

Nanoscale hydrodynamics near solids

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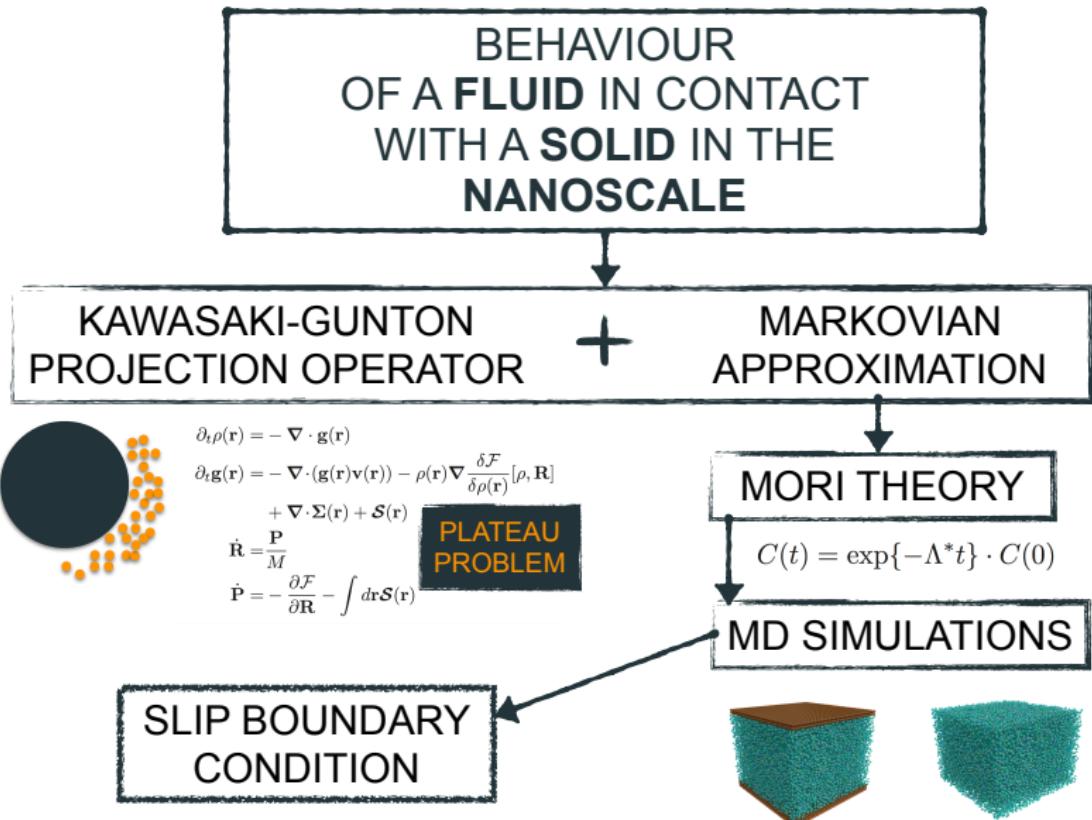


Agenda

- ① Introduction
- ② Nonequilibrium Statistical Mechanics
- ③ Hydrodynamics theory for liquids near solids
- ④ The plateau problem and the corrected Green-Kubo formula
- ⑤ Space and time locality for unconfined fluids

Introduction

Roadmap



Derivation of the slip boundary condition

- Through the measurement of the correlation of the transverse momentum and comparison with the predictions of continuum (local) hydrodynamics [**Bocquet1993, Chen2015**].
- Through linear response theory relating the force on the walls with the velocity of the fluid [**Bocquet1993, Petravic2007**].
- By formulating linear, in general non-Markovian, connections between friction forces and velocities [**Hansen2011**], where the meaning of this quantities is often understood implicitly.

The slip problem from first principles

- Hydrodynamic equations from the microscopic dynamics of a fluid [**Piccirelli1968**].
- Molecular Dynamics simulations in order to measure the transport coefficients that appear in the hydrodynamic equations in order to validate the theory.
- The slip boundary condition is measured from a microscopic definition of the slip lenght and the position of the atomic wall.

Nonequilibrium Statistical Mechanics

The Theory of Coarse-Graining (ToCG)

- The ToCG consists on eliminate the “useless” information about a system.
- We select the relevant variables or Coarse grained (CG) variables.
- Levels of description depending on the amount of information which one retains macroscopically.
 - Macroscopic level.
 - Microscopic level.
 - Mesoscopic level.

