Nanoscopic approach to dynamics of liquids

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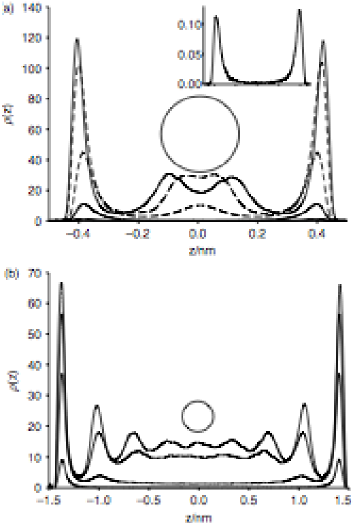
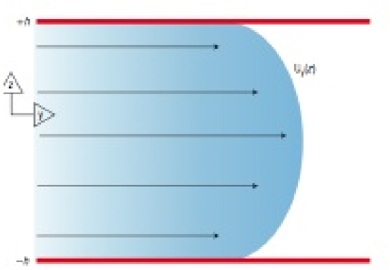
Motivations

- New areas of physics, materials science and chemistry come in at the nanoscale. At nanoscale dimensions different physical phenomena start to dominate.
- A central question in nanofluidics concerns the extent to which the hydrodynamic equations hold at the nanoscale.
- New techniques available: electrowetting, drop/bubble microfluidics, soft-substrate actuation, electro-osmotic pumps, electrophoresis, static mixing, flow focusing, etc.
- Nanofluidic computing where basic computing elements such as logic gates may be incorporated into very small scale devices. Enable nanofluidic technology by directly incorporating computing functions.

Transport in a nanochannel





A fluid in a pipe

Properties at the nanoscale

- When structures approach the size regime corresponding to molecular scaling lengths, new physical constraints are placed on the behavior of the fluid.
- Fluids exhibit new properties not observed in bulk, e.g. vastly increased viscosity near the pore wall; they may effect changes in thermodynamic properties and may also alter the chemical reactivity of species at the fluid-solid interface.
- Large demand for studying transport in nanofluidic devices, multiphase dynamics , interfacial phenomena
- At small scales Navier-Stokes equation breaks down
- Consider the discrete nature of fluids and hydrodynamics in a workable scheme
- Represent non ideal gas behavior via a bottom-up approach or coarse graining procedure instead of fine graining methods.

OUTLINE

- Kinetic approach: evolution equation for the 1-particle phase space distribution.
- Balance equations for conserved quantities. Hydrodynamics
- Transport coefficients.
- Lattice Boltzmann Equation implementation.
- Numerical test: Poiseuille flow of hard spheres in a narrow pore
- Conclusions.

Microscopic description of inhomogeneous fluids

Phenomenological **Langevin** equation:

$$\frac{d\mathbf{r}_n}{dt} = \mathbf{v}_n$$

$$m\frac{d\mathbf{v}_n}{dt} = \left[\mathbf{F}(\mathbf{r}_n) - \sum_{m(\neq n)} \nabla_{\mathbf{r}_n} U(|\mathbf{r}_n - \mathbf{r}_m|)\right] - m\gamma\mathbf{v}_n + \boldsymbol{\xi}_n(t)$$

$$\langle \xi_n^i(t)\xi_m^j(s)\rangle = 2\gamma m k_B T \delta_{mn}\delta^{ij}\delta(t-s)$$

How do we contract description from phase-space (6N-DIM) $\rightarrow$ diffusion ordinary 3d space?

Answ: At equilibrium via integral eqs. method or DFT.

Non-equilibrium...

