Nanoscale hydrodynamics near solids

Diego Duque Zumajo

June 2019

Departamento Física Fundamental
Universidad Nacional de Educación a Distancia

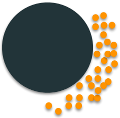
Agenda

Introduction

Roadmap

BEHAVIOUR
OF A **FLUID** IN CONTACT
WITH A **SOLID** IN THE
NANOSCALE

KAWASAKI-GUNTON PROJECTION OPERATOR + MARKOVIAN APPROXIMATION



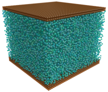
$$\partial_t \rho(\mathbf{r}) = -\boldsymbol{\nabla}\cdot \mathbf{g}(\mathbf{r})$$
$$\partial_t \mathbf{g}(\mathbf{r}) = -\boldsymbol{\nabla}\cdot(\mathbf{g}(\mathbf{r})\mathbf{v}(\mathbf{r})) - \rho(\mathbf{r})\boldsymbol{\nabla}\frac{\delta \mathcal{F}}{\delta\rho(\mathbf{r})}[\rho,\mathbf{R}] + \boldsymbol{\nabla}\cdot\boldsymbol{\Sigma}(\mathbf{r})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

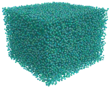
PLATEAU PROBLEM

MORI THEORY

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

MD SIMULATIONS





SLIP BOUNDARY CONDITION

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, conections 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 $\hat{A}$

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

- The trace symbol is given by

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

- Gibbs-Jaynes entropy functional

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

- The relevant ensemble takes the form

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

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

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

- 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

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

- 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 $\hat{A}_i(z)$

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

- 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

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

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

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

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

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

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

Kawsaki-Gunton projection operator. The irreversible term

- The irreversible term involves the memory kernel

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

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

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

- 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

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

- $\langle \cdots \rangle$ 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

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

Mori theory. Projected forces and projection operator

- The projected forces are given by

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

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

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

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

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

Mori theory. Correlations and averages

- The equilibrium time correlation matrix of the CG variables is

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

- 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 aproximation

- 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 aproximation

- 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 $\mathbf{p}_i = m_i \mathbf{v}_i$ $(i = 1, \cdots, N)$ of the liquid atoms plus the positions $\mathbf{q}_{i'}$ and momenta $\mathbf{p}_{i'} = m_{i'} \mathbf{v}_{i'}$ $(i' = 1, \cdots, N')$ 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

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

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

- The derivatives of the CG variables

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

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

The relevant enesemble

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

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

- The λ-dependent partition function is

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

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

$$\rho(\mathbf{r}) = \frac{\delta\Phi[\lambda]}{\delta\lambda_\rho(\mathbf{r})} \qquad \mathbf{R} = \frac{\partial\Phi[\lambda]}{\partial\boldsymbol{\lambda}_R}$$

$$\mathbf{g}(\mathbf{r}) = \frac{\delta\Phi[\lambda]}{\delta\boldsymbol{\lambda}_g(\mathbf{r})} \qquad \mathbf{P} = \frac{\partial\Phi[\lambda]}{\partial\boldsymbol{\lambda}_P}$$

The hydrodynamic functional

- The hydrodynamic functional

$$\begin{aligned}\mathcal{H}[\rho,\mathbf{g},\mathbf{R},\mathbf{P}] =& \Phi[\lambda_\rho,\boldsymbol{\lambda}_g,\boldsymbol{\lambda}_R,\boldsymbol{\lambda}_P] \\ & - \int d\mathbf{r}\rho(\mathbf{r})\lambda_\rho(\mathbf{r}) - \int d\mathbf{r}\mathbf{g}(\mathbf{r})\cdot\boldsymbol{\lambda}_g(\mathbf{r}) \\ & - \boldsymbol{\lambda}_R\cdot\mathbf{R} - \boldsymbol{\lambda}_P\cdot\mathbf{P}\end{aligned}$$

- The hydrodynamic functional is minus the entropy

$$\lambda_\rho(\mathbf{r}) = -\frac{\delta\mathcal{H}}{\delta\rho(\mathbf{r})} \qquad \boldsymbol{\lambda}_R = -\frac{\partial\mathcal{H}}{\partial\mathbf{R}}$$

$$\boldsymbol{\lambda}_g(\mathbf{r}) = -\frac{\delta\mathcal{H}}{\delta\mathbf{g}(\mathbf{r})} \qquad \boldsymbol{\lambda}_P = -\frac{\partial\mathcal{H}}{\partial\mathbf{P}}$$

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

- We may express the gran 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

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

- We have introduced the thermal wavelength and the chemical potential

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

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

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

- Finally, the hydrodynamic funcional $\mathcal{H}$ 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

