \exp\{-\lambda\cdot\hat{A}(z)\}$$

- The dissipative matrix is given by the Green-Kubo formula

$$D_{ij}(t) = \int_0^{\Delta t} dt' \left\langle \mathcal{Q}_t i\mathcal{L}\hat{A}_j \exp\{i\mathcal{L}t'\}\mathcal{Q}_t i\mathcal{L}\hat{A}_i \right\rangle^{\lambda(t)}$$

- The Kawasaki-Gunton projection operator is given by

$$\mathcal{Q}_{t'}\hat{F}(z) = \hat{F}(z) - \mathrm{Tr}[\overline{\rho}_{t'}\hat{F}] - \sum_i (\hat{A}_i(z) - a_i(t'))\frac{\partial}{\partial a_i(t')}\mathrm{Tr}[\overline{\rho}_{t'}\hat{F}]$$

Equations of nanohydrodynamics

$$
\begin{aligned}
\partial_t \rho(\mathbf{r}) &= -\boldsymbol{\nabla} \cdot \mathbf{g}(\mathbf{r}) \\
\partial_t \mathbf{g}(\mathbf{r}) &= -\boldsymbol{\nabla} \cdot (\mathbf{g}(\mathbf{r})\mathbf{v}(\mathbf{r})) - \rho(\mathbf{r}) \boldsymbol{\nabla} \frac{\delta \mathcal{F}}{\delta \rho(\mathbf{r})}[\rho, \mathbf{R}] + \boldsymbol{\nabla} \cdot \boldsymbol{\Sigma}(\mathbf{r}) + \boldsymbol{\mathcal{S}}(\mathbf{r}) \\
\dot{\mathbf{R}} &= \frac{\mathbf{P}}{M} \\
\dot{\mathbf{P}} &= -\frac{\partial \mathcal{F}}{\partial \mathbf{R}} - \int d\mathbf{r} \boldsymbol{\mathcal{S}}(\mathbf{r})
\end{aligned}
$$

- $\mathcal{F}[\rho, \mathbf{R}]$: free energy density functional of a fluid in the presence of a solid sphere.
- $\Sigma(\mathbf{r})$: fluid stress tensor.
- $\mathcal{S}(\mathbf{r})$: irreversible surface force density on the fluid.

The transport kernels

- The fluid stress tensor $\boldsymbol{\Sigma}(\mathbf{r})$ is given by

$$\boldsymbol{\Sigma}^{\alpha\beta}(\mathbf{r}) = \int d\mathbf{r}' \eta_{\mathbf{r}\mathbf{r}'}^{\alpha\beta\alpha'\beta'} \boldsymbol{\nabla}_{\mathbf{r}'}^{\beta'} \mathbf{v}^{\alpha'}(\mathbf{r}')$$

- The irreversible surface force density on the fluid $\mathcal{S}(\mathbf{r})$

$$\begin{aligned}\mathcal{S}^{\alpha}(\mathbf{r}) = &- \int d\mathbf{r}' \mathbf{G}_{\mathbf{r}\mathbf{r}'}^{\alpha\alpha'\beta'} \boldsymbol{\nabla}_{\mathbf{r}'}^{\beta'} \mathbf{v}^{\alpha'}(\mathbf{r}') + \boldsymbol{\nabla}_{\mathbf{r}}^{\beta} \int d\mathbf{r}' \mathbf{H}_{\mathbf{r}\mathbf{r}'}^{\alpha\beta\alpha'} (\mathbf{v}^{\alpha'}(\mathbf{r}') - \mathbf{V}^{\alpha'}) \\ &- \int d\mathbf{r}' \gamma_{\mathbf{r}\mathbf{r}'}^{\alpha\alpha'} (\mathbf{v}^{\alpha'}(\mathbf{r}') - \mathbf{V}^{\alpha'})\end{aligned}$$

The transport kernels

$$\boldsymbol{\eta}_{\mathbf{rr}'} \equiv \frac{1}{k_B T} \int_0^{\Delta t} dt' \langle \mathcal{Q}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}(t') \mathcal{Q}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^{\lambda(t)}$$

$$\mathbf{H}_{\mathbf{rr}'} \equiv \frac{1}{k_B T} \int_0^{\Delta t} dt' \langle \mathcal{Q}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}}(t') \mathcal{Q}_t \hat{\mathbf{F}}_{\mathbf{r}'}^{\mathrm{s}\to\mathrm{l}} \rangle^{\lambda(t)}$$

$$\mathbf{G}_{\mathbf{rr}'} \equiv \frac{1}{k_B T} \int_0^{\Delta t} dt' \langle \mathcal{Q}_t \hat{\mathbf{F}}_{\mathbf{r}}^{\mathrm{s}\to\mathrm{l}}(t') \mathcal{Q}_t \hat{\boldsymbol{\sigma}}_{\mathbf{r}'} \rangle^{\lambda(t)}$$

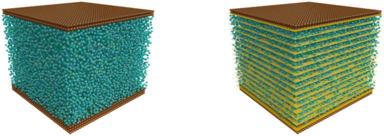
$$\gamma_{\mathbf{rr}'} \equiv \frac{1}{k_B T} \int_0^{\Delta t} dt' \langle \mathcal{Q}_t \hat{\mathbf{F}}_{\mathbf{r}}^{\mathrm{s}\to\mathrm{l}}(t') \mathcal{Q}_t \hat{\mathbf{F}}_{\mathbf{r}'}^{\mathrm{s}\to\mathrm{l}} \rangle^{\lambda(t)}$$

Simpler theory

- The amount of information to compute the hydrodynamic equations is exceedingly large:
  - $\boldsymbol{\eta}$ has 36 independent components.
  - **G** and **H** have 21 independent components.
  - γ has 9 independent components.
- The interactions felt by the fluid due to the walls are statistically planar and isotropic. We restric ourselves to planar flows.
- In order to compare the hydrodynamic equations with the MD simulations we need a discrete version of the theory.