Evolution eq. 1-particle phase-space distribution

- Kinetic equation

$$\partial_t f(\mathbf{r},\mathbf{v},t) + \mathbf{v}\cdot\nabla f(\mathbf{r},\mathbf{v},t) + \frac{\mathbf{F}^{ext}(\mathbf{r})}{m}\cdot\frac{\partial}{\partial \mathbf{v}} f(\mathbf{r},\mathbf{v},t) = \mathcal{Q}(\mathbf{r},\mathbf{v},t) + \mathcal{B}(\mathbf{r},\mathbf{v},t)$$

- Collision term

$$\mathcal{Q}(\mathbf{r},\mathbf{v},t) = \frac{1}{m}\nabla_{\mathbf{v}} \int d\mathbf{r}' \int d\mathbf{v}' f_2(\mathbf{r},\mathbf{v},\mathbf{r}',\mathbf{v}',t)\nabla_{\mathbf{r}} U(|\mathbf{r}-\mathbf{r}'|)$$

- Heat bath term $\mathcal{B}^{(DDFT)}(\mathbf{r},\mathbf{v},t) = \gamma[\frac{k_B T}{m}\frac{\partial^2}{\partial \mathbf{v}^2} + \frac{\partial}{\partial \mathbf{v}}\cdot\mathbf{v}]f(\mathbf{r},\mathbf{v},t)$
- Closure obtained from Decoupling (Molecular chaos)

$$f_2(\mathbf{r},\mathbf{v},\mathbf{r}',\mathbf{v}',t) \approx f(\mathbf{r},\mathbf{v},t) f(\mathbf{r}',\mathbf{v}',t) g_2(\mathbf{r},\mathbf{r}',t|n)$$

Approaches: DDFT and Kinetic equation

- When friction γ is large:

$$\partial_t n(\mathbf{r},t) = D\nabla\left[n(\mathbf{r},t)\nabla\frac{\delta\mathcal{F}}{\delta n(\mathbf{r},t)} - F(\mathbf{r})n(\mathbf{r},t)\right]. \tag{1}$$

- $\mathcal{F}$ free energy functional of density.
- Method works when colloidal particles due to the strong interaction with the solvent reach rapidly a local equilibrium. Velocity distrib. function is $\approx$ Maxwellian. Density evolves diffusively towards the equilibrium solution. Smoluchovski description appropriate.
- The Solvent acts as an HEAT BATH . **Noise and friction** are intimately connected through Fluctuation-dissipation.

Dynamics of molecular liquids vs. colloidal suspensions

- Colloidal dynamics is overdamped. Relaxation occurs via diffusion. (One conserved mode) No Galilei invariance.
- Molecular liquids have inertial dynamics, **5 conserved modes**
- First 5 (hydrodynamic) moments of $f(\mathbf{r}, \mathbf{v}, t)$ privileged status.
- Hard modes (short lived) absorb energy from the soft modes and restore global equilibrium.

How to combine microscopic and hydrodynamic description?

- **Eq. of state** requires better description of structure. Revised Enskog theory.
- Simplifly transport equation by exactly treating contributions to hydrodynamic modes while approximating non hydrodynamic terms via an exponential relaxation ansatz.
- $$\partial_t f(\mathbf{r},\mathbf{v},t) + \mathbf{v}\cdot\nabla f(\mathbf{r},\mathbf{v},t) + \frac{\mathbf{F}^{ext}(\mathbf{r})}{m}\cdot\frac{\partial}{\partial\mathbf{v}} f(\mathbf{r},\mathbf{v},t) =$$
  $$\frac{f_{loc}(\mathbf{r},\mathbf{v},t)}{nk_BT}\Big((\mathbf{v}-\mathbf{u})\cdot\mathbf{C}^{(1)}(\mathbf{r},t) + (\frac{m(\mathbf{v}-\mathbf{u})^2}{3k_BT}-1)C^{(2)}(\mathbf{r},t)\Big)+\mathcal{B}_{bgk}$$
- $$\mathcal{B}_{bgk}(\mathbf{r},\mathbf{v},t) \equiv -\nu_0[f(\mathbf{r},\mathbf{v},t) - f_{loc}(\mathbf{r},\mathbf{v},t)]$$
  $$f_{loc}(\mathbf{r},\mathbf{v},t) = n(\mathbf{r},t)[\tfrac{m}{2\pi k_B T(\mathbf{r},t)}]^{3/2}\exp\Big(-\tfrac{m(\mathbf{v}-\mathbf{u})^2}{2k_BT(\mathbf{r},t)}\Big).$$

Hydrodynamic description

- Continuity equation

$$\partial_t n(\mathbf{r},t) + \nabla \cdot (n(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)) = 0$$

