Stochastic Lattice Boltzmann and its Coupling to Soft Matter Systems

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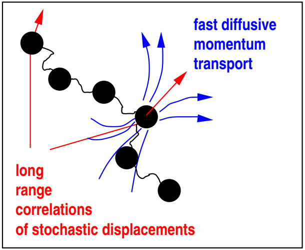
Hydrodynamic interactions



Navier–Stokes equation
(Green's function)
solvent viscosity η

$$\langle \Delta \vec{r}_i \otimes \Delta \vec{r}_j \rangle = 2 \overleftrightarrow{D}_{ij} \Delta t$$

Oseen tensor:

$$\overleftrightarrow{D}_{ij} = k_B T \overleftrightarrow{\mu}_{ij} = \frac{k_B T}{8 \pi \eta} \frac{1}{|\vec{r}_i - \vec{r}_j|} \left(\overleftrightarrow{1} + \hat{r}_{ij} \otimes \hat{r}_{ij} \right)$$

Brownian Dynamics (BD)

$$\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \Delta t \sum_j \overleftrightarrow{\mu}_{ij} \vec{F}_j(t) + \Delta \vec{r}_i$$

$$\langle \Delta \vec{r}_i \otimes \Delta \vec{r}_j \rangle = 2 \overleftrightarrow{D}_{ij} \Delta t$$

- For many Brownian particles, the correlation matrix becomes huge and **very** unwieldy!
- Exact calculation of stochastic term via Cholesky decomposition: $O(N^3)$
- Approximate solution via matrix Chebyshev expansion: $O(N^{2.25})$
- "P^3M"–like methods (Banchio & Brady): $O(N^{1.25} \ln N)$ (complicated, not considered here)
- $\Rightarrow$ In many cases, **explicit** momentum transport is desired (strictly $O(N)$!)

Brownian Dynamics vs. explicit solvent (ES)

BD	ES
$Sc = \infty$	$Sc \gg 1$
$Ma = 0$	$Ma \ll 1$
$Re = 0$	$Re \ll 1$
$Bo > 0$	$Bo > 0$

- Schmidt number $Sc = \nu / D$ (diffusive momentum transport vs. diffusive mass transport)
- Mach number $Ma = v/c$ (flow velocity vs. speed of sound; importance of fluid compressibility)
- Reynolds number $Re = vL/\nu$ (convective vs. diffusive momentum transport)
- "Boltzmann number" Bo: $\Delta x / x$ (thermal fluctuation vs. mean value, on the scale of an effective degree of freedom — depends on the degree of coarse–graining!)
  - Particle methods: $Bo = O(1)$
  - BD, discretized field theories: Bo freely adjustable!

Low Mach number physics

- only $u \ll a/h$ (lattice spacing / time step)
- only $u \ll c_s$
- $Ma = u/c_s \ll 1$
- low Mach number $\Rightarrow$
  compressibility does not matter $\Rightarrow$
  equation of state does not matter $\Rightarrow$
  choose ideal gas!

m_p particle mass:

$$p = \frac{\rho}{m_p} k_B T$$

$$c_s^2 = \frac{\partial p}{\partial \rho} = \frac{1}{m_p} k_B T$$

$$p = \rho c_s^2$$

$$k_B T = m_p c_s^2$$

“Boltzmann number”

- Ideal gas, temp. T, particle mass m_p, sound speed c_s:

$$k_B T = m_p c_s^2$$

- $c_s \sim a/h$ (a lattice spacing, h time step)
- c_s as small as possible

Example (water):
mass density $\rho = 10^3 kg/m^3$
sound speed realistic: $1.5 \times 10^3 m/s$
sound speed artificial: $c_s = 10^2 m/s$
temperature $T \approx 300K$, $k_B T = 4 \times 10^{-21} J$
particle mass: $m_p = 4 \times 10^{-25} kg$

	macroscopic scale	molecular scale
lattice spacing	$a = 1mm$	$a = 1nm$
time step	$h = 10^{-5} s$	$h = 10^{-11} s$
mass of a site	$m_a = 10^{-6} kg$	$m_a = 10^{-24} kg$
“Boltzmann number”	$Bo = (m_p/m_a)^{1/2} = 6 \times 10^{-10}$	$Bo = (m_p/m_a)^{1/2} = 0.6$