Discrete basis function

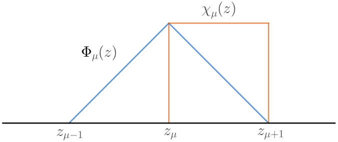
- N_{bin} bins with dimensions L_x, L_y, Δz (L_z/N_{bin}).



- Characteristic function $\chi_\mu(\mathbf{r})$ and finite element linear basis function $\Phi_\mu(\mathbf{r})$

$$\chi_\mu(\mathbf{r}) = \theta(z_{\mu+1} - z)\theta(z - z_\mu) = \chi_\mu(z)$$

$$\Phi_\mu(\mathbf{r}) = \chi_\mu(z)\frac{z_{\mu+1} - z}{\Delta z} + \chi_{\mu-1}(z)\frac{z - z_{\mu-1}}{\Delta z}$$



Mass matrix and dual basis functions

- The usual mass matrix of the finite element method is

$$M^{\Phi}_{\mu\nu} = \Big(\Phi_\mu \Phi_\nu \Big)$$

where we have introduce the notation $\Big(\cdots \Big) = \int d\mathbf{r} ...$

- We introduce the discrete velocity field in terms of $M^{\Phi}_{\mu\nu}$

$$\tilde{\mathbf{v}}_\mu = \sum_\nu \mathcal{V}_\mu [M^{\Phi}]^{-1}_{\mu\nu} \mathbf{v}_\nu$$

- We can contruct continuum and discrete fields from dual basis functions $\delta_\mu(\mathbf{r})$ and $\psi_\mu(\mathbf{r})$

$$v_\mu = \int d\mathbf{r} v(\mathbf{r}) \delta_\mu(\mathbf{r}), \qquad \overline{v}(\mathbf{r}) = \sum_\mu v_\mu \psi_\mu(\mathbf{r})$$

Discrete equations of nanohydrodynamics

$$\frac{d}{dt}\rho_\mu = \left(\overline{\rho}\;\overline{\mathbf{v}}\boldsymbol{\nabla}\delta_\mu\right)$$

$$\frac{d}{dt}\mathbf{g}_\mu = \left(\overline{\rho\mathbf{v}}\;\overline{\mathbf{v}}\cdot\boldsymbol{\nabla}\delta_\mu\right) - \sum_\nu \left(\overline{\rho}\delta_\mu\boldsymbol{\nabla}\delta_\nu\right)\frac{\partial F}{\partial\rho_\nu}(\rho)$$

$$- \sum_\nu \mathcal{V}_\nu \frac{\mathbf{n}\cdot\left[\boldsymbol{\eta}_{\mu\nu} - \boldsymbol{\eta}_{\mu-1\nu} - \boldsymbol{\eta}_{\mu\nu-1} + \boldsymbol{\eta}_{\mu-1\nu-1}\right]}{\Delta z^2} : \mathbf{n}\tilde{\mathbf{v}}_\nu$$

$$+ \sum_\nu \mathcal{V}_\nu \frac{\left[\mathbf{G}_{\mu\nu} - \mathbf{G}_{\mu\nu-1}\right]}{\Delta z}\cdot\mathbf{n}\tilde{\mathbf{v}}_\nu$$

$$+ \sum_\nu \mathcal{V}_\nu \frac{\mathbf{n}\cdot\left[\mathbf{H}_{\mu\nu} - \mathbf{H}_{\mu-1\nu}\right]}{\Delta z}\cdot\tilde{\mathbf{v}}_\nu$$

$$- \sum_\nu \mathcal{V}_\nu \gamma_{\mu\nu}\cdot\tilde{\mathbf{v}}_\nu$$

Symmetry assumptions

- The system is isotropic when we rotate it with respect to an axis perpendicular to the walls...
- ... and reflect it with respect to a plane containing the axis.
- Large simplification of the structure of the tensors $\boldsymbol{\eta}_{\mu\nu}$, $\mathbf{G}_{\mu\nu}$, $\mathbf{H}_{\mu\nu}$ and $\boldsymbol{\gamma}_{\mu\nu}$.
- Under the simplification we may separate the evolution of the selected variables in two contribution: normal and tangent.

Normal and tangent evolution

- The normal evolution

$$\frac{d}{dt}\rho_\mu = \left(\overline{\rho}\;\overline{v}^z \nabla^z \delta_\mu\right)$$
$$\frac{d}{dt}\mathbf{g}^z_\mu = \left(\overline{\rho}\;\overline{v}^z\;\overline{v}^z \nabla^z \delta_\mu\right) - \left(\overline{\rho}\delta_\mu \nabla^z \delta_\nu\right)\frac{\partial F}{\partial \rho_\nu}(\rho) + M^{\perp}_{\mu\nu}\mathcal{V}_\nu \tilde{v}^z_\nu$$

- The parallel evolution for $\alpha = x, y$

$$\frac{d}{dt}\mathbf{g}^\alpha_\mu = -M^{||}_{\mu\nu}\mathcal{V}_\nu \tilde{v}^\alpha_\nu$$

- The dissipative matrix for $\odot = ||, \perp$

$$M^{\odot}_{\mu\nu} = -\frac{\eta^{\odot}_{\mu\nu} - \eta^{\odot}_{\mu-1\nu} - \eta^{\odot}_{\mu\nu-1} + \eta^{\odot}_{\mu-1\nu-1}}{\Delta z^2} + \frac{G^{\odot}_{\mu\nu} - G^{\odot}_{\mu\nu-1}}{\Delta z} + \frac{H^{\odot}_{\mu\nu} - H^{\odot}_{\mu-1\nu}}{\Delta z} - \gamma^{\odot}_{\mu\nu}$$