- the momentum balance equation

$$mn[\partial_t u_j + u_i \partial_i u_j] + \partial_i P_{ij}^{(K)} - F_j n - C_j^{(1)}(\mathbf{r},t) = b_j^{(1)}(\mathbf{r},t)$$

- and the kinetic energy balance equation

$$\frac{3}{2} k_B n[\partial_t + u_i \partial_i] T + P_{ij}^{(K)} \partial_i u_j + \partial_i q_i^{(K)} - C^{(2)}(\mathbf{r},t) = b^{(2)}(\mathbf{r},t)$$

- C are are determined by interactions (self-consistent fields) and are gradients of the pressure tensor and heat flux.

$$C_i^{(1)}(\mathbf{r},t) = m \int d\mathbf{v} \mathcal{Q}(\mathbf{r},\mathbf{v},t) v_i = -\nabla_j P_{ij}^{(C)}(\mathbf{r},t) \qquad (2)$$

$$C^{(2)}(\mathbf{r},t) = -\nabla_i q_i^{(C)}(\mathbf{r},t) - P_{ij}^{(C)}(\mathbf{r},t) \nabla_i u_j(\mathbf{r},t) \qquad (3)$$

Interactions determine **pressure** and **transp. coefficients**

$$P_{bulk} = \frac{1}{d}\sum_{i=1}^{d}\left[P_{ii}^{(K)} + P_{ii}^{(C)}\right]_{bulk} = k_B T\left[n_b + \frac{2\pi}{3}n_b^2\sigma^3 g_2(\sigma)\right]$$

Rewrite interaction as a sum of specific forces:

$$\mathbf{C}^{(1)}(\mathbf{r},t) = n(\mathbf{r},t)\Big(\mathbf{F}^{mf}(\mathbf{r},t) + \mathbf{F}^{drag}(\mathbf{r},t) + \mathbf{F}^{viscous}(\mathbf{r},t)\Big). \quad (4)$$

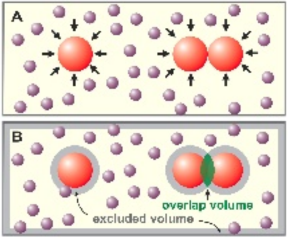
We identify the force, $\mathbf{F}^{mf}$, acting on a particle at $\mathbf{r}$ with the gradient of the so-called potential of mean force (attractive+repulsive):

$$\mathbf{F}^{mf}(\mathbf{r},t) = -k_B T\sigma^2 \int dkkg(\mathbf{r},\mathbf{r}+\sigma k,t)n(\mathbf{r}+\sigma k,t) + \mathbf{G}_{attr}(\mathbf{r},t) \quad (5)$$

For slowly varying densities

$$\mathbf{F}^{mf}(\mathbf{r},t) = -\nabla\mu_{int}^{\alpha}(\mathbf{r},t). \quad (6)$$

Asakura and Oosawa Entropic between hard spheres

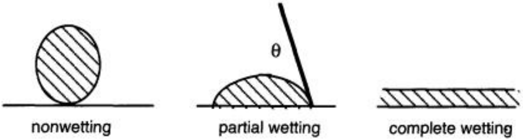


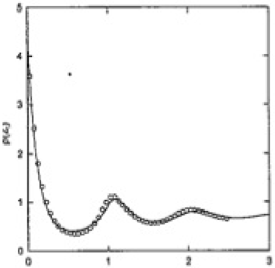
Spheres of radius R, separated a distance 2R + D, and immersed in fluid of particles with radius r, $\mathcal{F} = -k_B T \ln V'$

$$V' = V - \frac{8\pi}{3}(R+r)^3 + v_{overlap}$$

$$F = -\frac{\partial \mathcal{F}}{\partial D} = \frac{N k_B T}{V}\frac{\partial v_{overlap}}{\partial D} = -\rho k_B T \pi (r - D/2)(2R + r + D/2)$$

Fluids at substrates





Near a repulsive wall a dense fluid of hard spheres displays pronounced oscillations on a nanoscale.

