Nanoscale hydrodynamics near solids

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July 2019

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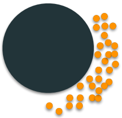
- The expression for γ suffers from the plateau problem.

BEHAVIOUR
FLUID - SOLID
IN THE **NANOSCALE**

KAWASAKI-GUNTON PROJECTION OPERATOR + MARKOVIAN APPROXIMATION



$$\begin{aligned}
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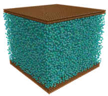
MORI THEORY

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

MD SIMULATIONS



SLIP BOUNDARY CONDITION

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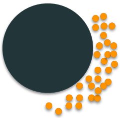

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Hydrodynamics theory for liquids near solids

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- The derivatives of the relevant variables

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

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

Kawasaki-Gunton projection operator

- Separation of timescales between the evolution of the averages of the CG variables, a_i, and the decay of the memory kernel

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

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- 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

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\begin{aligned}
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$$

- $\mathcal{F}[\rho, \mathbf{R}]$: 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 fluid stress tensor and the irreversible force

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

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

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

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

The transport kernels

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

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

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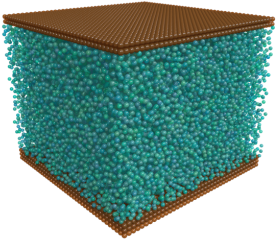
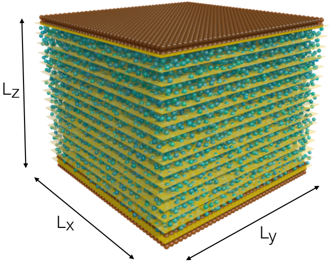
Discrete basis function I

N_{bin} bins with dimensions L_x, L_y, Δz. ($\Delta z = \frac{L_z}{N_{\text{bin}}}$).



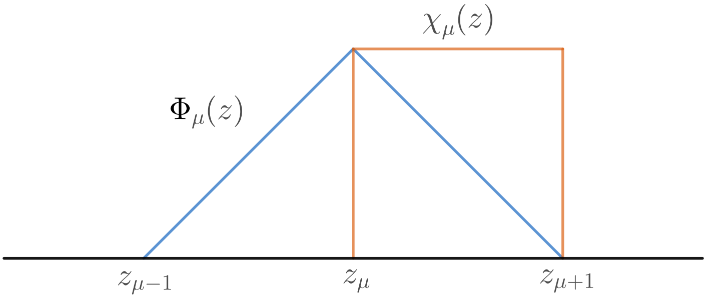


Discrete basis function II

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

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

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



Discrete equations of nanohydrodynamics

$$\frac{d}{dt}\rho_\mu = \int d\mathbf{r}\overline{\rho}\,\overline{\mathbf{v}}\boldsymbol{\nabla}\delta_\mu$$

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

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

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

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

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

Simpler theory

- The amount of information to compute the hydrodynamic equations is exceedingly large:
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  - **G** and **H** have 21 independent components.
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- Under the simplification we may separate the evolution of the selected variables in two contributions: normal and tangent.

The discrete transport kernels

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

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

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

Roadmap

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IN THE NANOSCALE

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MORI THEORY

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

MD SIMULATIONS

SLIP BOUNDARY CONDITION

Space and time locality for unconfined fluids

Mori's theory

- Linear dynamic equations for the correlations of $\hat{A}(t)$

$$\frac{d}{dt}C(t) = -L\cdot C^{-1}(0)\cdot C(t) - \int_0^t dt'\Gamma(t-t')\cdot C^{-1}(0)\cdot C(t')$$

where $L = \langle \hat{A} i\mathcal{L}\hat{A}^T\rangle$.

- Markovian approximation

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

- Mori's equation and Markovian approximation

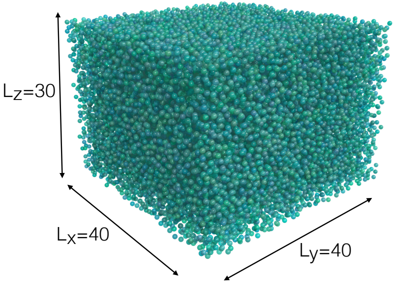
$$\frac{d}{dt}C(t) = -(L+M^*)\cdot C^{-1}(0)\cdot C(t) \equiv \Lambda^*\cdot C(t)$$

- Exponential matrix decay

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

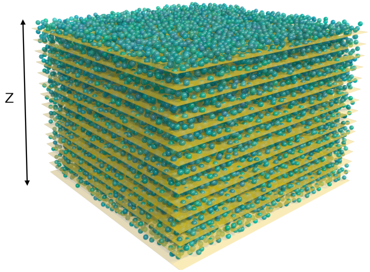
- **We need to find a constant matrix $\boldsymbol{\Lambda}^*$.**

Unconfined fluid. Simulation set up



- $L_x = 40$, $L_y = 40$, $L_z = 30$.
- 28749 particles.
- LJ potential truncated at $\sigma = 2.5$.
- $dt = 2 \cdot 10^{-4}$ in reduced units.