The entropy

- The average of the CG variables \hat{A}

$$a = \text{Tr}[\hat{A}\rho]$$

- The trace symbol is given by

$$\text{Tr} [\cdots] = \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \int dz' \cdots$$

- Gibbs-Jaynes entropy functional

$$S[\rho] = -\text{Tr} \left[\rho \ln \frac{\rho}{\rho_0} \right]$$

- The relevant ensemble takes the form

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

with $Z[\lambda]$ the partition function and λ the set of conjugate variables.

The entropy

- The average a with respect to the relevant ensemble is

$$a = \langle \hat{A} \rangle^\lambda = \text{Tr}[\bar{\rho} \hat{A}]$$

- If we introduce the thermodynamic potential $\Phi[\lambda] = -\ln Z[\lambda]$

$$a = \frac{\partial \Phi}{\partial \lambda}[\lambda]$$

- One to one connection between λ and a .
- The entropy is the Legendre transform of $\Phi[\lambda]$

$$\mathcal{S}[a] = -\Phi[\lambda[a]] + \lambda[a]a$$

which is related to the Gibbs-Jaynes entropy functional $\mathcal{S}[\rho]$ as

$$\mathcal{S}[a] = \mathcal{S}[\bar{\rho}]$$

- The averages a and λ are related through the entropy

$$\frac{\partial S}{\partial a} = \lambda$$

The dynamics

- The aim is to **derive equations of motion** for the time dependent average $a_i(t)$ of the CG variables $\hat{A}_i(z)$

$$a_i(t) = \text{Tr} \left[\hat{A}_i(z) \rho_t \right]$$

- ρ_t is the nonequilibrium solution of the Liouville equation

$$\rho_t(z) = \exp\{-i\mathcal{L}t\} \rho_0(z)$$

- We use two techniques:
 - ① The Kawasaki-Gunton projection operator.
 - ② Mori theory.

The dynamics. The Kawasaki-Gunton projection operator

For isolated systems with a time-independet Hamiltonian, the averages evolves according to the following equation

[Grabert1982]

$$\frac{\partial}{\partial t} a_i(t) = v_i(t) + \int_0^t dt' \sum_j K_{ij}(t, t') \lambda_j(t')$$

Kawasaki-Gunton projection operator. The reversible term

- The reversible term is given by

$$v_i(t) = \text{Tr}[\bar{\rho}_t i\mathcal{L}\hat{A}_i]$$

where $i\mathcal{L}$ is the Liouville operator and $\bar{\rho}_t$ is the **relevant ensemble** which maximizes the Gibbs-Jaynes entropy functional

$$S[\rho] = -\text{Tr} \left[\rho \ln \frac{\rho}{\rho_0} \right]$$

- The form of $\bar{\rho}_t$ is

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

where $Z[\lambda]$ is the partition function and $\rho_0 = \frac{1}{N!h^{3N}}$, with h being the Planck's constant.

Kawasaki-Gunton projection operator. The irreversible term

- The irreversible term involves the **memory kernel**

$$K_{ij}(t, t') = \text{Tr} \left[\bar{\rho}_{t'} \left(\mathcal{Q}_{t'} i\mathcal{L} \hat{A}_j \right) G_{t't} \left(\mathcal{Q}_t i\mathcal{L} \hat{A}_i \right) \right]$$

where the Kawasaki-Gunton projection operator $\mathcal{Q}_{t'}$ applied to an arbitrary function $\hat{F}(z)$ is

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

- The time ordered projected propagator $G_{t't}$ is given by

$$\begin{aligned} G_{t't} &= 1 + \sum_{n=1}^{\infty} \int_{t'}^t dt_1 \cdots \int_{t'}^{t_{n-1}} dt_n i\mathcal{L} \mathcal{Q}_{t_n} \cdots i\mathcal{L} \mathcal{Q}_{t_1} \\ &\equiv T_+ \exp \left\{ \int_{t'}^t dt'' i\mathcal{L} \mathcal{Q}_{t''} \right\} \end{aligned}$$

where T_+ ensures that the operators are ordered from left to right as time increases.

Kawasaki-Gunton projection operator. Markovian equation

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

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

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

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

- $\langle \dots \rangle$ denotes an equilibrium average.