The discrete transport kernels

$$\eta^{||}_{\mu\nu} = \frac{1}{k_B T}\int_0^{\tau} dt \left\langle \mathcal{Q}\hat{\boldsymbol{\sigma}}^{xz}_{\mu}(t)\mathcal{Q}\hat{\boldsymbol{\sigma}}^{xz}_{\nu}\right\rangle \quad \eta^{\perp}_{\mu\nu} = \frac{1}{k_B T}\int_0^{\tau} dt\langle \mathcal{Q}\hat{\boldsymbol{\sigma}}^{zz}_{\mu}(t)\mathcal{Q}\hat{\boldsymbol{\sigma}}^{zz}_{\nu}\rangle$$

$$G^{||}_{\mu\nu} = \frac{1}{k_B T}\int_0^{\tau} dt \left\langle \mathcal{Q}\hat{\mathbf{F}}^{x}_{\mu}(t)\mathcal{Q}\hat{\boldsymbol{\sigma}}^{xz}_{\nu}\right\rangle \quad G^{\perp}_{\mu\nu} = \frac{1}{k_B T}\int_0^{\tau} dt \left\langle \mathcal{Q}\hat{\mathbf{F}}^{z}_{\mu}(t)\mathcal{Q}\hat{\boldsymbol{\sigma}}^{zz}_{\nu}\right\rangle$$

$$H^{||}_{\mu\nu} = \frac{1}{k_B T}\int_0^{\tau} dt \left\langle \mathcal{Q}\hat{\boldsymbol{\sigma}}^{xz}_{\mu}(t)\mathcal{Q}\hat{\mathbf{F}}^{x}_{\nu}\right\rangle \quad H^{\perp}_{\mu\nu} = \frac{1}{k_B T}\int_0^{\tau} dt \left\langle \mathcal{Q}\hat{\boldsymbol{\sigma}}^{zz}_{\mu}(t)\mathcal{Q}\hat{\mathbf{F}}^{z}_{\nu}\right\rangle$$

$$\gamma^{||}_{\mu\nu} = \frac{1}{k_B T}\int_0^{\tau} dt \left\langle \mathcal{Q}\hat{\mathbf{F}}^{x}_{\mu}(t)\mathcal{Q}\hat{\mathbf{F}}^{x}_{\nu}\right\rangle \quad \gamma^{\perp}_{\mu\nu} = \frac{1}{k_B T}\int_0^{\tau} dt \left\langle \mathcal{Q}\hat{\mathbf{F}}^{z}_{\mu}(t)\mathcal{Q}\hat{\mathbf{F}}^{z}_{\nu}\right\rangle$$

Summary

-
- We have obtained a set of nonlocal transport coefficients that are include in the nanohydrodynamic equations.

Space and time locality for unconfined fluids

Mori's theory

- Linear dynamic equations not only for the averages of the relevant variables but also for their correlations
$$\frac{d}{dt}C(t) = -L\cdot C^{-1}(0)\cdot C(t) - \int_0^t dt'\Gamma(t-t')\cdot C^{-1}(0)\cdot C(t')$$
where the following matrices have been introduced
$$L = \langle \hat{A} i\mathcal{L}\hat{A}^T\rangle$$
$$C(0) = \langle \hat{A}\hat{A}^T\rangle$$
$$\Gamma(t) = \langle F^+(t)F^{+T}(0)\rangle$$
- The projected forces are given by
$$F^+(t) = \exp\{\mathcal{Q}i\mathcal{L}t\}\mathcal{Q}i\mathcal{L}\hat{A}$$
- $\mathcal{Q} = 1 - \mathcal{P}$ where $\mathcal{P}$ is Mori's projector
$$\mathcal{P}\hat{F}(z) = \langle \hat{F}\rangle + \langle \hat{F}\hat{A}^T\rangle\cdot C^{-1}(0)\cdot \hat{A}(z)$$

Markovian approximation

- Memory-less term

$$\int_0^t dt' \Gamma(t-t') \cdot C^{-1}(0) \cdot C(t') \simeq M^* C^{-1}(0) C(t)$$

- Expression for the correlations

$$\begin{aligned} \frac{d}{dt} C(t) &= -(L + M^*) \cdot C^{-1}(0) \cdot C(t) \\ &\equiv \Lambda^* \cdot C(t) \end{aligned}$$

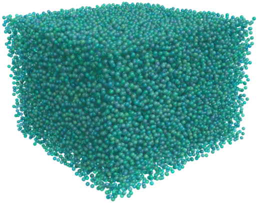
- For a linear Markovian theory the only possibility for a correlation is to decay in an exponential matrix way

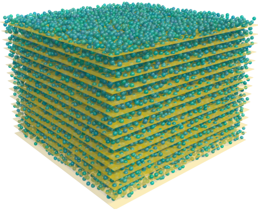
$$C(t) = \exp\{-\Lambda^*(t-\tau)\} \cdot C(\tau)$$

