Simulating the dynamics of a single polymer chain in solution: Lattice Boltzmann vs. Brownian Dynamics

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Hydrodynamic interactions

Navier–Stokes equation
solvent viscosity $\eta$

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

Oseen tensor:

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

\[ \vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \Delta t \sum_j \vec{\mu}_{ij} F_j(t) + \Delta \vec{r}_i \]

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

- 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: \( O(N^{2.25}) \)
- “P3M”–like methods (Banchio & Brady): \( O(N^{1.25 \ln N}) \) (complicated, not considered here)
- \( \Rightarrow \) In many cases, **explicit** momentum transport is desired (strictly \( O(N) \)!)
Lattice Boltzmann (LB)

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

- \( \vec{c}_i \) small set of velocities
- \( \vec{c}_i h \) connects two sites
- \( n_i(\vec{r}, t) \): real number, mass density on site \( \vec{r} \) corresponding to velocity \( \vec{c}_i \)

\[
n_i(\vec{r} + \vec{c}_i h, t + h) = n_i^*(\vec{r}, t) = n_i(\vec{r}, t) + \Delta_i(\vec{r}, t)
\]
Conservation laws, symmetries

\[ n_i(\vec{r} + \vec{c}_i h, t + h) = n_i^*(\vec{r}, t) = n_i(\vec{r}, t) + \Delta_i \{ n_i(\vec{r}, t) \} \]

\[ \rho = \sum_i n_i \]

\[ \vec{j} = \rho \vec{u} = \sum_i n_i \vec{c}_i \]

\[ \sum_i \Delta_i = \sum_i \Delta_i \vec{c}_i = 0 \]

- mass conservation
- momentum conservation
- locality
- rotational symmetry (lattice!)
- Galilei invariance (finite number of velocities)
Lattice Boltzmann algorithm

- $\rho = \sum_i n_i$
- $\vec{j} = \sum_i n_i \vec{c}_i$, $\vec{u} = \vec{j}/\rho$
- $\vec{\Pi} = \sum_i n_i \vec{c}_i \otimes \vec{c}_i$
- $n_i^{eq}(\rho, \vec{u}) = w_i \rho \left(1 + \frac{\vec{u} \cdot \vec{c}_i}{c_s^2} + \frac{(\vec{u} \cdot \vec{c}_i)^2}{2c_s^4} - \frac{\vec{u}^2}{2c_s^2}\right)$, such that
- $\sum_i n_i^{eq} = \rho$
- $\sum_i n_i^{eq} \vec{c}_i = \vec{j}$
- $\sum_i n_i^{eq} \vec{c}_i \otimes \vec{c}_i = \rho c_s^2 + \rho \vec{u} \otimes \vec{u}$
- linear relaxation: $\Delta_i^{det} = \sum_j L_{ij}(n_j - n_j^{eq})$
- addition of noise: $\Delta_i^{stoch}$
- streaming
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
"Bare" vs. effective friction constant

\( D_0 \): long–time diffusion coefficient

\( D_0 > k_B T / \zeta_{bare} \) (due to long time tail)

\( \vec{F} = \text{const.}, \vec{V} = \text{const.} \)

\[
\vec{V} = \frac{1}{\zeta_{bare}} \vec{F} + \vec{u}_{av}
\]

\[
\vec{u} \approx \frac{1}{8\pi \eta r} \left( \hat{1} + \hat{r} \otimes \hat{r} \right) \vec{F}
\]

\[
\vec{u}_{av} = \frac{1}{g \eta a} \vec{F}
\]

\[
\frac{1}{\zeta_{eff}} = \frac{1}{\zeta_{bare}} + \frac{1}{g \eta a}
\]

Stokes contribution from interpolation with range \(a\).

This regularizes the theory (no point particles in nature!)

\( \zeta_{bare} \): no physical meaning!

Match \( \zeta_{eff} \) with the BD friction coefficient!
Finite size effects

Study diffusion / sedimentation of a single object

- $L = \infty$: $u(r) \sim 1/r$
- $F \sim \eta R v = \eta R^2 (v/R)$
- area $R^2$, shear gradient $v/R$

- $L < \infty$: homogeneous background force (no net acceleration)
- backflow due to momentum conservation
- additional shear gradient $v/L$
- additional force
  $\eta R^2 (v/L) = \eta R v (R/L)$
- finite size effect $\sim R/L$
Brownian Dynamics vs. Lattice Boltzmann