The dynamics. Mori theory

The Mori's exact Generalized Langevin equation [**Mori1965**] is

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

where the following matrices have been introduced

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

$$C(0) = \langle \hat{A} \hat{A}^T \rangle$$

$$\Gamma(t) = \langle F^+(t) F^{+T}(0) \rangle$$

Mori theory. Projected forces and projection operator

- The projected forces are given by

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

- $F^+(t)$ have zero mean and are uncorrelated from previous values of the CG variables

$$\langle F^+(t) \rangle = 0$$

$$\langle \hat{A} F^+(t) \rangle = 0 \quad t \geq 0$$

- The projection operator Q is defined as $Q = 1 - P$ where P is **Mori's projector** whose effect on an arbitrary phase function $\hat{F}(z)$ is

$$P \hat{F}(z) = \langle \hat{F} \rangle + \langle \hat{F} \hat{A}^T \rangle \cdot C^{-1}(0) \cdot \hat{A}(z)$$

Mori theory. Correlations and averages

- The equilibrium time correlation matrix of the CG variables is

$$C(t) = \langle \hat{A}(t)\hat{A}^T \rangle$$

- Mori's equation for correlations

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

- The time-dependent average of the CG variables is defined as

$$a(t) = \int dz \rho_0(z) \exp\{i\mathcal{L}t\} \hat{A}(z)$$

- Mori's equation for averages

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

Mori theory. Markovian approximation

- The linear integro-differential term can be approximated by a memory-less term

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

- Evolution equation for the correlations

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

- The **relaxation matrix** Λ^* is defined as

$$\Lambda^* \equiv (L + M^*) \cdot C^{-1}(0)$$

Mori theory. Markovian approximation

- The only possibility for a correlation is to decay in an exponential matrix way

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

- At short times

$$\frac{d}{dt} C(0) = -L$$

which is only possible if $M^* = 0$.

- The correlations will decay in an exponential (Markovian) way only after the time τ beyond which memory is lost.

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

- Onsager's regression hypothesis

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

Summary

- Kawasaki-Gunton equation with Markovian approximation

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

- Mori equation with Markovian approximation

$$\frac{d}{dt} C(t) = \Lambda^* C(t)$$

- Exponential decay of the matrix of correlations after a time τ .

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

Hydrodynamics theory for liquids near solids

The system

- Liquid system of N particles interacting with a solid sphere of N' particles.
- The system is described by the set of all positions \mathbf{q}_i and momenta $\mathbf{p}_i = m_i \mathbf{v}_i$ ($i = 1, \dots, N$) of the liquid atoms plus the positions $\mathbf{q}_{i'}$ and momenta $\mathbf{p}_{i'} = m_{i'} \mathbf{v}_{i'}$ ($i' = 1, \dots, N'$) of the atoms of the solid sphere.
- The microstate $z = q, p, q', p'$.
- The microstate of the system evolves according to Hamilton's equations

$$H(z) = \sum_i^N \frac{p_i^2}{2m_i} + \sum_{i'}^{N'} \frac{p_{i'}^2}{2m_{i'}} + U(z)$$

The CG variables

- The CG 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 CG variables

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

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

The relevant ensemble

- The ensemble which maximizes the Gibbs-Jaynes entropy functional is

$$\begin{aligned}\bar{\rho}(z) = & \frac{1}{\Xi[\lambda]} \rho_0 \exp \{-\beta H(z)\} \\ & \times \exp \left\{ -\beta \int d\mathbf{r} (\lambda_\rho(\mathbf{r}) \cdot \hat{\rho}_{\mathbf{r}}(z) + \boldsymbol{\lambda}_g(\mathbf{r}) \cdot \hat{\mathbf{g}}_{\mathbf{r}}(z)) \right\} \\ & \times \exp \left\{ -\beta \boldsymbol{\lambda}_R \cdot \hat{\mathbf{R}}(z) - \beta \boldsymbol{\lambda}_P \cdot \hat{\mathbf{P}}(z) \right\}\end{aligned}$$

- The λ -dependent partition function is

$$\begin{aligned}\Xi[\lambda] \equiv & \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \int dq dp dq' dp' \\ & \times \exp \left\{ -\beta H - \beta \sum_{i=1}^N m \lambda_\rho(\mathbf{q}_i) - \beta \sum_{i=1}^N \mathbf{p}_i \cdot \boldsymbol{\lambda}_g(\mathbf{q}_i) \right\} \\ & \times \exp \left\{ -\beta \boldsymbol{\lambda}_R \cdot \hat{\mathbf{R}}(z) - \beta \boldsymbol{\lambda}_P \cdot \hat{\mathbf{P}}(z) \right\}\end{aligned}$$

The grand potential

- The λ -dependent grand-canonical potential is given by

$$\Phi[\lambda] \equiv -k_B T \ln \Xi[\lambda]$$

- There is a one to one connection between the averages of the CG variables and the conjugates ones

$$\begin{aligned}\rho(\mathbf{r}) &= \frac{\delta\Phi[\lambda]}{\delta\lambda_\rho(\mathbf{r})} & \mathbf{R} &= \frac{\partial\Phi[\lambda]}{\partial\lambda_R} \\ \mathbf{g}(\mathbf{r}) &= \frac{\delta\Phi[\lambda]}{\delta\lambda_g(\mathbf{r})} & \mathbf{P} &= \frac{\partial\Phi[\lambda]}{\partial\lambda_P}\end{aligned}$$