- **We need to find a constant matrix $\boldsymbol{\Lambda}^*$.**

Simpler case: unconfined fluid

- The system





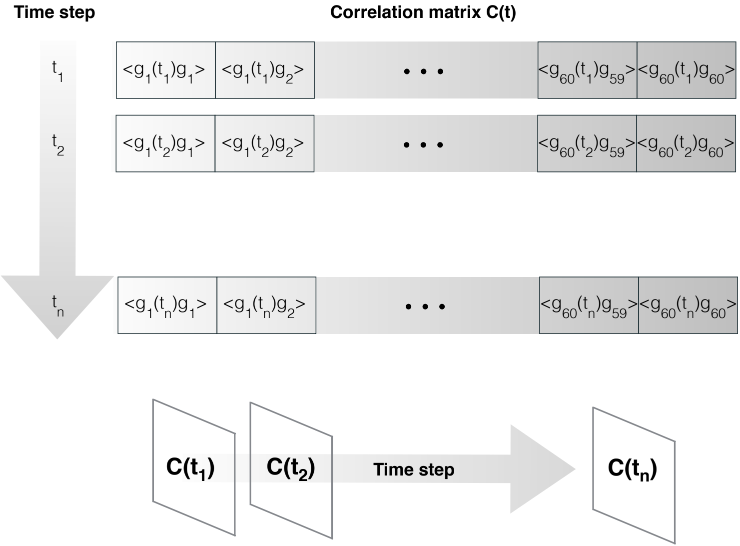
- The relevant variable

$$\hat{\mathbf{g}}_\mu(z) = \sum_i^N \mathbf{p}_i \delta_\mu(\mathbf{r}_i)$$

Simulation set up

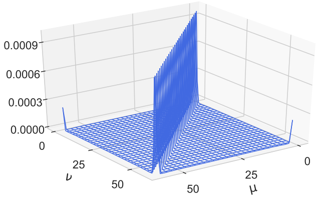
- Simulation of 28749 particles interacting with a LJ potential truncated at $\sigma = 2.5$.
- Box size 40x40x30.
- $dt = 0.002$ in reduced units.
- Equilibration stage
  - Langevin thermostat for 10^5 timesteps: $T = 2.0$, $\rho = 0.6$.
  - NVE microcanonical conditions for a further 10^5 timesteps.
- Production stage
  - 1.5×10^6 timesteps.
  - z axis binned in 60 bins μ. $\boldsymbol{\Delta z = 0.5\sigma}$.
  - $g_\mu^x(t)$ recorded every 10 timesteps.

Building the correlation matrix $C(t)$

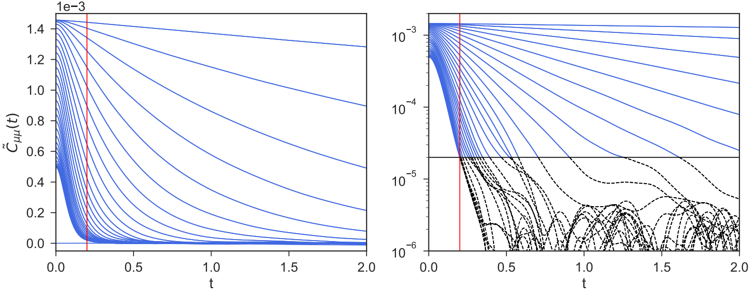


The correlation matrix $C(t)$ and its eigenvalues $\tilde{C}_{\mu\mu}$

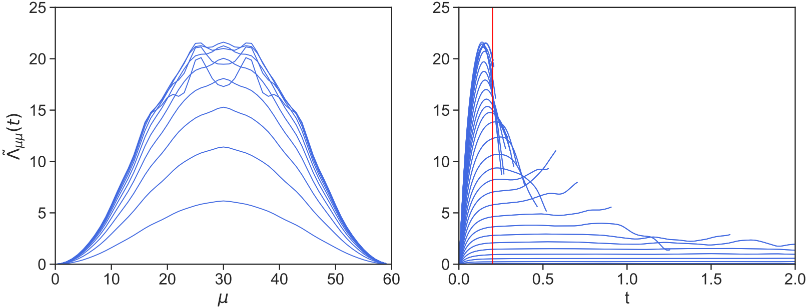
- The correlation matrix $C(t)$ at $t = 0$ (left) and $t = 0.6$ (right)



- The evolution of the different eigenvalues $\tilde{C}_{\mu\mu}(t)$.



Validation of the Markovian approximation

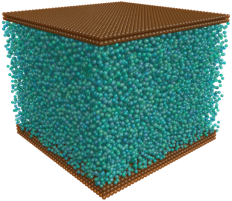


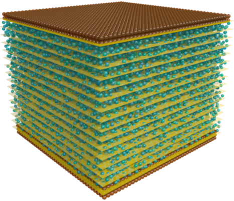
In the left panel, in ascending order the plotted times go from $t = 0$ to $t = 0.20$ in intervals of 0.02. In the right pannel the time evolution of $\tilde{\Lambda}_{\mu\mu}(t)$.

Markovian behaviour near solids

The system and the CG variables

- The system





- The CG variables and its correlation

$$\hat{\mathbf{g}}^x_\mu = \sum_i^N \mathbf{p}_i \delta_\mu(\mathbf{q}_i), \quad \hat{g}^T = (\hat{\mathbf{g}}^x_1, \cdots, \hat{\mathbf{g}}^x_{N_{\mathrm{bin}}}), \quad C(t) = \left\langle \hat{g}(t)\hat{g}^T \right\rangle$$

Simulation set up

- Simulation of 28175 fluid particles interacting with a LJ potential truncated at $\sigma = 2.5$.
- Two solid walls in the xy plane confine the fluid.
- Box size 40x40x33.
- $dt = 0.002$ in reduced units.
- Equilibration stage
  - Langevin thermostat for 10^5 timesteps: $T = 2.0$, $\rho = 0.6$.
  - NVE microcanonical conditions for a further 10^5 timesteps.
- Production stage
  - 12×10^6 timesteps.
  - z axis binned in 66 bins μ $\boldsymbol{\Delta z = 0.5\sigma}$ or 33 bins μ $\boldsymbol{\Delta z = 2\sigma}$.
  - $g_\mu^x(t)$ recorded every 2 timesteps.