Consequences

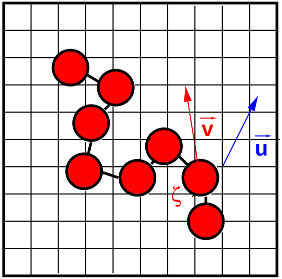
- solvent $\equiv$ just a medium to transmit momentum!
- easy and simple representation
- lattice model with momentum conservation
- ideal gas
- inclusion of thermal fluctuations

Stochastic Lattice Boltzmann!

Coupling lattice Boltzmann $\leftrightarrow$ Molecular Dynamics

(P. Ahlrichs & B. D. 1999)

- particle system: stochastic Molecular Dynamics
- solvent: stochastic lattice Boltzmann
- *dissipative* coupling:



- $\vec{F} = -\zeta(\vec{v} - \vec{u})$
- $\vec{u}$: interpolation from surroundings
- momentum conservation
- fluctuation–dissipation theorem

yields hydrodynamic interactions on large scales

Equations of motion, continuum limit

$$\vec{u}_i \equiv \int d^3\vec{r}\sigma_i(\vec{r}_i, \vec{r})\vec{u}\,(\vec{r})$$

$$\begin{aligned}\frac{d}{dt}\vec{r}_i &= \frac{1}{m_i}\vec{p}_i \\ \frac{d}{dt}\vec{p}_i &= \vec{F}_i - \zeta_i\left(\frac{1}{m_i}\vec{p}_i - \vec{u}_i\right) + \vec{f}_i\end{aligned}$$

$$\partial_t\rho + \partial_\alpha j_\alpha = 0$$

$$\partial_t j_\alpha + \partial_\beta\left(p\delta_{\alpha\beta} + \rho u_\alpha u_\beta\right) = \partial_\beta\eta_{\alpha\beta\gamma\delta}\partial_\gamma u_\delta + \partial_\beta Q_{\alpha\beta}$$

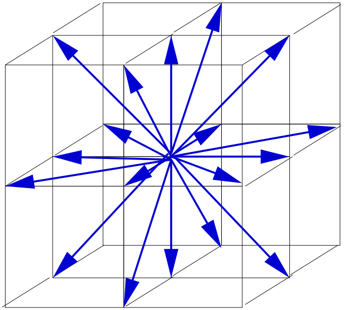
$$+\sum_i\left[\zeta_i\left(\frac{1}{m_i}p_{i\alpha} - u_{i\alpha}\right) - f_{i\alpha}\right]\sigma_i\left(\vec{r}_i, \vec{r}\right)$$

Fluctuation–dissipation relations

$$
\begin{aligned}
\langle f_{i\alpha} \rangle &= 0 \\
\langle Q_{\alpha\beta} \rangle &= 0 \\
\left\langle f_{i\alpha}(t) \, f_{j\beta}(t') \right\rangle &= 2 k_B T \zeta_i \delta_{ij} \delta_{\alpha\beta} \delta \left(t - t' \right) \\
\left\langle Q_{\alpha\beta}(\vec{r}, t) \, Q_{\gamma\delta}(\vec{r}', t') \right\rangle &= 2 k_B T \eta_{\alpha\beta\gamma\delta} \delta \left(\vec{r} - \vec{r}' \right) \delta \left(t - t' \right)
\end{aligned}
$$

Proof for the coupled system: See B. D. & A. J. C. Ladd, Advances in Polymer Science 221, 89 (2009).

