

# Nanoscale hydrodynamics near solids

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# Motivation

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

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

- Bocquet and Barrat [**Bocquet1993**]

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

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

## BEHAVIOUR FLUID - SOLID IN THE NANOSCALE

KAWASAKI-GUNTON  
PROJECTION OPERATOR + MARKOVIAN APPROXIMATION



$$\partial_t \rho(\mathbf{r}) = -\nabla \cdot \mathbf{g}(\mathbf{r})$$

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

$$\dot{\mathbf{R}} = \frac{\mathbf{P}}{M}$$

$$\dot{\mathbf{P}} = -\frac{\partial \mathcal{F}}{\partial \mathbf{R}} - \int d\mathbf{r} \mathcal{S}(\mathbf{r})$$

MORI THEORY

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

MD SIMULATIONS

SLIP BOUNDARY CONDITION



# **Hydrodynamics theory for liquids near solids**

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## 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

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

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

- The derivatives of the relevant variables

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

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

## Kawasaki-Gunton projection operator

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

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

- **Reversible term:**  $\nu_i = \text{Tr}[\bar{\rho}_t i \mathcal{L} \hat{A}_i]$
- The relevant ensemble:

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

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

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

- The Kawasaki-Gunton projection operator is given by

$$Q_{t'} \hat{F}(z) = \hat{F}(z) - \text{Tr}[\bar{\rho}_{t'} \hat{F}] - \sum_i (\hat{A}_i(z) - a_i(t')) \frac{\partial}{\partial a_i(t')} \text{Tr}[\bar{\rho}_{t'} \hat{F}]$$

# Equations of nanohydrodynamics

$$\partial_t \rho(\mathbf{r}) = -\nabla \cdot \mathbf{g}(\mathbf{r})$$

$$\partial_t \mathbf{g}(\mathbf{r}) = -\nabla \cdot (\mathbf{g}(\mathbf{r}) \mathbf{v}(\mathbf{r})) - \rho(\mathbf{r}) \nabla \frac{\delta \mathcal{F}}{\delta \rho(\mathbf{r})} [\rho, \mathbf{R}] + \nabla \cdot \boldsymbol{\Sigma}(\mathbf{r}) + \mathcal{S}(\mathbf{r})$$

$$\dot{\mathbf{R}} = \frac{\mathbf{P}}{M}$$

$$\dot{\mathbf{P}} = -\frac{\partial \mathcal{F}}{\partial \mathbf{R}} - \int d\mathbf{r} \mathcal{S}(\mathbf{r})$$

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

# The transport kernels

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

$$\Sigma^{\alpha\beta}(\mathbf{r}) = \int d\mathbf{r}' \eta_{\mathbf{rr}'}^{\alpha\beta\alpha'\beta'} \nabla_{\mathbf{r}'}^{\beta'} \mathbf{v}^{\alpha'}(\mathbf{r}')$$

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

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

# The transport kernels

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

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

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

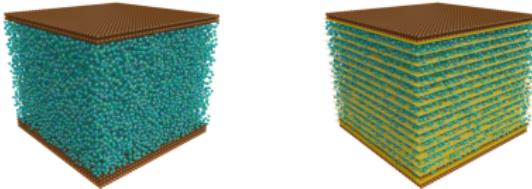
$$\gamma_{\mathbf{rr}'} \equiv \frac{1}{k_B T} \int_0^{\Delta t} dt' \langle \mathcal{Q}_t \hat{\mathbf{F}}_{\mathbf{r}}^{s \rightarrow l}(t') \mathcal{Q}_t \hat{\mathbf{F}}_{\mathbf{r}'}^{s \rightarrow l} \rangle^{\lambda(t)}$$

## Simpler theory

- The amount of information to compute the hydrodynamic equations is exceedingly large:
  - $\eta$  has 36 independent components.
  - $\mathbf{G}$  and  $\mathbf{H}$  have 21 independent components.
  - $\gamma$  has 9 independent components.
- The interactions felt by the fluid due to the walls are statistically planar and isotropic. We restrict 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

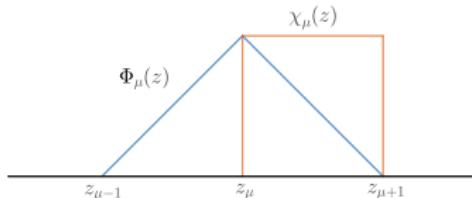
- $N_{\text{bin}}$  bins with dimensions  $L_x, L_y, \Delta z$  ( $L_z/N_{\text{bin}}$ ).



- 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

$$M_{\mu\nu}^\Phi = \left( \Phi_\mu \Phi_\nu \right)$$

where we have introduced the notation  $\left( \cdots \right) = \int d\mathbf{r} \dots$

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

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

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

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

# Discrete equations of nanohydrodynamics

$$\begin{aligned}\frac{d}{dt} \rho_\mu &= \left( \bar{\rho} \bar{\mathbf{v}} \nabla \delta_\mu \right) \\ \frac{d}{dt} \mathbf{g}_\mu &= \left( \bar{\rho} \bar{\mathbf{v}} \bar{\mathbf{v}} \cdot \nabla \delta_\mu \right) - \sum_{\nu} \left( \bar{\rho} \delta_\mu \nabla \delta_\nu \right) \frac{\partial F}{\partial \rho_\nu}(\rho) \\ &\quad - \sum_{\nu} \mathcal{V}_\nu \frac{\mathbf{n} \cdot [\eta_{\mu\nu} - \eta_{\mu-1\nu} - \eta_{\mu\nu-1} + \eta_{\mu-1\nu-1}]}{\Delta z^2} : \mathbf{n} \tilde{\mathbf{v}}_\nu \\ &\quad + \sum_{\nu} \mathcal{V}_\nu \frac{[\mathbf{G}_{\mu\nu} - \mathbf{G}_{\mu\nu-1}]}{\Delta z} \cdot \mathbf{n} \tilde{\mathbf{v}}_\nu \\ &\quad + \sum_{\nu} \mathcal{V}_\nu \frac{\mathbf{n} \cdot [\mathbf{H}_{\mu\nu} - \mathbf{H}_{\mu-1\nu}]}{\Delta z} \cdot \tilde{\mathbf{v}}_\nu \\ &\quad - \sum_{\nu} \mathcal{V}_\nu \gamma_{\mu\nu} \cdot \tilde{\mathbf{v}}_\nu\end{aligned}$$

## 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  $\eta_{\mu\nu}$ ,  $\mathbf{G}_{\mu\nu}$ ,  $\mathbf{H}_{\mu\nu}$  and  $\gamma_{\mu\nu}$ .
- 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

$$\frac{d}{dt} \rho_\mu = \left( \bar{\rho} \bar{v}^z \nabla^z \delta_\mu \right)$$