Reciprocal space

- Eigenvalues $\tilde{C}_\mu$ and eigenvectors u_μ

$$C(t) = \sum_{\mu}^{N_{\mathrm{bin}}} \tilde{C}_\mu(t) u_\mu(t) \otimes u_\mu^T(t)$$

- Unitary matrix $E(t)$

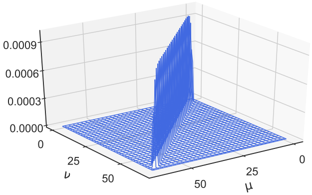
$$E^{-1}(t) \cdot C(t) \cdot E(t) = \tilde{C}(t)$$

- We observed that $\dot{E} \simeq 0$.
- The predictions of $C(t)$ in the reciprocal space

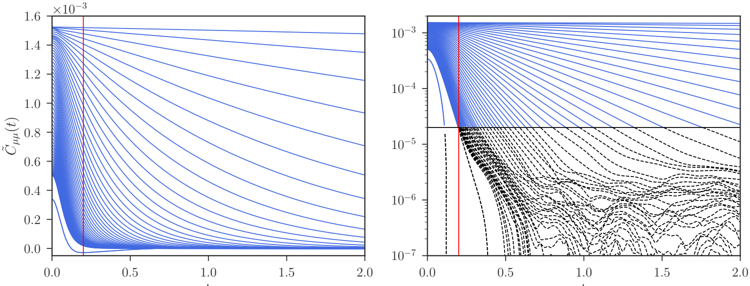
$$\tilde{C}_\mu(t) = \exp\{-\tilde{\Lambda}_{\mu\mu}(t - \tau)\} \tilde{C}_\mu(\tau)$$

Thin bins ($\Delta z = 0.5\sigma$)

- $C_{\mu\nu}(t)$ for $t = 0$ (left) and $t = 0.6$ (right).

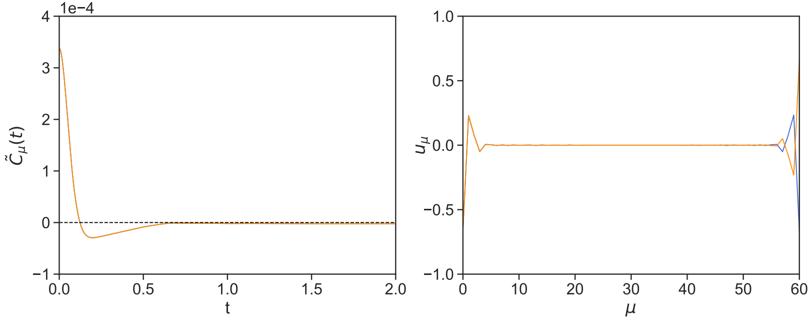


- Evolution of different eigenvalues $\tilde{C}_{\mu\nu}(t)$



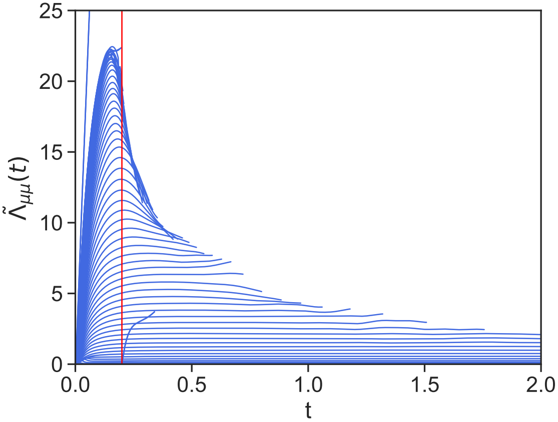
Eigenvalues and eigenvectors near the walls ($\Delta z = 0.5\sigma$)

The eigenvalues $\tilde{C}_\mu(t)$ of the correlation matrix $C(t)$ for $\mu = 59, 60$ which are identical and superimpose (left) and the corresponding eigenvectors u_μ in blue and orange, respectively (right).



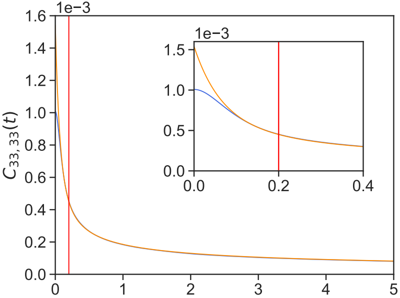
$\tilde{\Lambda}(t)$ $(\Delta z = 0.5\sigma)$

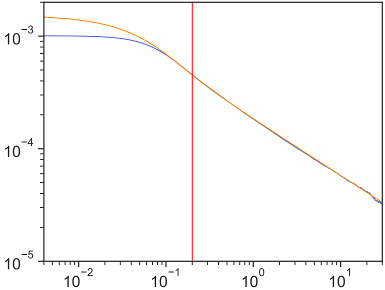
Diagonal elements $\tilde{\Lambda}_{\mu\mu}(t)$ of $\Lambda(t)$ in the reciprocal space. After a time $\tau = 0.2$ we observe a nice plateau for the lower modes.



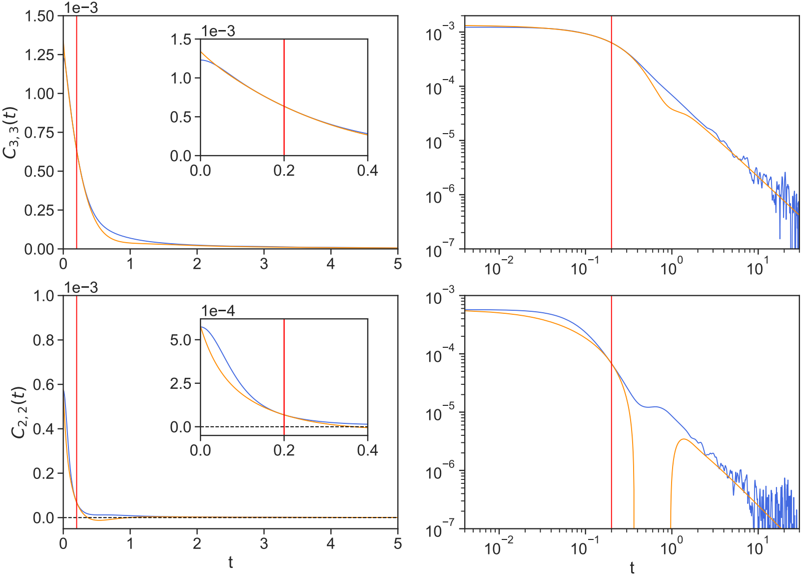
Predicted correlations in the bulk ($\Delta z = 0.5\sigma$)

In the middle of the canal the predicted correlation fits perfectly the measured correlation after a time $\tau = 0.2$



