

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 γ 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

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

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

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

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

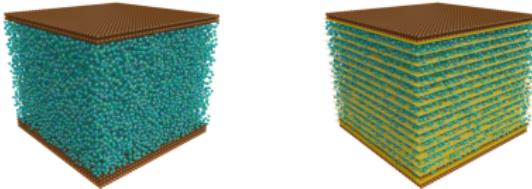
$$\gamma_{\mathbf{rr}'} \equiv \frac{1}{k_B T} \int_0^{\Delta t} dt' \langle \mathcal{Q}_t \hat{\mathbf{F}}_{\mathbf{r}}^{s \rightarrow l}(t') \mathcal{Q}_t \hat{\mathbf{F}}_{\mathbf{r}'}^{s \rightarrow l} \rangle^{\lambda(t)}$$

Simpler theory

- The amount of information to compute the hydrodynamic equations is exceedingly large:
 - η has 36 independent components.
 - \mathbf{G} and \mathbf{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 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

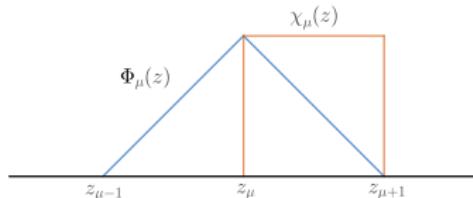
- N_{bin} bins with dimensions $L_x, L_y, \Delta z$ (L_z/N_{bin}).



- 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

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

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

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

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

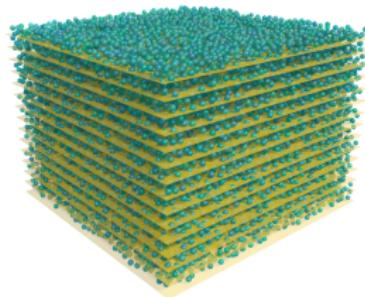
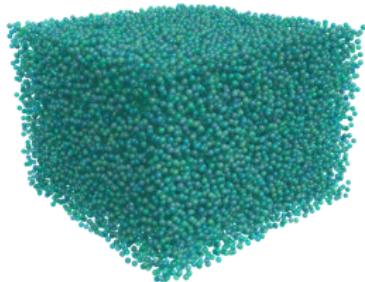
- For a linear Markovian theory the only possibility for a correlation is to decay in an exponential matrix way

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

- We need to find a constant matrix Λ^* .

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

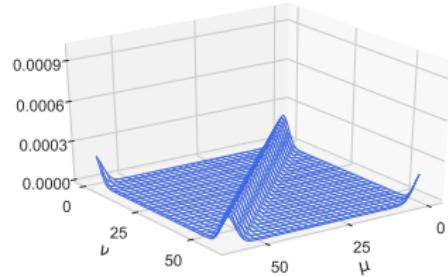
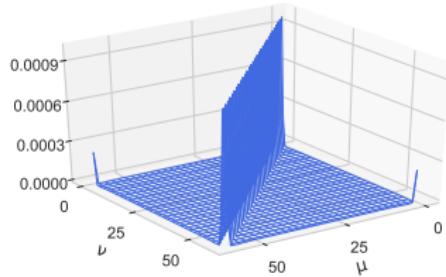
Building the correlation matrix $C(t)$

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	$\langle g_1(t_n)g_1 \rangle$	$\langle g_1(t_n)g_2 \rangle$	• • •	$\langle g_{60}(t_n)g_{59} \rangle$ $\langle g_{60}(t_n)g_{60} \rangle$

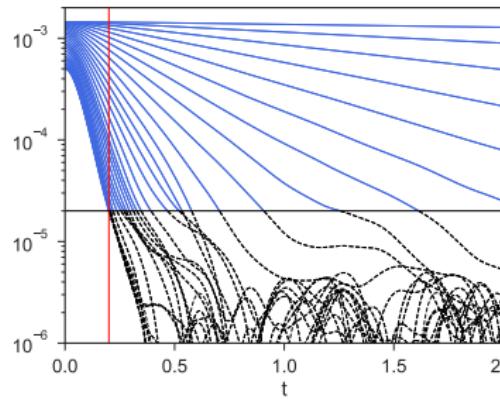
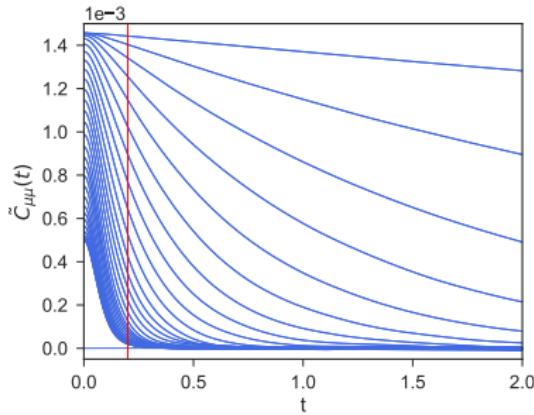