The hydrodynamic functional

- The hydrodynamic functional

$$\begin{aligned}\mathcal{H}[\rho, \mathbf{g}, \mathbf{R}, \mathbf{P}] = & \Phi[\lambda_\rho, \lambda_g, \lambda_R, \lambda_P] \\ & - \int d\mathbf{r} \rho(\mathbf{r}) \lambda_\rho(\mathbf{r}) - \int d\mathbf{r} \mathbf{g}(\mathbf{r}) \cdot \lambda_g(\mathbf{r}) \\ & - \lambda_R \cdot \mathbf{R} - \lambda_P \cdot \mathbf{P}\end{aligned}$$

- The hydrodynamic functional is minus the entropy

$$\begin{array}{ll}\lambda_\rho(\mathbf{r}) = -\frac{\delta \mathcal{H}}{\delta \rho(\mathbf{r})} & \lambda_R = -\frac{\partial \mathcal{H}}{\partial \mathbf{R}} \\ \lambda_g(\mathbf{r}) = -\frac{\delta \mathcal{H}}{\delta \mathbf{g}(\mathbf{r})} & \lambda_P = -\frac{\partial \mathcal{H}}{\partial \mathbf{P}}\end{array}$$

The grand potential of a fluid in the presence of a sphere

- We may express the grand potential $\Phi[\lambda]$ as a sum of two contributions

$$\Phi[\lambda] = \Phi^{\text{pos}}[\mu, \boldsymbol{\lambda}_R] - \frac{M'}{2} \boldsymbol{\lambda}_P^2,$$

where we have defined the following grand potential

$$\begin{aligned}\Phi^{\text{pos}}[\mu, \boldsymbol{\lambda}_R] &\equiv -k_B T \ln \sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{dq}{\Lambda^{3N}} \frac{dq'}{\Lambda^{3N'}} \\ &\times \exp \left\{ -\beta \left(U - \sum_{i=1}^N \mathbf{m} \cdot \boldsymbol{\mu}(\mathbf{q}_i) + \boldsymbol{\lambda}_R \cdot \hat{\mathbf{R}} \right) \right\}\end{aligned}$$

- We have introduced the thermal wavelength and the chemical potential

$$\Lambda = \left(\frac{h^2 \beta}{2\pi m} \right)^{\frac{1}{2}}, \quad \mu(\mathbf{r}) \equiv \frac{1}{2} \lambda_g^2(\mathbf{r}) - \lambda_\rho(\mathbf{r})$$

The free energy

- The Legendre transform of the grand potential for a simple fluid gives the classic free energy density functional.
- The free energy functional $\mathcal{F}[\rho, \mathbf{R}]$ of a structured fluid in the presence of a solid sphere is

$$\mathcal{F}[\rho, \mathbf{R}] \equiv \Phi^{\text{pos}}[\mu, \boldsymbol{\lambda}_R] + \int d\mathbf{r} \rho(\mathbf{r}) \mu(\mathbf{r}) - \boldsymbol{\lambda}_R \cdot \mathbf{R},$$

- Finally, the hydrodynamic functional \mathcal{H} takes the form

$$\frac{\delta \mathcal{H}}{\delta \rho(\mathbf{r})} [\rho, \mathbf{g}, \mathbf{R}, \mathbf{P}] = \frac{\mathbf{v}^2(\mathbf{r})}{2} + \frac{\delta \mathcal{F}}{\delta \rho(\mathbf{r})} [\rho, \mathbf{R}]$$

The transport equations. Reversible term

- The reversible term has the form

$$v_i(t) = \text{Tr}[\bar{\rho}_t i \mathcal{L} \hat{A}_i]$$

- Reversible equations for the CG variables

$$\partial_t \rho(\mathbf{r})|_{\text{rev}} = -\nabla \cdot \mathbf{g}(\mathbf{r})$$

$$\partial_t \mathbf{g}(\mathbf{r})|_{\text{rev}} = -\nabla \cdot (\mathbf{g}(\mathbf{r}) \mathbf{v}(\mathbf{r})) - \rho(\mathbf{r}) \nabla \frac{\delta \mathcal{F}}{\delta \rho(\mathbf{r})} [\rho, \mathbf{R}]$$

$$\partial_t \mathbf{R}|_{\text{rev}} = \frac{\mathbf{P}}{M}$$

$$\partial_t \mathbf{P}|_{\text{rev}} = -\frac{\partial \mathcal{F}}{\partial \mathbf{R}} [\rho, \mathbf{R}]$$

- No approximations.
- They conserve the hydrodynamic functional \mathcal{H} .