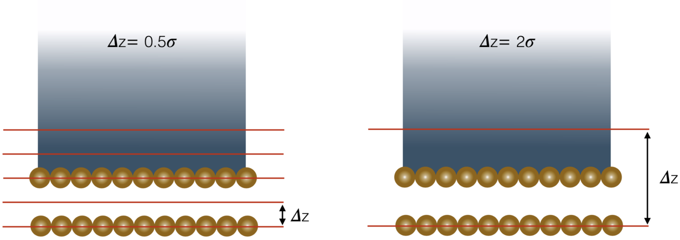


Predicted correlations near the walls ($\Delta z = 0.5\sigma$)

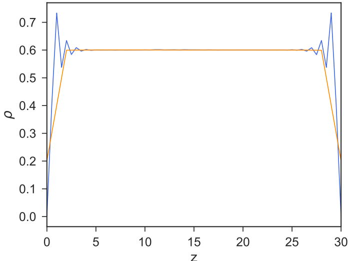


From $\Delta z = 0.5\sigma$ to $\Delta z = 2\sigma$

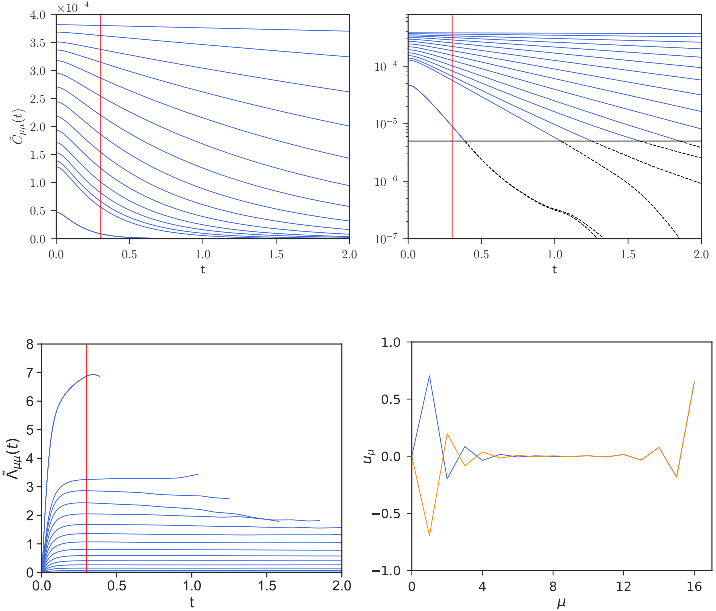
- We change the size of the bin



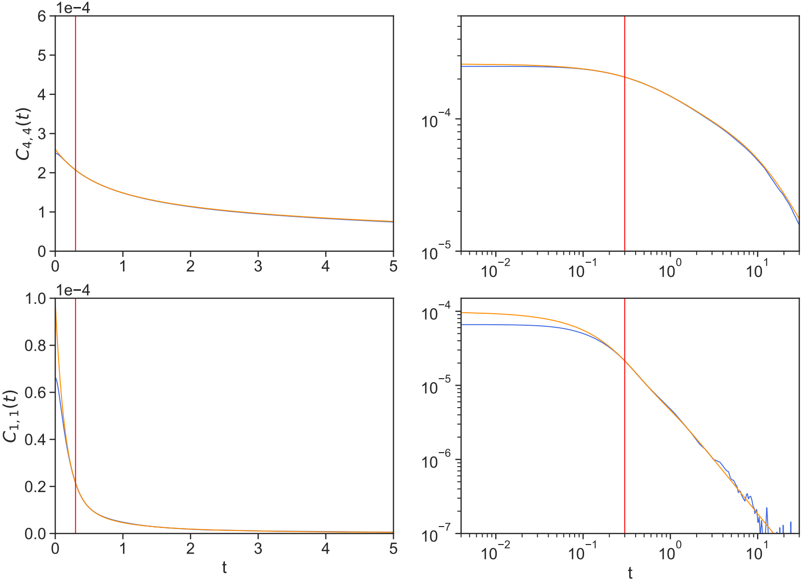
- The thick bins do not capture the layering of the density field



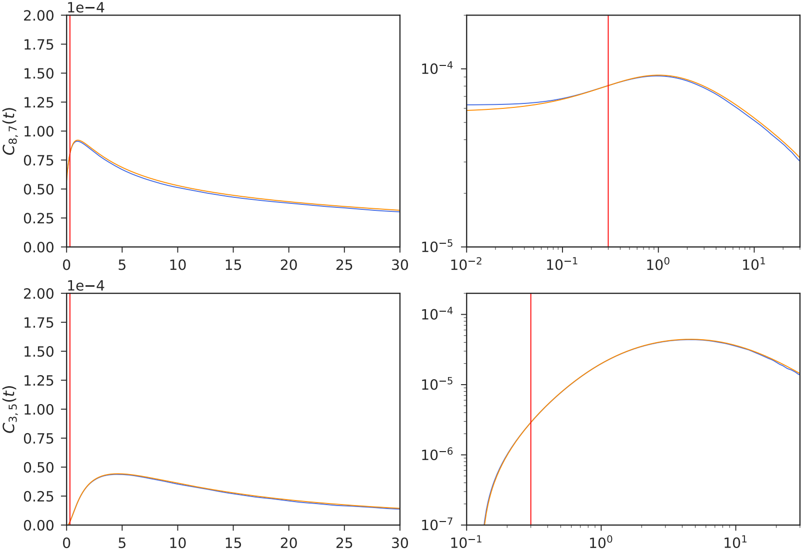
Eigenvalues $\tilde{C}_{\mu\mu}(t)$ ($\Delta = 2\sigma$)



Predicted auto-correlations ($\Delta z = 2\sigma$)



Predicted cross-correlations ($\Delta z = 2\sigma$)



The slip boundary condition

Strategy

Esto habrá que cambiarlo. No muestro las predicciones de C(t) aunque sí que vimos que el teorema se cumple. Directamente plug flow

1. Compute the viscosity (η) and friction kernels (G, H, γ).
2. Corrected Green-Kubo expression which avoid the plateau problem.
3. Predict the evolution of the correlation matrix, $C(t)$, with that transport kernels.
4. Onsager's hypothesis.
5. Navier slip boundary condition $\rightarrow$ slip length.
6. Check that the slip boundary condition is satisfied by a plug flow.
7. The slip lenght is independent on the channel width.