<table>
<thead>
<tr>
<th></th>
<th>BD</th>
<th>LB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ma = 0$</td>
<td>$Ma \ll 1$</td>
<td></td>
</tr>
<tr>
<td>$Sc = \infty$</td>
<td>$Sc \gg 1$</td>
<td></td>
</tr>
<tr>
<td>$Re = 0$</td>
<td>$Re \ll 1$</td>
<td></td>
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<tr>
<td>$Bo &gt; 0$</td>
<td>$Bo &gt; 0$</td>
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- Schmidt number $Sc = \nu/D$ (diffusive momentum transport vs. diffusive mass transport)
- Mach number $Ma = \nu/c$ (flow velocity vs. speed of sound; importance of fluid compressibility)
- Reynolds number $Re = \nu L/\nu$ (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!
Necessity of thermal fluctuations

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

<table>
<thead>
<tr>
<th></th>
<th>macroscopic scale</th>
<th>molecular scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>lattice spacing</td>
<td>$a = 1 \text{mm}$</td>
<td>$a = 1 \text{nm}$</td>
</tr>
<tr>
<td>time step</td>
<td>$h = 10^{-5} \text{s}$</td>
<td>$h = 10^{-11} \text{s}$</td>
</tr>
<tr>
<td>mass of a site</td>
<td>$m_a = 10^{-6} \text{kg}$</td>
<td>$m_a = 10^{-24} \text{kg}$</td>
</tr>
<tr>
<td>“Boltzmann number”</td>
<td>$Bo = (m_p/m_a)^{1/2}$</td>
<td>$Bo = (m_p/m_a)^{1/2}$</td>
</tr>
<tr>
<td></td>
<td>$= 6 \times 10^{-10}$</td>
<td>$= 0.6$</td>
</tr>
</tbody>
</table>
Low Mach number physics

Low Mach number ⇒
compressibility does not matter ⇒
equation of state does not matter ⇒
choose ideal gas!
m\(_p\) particle mass:

\[
p = \frac{\rho}{m_p} k_B T
\]

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

\[
p = \rho c_s^2
\]

\[
k_B T = m_p c_s^2
\]
Occupation numbers in local thermal equilibrium
(Phys. Rev. E 76, 036704 (2007))

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

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

- $m_p$ mass of an LB particle
- $\mu = m_p/a^3$ $\Rightarrow$ $n_i = \mu \nu_i$ and $\mu \bar{\nu}_i = w_i \rho$
- $n_i^{eq}$ via maximization of $P$
- saddle point approximation around $n_i^{eq}$
Modes

\[ n_{i}^{\text{neq}} = n_{i} - n_{i}^{\text{eq}} \]

theory of fluctuations \( \Rightarrow \)

\[ \langle n_{i}^{\text{neq}}^2 \rangle = w_{i} \rho \mu \]

with \( \mu = m_{p}/a^{3} = k_{B} T/(a^{3} c_{s}^{2}) \Rightarrow \) normalization:

\[ \hat{n}_{i}^{\text{neq}} = \frac{n_{i}^{\text{neq}}}{\sqrt{w_{i} \rho \mu}} \]

modes via orthonormal transformation \( \hat{e}_{ki} \):

\[ \hat{m}_{k}^{\text{neq}} = \sum_{i} \hat{e}_{ki} \hat{n}_{i}^{\text{neq}} \]

- \( m_{0} \propto \rho \)
- \( (m_{1}, m_{2}, m_{3}) \propto \vec{j} \)
- \( m_{4} \in \text{span}(\rho, \Pi_{\alpha\alpha}) \) (bulk stress)
- \( \text{span}(m_{5}, \ldots, m_{9}) = \text{span}(\bar{\Pi}_{\alpha\beta}) \) (5 shear stresses)
- kinetic (or “ghost”) modes \( m_{10}, \ldots, m_{18} \)
Mode update: Relaxation and noise

\[ P \left( \{ \hat{m}_k^{neq} \} \right) \propto \exp \left( -\frac{1}{2} \sum_{k \geq 4} \hat{m}_k^{neq^2} \right) \]

\[ \hat{m}_k^{*neq} = \gamma_k \hat{m}_k^{neq} + (1 - \gamma_k^2)^{1/2} r_k \]

\( r_k \) Gaussian with

\[ \langle r_k \rangle = 0 \quad \langle r_k^2 \rangle = 1 \]

satisfies detailed balance!