Unconfined fluid. Simulation set up



- Equilibration stage
  - Langevin thermostat for 10^5 timesteps: $T = 2.0$, $\rho = 0.6$.
  - NVE microcanonical conditions for a further 10^5 timesteps.

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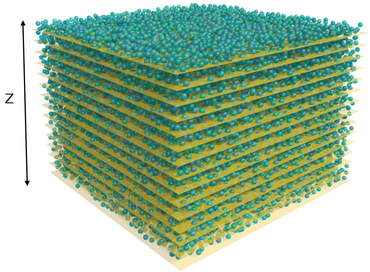

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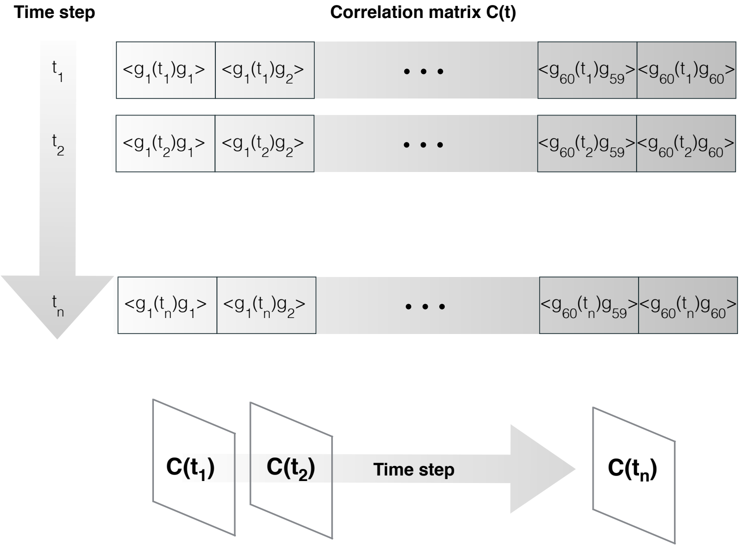
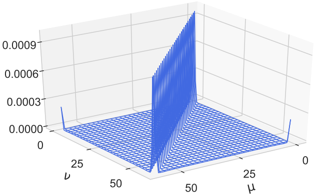
- Production stage
    - 1.5×10^6 timesteps.
    - z axis binned in 60 bins μ. $\mathbf{\Delta z = 0.5\boldsymbol{\sigma}}$.
    - $g_\mu^x(t)$ recorded every 10 timesteps.

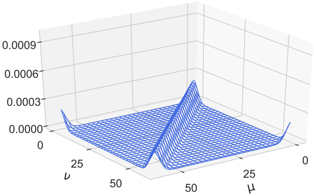
Building the correlation matrix $C(t)$



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)





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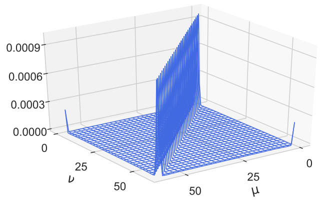
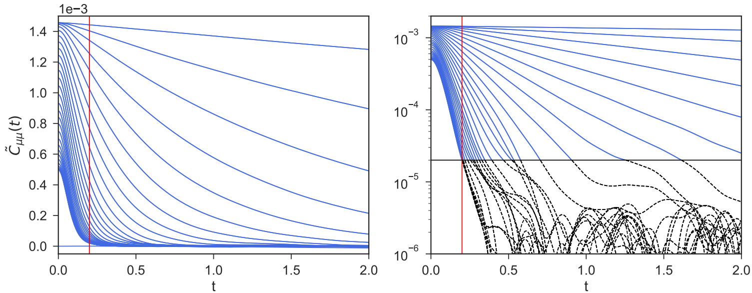
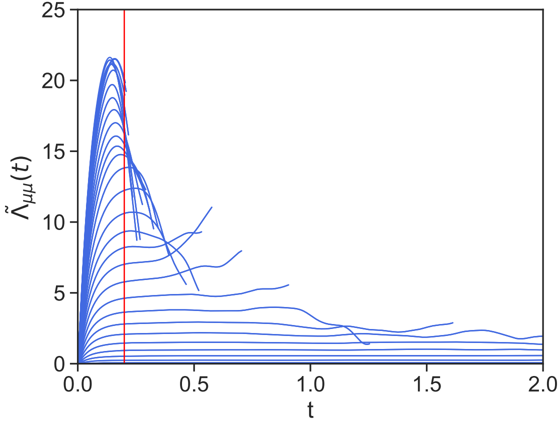


- The evolution of the different eigenvalues $\tilde{C}_{\mu\mu}(t)$.