Non equilibrium forces

The drag force is proportional to the velocity difference between impurity and fluid:

$$F_i^{drag}(\mathbf{r},t) = -\gamma_{ij}(\mathbf{r})[u_j^{impurity}(\mathbf{r}) - u_j(\mathbf{r})] \quad (7)$$

In the homogeneous case microscopic expression is

$$\hat{\gamma}_{ij} \approx \frac{8}{3}(\pi m k_B T)^{1/2}\sigma^2 g n \delta_{ij} \quad (8)$$

In the limit of small Reynolds numbers obtain mass concentration advection-diffusion equation:

$$\partial_t c + \mathbf{u}\cdot\nabla c = \frac{K_B T}{\gamma}\nabla\Big[(c(1-c)\nabla\Delta\mu\Big] \quad (9)$$

with $c = \rho^A/\rho$ and $\Delta\mu \equiv \frac{1}{m^A}\mu^A - \frac{1}{m^B}\mu^B$,

$$D = \frac{k_B T}{\gamma} \quad (10)$$

Diffusion current

$$\partial_t \rho^A + \nabla \cdot (\rho^A \mathbf{u}) + \nabla \cdot \mathbf{J} = 0$$

$$\mathbf{J} = -m^A m^B \frac{n^2}{\rho} \Big(D^{AB} \mathbf{d}^A + D_T \frac{1}{T} \nabla T \Big)$$

Chemical force

$$\mathbf{d}^A = \frac{\rho^A \rho^B}{\rho n k_B T} \Big\{ \frac{1}{m^A} \nabla \mu^A|_T - \frac{1}{m^B} \nabla \mu^B|_T - \Big(\frac{\mathbf{F}^A(\mathbf{r})}{m^A} - \frac{\mathbf{F}^B(\mathbf{r})}{m^B} \Big) \Big\},$$

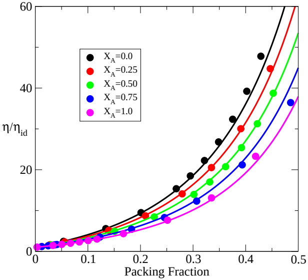
$$D^{AB} = \frac{3}{8n} \frac{(k_B T)^{1/2}}{(2\pi \mu_{AB})^{1/2} (\sigma_{AB})^2 g_{AB}}.$$

$$D_T = \alpha D^{AB}$$

Viscous force force and shear viscosity

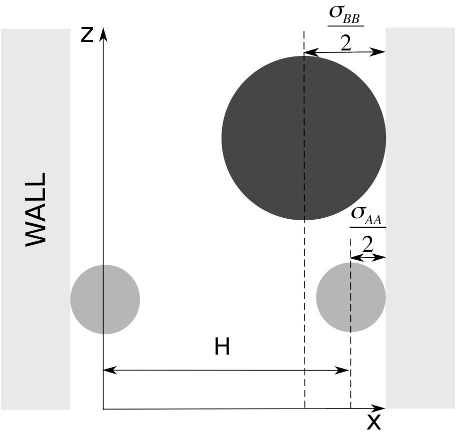
Viscous force of non local character:

$$F_i^{viscous}(\mathbf{r}, t) = \int d\mathbf{r}' H_{ij}(\mathbf{r}, \mathbf{r}')[u_j(\mathbf{r}') - u_j(\mathbf{r})]. \quad (11)$$



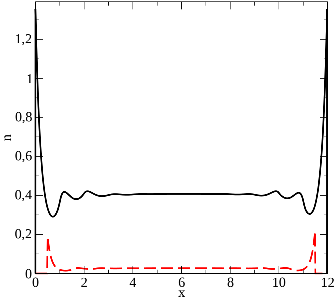
$$F_z^{viscous} = \frac{4}{15}\sqrt{\pi m k_B T} n \sigma^4 g \left(\frac{\partial^2 u_z}{\partial x^2} + \frac{\partial^2 u_z}{\partial y^2}\right) \quad (12)$$

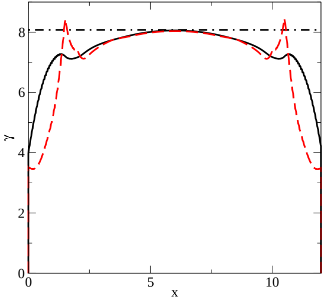
Inhomogeneous Diffusion in a slit



Microscopic profiles and mobility tensor

Diffusion is normal, but non isotropic, parallel and normal mobility are different