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

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

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

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

$$M_{\mu\nu}^\odot = -\frac{\eta_{\mu\nu}^\odot - \eta_{\mu-1\nu}^\odot - \eta_{\mu\nu-1}^\odot + \eta_{\mu-1\nu-1}^\odot}{\Delta z^2} + \frac{G_{\mu\nu}^\odot - G_{\mu\nu-1}^\odot}{\Delta z}$$
$$+ \frac{H_{\mu\nu}^\odot - H_{\mu-1\nu}^\odot}{\Delta z} - \gamma_{\mu\nu}^\odot$$

# The discrete transport kernels

$$\begin{aligned}\eta_{\mu\nu}^{\parallel} &= \frac{1}{k_B T} \int_0^\tau dt \left\langle \mathcal{Q} \hat{\sigma}_\mu^{xz}(t) \mathcal{Q} \hat{\sigma}_\nu^{xz} \right\rangle & \eta_{\mu\nu}^{\perp} &= \frac{1}{k_B T} \int_0^\tau dt \left\langle \mathcal{Q} \hat{\sigma}_\mu^{zz}(t) \mathcal{Q} \hat{\sigma}_\nu^{zz} \right\rangle \\ G_{\mu\nu}^{\parallel} &= \frac{1}{k_B T} \int_0^\tau dt \left\langle \mathcal{Q} \hat{\mathbf{F}}_\mu^x(t) \mathcal{Q} \hat{\sigma}_\nu^{xz} \right\rangle & G_{\mu\nu}^{\perp} &= \frac{1}{k_B T} \int_0^\tau dt \left\langle \mathcal{Q} \hat{\mathbf{F}}_\mu^z(t) \mathcal{Q} \hat{\sigma}_\nu^{zz} \right\rangle \\ H_{\mu\nu}^{\parallel} &= \frac{1}{k_B T} \int_0^\tau dt \left\langle \mathcal{Q} \hat{\sigma}_\mu^{xz}(t) \mathcal{Q} \hat{\mathbf{F}}_\nu^x \right\rangle & H_{\mu\nu}^{\perp} &= \frac{1}{k_B T} \int_0^\tau dt \left\langle \mathcal{Q} \hat{\sigma}_\mu^{zz}(t) \mathcal{Q} \hat{\mathbf{F}}_\nu^z \right\rangle \\ \gamma_{\mu\nu}^{\parallel} &= \frac{1}{k_B T} \int_0^\tau dt \left\langle \mathcal{Q} \hat{\mathbf{F}}_\mu^x(t) \mathcal{Q} \hat{\mathbf{F}}_\nu^x \right\rangle & \gamma_{\mu\nu}^{\perp} &= \frac{1}{k_B T} \int_0^\tau dt \left\langle \mathcal{Q} \hat{\mathbf{F}}_\mu^z(t) \mathcal{Q} \hat{\mathbf{F}}_\nu^z \right\rangle\end{aligned}$$

## Summary

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

## **Space and time locality for unconfined fluids**

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## 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

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

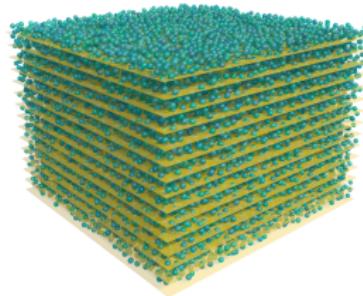
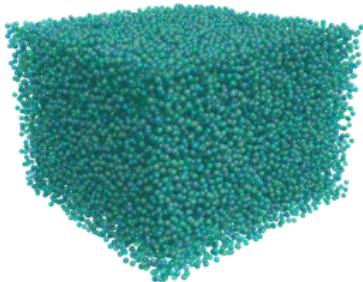
- For a linear Markovian theory the only possibility for a correlation is to decay in an exponential matrix way

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

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

## 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  $40 \times 40 \times 30$ .
- $dt = 0.002$  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
  - $1.5 \times 10^6$  timesteps.
  - $z$  axis binned in 60 bins  $\mu$ .  $\Delta z = 0.5\sigma$ .
  - $g_\mu^x(t)$  recorded every 10 timesteps.

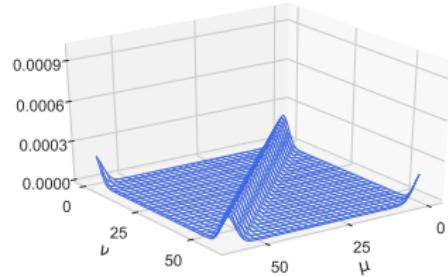
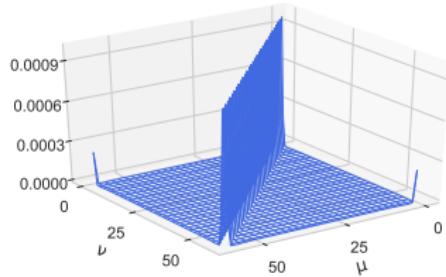
# Building the correlation matrix $C(t)$

Time step	Correlation matrix $C(t)$			
$t_1$	$\langle g_1(t_1)g_1 \rangle$	$\langle g_1(t_1)g_2 \rangle$	• • •	$\langle g_{60}(t_1)g_{59} \rangle$ $\langle g_{60}(t_1)g_{60} \rangle$
$t_2$	$\langle g_1(t_2)g_1 \rangle$	$\langle g_1(t_2)g_2 \rangle$	• • •	$\langle g_{60}(t_2)g_{59} \rangle$ $\langle g_{60}(t_2)g_{60} \rangle$
$t_n$	$\langle g_1(t_n)g_1 \rangle$	$\langle g_1(t_n)g_2 \rangle$	• • •	$\langle g_{60}(t_n)g_{59} \rangle$ $\langle g_{60}(t_n)g_{60} \rangle$

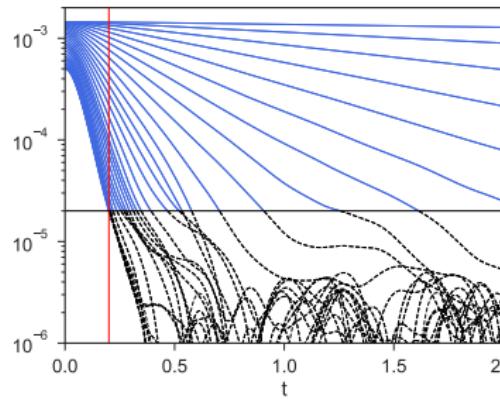
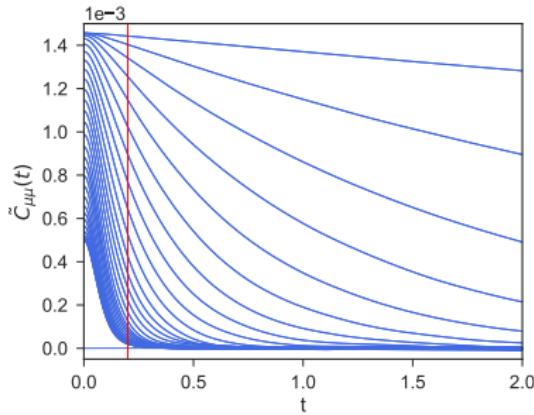