Correlation matrix $C(t)$

- We measure the correlation matrix $C(t) = \left\langle \hat{g}(t)\hat{g}^T \right\rangle$
- The time derivative of the correlation matrix

$$\frac{d}{dt}C(t) = -\int_0^t dt' \left\langle i\mathcal{L}\hat{g}(t')i\mathcal{L}\hat{g}^T \right\rangle = -k_B T M(t)$$

- The Green-Kubo running integral

$$M(t) = \frac{1}{k_B T}\int_0^t dt' \langle i\mathcal{L}\hat{g}(t')i\mathcal{L}\hat{g}^T \rangle$$

- The time derivative of the momentum is

$$i\mathcal{L}\hat{g}_\mu(z) = \hat{F}_\mu(z) - \frac{\hat{\sigma}_\mu(z) - \hat{\sigma}_{\mu-1}(z)}{\Delta z}$$

  where $\hat{F}_\mu = \hat{\mathbf{F}}_\mu^x$ and $\hat{\sigma}_\mu = \hat{\boldsymbol{\sigma}}_\mu^{xz}$.
- Therefore, the Green-Kubo running integral takes the form

$$M(t) = F^T \cdot \eta(t) \cdot F + G(t) \cdot F + F^T \cdot H(t) + \gamma(t)$$

  where F is the bi-diagonal fordward finite difference operator.

The nonlocal transport matrices

$$\eta_{\mu\nu}(t) = \frac{1}{k_B T}\int_0^t dt' \left\langle \hat{\boldsymbol{\sigma}}^{xz}_{\mu}(t')\hat{\boldsymbol{\sigma}}^{xz}_{\nu}\right\rangle$$

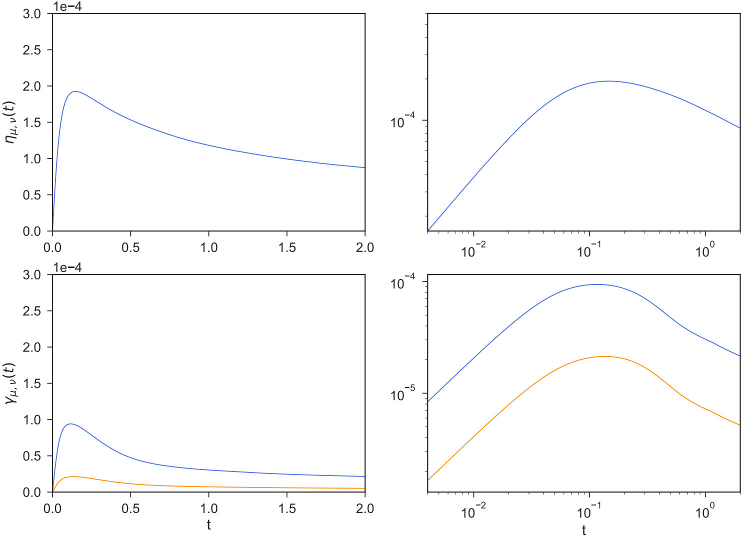
$$G_{\mu\nu}(t) = \frac{1}{k_B T}\int_0^t dt' \left\langle \hat{\mathbf{F}}^{x}_{\mu}(t')\hat{\boldsymbol{\sigma}}^{xz}_{\nu}\right\rangle$$

$$H_{\mu\nu}(t) = \frac{1}{k_B T}\int_0^t dt' \left\langle \hat{\boldsymbol{\sigma}}^{xz}_{\mu}(t')\hat{\mathbf{F}}^{x}_{\nu}\right\rangle$$

$$\gamma_{\mu\nu}(t) = \frac{1}{k_B T}\int_0^t dt' \left\langle \hat{\mathbf{F}}^{x}_{\mu}(t')\hat{\mathbf{F}}^{x}_{\nu}\right\rangle$$

The plateau problem

$\eta_{10,10}(t)$ (middle of the channel), $\gamma_{1,1}$ (blue) and $\gamma_{2,2}$ (orange).



Corrected Green-Kubo expression

- Mori's theory and Markovian approximation

$$\frac{d}{dt}C(t) = -k_B T(\cancel{L} + M^*) \cdot C^{-1}(0) \cdot C(t)$$

- We also have $\frac{d}{dt}C(t) = -k_B T \cdot M(t)$
- The *corrected* Green-Kubo formula $M^* = M(\tau) \cdot C^{-1}(\tau) \cdot C(0)$
- The evolution of the correlation matrix

$$\frac{d}{dt}C(t) = -k_B T \cdot M(\tau) \cdot C^{-1}(\tau) \cdot C(t)$$

- The evolution of the momentum field

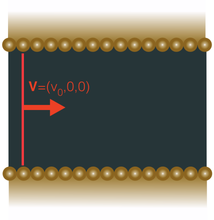
$$\frac{d}{dt}g(t) = -k_B T \cdot M(\tau) \cdot C^{-1}(\tau) \cdot g(t)$$

- The evolution of the velocity field

$$\frac{d}{dt}v(t) = -k_B T \cdot M(\tau) \cdot C^{-1}(\tau) \cdot \mathcal{V} \cdot \underbrace{C^{-1}(\tau) \cdot C(0) \cdot v(t)}_{\overline{v}(t)}$$

Plug flow simulation

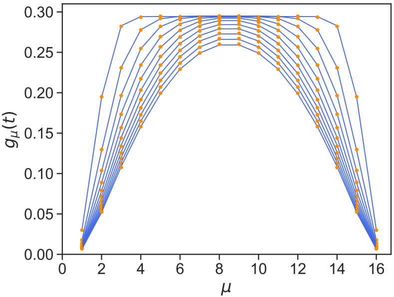
- Simulations to generate a nonequilibrium plug flow.
- Add to the thermal velocity of each fluid atom the same velocity **V**



- Increase the kinetic energy $\rightarrow$ Increase the temperature.
- Rescale the resulting velocities in order to remain at the same temperature.
- Average over 5000 simulations with different initial configurations.
- $g_{\mu}^{x})(t)$ recorded every 2 timesteps.