Velocity profiles

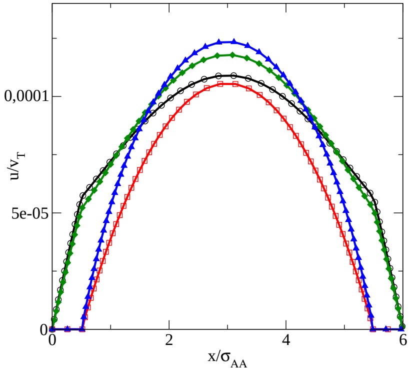
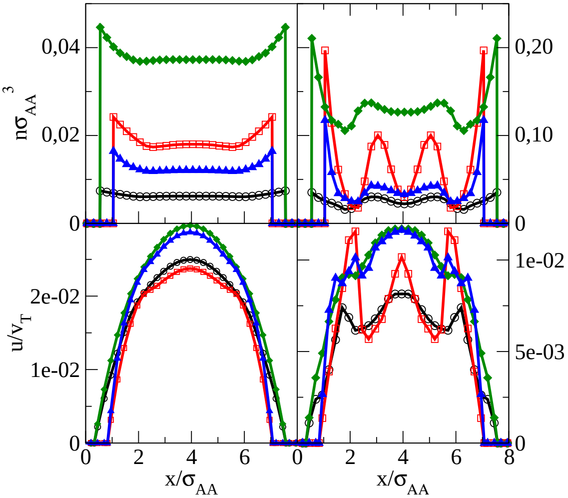


Figure: Velocity profiles of the two species for a channel of width $H = 6\sigma_{AA}$ and load $F = 0.001$. according to the toy model.

Self-consistent Numerical solution of transport equation



Lattice Boltzmann in a nutshell

Lattice Boltzmann strategy is applied as a numerical solver. Based on discretization of velocities on a lattice. No hydrodynamic equations need to be solved.

- The distribution function is replaced by an array of 19 populations, $f(\mathbf{r},\mathbf{v},t) \to f_i(\mathbf{r},t)$. Minimal velocity set employed ($D3Q19$, $D3Q27$)
- The propagation of the populations achieved via a time discretization to first order and a forward Euler update:

$$\partial_t f_i(\mathbf{r},t) + \mathbf{v}_i \cdot \partial_{\mathbf{r}} f_i(\mathbf{r},t)] \simeq \frac{f_i(\mathbf{r}+\mathbf{v}_i\delta t, t+\delta t) - f_i(\mathbf{r},t)}{\delta t}$$

- Collisional stage

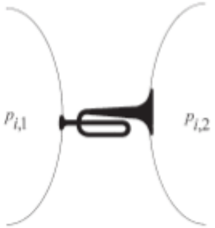
$$f_i(\mathbf{r}+\mathbf{c}_i, t+1) - f_i(\mathbf{r},t) = w_i \sum_{l=0}^{K} \frac{1}{v_T^{2l} l!} C_{\underline{\alpha}}^{(l)}(\mathbf{r},t) h_{\underline{\alpha}}^{(l)}(\mathbf{c}_i) + \frac{f_i^{loc}(\mathbf{r},t) - f_i(}{\tau_0}$$

For a practical scheme we need to

- Evaluate integrals by Gauss quadratures in r-space
- Have a good representation of the radial distribution function Fischer-Methfessel (1980)
- Boundary conditions simple (eg no-slip via bounce-back)
- Disentanglement of spatial/velocity discretization (i.e. $u\nabla u$ term in NS eq.). No need to solve Poisson eqn for pressure.
- Navier-Stokes is recovered for small gradients .

Conclusions

- Starting from a microscopic level we have obtained a governing eq. for $f(\mathbf{r}, \mathbf{v}, t)$ describing both equilibrium structural properties and transport properties.
- Hydrodynamic vs. non-hydrod. modes splitting proves a convenient route.
- Attractive potential tails: contribute to the energy of the fluid, but less important for collisional dissipation.
- Future work must include more general interactions and geometries.



. Schematic representation of transport through an object of complicated shape, with two openings.

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