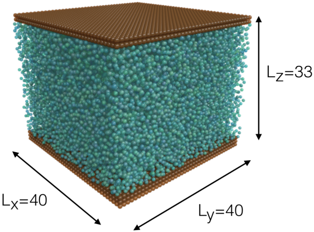
Validation of the Markovian approximation

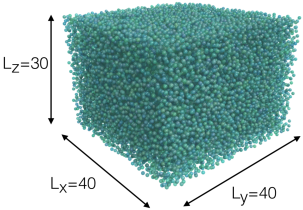
$$\tilde{\Lambda}_{\mu\mu} = -\frac{1}{\tilde{C}_{\mu\mu}(t)} \frac{d\tilde{C}_{\mu\mu}}{dt}(t)$$



Markovian behaviour near solids

Confined fluid. Simulation set up





- $L_x = 40$, $L_x = 40$, $L_z = 33$.
- 28175 particles.
- LJ potential truncated at $\sigma = 2.5$.
- $dt = 2 \cdot 10^{-3}$ in reduced units.

Confined fluid. Simulation set up

- Equilibration stage
    - Langevin thermostat for 10^5 timesteps: $T = 2.0$, $\rho = 0.6$.
    - NVE microcanonical conditions for a further 10^5 timesteps.

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  - 12×10^6 timesteps.
  - $g_\mu^x(t)$ recorded every 2 timesteps.
  - z axis binned in 66 bins μ ($\boldsymbol{\Delta z = 0.5\sigma}$).

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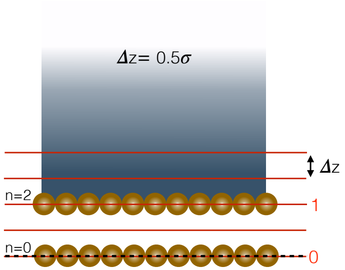
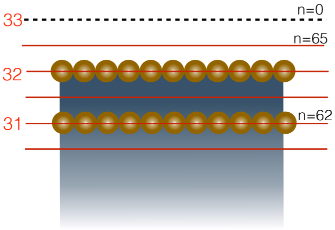
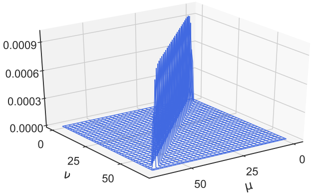
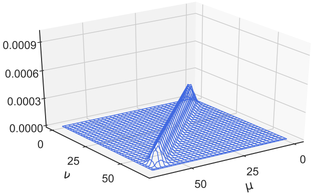




Thin bins ($\Delta z = 0.5\sigma$)

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





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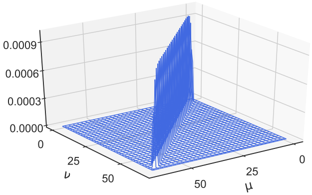
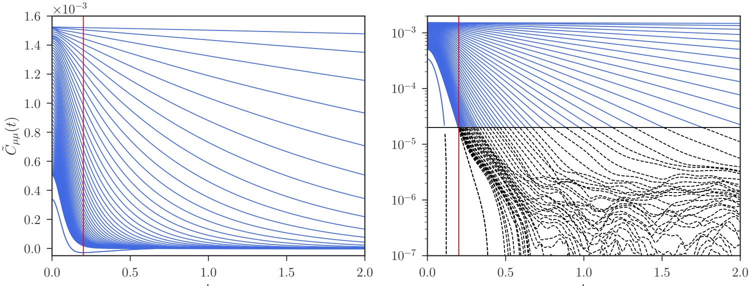
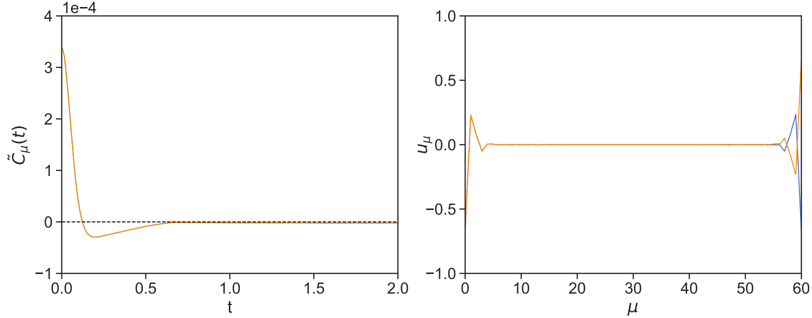


- Evolution of different eigenvalues $\tilde{C}_{\mu\nu}(t)$



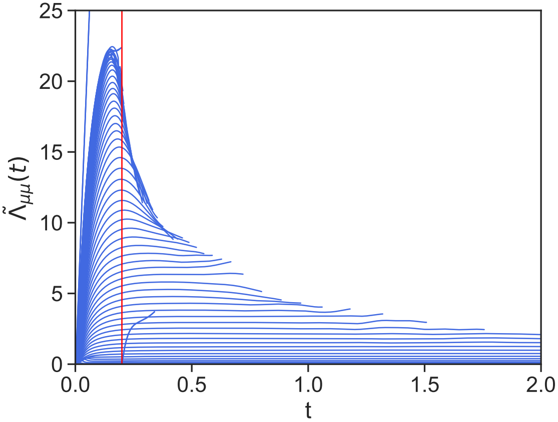
Eigenvalues and eigenvectors near the walls ($\Delta z = 0.5\sigma$)

Eigenvalues $\tilde{C}_\mu(t)$ of $C(t)$ for $\mu = 59, 60$ and the corresponding eigenvectors u_μ in blue and orange, respectively.