# The correlation matrix $C(t)$ and its eigenvalues $\tilde{C}_{\mu\mu}$

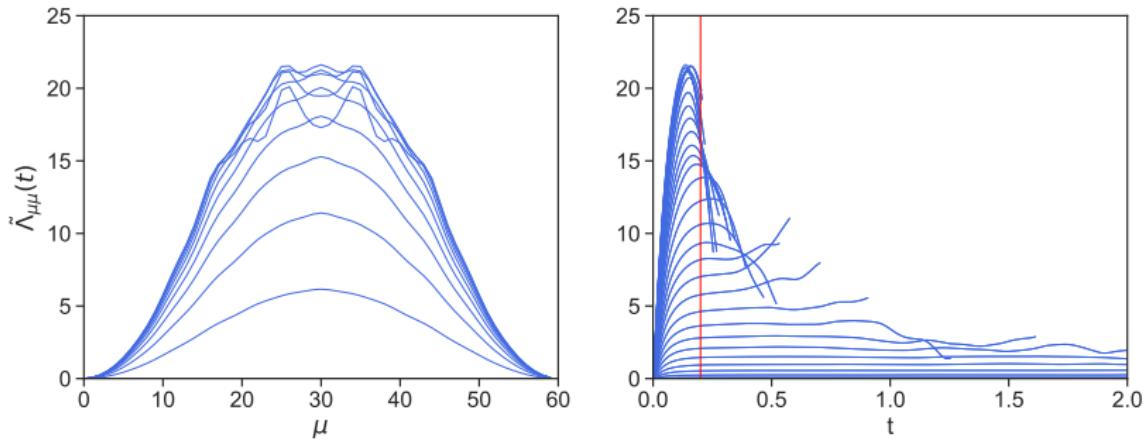
- The correlation matrix  $C(t)$  at  $t = 0$  (left) and  $t = 0.6$  (right)



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



# Validation of the Markovian approximation



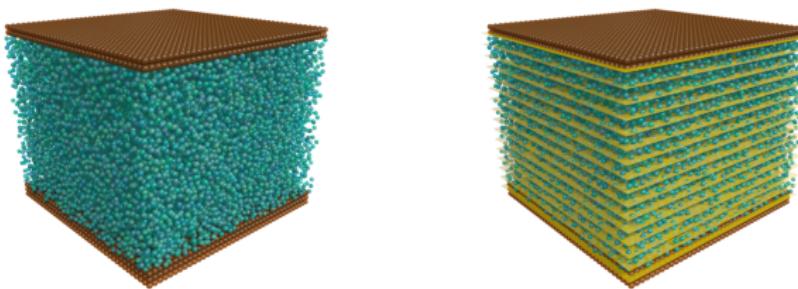
In the left panel, in ascending order the plotted times go from  $t = 0$  to  $t = 0.20$  in intervals of 0.02. In the right panel the time evolution of  $\tilde{\Lambda}_{\mu\mu}(t)$ .

## **Markovian behaviour near solids**

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## The system and the CG variables

- The system



- The CG variables and its correlation

$$\hat{\mathbf{g}}_\mu^x = \sum_i^N \mathbf{p}_i \delta_\mu(\mathbf{q}_i), \quad \hat{\mathbf{g}}^T = (\hat{\mathbf{g}}_1^x, \dots, \hat{\mathbf{g}}_{N_{\text{bin}}}^x), \quad C(t) = \langle \hat{\mathbf{g}}(t) \hat{\mathbf{g}}^T \rangle$$

## 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  $40 \times 40 \times 33$ .
- $dt = 0.002$  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
  - $12 \times 10^6$  timesteps.
  - $z$  axis binned in 66 bins  $\mu \Delta z = 0.5\sigma$  or 33 bins  $\mu \Delta z = 2\sigma$ .
  - $g_\mu^x(t)$  recorded every 2 timesteps.

# Reciprocal space

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

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

- Unitary matrix  $E(t)$

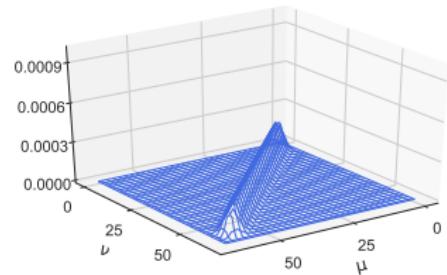
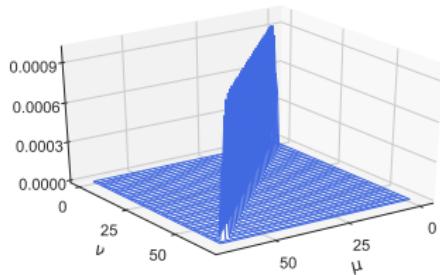
$$E^{-1}(t) \cdot C(t) \cdot E(t) = \tilde{C}(t)$$

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

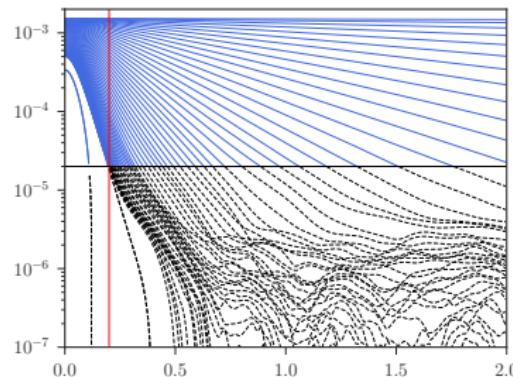
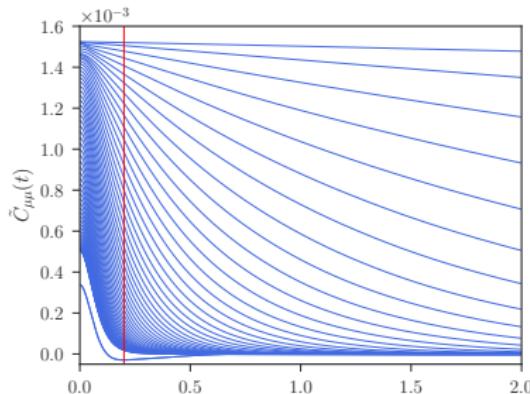
$$\tilde{C}_\mu(t) = \exp\{-\tilde{\Lambda}_{\mu\mu}(t - \tau)\} \tilde{C}_\mu(\tau)$$