- \( \gamma_4 \rightarrow \) bulk viscosity
- \( \gamma_5 = \ldots = \gamma_9 \rightarrow \) shear viscosity
- \( \gamma_{10} = \ldots = \gamma_{18} = 0 \) easiest choice
Provide *quantitative* comparison between BD and LB:

- Results on static and dynamic properties
- Efficiency
- Standard benchmark system: Single polymer chain in solvent
Static structure factor

\[ S(k) = \frac{1}{N} \sum_{ij} \left\langle \exp \left[ i \mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j) \right] \right\rangle \propto k^{-1/\nu} \]

for \( R^{-1} \ll k \ll a^{-1} \)
Lattice Boltzmann vs. Brownian Dynamics
B. Dünweg
U. Schiller
Hydrodynamic interactions
Brownian Dynamics
Lattice Boltzmann
Fluctuations
BD vs. LB
Results
Summary

Diffusion constant

![Graph showing diffusion constant vs. inverse length](image-url)

- \( \bar{D}_{cm} \)
- \( 1/L \)
- \( x 10^{-3} \)
Rouse modes

\[ \vec{X}_p = \frac{1}{N} \sum_{n=1}^{N} \vec{r}_n \cos \left( \frac{p \pi N}{N} \left( n - \frac{1}{2} \right) \right) \]
Rouse modes: Weak finite size effects

- internal forces cancel in leading order
- $\Rightarrow$ finite size effect $L^{-3}$
Scaling of dynamic structure factor

$\frac{k}{\nu} S(k, t)$

$k^2 t^{2/z}, z = 3.7$

$k^2 t^{2/z}, z = 3$

$k^2 t^{2/z}, z = 2.75$

$\frac{k}{\nu} S(k, t)$
CPU scaling: Single polymer chain

\[ R \sim a N^\nu \quad \nu \approx 0.59 \]

- BD: \( N^{2.25} \)
- LB: \( N^{3\nu} \approx N^{1.8} \) (but with unfavorable prefactor)
  - box size \( L \)
  - \( L \sim a N^\nu \)
  - \( L^3 \sim a^3 N^{3\nu} \)

- For typical chain lengths, BD is nearly two orders of magnitude faster
LB vs. BD: Comparison of efficiency

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

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

- $M$ chains of length $N$ in box of size $L$; blob picture:
  - "blob size" $\xi$
    - $\xi \sim an^\nu$
    - $R \sim \xi (N/n)^{1/2}$
    - $L \sim R$
    - $L^3/\xi^3 \sim M(N/n)$
    - $M \sim (N/n)^{1/2}$

- LB effort: slightly decreased (chain shrinkage) by factor $(n/N)^{3\nu-3/2} \approx 1/3$ for $N/n = 30$
- BD effort: increased by factor $M^{2.25} \sim (N/n)^{1.125} \approx 50$ (but HI with periodic images)
- BD can only compete (if at all) by using FFT acceleration
Summary

- Hydrodynamic interactions via dissipative coupling
  MD / LB: Simple, versatile, efficient
- Single–chain polymer dynamics: BD more efficient
- *Quantitative* agreement between BD and LB+MD
Chebyshev approximation

Polynomial approximation:

\[
\frac{\leftrightarrow 1/2}{D} \approx \sum_{k=0}^{L} a_k \leftrightarrow D
\]

\[
\frac{\leftrightarrow 1/2}{\vec{R}} \approx \sum_{k=0}^{L} a_k \leftrightarrow D \vec{R}
\]

\[
\frac{\leftrightarrow k}{D \vec{R}} = \frac{\leftrightarrow k-1}{DD \vec{R}}
\]

- Each term: \(O(N^2)\)
- Number of needed terms: Typically \(O(N^{0.25})\)

Coefficients \(a_k\) (pre-computed) depend on:

- \(L\)th order Chebyshev approximation to \(x^{1/2}\)
- \(\lambda_{\text{min}}, \lambda_{\text{max}}\), where all eigenvalues of \(\vec{D}\) obey \(\lambda_{\text{min}} \leq \lambda_i \leq \lambda_{\text{max}}\)
Equations of motion, continuum limit

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

\[
\frac{d}{dt} \vec{r}_i = \frac{1}{m_i} \vec{p}_i
\]

\[
\frac{d}{dt} \vec{p}_i = \vec{F}_i - \zeta_i \left( \frac{1}{m_i} \vec{p}_i - \vec{u}_i \right) + \vec{f}_i
\]

\[
\partial_t \rho + \partial_\alpha j_\alpha = 0
\]

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

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

\[ \langle f_{i\alpha} \rangle = 0 \]
\[ \langle Q_{\alpha\beta} \rangle = 0 \]
\[ \langle f_{i\alpha}(t) f_{j\beta}(t') \rangle = 2k_B T \zeta_i \delta_{ij} \delta_{\alpha\beta} \delta(t - t') \]
\[ \langle Q_{\alpha\beta}(\vec{r}, t) Q_{\gamma\delta}(\vec{r}', t') \rangle = 2k_B T \eta_{\alpha\beta\gamma\delta} \delta(\vec{r} - \vec{r}') \delta(t - t') \]
Chapman–Enskog expansion