The transport equations. Irreversible term

- The irreversible term has the form $\sum_j D_{ij}(t) \lambda_j(t)$
- With $D_{ij}(t) = \int_0^{\Delta t} dt' \left\langle Q_t i \mathcal{L} \hat{A}_j \exp\{i \mathcal{L} t'\} Q_t i \mathcal{L} \hat{A}_i \right\rangle^{\lambda(t)}$
- Large simplification of the friction matrix because $Q i \mathcal{L} \hat{\rho}_r = 0$ and $Q i \mathcal{L} \hat{\mathbf{R}}_\mu = 0$
- Irreversible equations for the CG variables

$$\begin{aligned}\partial_t \mathbf{g}^\alpha(\mathbf{r})|_{\text{irr}} &= \nabla_{\mathbf{r}}^\beta \boldsymbol{\Sigma}^{\alpha\beta}(\mathbf{r}) + \mathcal{S}^\alpha(\mathbf{r}) \\ \frac{d}{dt} \mathbf{P}^\alpha(t) \Big|_{\text{irr}} &= - \int d\mathbf{r}' \mathcal{S}^\alpha(\mathbf{r}'),\end{aligned}$$

The transport equations. Irreversible term

- The fluid **stress tensor**

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

- The **irreversible surface force density** on the fluid

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

Irreversible term. Nonlocal transport coefficients

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

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

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

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

Final equations of nanohydrodynamics

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

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

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

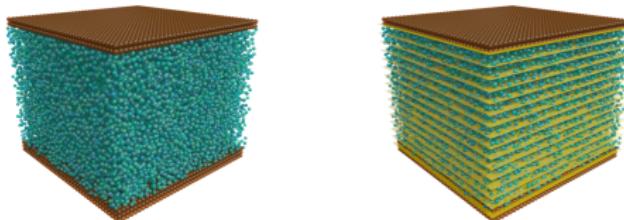
$$\dot{\mathbf{P}} = - \frac{\partial \mathcal{F}}{\partial \mathbf{R}} - \int d\mathbf{r} \boldsymbol{\mathcal{S}}(\mathbf{r})$$

From continuum to discrete theory

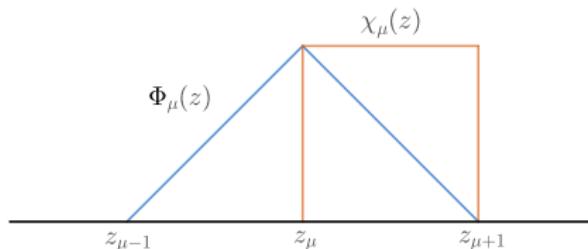
- The amount of information required in the hydrodynamic equations is exceedingly large.
 - η 36 independent components.
 - \mathbf{H} and \mathbf{G} 21 independent components.
 - γ 9 independent components.
- We need a simpler theory.
 - Planar walls.
 - Isotropic walls: invariant under translations in the plane of the wall, and under rotations around an axis perpendicular to the walls.
- Discrete version in order to compute MD simulations.

The discrete basis function set

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



- The characteristic function $\chi_\mu(z)$ and the finite element linear basis function $\Phi_\mu(z)$.



The discrete basis function set

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

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

- The discrete Dirac δ function is defined in terms of $\Phi_\mu(z)$

$$\delta_\mu(\mathbf{r}) \equiv \frac{\Phi_\mu(\mathbf{r})}{\mathcal{V}_\mu}$$

- And the interpolant basis function takes the form

$$\psi_\mu(\mathbf{r}) = \mathcal{V}_\mu \sum_\nu \left[M^\Phi \right]_{\mu\nu}^{-1} \Phi_\nu(\mathbf{r})$$

- The usual mass matrix of the finite element method is

$$M_{\mu\nu}^\Phi = \int d\mathbf{r} \Phi_\mu(\mathbf{r}) \Phi_\nu(\mathbf{r})$$

The discrete CG variables

- The discrete CG variables

$$\hat{\rho}_\mu = \sum_i^N m_i \delta_\mu(\mathbf{q}_i), \quad \hat{\mathbf{g}}_\mu = \sum_i^N \mathbf{p}_i \delta_\mu(\mathbf{q}_i)$$

- The time derivatives

$$i\mathcal{L}\hat{\rho}_\mu = \sum_{i=1}^N \mathbf{p}_i \cdot \nabla \delta_\mu(\mathbf{q}_i), \quad i\mathcal{L}\hat{\mathbf{g}}_\mu = \sum_{i=1}^N \mathbf{p}_i \mathbf{v}_i \cdot \nabla \delta_\mu(\mathbf{q}_i) + \hat{\mathbf{F}}_\mu$$