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

- Reversible equations for the CG variables

$$\begin{aligned}
\partial_t \rho(\mathbf{r})\big|_{\mathrm{rev}} &= -\boldsymbol{\nabla}\cdot\mathbf{g}(\mathbf{r}) \\
\partial_t \mathbf{g}(\mathbf{r})\big|_{\mathrm{rev}} &= -\boldsymbol{\nabla}\cdot(\mathbf{g}(\mathbf{r})\mathbf{v}(\mathbf{r})) - \rho(\mathbf{r})\boldsymbol{\nabla}\frac{\delta\mathcal{F}}{\delta\rho(\mathbf{r})}[\rho,\mathbf{R}] \\
\partial_t\, \mathbf{R}\big|_{\mathrm{rev}} &= \frac{\mathbf{P}}{M} \\
\partial_t\, \mathbf{P}\big|_{\mathrm{rev}} &= -\frac{\partial\mathcal{F}}{\partial\mathbf{R}}[\rho,\mathbf{R}]
\end{aligned}$$

- 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 $D_{ij}(t) = \int_0^{\Delta t} dt' \left\langle \mathcal{Q}_t i\mathcal{L}\hat{A}_j \exp\{i\mathcal{L}t'\}\mathcal{Q}_t i\mathcal{L}\hat{A}_i \right\rangle^{\lambda(t)}$
- Large simplificatin of the friction matrix because $\mathcal{Q}i\mathcal{L}\hat{\rho}_{\mathbf{r}} = 0$ and $\mathcal{Q}i\mathcal{L}\hat{\mathbf{R}}_\mu = 0$
- Irreversible equations for the CG variables

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

The transport equations. Irreversible term

- The fluid stress tensor

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

- The irreversible surface force density on the fluid

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

Irreversible term. Nonlocal transport coefficients

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

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

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

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

Final equations of nanohydrodynamics

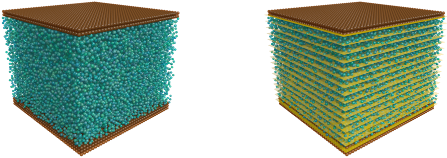
$$
\begin{aligned}
\partial_t \rho(\mathbf{r}) &= -\,\boldsymbol{\nabla}\cdot\mathbf{g}(\mathbf{r})\\
\partial_t \mathbf{g}(\mathbf{r}) &= -\,\boldsymbol{\nabla}\cdot(\mathbf{g}(\mathbf{r})\mathbf{v}(\mathbf{r})) - \rho(\mathbf{r})\boldsymbol{\nabla}\frac{\delta\mathcal{F}}{\delta\rho(\mathbf{r})}[\rho,\mathbf{R}]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

From continuum to discrete theory

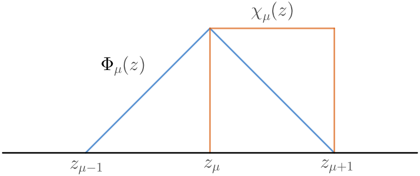
- The amount of information required in the hydrodynamic equations is exceedingly large.
  - η 36 independent components.
  - **H** and **G** 21 independent components.
  - γ 9 independent components.
- We need a simpler theory.
  - Planar walls.
  - Isotropic walls: invariant under translations in the 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 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 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

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

- The usual mass matrix of the finite element method is

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

The discrete CG variables

- The discrete CG variables

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

- The time derivatives

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

The discrete equations of nanohydrodynamics

- The equation for the density

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

- The normal component of the momentum

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

- The dissipative matrix is defined as

$$\begin{aligned} M^\perp_{\mu\nu} = &- \frac{\eta^\perp_{\mu\nu} - \eta^\perp_{\mu-1\nu} - \eta^\perp_{\mu\nu-1} + \eta^\perp_{\mu-1\nu-1}}{\Delta z^2} \\ &+ \frac{G^\perp_{\mu\nu} - G^\perp_{\mu\nu-1}}{\Delta z} + \frac{H^\perp_{\mu\nu} - H^\perp_{\mu-1\nu}}{\Delta z} - \gamma^\perp_{\mu\nu} \end{aligned}$$

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

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

The transport kernels

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

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

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

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

Summary

- 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

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

- Rationale justifying the Markovian approximation

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

with the normalized correlation $c(t)$ as $C^{-1}(0)C(t)$.

- Where we have introduced the *projected* Green-Kubo running integral

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

Corrected Green-Kubo formula

Space and time locality for unconfined fluids

CG variables

Markovian behaviour in confined fluids

The system

The slip boundary condition

The system

Conclusions and future directions

Conclusions

Future directions

Important references