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

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

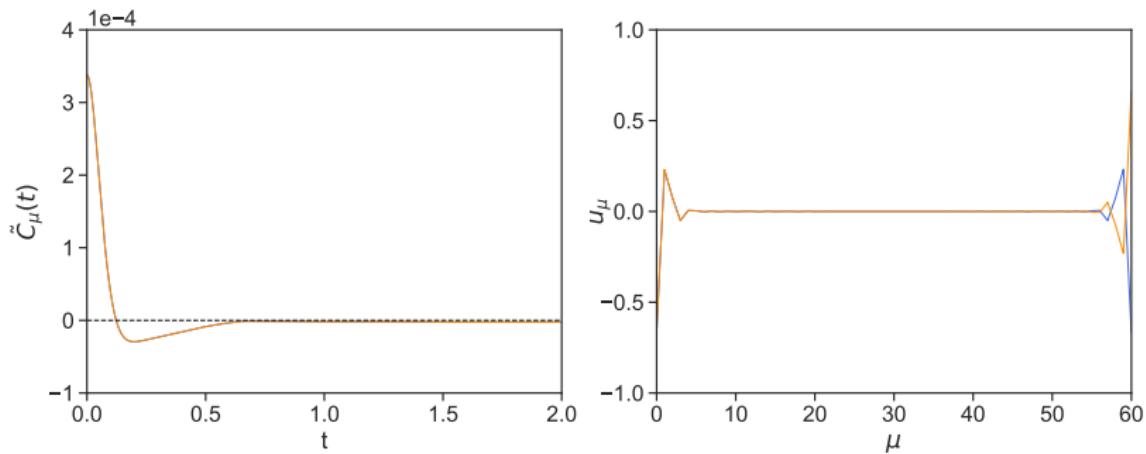


- Evolution of different eigenvalues  $\tilde{C}_{\mu\nu}(t)$



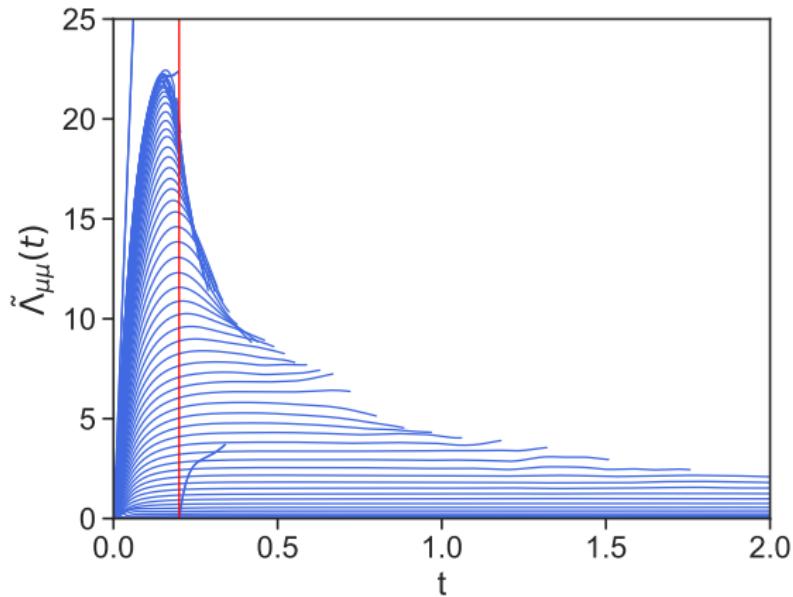
## Eigenvalues and eigenvectors near the walls ( $\Delta z = 0.5\sigma$ )

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  $u_\mu$  in blue and orange, respectively (right).



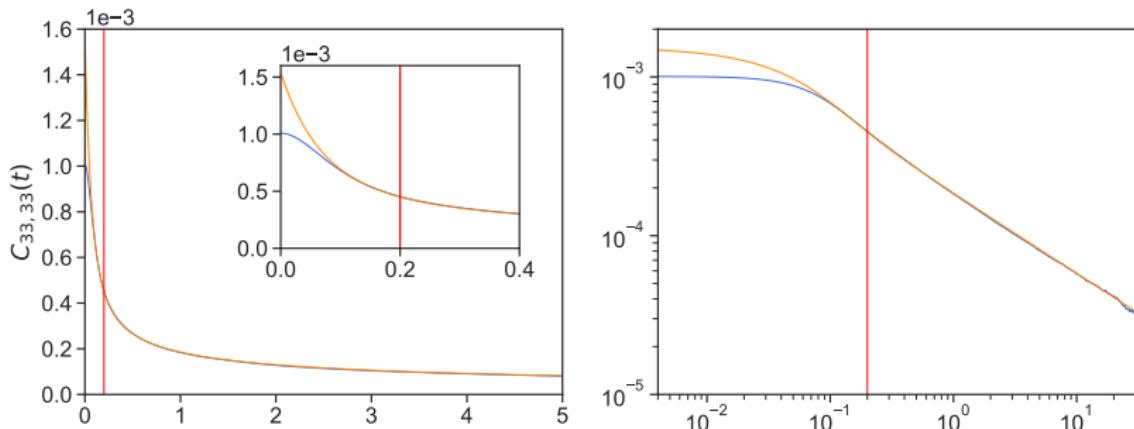
$$\tilde{\Lambda}(t) \ (\Delta z = 0.5\sigma)$$

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.