The discrete equations of nanohydrodynamics

- The equation for the density

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

- The normal component of the momentum

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

- The dissipative matrix is defined as

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

- The parallel component \mathbf{g}_μ^α for $\alpha = x, y$ of the discrete momentum density

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

The 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

- Isothermal hydrodynamic theory for simple fluids in the presence of a solid sphere.
- Kawasaki-Gunton operator to obtain the evolution equations for the average of the CG variables.
- Markovian approximation: the CG variables should be slow in order to have memoryless equation.
- The theory describes the interaction fluid-solid in terms of irreversible surfaces forces.
- Hydrodynamic discrete theory for planar geometries and flows involving discrete mass and momentum density variables defined in terms of finite element basis functions.

The plateau problem and the corrected Green-Kubo formula

Plateau problem

- Approximation of the linear integro-differential term

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

- Rationale justifying the Markovian approximation

$$\int_0^t dt' \Gamma(t-t') \cdot c(t') \simeq \int_0^t dt' \Gamma(t-t') \cdot c(t) \equiv M^+(t) \cdot c(t)$$

- The **projected** Green-Kubo running integral

$$M^+(t) = \int_0^t dt' \left\langle \left(\exp\{Q i \mathcal{L} t'\} Q i \mathcal{L} \hat{A} \right) Q i \mathcal{L} \hat{A}^T \right\rangle$$

- The **unprojected** Green-Kubo running integral is

$$M(t) \equiv \int_0^t dt' \left\langle \left(\exp\{i \mathcal{L} t'\} i \mathcal{L} \hat{A} \right) Q i \mathcal{L} \hat{A}^T \right\rangle$$

Plateau problem

- After performing the running integrals

$$M^+(t) = \left\langle \left(\exp\{Q i \mathcal{L} t\} \hat{A} \right) Q i \mathcal{L} \hat{A}^T \right\rangle$$

$$M(t) = \left\langle \left(\exp\{i \mathcal{L} t\} \hat{A} \right) Q i \mathcal{L} \hat{A}^T \right\rangle$$

- $M^+(t) \approx M(t)$ when large separation of timescales.
- $M(t)$ should have a plateau after a time τ .
- For an ergodic system the correlations computed with the unprojected dynamics decay to zero

$$\begin{aligned}\lim_{t \rightarrow \infty} M(t) &= \lim_{t \rightarrow \infty} \left\langle \left(\exp\{i \mathcal{L} t\} \hat{A} \right) Q i \mathcal{L} \hat{A}^T \right\rangle \\ &= \langle \hat{A} \rangle \langle Q i \mathcal{L} \hat{A}^T \rangle = 0\end{aligned}$$

Corrected Green-Kubo formula

- Action of Mori projector operator on the phase function $i\mathcal{L}\hat{A}$

$$\mathcal{Q}i\mathcal{L}\hat{A} = i\mathcal{L}\hat{A} + L \cdot C^{-1}(0) \cdot \hat{A}$$

- Therefore, we may express $M(t)$

$$M(t) = -\frac{d}{dt}C(t) - L \cdot c(t)$$

(Remember that $L = \langle \hat{A}i\mathcal{L}\hat{A}^T \rangle$)

- With $\frac{d}{dt}C(t) = -\lambda^* \cdot C(t)$ and $\lambda^* = (L + M^*) \cdot C^{-1}(0)$ we obtain

$$M(\tau) \simeq M^* \cdot c(\tau)$$

- The new corrected Green-Kubo formula does not suffer from the plateau problem by construction

$$M^* = \int_0^\tau dt \left\langle \mathcal{Q}i\mathcal{L}\hat{A}(t)i\mathcal{L}\hat{A}^T \right\rangle \cdot c^{-1}(\tau)$$

Corrected Green-Kubo formula

- We introduce the time dependent matrix

$$\Lambda(t) \equiv -\frac{d}{dt} C(t) \cdot C^{-1}(t)$$

- If the Markovian approximation is correct, after a time τ , $\Lambda(t)$ should become a time-independent matrix

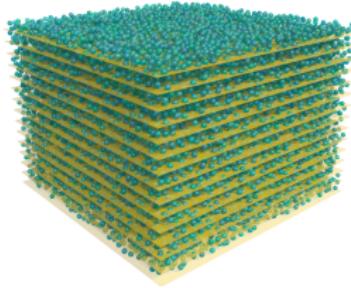
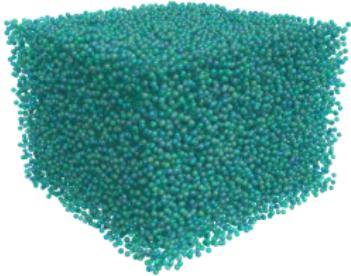
$$\lim_{t \rightarrow \infty} \Lambda(t) = \Lambda^*$$