Fluctuating lattice Boltzmann



- linearized Boltzmann equation (kinetic theory of gases)
- fully discretized
- sites $\vec{r}$, lattice spacing a
- time t, time step h

$$n_i(\vec{r} + \vec{c}_i h, t + h) = n_i^\star(\vec{r}, t) = n_i(\vec{r}, t) + \Delta_i(\vec{r}, t)$$

- n_i mass density associated with velocity $\vec{c}_i$
- conserved mass density $\rho = \sum_i n_i$
- conserved momentum density $\vec{j} = \rho \vec{u} = \sum_i n_i \vec{c}_i$
- collision term Δ_i: stochastic variable

Deterministic D3Q19 model

- $\rho = \sum_i n_i$, $\vec{j} = \sum_i n_i \vec{c}_i$, $\vec{u} = \vec{j}/\rho$
- $\overleftrightarrow{\Pi} = \sum_i n_i \vec{c}_i \otimes \vec{c}_i$
- $n_i^{eq}(\rho, \vec{u}) = w_i \rho \left(1 + \frac{\vec{u}\cdot\vec{c}_i}{c_s^2} + \frac{(\vec{u}\cdot\vec{c}_i)^2}{2c_s^4} - \frac{u^2}{2c_s^2}\right)$, such that
- $\sum_i n_i^{eq} = \rho$, $\sum_i n_i^{eq} \vec{c}_i = \vec{j}$
- $\overleftrightarrow{\Pi}^{eq} = \sum_i n_i^{eq} \vec{c}_i \otimes \vec{c}_i = \rho c_s^2 + \rho \vec{u} \otimes \vec{u}$
- this *fixes*:
  - $w_i(0) = 1/3$
  - $w_i(nn) = 1/18$
  - $w_i(nnn) = 1/36$
  - $c_s = (1/\sqrt{3})(a/h)$
- linear relaxation: $\Delta_i = \sum_j L_{ij}(n_j - n_j^{eq})$
- streaming

- Chapman–Enskog:
  Navier–Stokes in the hydrodynamic limit
- $\overleftrightarrow{\Pi}$ relaxation rates $\leftrightarrow$ viscosities

Inclusion of noise

- Ladd JFM 1994: Noise acts *only* on the stress
- Adhikari / Stratford / Cates / Wagner EPL 2005: Noise should act on *all* non–conserved degrees of freedom
- B. D. / Schiller / Ladd PRE 2007: Confirmation based on the detailed–balance principle; restriction to stresses *only* correct in the hydrodynamic limit

Poisson statistics

- ν_i # of LB particles in velocity bin i
- contact with a large reservoir
- Poisson + constraints of conserved mass and momentum:

$$P(\{\nu_i\}) \propto \left(\prod_i \frac{\xi_i^{\nu_i}}{\nu_i!} \exp(-\xi_i) \right) \delta\left(\sum_i \mu \nu_i - \rho \right) \delta\left(\sum_i \mu \vec{c}_i \nu_i - \vec{j} \right)$$

- m_p mass of an LB particle
- $\mu = m_p / a^3 \Rightarrow n_i = \mu \nu_i$ and $\mu \xi_i = w_i \rho$
- Stirling: $\nu_i! \approx \exp(\nu_i \ln \nu_i - \nu_i)$

hence,

$$P\left(\{n_i\}\right) \quad \propto \quad \exp\left(S\left(\{n_i\}\right)\right)$$
$$\delta\left(\sum_i n_i - \rho\right) \delta\left(\sum_i n_i \vec{c}_i - \vec{j}\right)$$

with

$$S\left(\{n_i\}\right) = \frac{1}{\mu} \sum_i \rho w_i \left(\frac{n_i}{\rho w_i} - \frac{n_i}{\rho w_i} \ln \frac{n_i}{\rho w_i} - 1 \right)$$

mean square fluctuations $\propto \mu$ (degree of coarse–graining)

