Nanoscale hydrodynamics near solids

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Agenda

1. Introduction

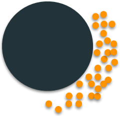
2. Nonequilibrium Statistical Mechanics

Introduction

Roadmap

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

KAWASAKI-GUNTON PROJECTION OPERATOR + MARKOVIAN APPROXIMATION



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

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

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

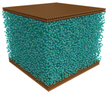
$$\dot{\mathbf{P}} = -\frac{\partial\mathcal{F}}{\partial\mathbf{R}} - \int d\mathbf{r}\,\boldsymbol{\mathcal{S}}(\mathbf{r})$$

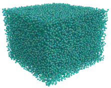
PLATEAU PROBLEM

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 Kawasaki-Gunton projection operator

- Set of CG variables $\hat{A}_i(z)$ and their conjugates variables $\lambda_i(t)$, related through the entropy $\frac{\delta S}{\delta a} = \lambda$.
- The aim is to derive equations of motion for the time dependent average $a_i(t)$ of the CG variables $\hat{A}_i(z)$

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

- For isolated systems with a time-independet Hamiltonian,the averages evolves according to the following equation [**Grabert1982**]

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

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.

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.

Markovian equation. Kawasaki-Gunton projection operator

- Whenever a clear separation of timescales exists between the evolution of the averages and the decay of the memory kernel can be approximate by the memory-less equation

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

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

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