Nanoscale hydrodynamics near solids

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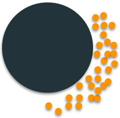
Agenda

Introduction

Roadmap

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

KAWASAKI-GUNTON PROJECTION OPERATOR + MARKOVIAN APPROXIMATION



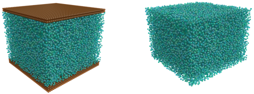
$$\partial_t \rho(\mathbf{r}) = -\boldsymbol{\nabla}\cdot\mathbf{g}(\mathbf{r})$$
$$\partial_t \mathbf{g}(\mathbf{r}) = -\boldsymbol{\nabla}\cdot(\mathbf{g}(\mathbf{r})\mathbf{v}(\mathbf{r})) - \rho(\mathbf{r})\boldsymbol{\nabla}\frac{\delta\mathcal{F}}{\delta\rho(\mathbf{r})}[\rho,\mathbf{R}] + \boldsymbol{\nabla}\cdot\boldsymbol{\Sigma}(\mathbf{r})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

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.
- Coarse grained (CG) variables.
- Levels of description depending on the amount of information which one retains macroscopically.
    - Macroscopic level.
    - Microscopic level.
    - Mesoscopic level.

The dynamics

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

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

- The trace symbol is given by

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

- ρ_t is the nonequilibrium solution of the Liouville equation

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

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

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

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

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

- 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.

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

Summary

- Kawasaki-Gunton and Mori theory.
- Exponential decay of the matrix of correlations after a time τ.

Continuum hydrodynamics theory for liquids near solids