Multi–time scale analysis: $\varepsilon \ll 1$ (e. g. $\varepsilon = 10^{-3}$):

$$\vec{r}_1 = \varepsilon \vec{r}$$

interpretation: “coarse–grained ruler”:
$1\mu m$ instead of 978nm

$$t_1 = \varepsilon t$$

interpretation: “coarse–grained clock”:
$1ns$ instead of 837ps

$$t_2 = \varepsilon^2 t$$

interpretation: “yet more coarse–grained clock”:
$1\mu s$ instead of 976ns572ps

- $t_1$ to capture wave–like phenomena
- $t_2$ to capture diffusive phenomena
- location in space and time: read off $\vec{r}_1$, $t_1$, $t_2$

Macroscopic limit is obtained for $\varepsilon \to 0$. 
\[ \vec{r} = \varepsilon^{-1}\vec{r}_1 \]

\( \vec{r}_1 \) fixed \( \Rightarrow \vec{r} \) varies with \( \varepsilon \) \( \Rightarrow \)

\[
\begin{align*}
n_i & = n_i^{(0)} + \varepsilon n_i^{(1)} + O(\varepsilon^2) \\
\Delta_i & = \Delta_i^{(0)} + \varepsilon \Delta_i^{(1)} + \varepsilon^2 \Delta_i^{(2)} + O(\varepsilon^3)
\end{align*}
\]

LBE:

\[
n_i(\vec{r}_1 + \varepsilon \vec{c}_i h, t_1 + \varepsilon h, t_2 + \varepsilon^2 h) - n_i(\vec{r}_1, t_1, t_2) = \Delta_i(\vec{r}_1, t_1, t_2)
\]

- Taylor expansion wrt \( \varepsilon \)
- truncate after 2nd order
- hierarchy of LBEs
- moments: \( \sum_i \ldots, \sum_i \vec{c}_i \ldots, \sum_i \vec{c}_i \otimes \vec{c}_i \ldots \)
- hierarchy of moment equations
- transform back to \( \vec{r}, t \)
- \( \equiv \) (fluctuating) Navier–Stokes
Zimm model

\[ \langle \Delta \vec{r}_i \otimes \Delta \vec{r}_j \rangle \sim \frac{k_B T}{\eta} \frac{1}{|\vec{r}_i - \vec{r}_j|} \]

\[ D \propto \frac{1}{R} \quad \tau_R \propto \frac{R^2}{D} \propto R^3 \quad z = 3 \]
Dynamic scaling

monomer mean square displacement:

\[ \log \Delta r^2 \]

\[ R^2 \]

\[ a^2 \]

\[ \log t \]

\[ \tau_a \]

\[ \tau_R \sim R^z \]

dynamic structure factor:

\[ S(k, t) = \frac{1}{N} \sum_{ij} \left\langle \exp \left[ i \vec{k} \cdot (\vec{r}_i(t) - \vec{r}_j(0)) \right] \right\rangle \]

\[ S(k, t) = k^{-1/\nu} f \left( k^2 t^{2/z} \right) \]
Semidilute solution: Mean square displacements: Crossover Zimm → Rouse

\[ \langle \Delta r^2 \rangle / (At^{2/3}) \]

- Log-log plot showing the crossover from Zimm to Rouse behavior.
- "Dilute" behavior at low concentrations (Zimm, \( z=3 \)).
- "Concentrated" behavior at high concentrations (Rouse, \( z=4 \)).

\[ <\Delta r^2>/At^{2/3} \]

- Parameters: \( c=0.231 \), \( c=0.134 \), \( c=0.0734 \).

- Scale: \( t/c^{2.3} \sim t/\tau_{\xi} \).
Dynamic single–chain structure factor

- “incomplete screening” is a short–time effect
  (P. Ahlrichs, R. Everaers, B. D. 2001)
- screening results from chain–chain collisions
- waiting time = blob relaxation time
Polymer motion in a turbulent flow (preliminary)

- multiscale approach:
- DNS of homogeneous turbulence (spectral code, J. Schumacher)
- flow field around tracer particles → initial and boundary conditions for LB+MD
- no back–coupling!

\[
\frac{d\vec{x}_L}{dt} = \bar{u}(\vec{x}_L(x_0,0), t)
\]
Chain stretching

\[ \frac{l_C}{l_K} = 1.72 \]

\[ \frac{\tau_Z}{\tau_K} = 11.6 \]
Histogram end–to–end distance

- w/o flow
- L=1, Wi=10
- L=2, Wi=40

P(R_{ee}) vs. R_{ee}/l_C
Consistency spectral code – LB

- vorticity vs. time
- solid lines: spectral code
- dotted lines: LB