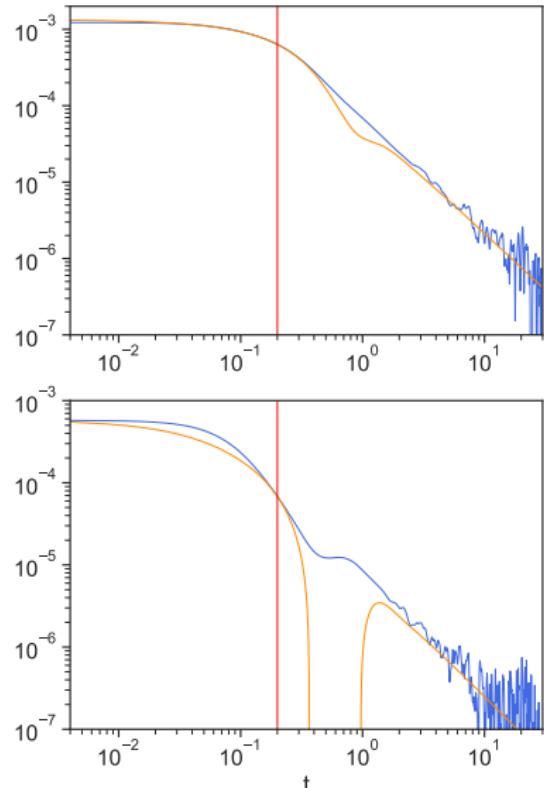
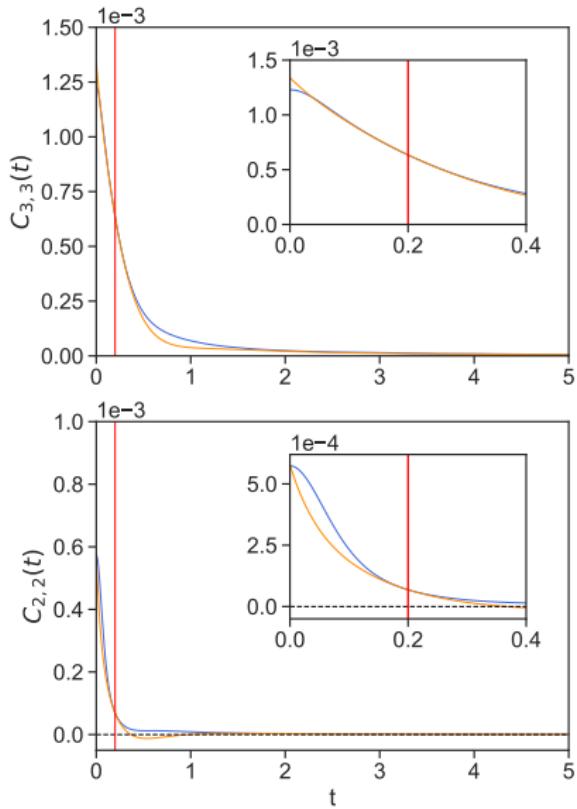