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

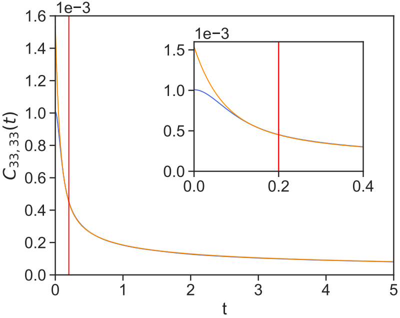
Diagonal elements $\tilde{\Lambda}_{\mu\mu}(t)$ of $\Lambda(t)$ in the reciprocal space. After a time $\tau = 0.2$ we observe a nice plateau for the lower modes.

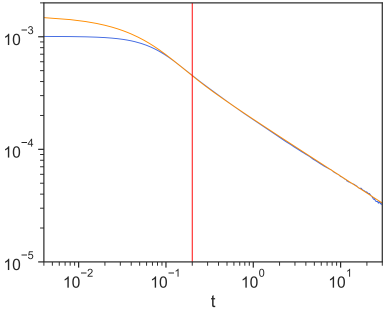


Predicted correlations in the bulk ($\Delta z = 0.5\sigma$)

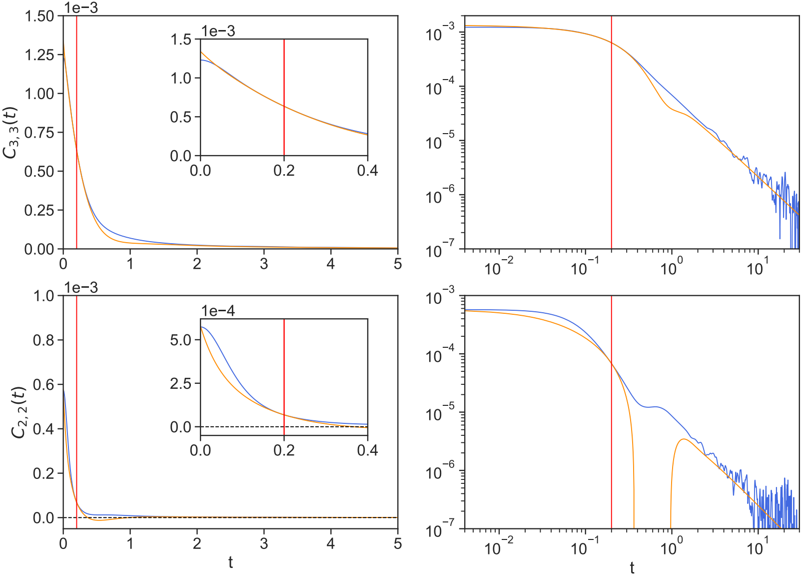
$$C(t) = \exp\{-\Lambda^*(t-\tau)\cdot C(\tau)\}$$

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



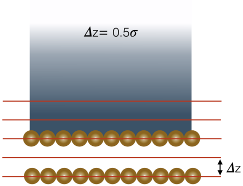


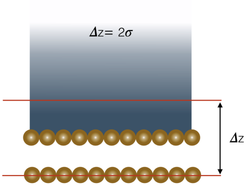
Predicted correlations near the walls ($\Delta z = 0.5\sigma$)



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

- We change the size of the bin





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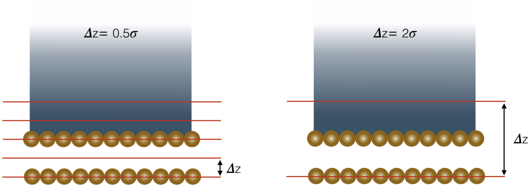
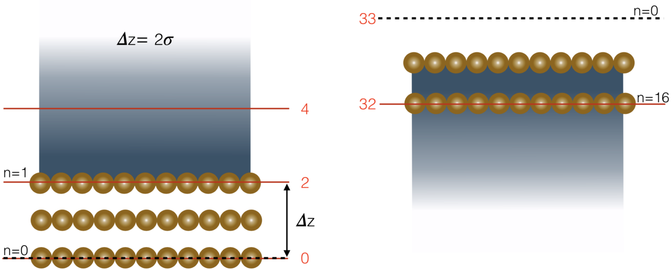
- We change the size of the bin