The correlation matrix $C(t)$ and its eigenvalues $\tilde{C}_{\mu\mu}$

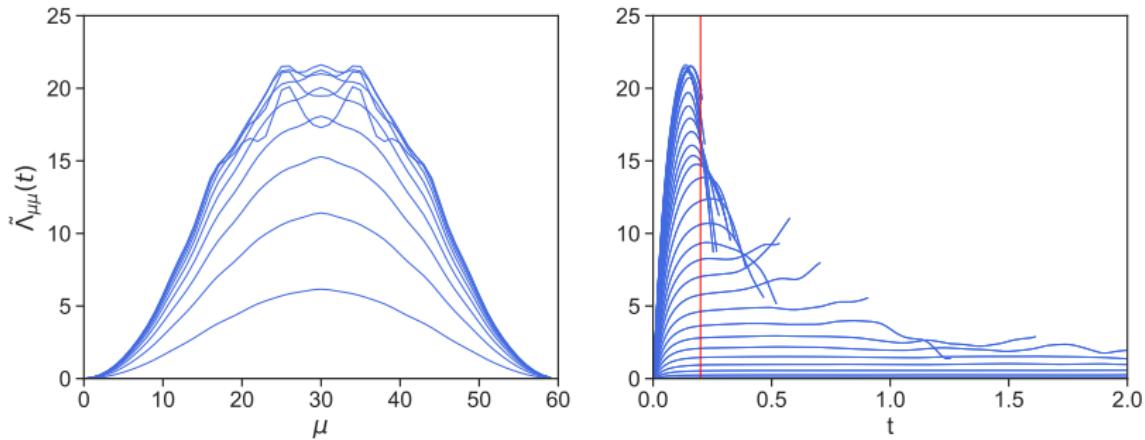
- The correlation matrix $C(t)$ at $t = 0$ (left) and $t = 0.6$ (right)



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



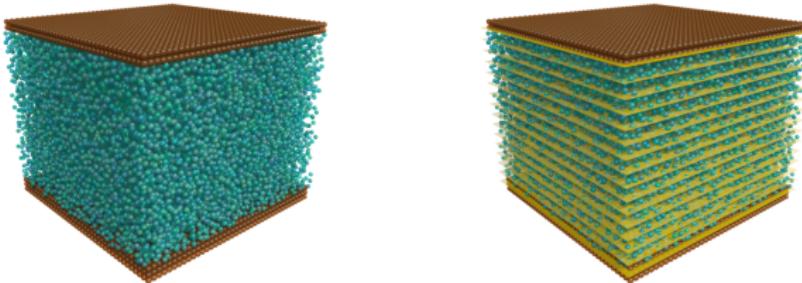
Validation of the Markovian approximation



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

- The system



- The CG variable 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
 - 12×10^6 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}_μ and eigenvectors u_μ

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

- Unitary matrix $E(t)$

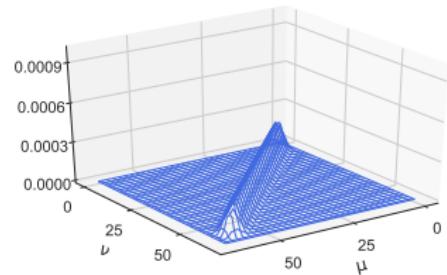
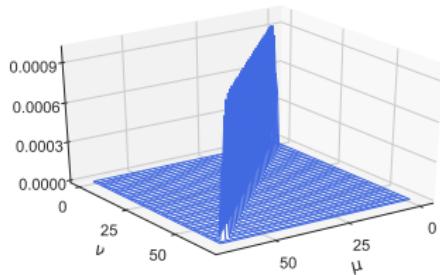
$$E^{-1}(t) \cdot C(t) \cdot E(t) = \tilde{C}(t),$$

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

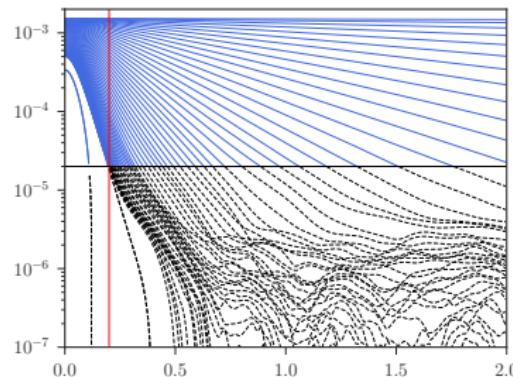
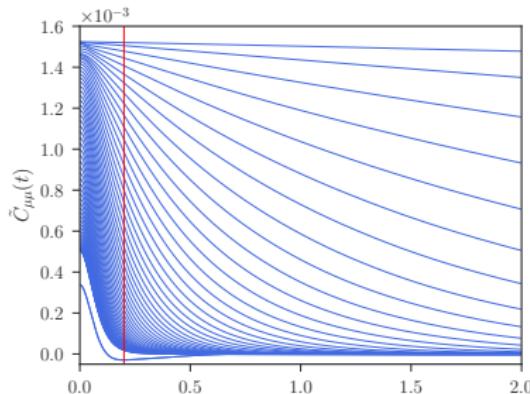
$$\tilde{C}_\mu(t) = \exp\{-\tilde{\Lambda}_{\mu\mu}(t - \tau)\} \tilde{C}_\mu(\tau)$$

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

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

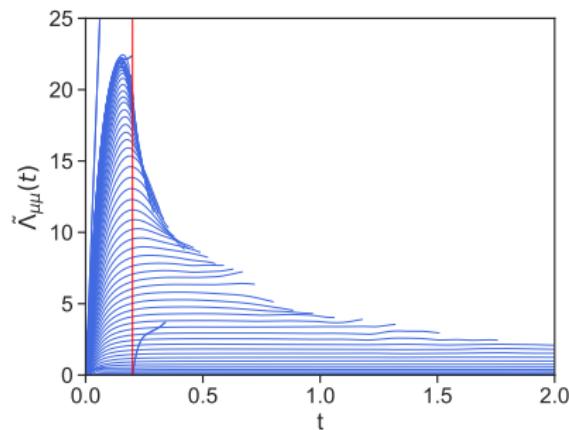


- Evolution of different eigenvalues $\tilde{C}_{\mu\nu}(t)$



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

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.



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).