## Predicted correlations in the bulk ( $\Delta z = 0.5\sigma$ )

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

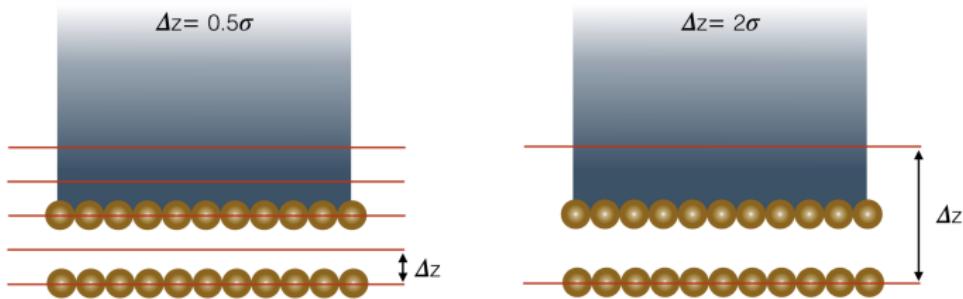


# Predicted correlations near the walls ( $\Delta z = 0.5\sigma$ )

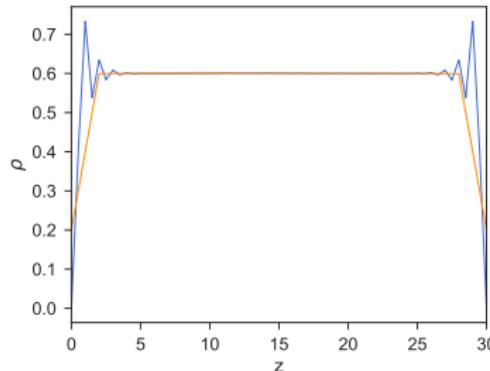


## From $\Delta z = 0.5\sigma$ to $\Delta z = 2\sigma$

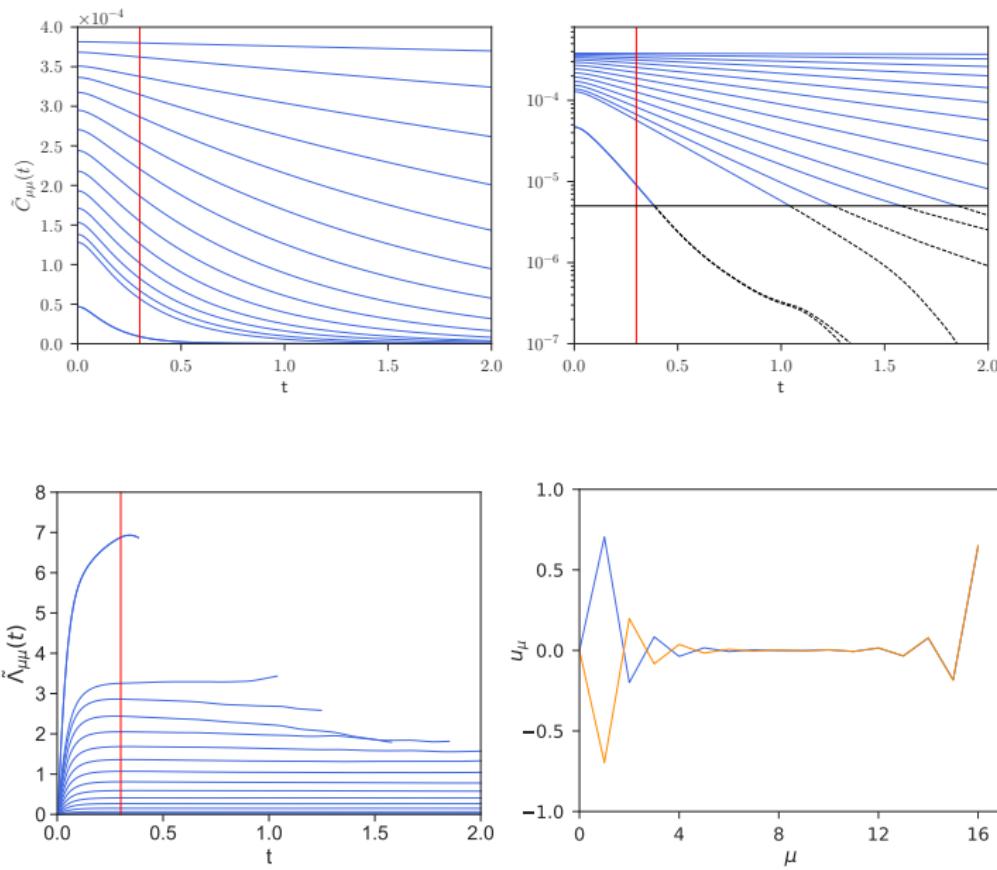
- We change the size of the bin



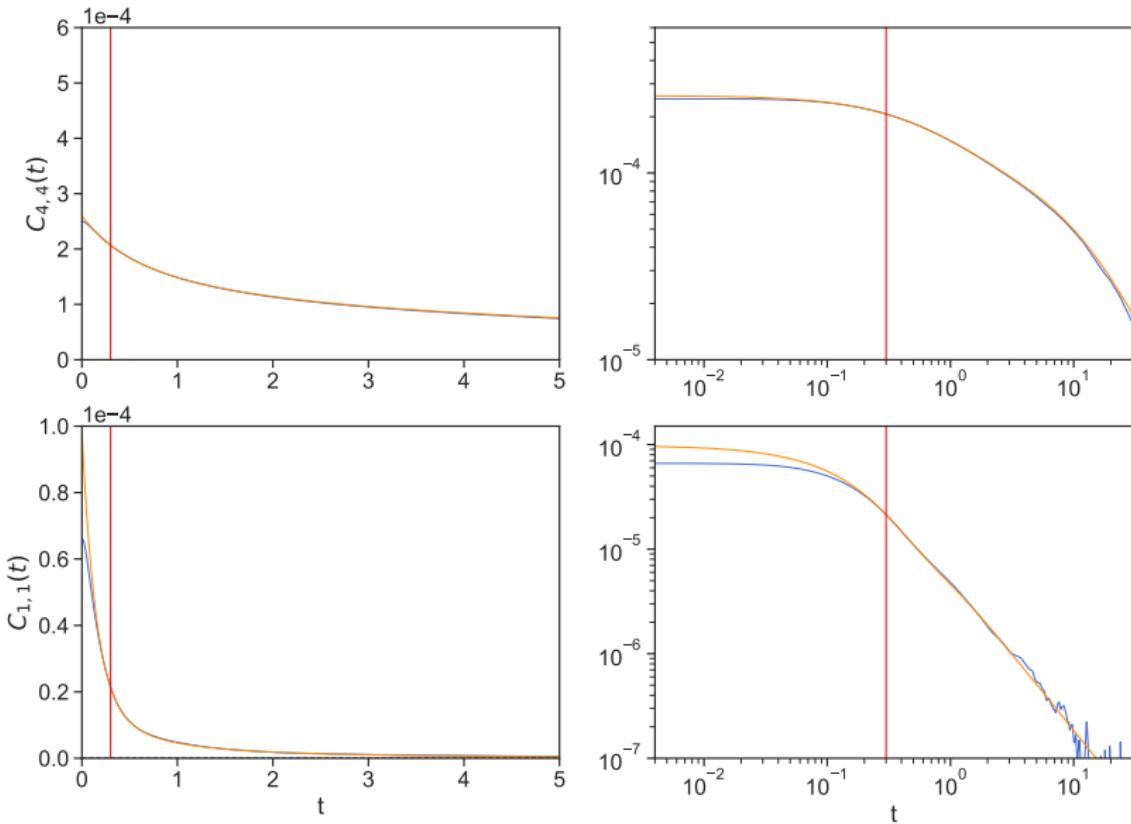
- The thick bins do not capture the layering of the density field



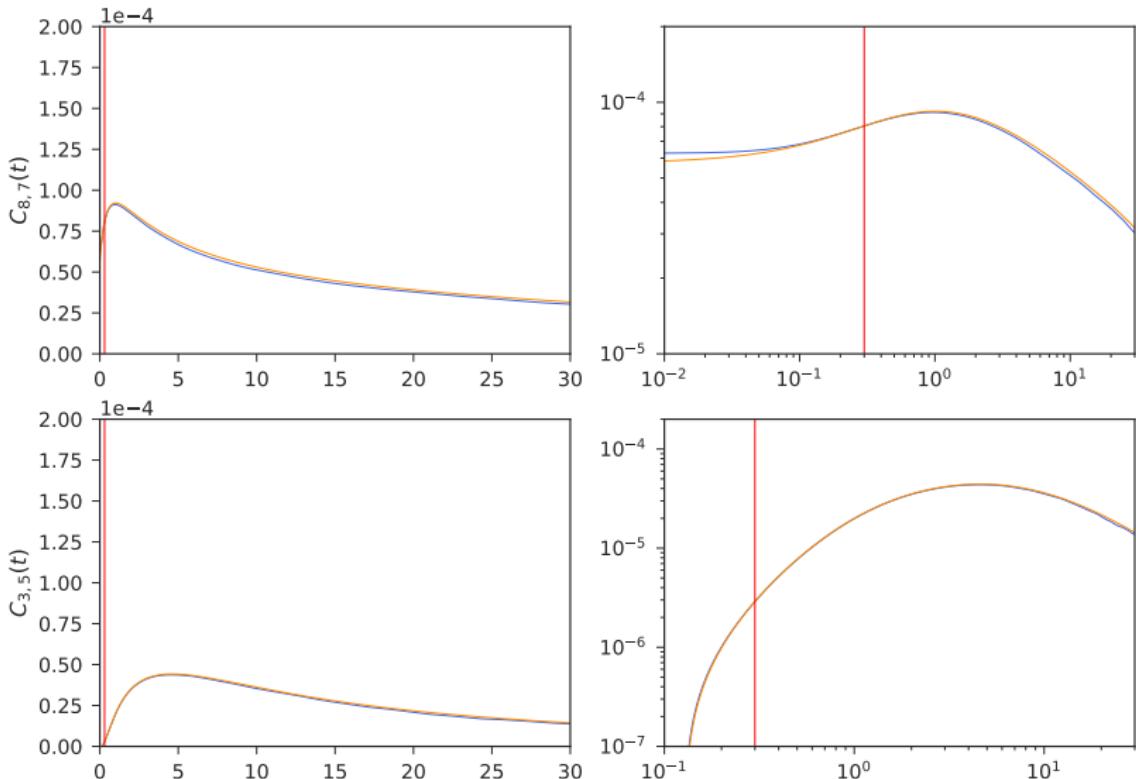
# Eigenvalues $\tilde{C}_{\mu\mu}(t)$ ( $\Delta = 2\sigma$ )



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



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



## The slip boundary condition

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## Strategy

- ① Compute the viscosity ( $\eta$ ) and friction kernels ( $G, H, \gamma$ ).
- 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  $C(t) = \langle \hat{g}(t)\hat{g}^T \rangle$
- 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 forward finite difference operator.