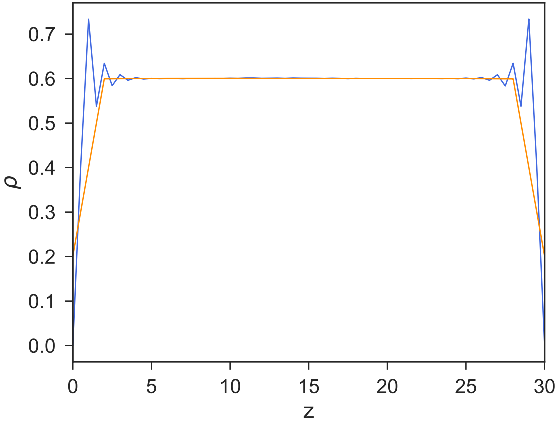


- We need to add a new layer of solid atoms

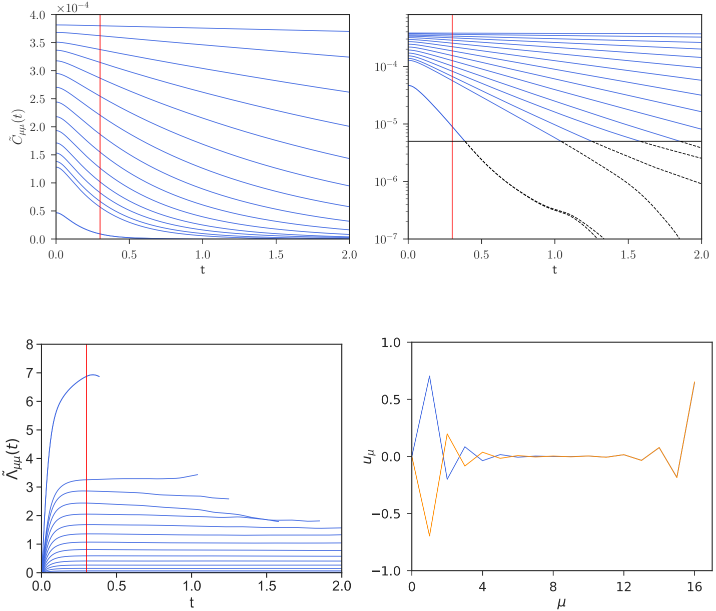


The density layering

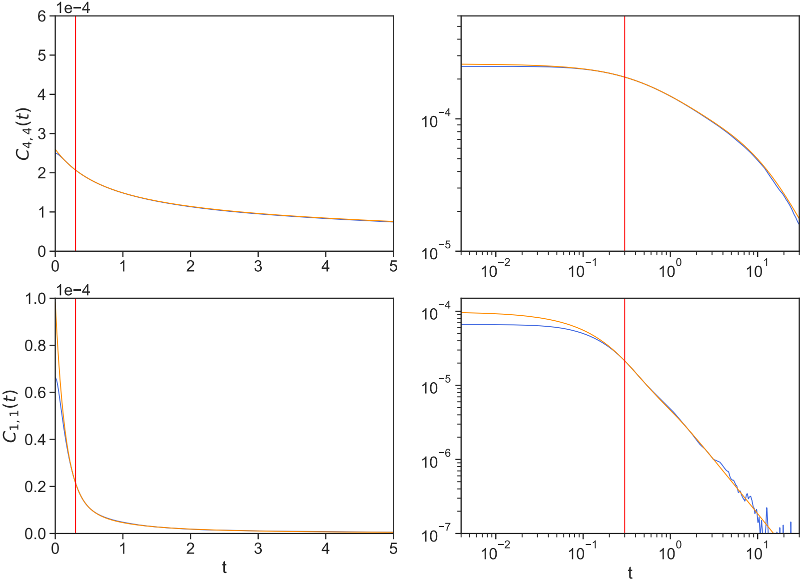
The thick bins do not capture the layering of the density field.



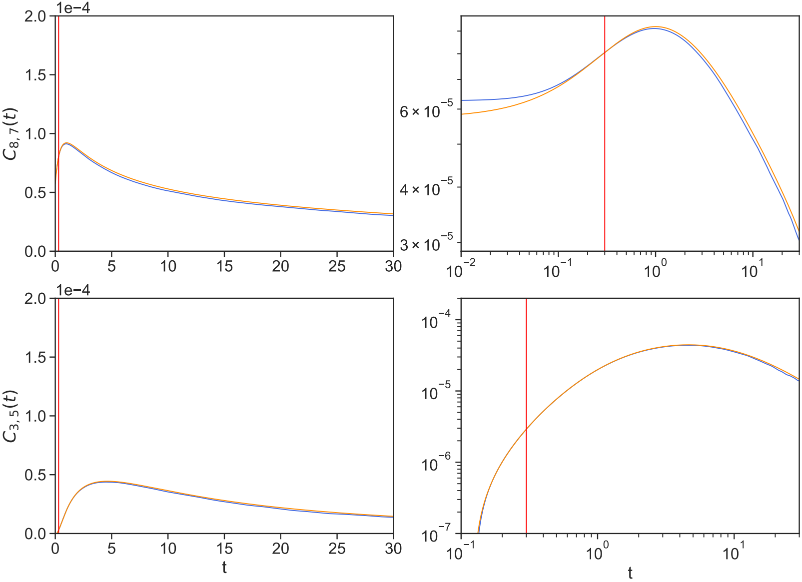
Eigenvalues $\tilde{C}_{\mu\mu}(t)$ ($\Delta = 2\sigma$)