- Therefore, the time-independent friction matrix M^*

$$M^* = -L + \Lambda^* \cdot C(0)$$

Space and time locality for unconfined fluids

CG variables



$$\hat{\mathbf{g}}_\mu(z) = \sum_i^N \mathbf{p}_i \delta_\mu(\mathbf{r}_i) \quad i\mathcal{L}\hat{\mathbf{g}}_\mu(z) = -\frac{\hat{\sigma}_\mu^{xz} - \hat{\sigma}_{\mu-1}^{xz}}{\Delta z}$$

The Green-Kubo running integral $M(t)$ and $\eta(t)$

- The Markovian dynamics given by Mori theory ($L = 0$)

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

- M^* is related to the standard Green-Kubo running integral

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

- We may express $M(t)$ as $M(t) = -\Delta \cdot \eta(t)$, where Δ is the discrete Laplacian matrix and the nonlocal shear viscosity

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

The friction matrix M^* and the nonlocal shear viscosity matrix

- Link between the momentum correlation matrix and the stress correlation matrix

$$\frac{d}{dt} C(t) = k_B T \Delta \cdot \eta(t)$$

- By analogy

$$M(t) = -\Delta \cdot \eta(t) \quad \rightarrow \quad M^* = -\Delta \cdot \eta^*$$

- The Markovian dynamics becomes

$$\frac{d}{dt} C(t) = k_B T \Delta \cdot \eta^* \cdot c(t)$$

- We would like to obtain η^* from $\eta(t)$

$$\Delta \cdot \eta(t) = \Delta \cdot \eta^* \cdot c(t)$$

- Δ and $c(t)$ are not invertible!

Fourier space

- The unitary matrix and its inverse

$$E_{\mu\nu} = \frac{1}{\sqrt{N_{\text{bin}}}} \exp \left\{ i \frac{2\pi}{N_{\text{bin}}} \mu\nu \right\}$$
$$E_{\mu\nu}^{-1} = \frac{1}{\sqrt{N_{\text{bin}}}} \exp \left\{ -i \frac{2\pi}{N_{\text{bin}}} \mu\nu \right\}$$

- E_μ and $E_{\mu\nu}^{-1}$ diagonalizes any traslation invariant and periodic matrix $A_{\mu\nu}$

$$\tilde{A} = E^{-1} \cdot A \cdot E$$

The nonlocal viscosity and nonlocal kinematic viscosity

- Therefore

$$\tilde{\Delta} \cdot \tilde{\eta}(t) = \tilde{\Delta} \cdot \tilde{\eta}^* \cdot \tilde{c}(t) \quad \rightarrow \quad \tilde{\eta}_{\mu\mu}^* = \frac{\tilde{\eta}_{\mu\mu}(t)}{\tilde{c}_{\mu\mu}(t)}$$

- The nonlocal kinematic viscosity is defined as

$$\nu^* \equiv \eta^* \cdot \mathcal{V} \cdot \rho^{-1}$$

where \mathcal{V} is a diagonal matrix that contains the volume \mathcal{V}_μ of the bins and ρ is the mass density matrix

- In Fourier space ν_μ is a diagonal matrix

$$\tilde{\nu}_\mu^* = \frac{\mathcal{V}_\mu \tilde{\eta}_\mu^*}{\tilde{\rho}_\mu}$$

- And the dynamic equation for the correlations

$$\frac{d}{dt} C(t) = \Delta \cdot \nu^* \cdot C(t)$$

Local predictions

- The local approximation of the nonlocal viscosity matrix ν is

$$\nu_{\mu\mu'} \simeq \nu_0 \delta_{\mu\mu'}$$

where the local kinematic viscosity is given by

$$\nu_0 \equiv \sum_{\mu'} \nu_{\mu\mu'} \quad \forall \mu$$

- Therefore, the local in space prediction

$$C(t) = \exp \{ \Delta \cdot \nu_0 (t - \tau) \} C(\tau)$$

- The local in time prediction

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

Simulations

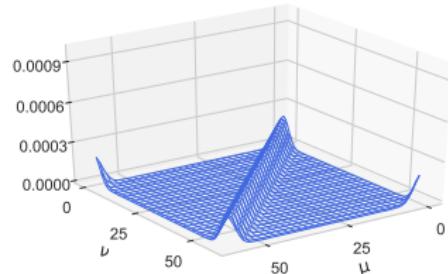
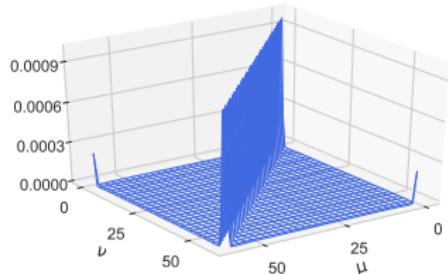
- ① Validation the Markovian approximation.
- ② The nonlocal viscosity ($\eta(t)$ and $\eta^*(t)$).
- ③ The nonlocal kinematic viscosity ($\nu(t)$ and $\nu^*(t)$).
- ④ Prediction of the correlations (local and nonlocal).