# The nonlocal transport matrices

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

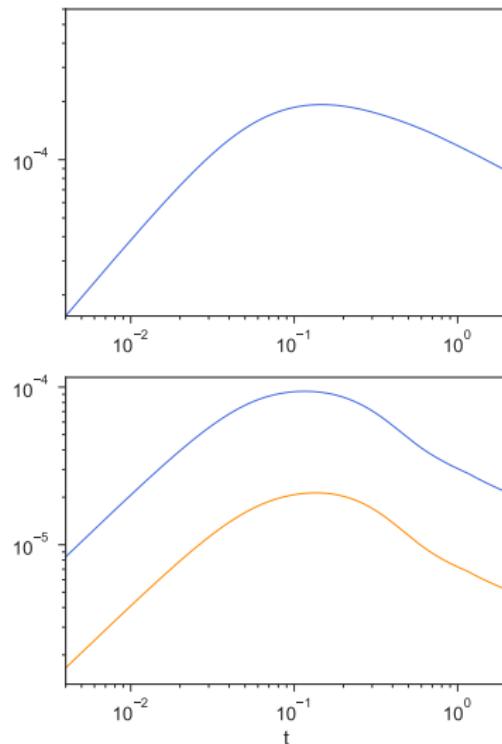
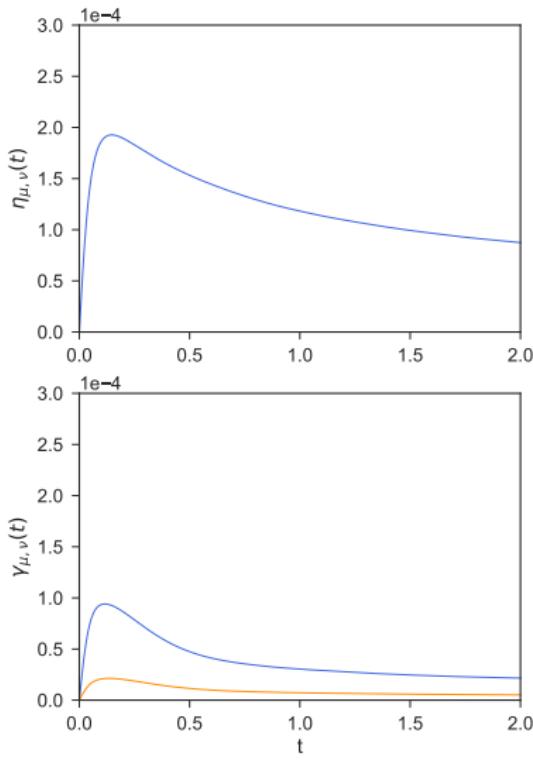
$$G_{\mu\nu}(t) = \frac{1}{k_B T} \int_0^t dt' \left\langle \hat{\mathbf{F}}_\mu^x(t') \hat{\sigma}_\nu^{xz} \right\rangle$$

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

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

# 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

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

- The evolution of the momentum field

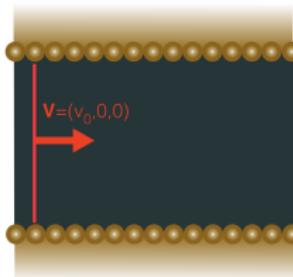
$$\frac{d}{dt} g(t) = -k_B T \cdot M(\tau) \cdot C^{-1}(\tau) \cdot g(t)$$

- The evolution of the velocity field

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

## Plug flow simulation

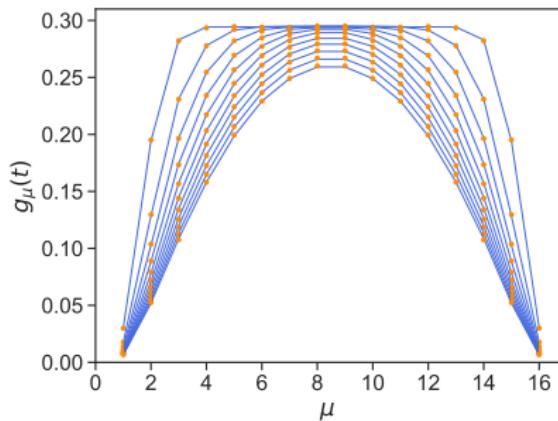
- Simulations to generate a nonequilibrium plug flow.
- Add to the thermal velocity of each fluid atom the same velocity  $\mathbf{V}$



- Increase the kinetic energy → 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.

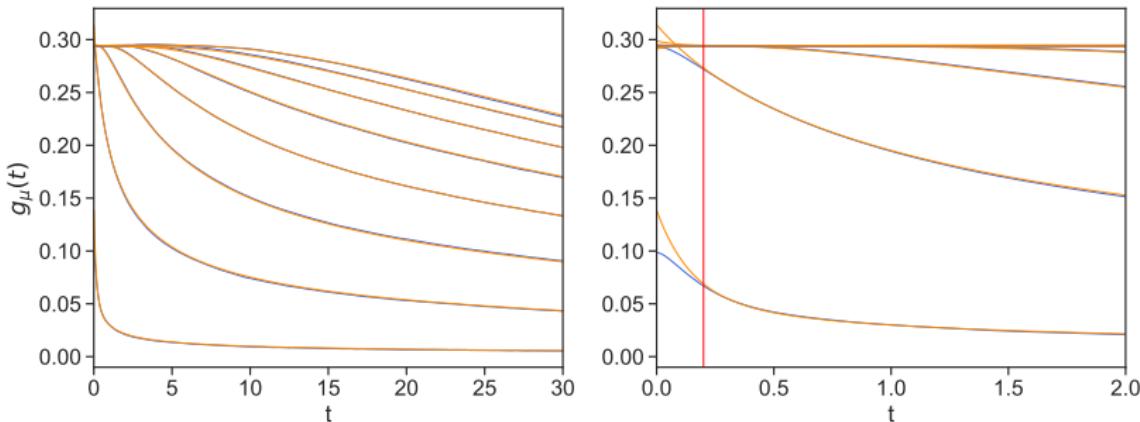
## Plug flow predictions

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



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

## Plug flow predictions



- The measured momentum average and the predictions for modes  $\mu = 1, 2, \dots, 8$  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

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

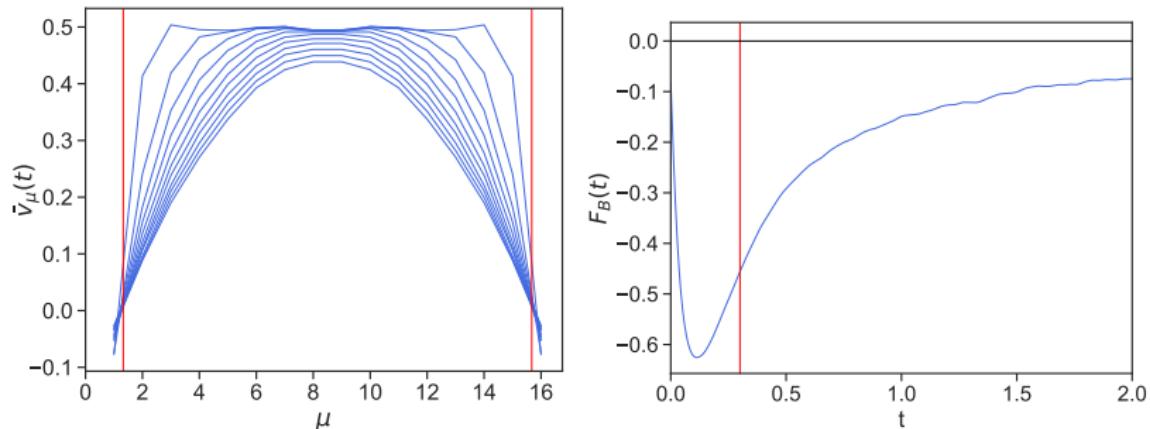
- $z_{\text{wall}}$ : position of the wall.
- $\bar{\mathbf{v}}_{\text{wall}}^x$ : velocity at  $z_{\text{wall}}$ .
- $\dot{\bar{\gamma}}_{\text{wall}}$ : shear rate.