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



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



Roadmap

BEHAVIOUR
FLUID - SOLID
IN THE NANOSCALE

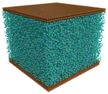
KAWASAKI-GUNTON PROJECTION OPERATOR + MARKOVIAN APPROXIMATION

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

MORI THEORY

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

MD SIMULATIONS



SLIP BOUNDARY CONDITION

The slip boundary condition

Strategy

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 average of the momentum profile, $g(t)$, with that transport kernels.
4. Navier slip boundary condition $\rightarrow$ slip length.
5. Check that the slip boundary condition is satisfied by a plug flow.
6. Compare nonlocal and local theories.

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

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

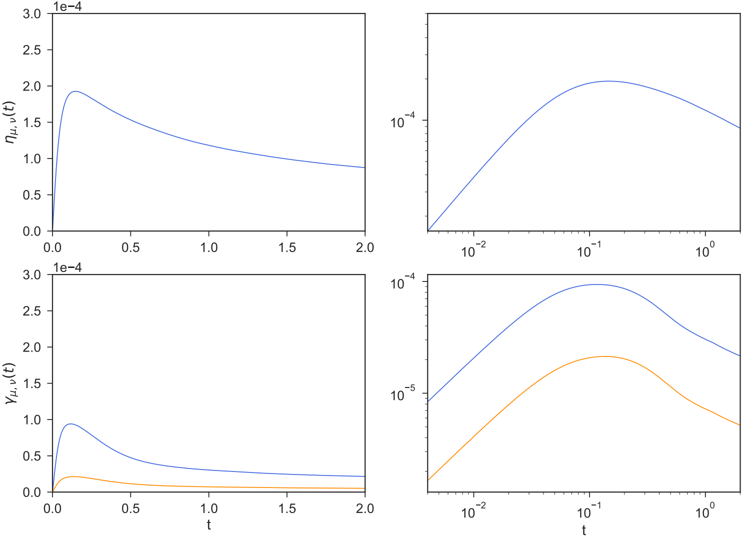
$$G_{\mu\nu}(t) = \frac{1}{k_B T} \int_0^t dt' \left\langle \hat{\mathbf{F}}^{x}_{\mu}(t') \hat{\boldsymbol{\sigma}}^{xz}_{\nu} \right\rangle$$

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

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

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

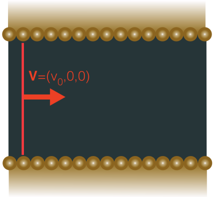
$$\frac{d}{dt}g(t) = -k_B T \cdot M(\tau)\cdot C^{-1}(\tau)\cdot g(t)$$

- 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

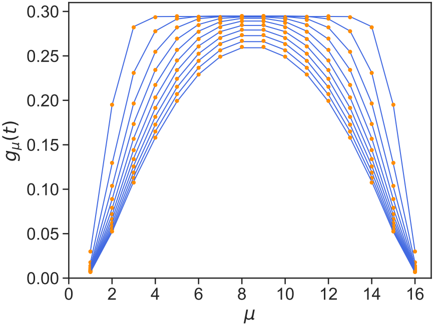
- Simulations to generate a nonequilibrium plug flow.
- Add to the thermal velocity of each fluid atom the same velocity **V**



- 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.

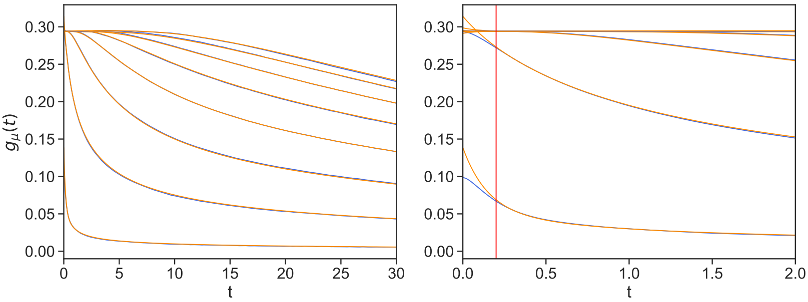
Plug flow predictions

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



The measured momentum average and the predictions for $\tau = 0.3$ at times $t = 1, 3, \ldots, 21$ 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 time 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

$$\overline{\mathbf{v}}_\mu^x = \overline{\mathbf{v}}_{\mathrm{wall}}^x + \dot{\overline{\gamma}}_{\mathrm{wall}}(\mu \Delta z - z_{\mathrm{wall}})$$