Simulation set up

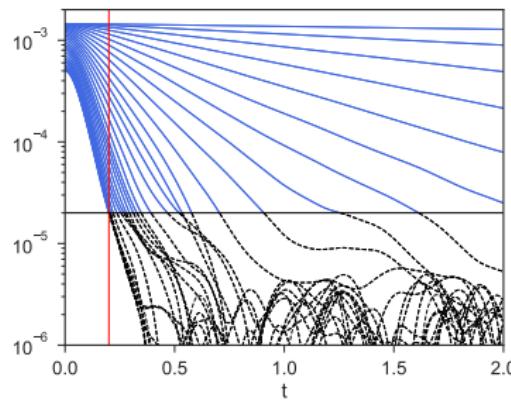
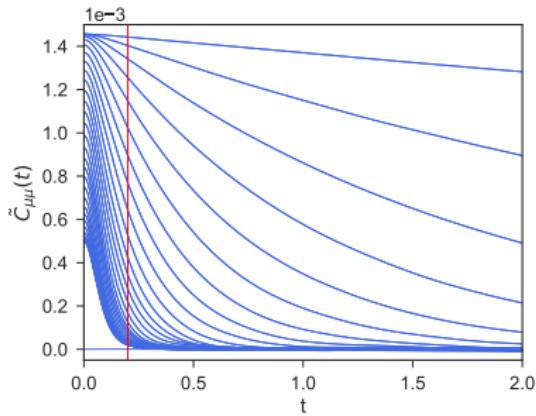
- Simulation of 28749 particles interacting with a LJ potential truncated at $\sigma = 2.5$.
- Box size $40 \times 40 \times 30$ binned in 60 bins along z axis. $\Delta z = 0.5\sigma$
- $dt = 0.002$ in reduced units.
- Equilibration stage
 - Langevin thermostat for 10^5 timesteps: $T = 2.0$, $\rho = 0.6$.
 - NVE microcanonical conditions for a further 10^5 timesteps.
- Production stage
 - 1.5×10^6 timesteps.
 - z axis binned in 60 bins μ .
 - $g_\mu^x(t)$ and $\rho_\mu(t)$ recorded every 10 timesteps.

The correlation matrix $C(t)$

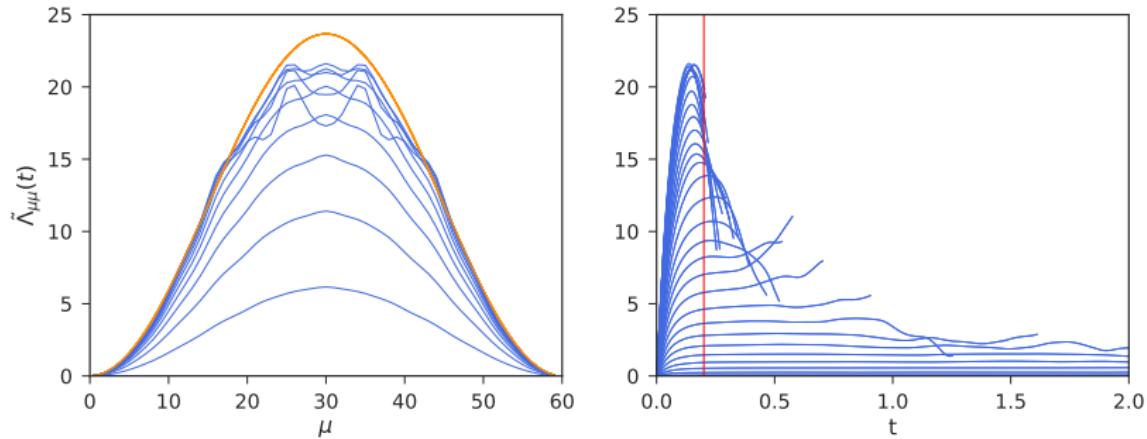
- The correlation matrix $C(t)$ at $t = 0$ (left) and $t = 0.6$ (right)



- 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. The orange line is the local approximation equation with a value of the local kinematic viscosity of $\nu_0 = 1.48$.