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

The Navier slip boundary condition and the slip length  $\delta$

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

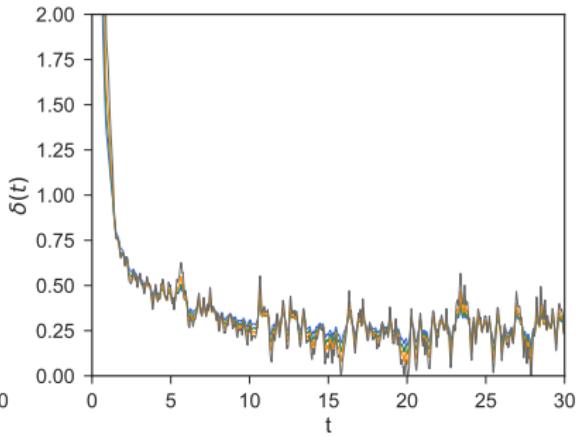
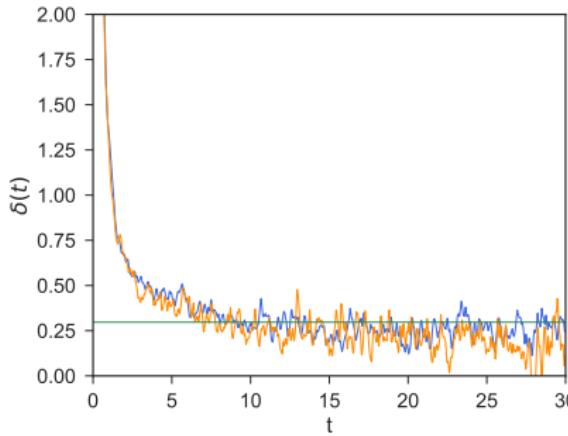
## Linear approximation for the velocity and force on the slab



- 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  $\delta(t) = \frac{\bar{v}_{\text{wall}}^x(t)}{\dot{\gamma}_{\text{wall}}(t)}$
- The slip length 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  $\tau$  (right).

## Local hydrodynamic model with boundary conditions

- The discrete version of the local equation

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

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

where the kinematic viscosity is  $\nu = \frac{\eta}{\rho}$ .

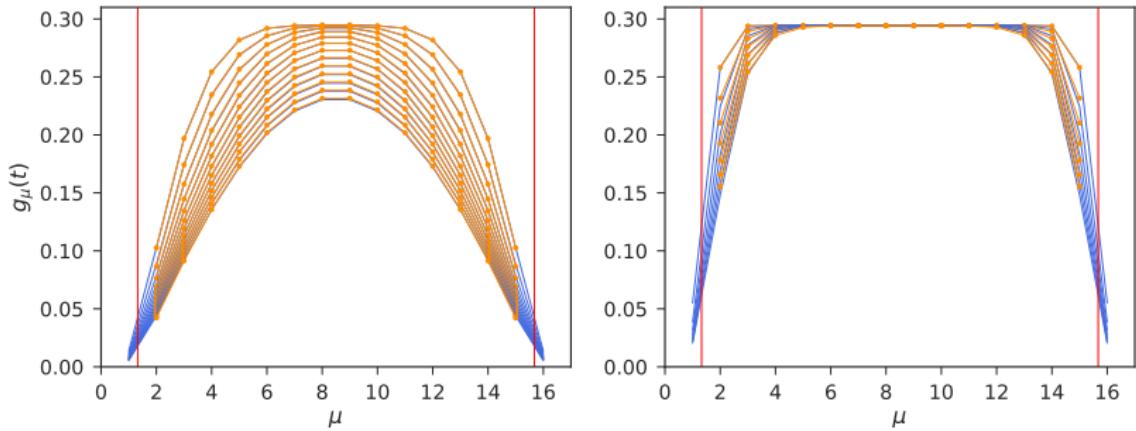
- Nonlocal hydrodynamic equation

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

- We use the slip boundary condition  $\dot{\bar{\gamma}}_{\text{wall}} = \delta \dot{\bar{\gamma}}_{\text{wall}}$  applied at  $z_{\text{wall}}$ .

# The local predictions

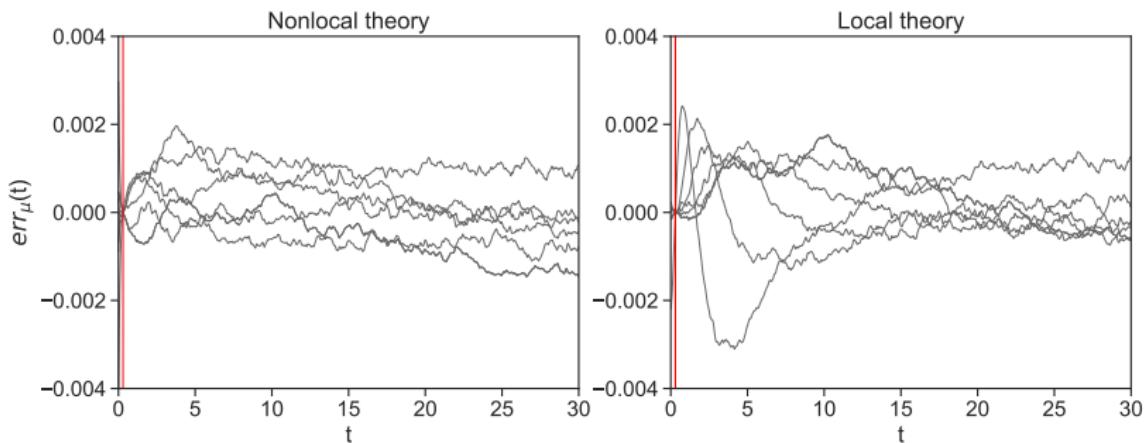
$$g(t) = \exp\{\nu\Delta'(t - \tau)\}g(\tau)$$



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

# Comparison of the error between local and nonlocal theories

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



# 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

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

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

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- 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.
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- **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*

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