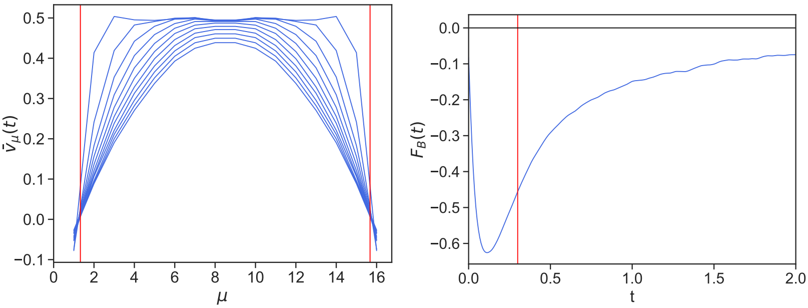
   - z_{wall}: position of the wall.
   - $\overline{\mathbf{v}}_{\mathrm{wall}}^x$: velocity at z_{wall}.
   - $\dot{\overline{\gamma}}_{\mathrm{wall}}$: shear rate.

3. The force on the boundary slab is vanishingly small.

The Navier slip boundary condition and the slip length δ

$$\overline{\mathbf{v}}_{\mathrm{wall}}^x = \delta \dot{\overline{\gamma}}_{\mathrm{wall}} = \frac{\eta - G}{\gamma - H} \dot{\overline{\gamma}}_{\mathrm{wall}}$$

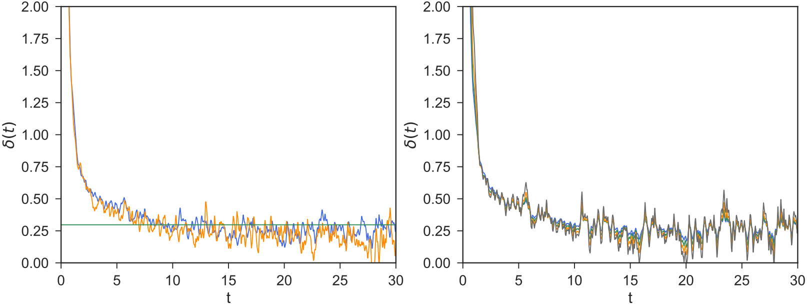
Linear approximation for the velocity and force on the slab



- 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 $\delta(t) = \frac{\overline{\mathbf{v}}^x_{\text{wall}}(t)}{\dot{\overline{\gamma}}_{\text{wall}}(t)}$
- 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

- The disrete version of the local equation $\partial_t g(z,t) = \nu \frac{\partial^2}{\partial z^2} g(z,t)$

$$\frac{d}{dt} g_\mu(t) = \nu \frac{1}{\Delta z^2} \left(g_{\mu-1}(t) + g_{\mu+1}(t) - 2 g_\mu(t)\right)$$

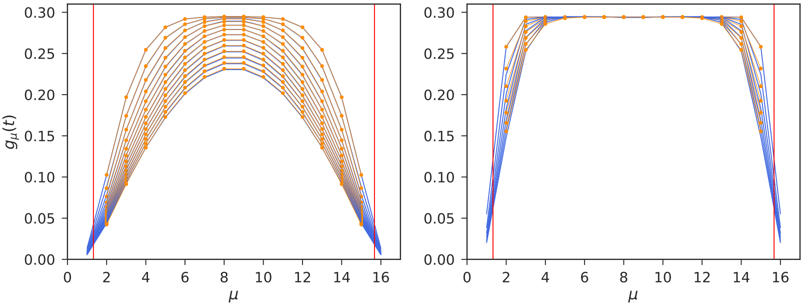
  where the kinematic viscosity is $\nu = \frac{\eta}{\rho}$.
- Nonlocal hydrodynamic equation

$$\frac{d}{dt}\mathbf{g}^x_\mu(t) = -\sum_\nu \mathcal{V}_\nu \frac{[\eta_{\mu\nu} - \eta_{\mu-1\nu} - \eta_{\mu\nu-1} + \eta_{\mu-1\nu-1}]}{\Delta z^2} \overline{\mathbf{v}}^x_\nu + \sum_\nu \mathcal{V}_\nu \frac{[G_{\mu\nu} - G_{\mu\nu-1}]}{\Delta z} \overline{\mathbf{v}}^x_\nu + \sum_\nu \mathcal{V}_\nu \frac{[H_{\mu\nu} - H_{\mu-1\nu}]}{\Delta z} \overline{\mathbf{v}}^x_\nu - \sum_\nu \mathcal{V}_\nu \gamma_{\mu\nu} \overline{\mathbf{v}}^x_\nu$$

- We use the slip boundary condition $\overline{\mathbf{v}}^x_{\mathrm{wall}} = \delta \dot{\overline{\gamma}}_{\mathrm{wall}}$ applied at z_{wall}.