Maximizing P

Lagrange multipliers λ_ρ, $\vec{\lambda}_{\vec{j}}$

$$
\begin{aligned}
\frac{\partial S}{\partial n_i} + \lambda_\rho + \vec{\lambda}_{\vec{j}} \cdot \vec{c}_i &= 0 \\
\sum_i n_i - \rho &= 0 \\
\sum_i n_i \vec{c}_i - \vec{j} &= 0
\end{aligned}
$$

approximate solution up to $O(u^2)$:

$$
n_i^{eq} = w_i \rho \left(1 + \frac{\vec{u} \cdot \vec{c}_i}{c_s^2} + \frac{(\vec{u} \cdot \vec{c}_i)^2}{2 c_s^4} - \frac{u^2}{2 c_s^2} \right)
$$

Gaussian approximation for fluctuations

$$n_i^{neq} = n_i - n_i^{eq}$$

$$P\left(\{n_i\}\right) \propto \exp\left(S\right) \delta\left(\sum_i n_i - \rho\right) \delta\left(\sum_i n_i \vec{c}_i - \vec{j}\right)$$

$u = 0$ approximation:

$$P\left(\{n_i^{neq}\}\right) \propto \exp\left(-\sum_i \frac{\left(n_i^{neq}\right)^2}{2\mu\rho w_i}\right) \delta\left(\sum_i n_i^{neq}\right) \delta\left(\sum_i \vec{c}_i \, n_i^{neq}\right)$$

$$n_i^{neq} = \left(\mu\rho w_i\right)^{1/2} x_i$$

$$P \propto \exp\left(-\frac{1}{2}\sum_i x_i^2\right) \delta\left(\sum_i \sqrt{w_i}\, x_i\right) \delta\left(\sum_i \sqrt{w_i}\, \vec{c}_i \, x_i\right)$$

Modes

orthogonal transformation:

$$x_i = \sum_j \hat{e}_{ij} m_j$$

$$\sum_i x_i^2 = \sum_i m_i^2$$

- mass mode:
  $m_0 \propto \sum_i \sqrt{w_i} x_i = 0$
- momentum modes:
  $m_1 \propto \sum_i \sqrt{w_i} x_i c_i^x = 0$
  $m_2 \propto \sum_i \sqrt{w_i} x_i c_i^y = 0$
  $m_3 \propto \sum_i \sqrt{w_i} x_i c_i^z = 0$
- bulk stress mode:
  $m_4 \propto \sum_i \sqrt{w_i} x_i (c_i^2 - 1)$
- shear stress modes:
  $m_5 \propto \sum_i \sqrt{w_i} x_i c_i^x c_i^y$
  $m_6, \ldots, m_9$
- ghost modes:
  $m_{10}, \ldots, m_{18}$

Detailed balance

$$P(\{m_i\}) \propto \exp\left(-\frac{1}{2}\sum_{i\geq 4} m_i^2\right)$$

$$\frac{\omega(m \to m^\star)}{\omega(m^\star \to m)} = \frac{\exp\left(-m^{\star 2}/2\right)}{\exp\left(-m^2/2\right)}$$

$$m^\star = \gamma m + \varphi r$$

r Gaussian random number with $\langle r \rangle = 0$ and $\langle r^2 \rangle = 1$

$$\omega(m \to m^\star) = (2\pi\varphi^2)^{-1/2} \exp\left(-\frac{(m^\star - \gamma m)^2}{2\varphi^2}\right)$$

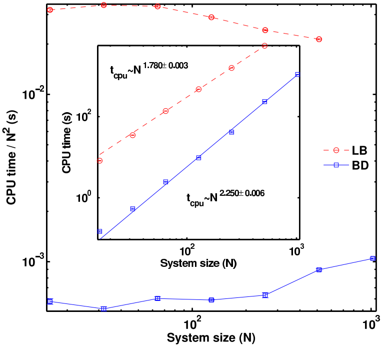
detailed balance holds if

$$\varphi = (1 - \gamma^2)^{1/2}$$

- **All** modes should be thermalized!
- Chapman–Enskog: Hydrodynamic limit is Landau–Lifshitz noise!