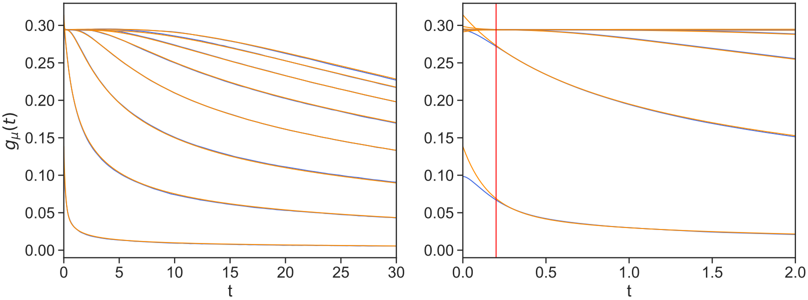
Plug flow predictions

$$g(t) = \exp\{-\Lambda^*(t-\tau)\} \cdot g(\tau)$$



The measured momentum average and the predictions for $\tau = 0.3$ at times $t = 1, 3, ..., 21$ in descending order.

Plug flow predictions



- The measured momentum average and the predictions for modes $\mu = 1, 2, ..., 8$ in ascending order. Zoom at short times.
- Only after the tine in which the transport matrix reached a plateau, and hence a Markovian theory holds, it is expected that we get correct predictions.

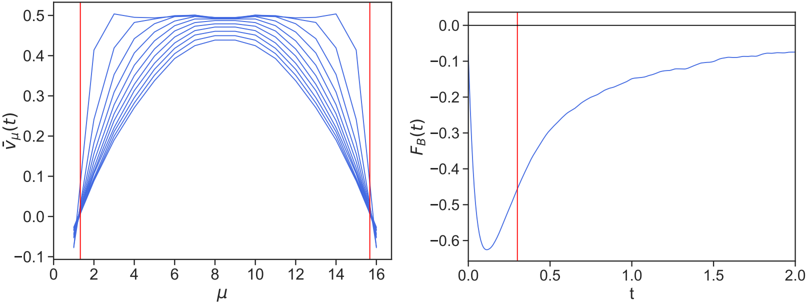
The boundary condition from pillbox argument

Boundary slab of made of B bins near one of the walls.

1. The momentum obeys the dynamics
$$\frac{d}{dt} g(t) = -k_B T \cdot M(\tau) \cdot C^{-1}(\tau) \cdot g(t)$$
2. The velocity field inside the boundary slab is linear
$$\overline{\mathbf{v}}^x_\mu = \overline{\mathbf{v}}^x_{\mathrm{wall}} + \dot{\overline{\gamma}}_{\mathrm{wall}}(\mu \Delta z - z_{\mathrm{wall}})$$
   - z_{wall}: position of the wall.
   - $\overline{\mathbf{v}}^x_{\mathrm{wall}}$: velocity at z_{wall}.
   - $\dot{\overline{\gamma}}_{\mathrm{wall}}$: shear rate.
3. The force on the boundary slab is vanishingly small.

The Navier slip boundary condition and the slip length δ
$$\overline{\mathbf{v}}^x_{\mathrm{wall}} = \delta \dot{\overline{\gamma}}_{\mathrm{wall}} = \frac{\eta - G}{\gamma - H} \dot{\overline{\gamma}}_{\mathrm{wall}}$$

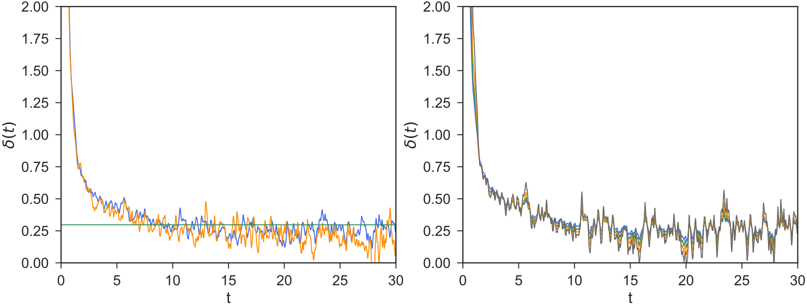
Linear approximation for the velocity and force on the slab



- The linear approximation for the velocity depends on the width of the boundary slab B. We choose $B = 2$.
- The force on the slab boundary vanishes for times larger than $t = 2$.

Validation of the slip boundary condition

- The slip length is measured from $\delta(t) = \frac{\overline{\mathbf{v}}^{x}_{\mathrm{wall}}(t)}{\dot{\overline{\gamma}}_{\mathrm{wall}}(t)}$
- The slip lenght has to be constant according to $\delta = \frac{\eta - G}{\gamma - H}$



- The slip length does not depend on the channel width (left) and is roughly independent of the actual value of τ (right).

Local hydrodynamic model with boundary conditions

- We asess the local hydrodynamic equation (tangential component of the Navier-Stokes equation)

$$\partial_t g(z,t) = \nu \frac{\partial^2}{\partial z^2} g(z,t)$$

  with the slip boundary condition $\bar{\mathbf{v}}^x_{\mathrm{wall}} = \delta \dot{\bar{\gamma}}_{\mathrm{wall}}$ applied at z_{wall}.
- The kinematic viscosity is $\nu = \frac{\eta}{\rho}$.