The local predictions

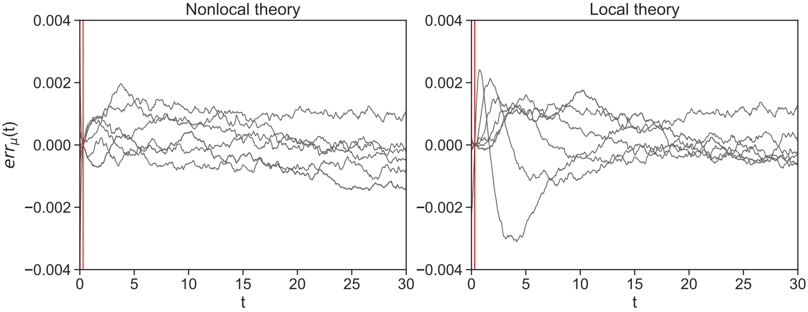
$$g(t) = \exp\{\nu\Delta'(t-\tau)\}g(\tau)$$



Local prediction compared with the measured momentum density profile. Times are $t = 5, 7, \cdots, 29$ (left panel) in descending order. Times $t = 0.3, 0.6, \cdots 2.1$ (right panel).

Comparison of the error between local and nonlocal theories

$$err_{\mu}(t) = g_{\mu}(t) - g_{\mu}^{\mathrm{predict}}(t)$$



Conclusions

Future Directions

1. Non-Markovian effects may be related to the “hard” nature of the crystal.
   - More realistic models for the solid wall.
   - Change the thermodynamic point.
   - Hydrofobicity or hydrofillicity affect the conclusions.
2. Non-isothermal theory.
   - New CG variables

$$\hat{e}_{\mathbf{r}}(z) = \sum_i^N e_i \delta(\mathbf{r} - \mathbf{q}_i) \qquad \hat{E}(z) = \sum_{i'}^{N'} e_{i'}$$

   - Solve the problem of thermal boundary conditions.
   - Understand the heat transfer between solids and fluid, specifically between nanoparticles and molten salts.

Relevant references

- D.Camargo, J.A. de la Torre, **D.Duque-Zumajo**, P.Español, R.Delgado-Buscalioni, and F. Chejne. Nanoscale hydrodynamics near solids. *Journal of Chemical Physics*, 148(6), 2018.
- P.Español, J.A.de la Torre, and **D.Duque-Zumajo**. Solution to the plateau problem in the Green-Kubo formula. *Physical Review E*, 99(2), 2019.
- **D. Duque-Zumajo**, D. Camargo, J. A. de la Torre, F. Chejne, and Pep Español. Discrete hydrodynamics for planar flows with confining walls. *Physical Review E*, 2019.
- **D. Duque-Zumajo**, J. A. de la Torre, and Pep Español. Slip and non-Markovian effects in nanohydrodynamics (in preparation). *Physical Review Letters*, 2019.
- **D. Duque-Zumajo**, D. Camargo, J. A. de la Torre, Farid Chejne, and Pep Español. Discrete hydrodynamics near solid walls: non-Markovian effects and slip (in preparation). *Physical Review E*, 2019.

Nanoscale hydrodynamics near solids

July 2019

Diego Duque Zumajo

Dual basis functions and mass matrix

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

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

- 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 $M^{\Phi}_{\mu\nu}$

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

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 $\odot = ||, \perp$

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

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

$$L = \langle \hat{A} i\mathcal{L}\hat{A}^T\rangle$$
$$C(0) = \langle \hat{A}\hat{A}^T\rangle$$
$$\Gamma(t) = \langle F^+(t)F^{+T}(0)\rangle$$

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$$\begin{aligned} L &= \langle \hat{A} i\mathcal{L}\hat{A}^T\rangle \\ C(0) &= \langle \hat{A}\hat{A}^T\rangle \\ \Gamma(t) &= \langle F^+(t)F^{+T}(0)\rangle \end{aligned}$$

- The projected forces are given by

$$F^+(t) = \exp\{\mathcal{Q}i\mathcal{L}t\}\mathcal{Q}i\mathcal{L}\hat{A}$$

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$$\frac{d}{dt}C(t) = -L\cdot C^{-1}(0)\cdot C(t) - \int_0^t dt'\Gamma(t-t')\cdot C^{-1}(0)\cdot C(t')$$
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$$L = \langle \hat{A} i\mathcal{L}\hat{A}^T\rangle$$
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- 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 $\boldsymbol{\Lambda}^*$.**