LB vs. BD: One simple comparison

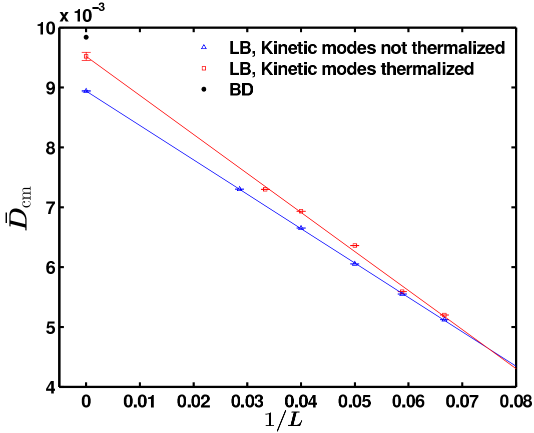
Pham / Schiller / Prakash / B. D. JCP 2009



- system: single polymer chain, good solvent, thermal equilibrium
- BD: infinite system
- LB+MD: 3 boxes with periodic boundary conditions, size L, extrapolation $L \to \infty$

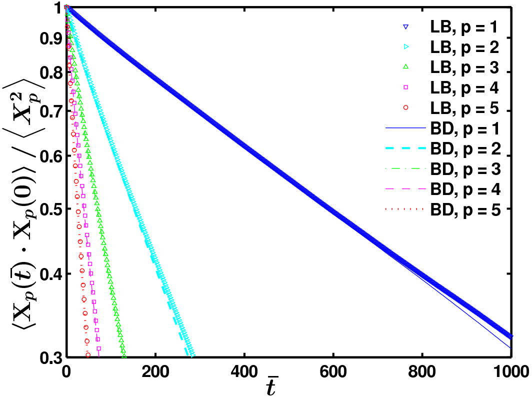
- BD: CPU $\propto N^{2.25}$
- LB+MD: $\sqrt{\langle R^2 \rangle}/L = const.$, CPU $\propto L^3 \propto R^3 \propto N^{3\nu} \propto N^{1.8}$

Diffusion constant



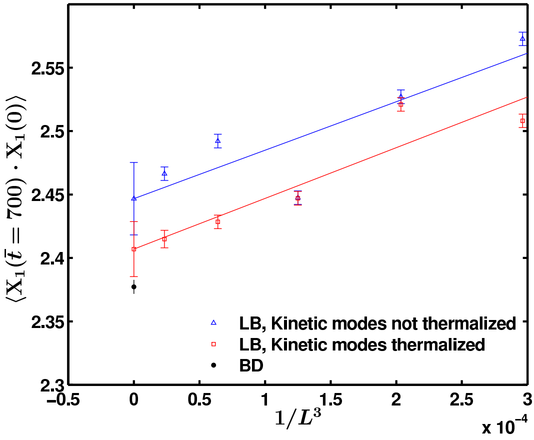
Rouse modes

$$\vec{X}_p = \frac{1}{N} \sum_{n=1}^{N} \vec{r}_n \cos\left[\frac{p\pi}{N}\left(n - \frac{1}{2}\right)\right]$$



Rouse modes: Weak finite size effects

- internal forces cancel in leading order
- $\Rightarrow$ "dipolar" interaction with periodic images
- $\Rightarrow$ finite size effect L^{-3}



Conclusions

- dissipative coupling LB+MD: simple, versatile, efficient
- rigorous understanding of thermal fluctuations in ideal–gas LB models
- rigorous understanding of the fluctuation–dissipation theorem for the coupled system
- thermal noise is necessary for all LB modes, *and* for the Brownian particles
- *quantitative* agreement between Brownian Dynamics and LB+MD
- BD: for highly dilute systems with few Brownian particles
- LB+MD: advisable for systems with many particles