Soft Matter Simulation

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Course Outline

- Lecture 5 – Mesoscale Simulations
  - Lattice Gas Automata
  - Lattice Boltzmann
  - Dissipative particle dynamics
Coarse-Graining

Molecular Dynamics  Coarse-Grained MD  Meso-Scale Methods  Continuum Methods

Coarse-Graining
Lattice Gas Automata (LGA)

- Idealized system where space and time are discrete
- Regular lattice of cells characterized by a set of boolean state variables i.e. 0 or 1
- Point particles move and collide
Lattice Gas Automata (LGA)

**streaming step**  
flow simulation by moving representative particles  
one node per time step

**collision step**
Lattice Gas Automata (LGA)

- Advantages
  - Stability
  - Easy to introduce boundary conditions
  - High performance computing due to intrinsic parallel structure

- Disadvantages
  - Statistical noise
  - Lack of invariance
  - Velocity dependent pressure
Lattice Boltzmann

- Powerful technique for the computational modeling of a wide variety of complex fluid flow
  - single and multiphase flow in complex geometries

- It is a discrete computational method based upon the Boltzmann equation
Lattice Boltzmann

- Considers a typical volume element of fluid to be composed of a collection of particles that are represented by a particle velocity distribution function for each fluid component at each grid point.

- The time is counted in discrete time steps and the fluid particles can collide with each other as they move, possibly under applied forces.

- The rules governing the collisions are designed such that the time-average motion of the particles is consistent with the Navier-Stokes equation.
Why Lattice Boltzmann Method?

- This method naturally accommodates a variety of boundary conditions such as the pressure drop across the interface between two fluids and wetting effects at a fluid-solid interface. It is an approach that bridges microscopic phenomena with the continuum macroscopic equations.

- Further, it can model the time evolution of systems.
The kinetic nature of the LBM introduces three important features that distinguish it from other numerical methods.

1. First, the convection operator (or streaming process) of the LBM in phase space (or velocity space) is linear.
2. Second, the incompressible Navier-Stokes (NS) equations can be obtained in the nearly incompressible limit of the LBM.
3. Third, the LBM utilizes a minimal set of velocities in phase space.
Lattice Boltzmann Equations

\[ f_i(x + e_i \Delta x, t + \Delta t) = f_i(x, t) + \Omega_i(f(x, t)), \quad (i = 0, 1, ..., M), \]

- \( f_i \) is the particle velocity distribution function along the \( i \)th direction

\[ \Omega_i = \Omega_i(f(x, t)) \]

- \( \Omega \) is the collision operator which represents the rate of change of \( f_i \) resulting from collision. \( \Delta t \) and \( \Delta x \) are time and space increments, respectively
Boundary Conditions in the LBM

- Wall boundary conditions
  - Originally taken from the LG method
  - E.g. a particle distribution function bounce-back scheme used at walls to obtain no-slip velocity conditions
- For a node near a boundary, some of its neighboring nodes lie outside the flow domain
  - Therefore the distribution functions at these no-slip nodes are not uniquely defined. The bounce-back scheme is a simple way to fix these unknown distributions on the wall node
Improved Boundary Conditions in LBM

- To improve the numerical accuracy of the LBM, other boundary treatments have been proposed:
  - Including velocity gradients in the equilibrium distribution function at the wall nodes
  - Hydrodynamic boundary conditions on no-slip walls by enforcing a pressure constraint
  - Slip velocity near wall nodes could be induced by the bounce-back scheme and proposed to use a counter slip velocity to cancel that effect
LBM

velocity

0.04
0.03
0.02
0.01
0.00
LBM Software

- **DL_MESO**
  - Multi-component/multi-phase/2D & 3D – Free

- **LBHydra**
  - capable of modeling laminar and turbulent flows, heat and mass transport, and multiple phase and multiple component fluids in complex and changing fluid flow 2D & 3D geometries – Free

- **Taxila LBM**
  - Multi-component/multi-phase/2D & 3D – Free

- **PowerFLOW**
  - CFD code which uses LBM, created and distributed by Exa Corp – Non-free
DPD

- DPD allows modeling of meso-phase structures and behaviour
- Soft beads are used to represent several atoms
- DPD preserves hydrodynamics
  - Advantageous over dynamic DFT or MC methods for evolving ordered thermodynamic equilibriums
Molecular Dynamics

- Uses classical Newtonian mechanics to model the system

- Needs a ‘force field’ for the atomic parameters

\[ E_{ff} = \sum_{\text{bonds}} E_{\text{bonds}} + \sum_{\text{angles}} E_{\text{angles}} + \sum_{\text{torsions}} E_{\text{torsions}} + \sum_{i}^{N} \sum_{j>i}^{N} (E_{\text{vdw}} + E_{\text{el}}) \]
DPD Intermolecular Terms

- MD force field is typically L-J type interactions
- DPD has 3 intermolecular forces
  - Conservative, $F^C$
  - Random, $F^R$
  - Dissipative, $F^D$

\[
F = F^C + F^R + F^D
\]
Conservative force, $F^C$

- Soft repulsive force
  - This is the repulsion between two beads

$$F^C_i = \begin{cases} 
\sum_{j \neq i} \left[ a_{ij} \left( 1 - \frac{r_{ij}}{r_c} \right) \right] & \text{if } r_{ij} < r_c \\
0 & \text{if } r_{ij} \geq r_c 
\end{cases}$$

![Graph showing the force $f^c(r)$ in kJ mol$^{-1}$ Å$^{-1}$ as a function of distance $r$ in Å]
Random force, $F^R$

- Random force
  - This force represents a random aspect to the motion
    
    $$F^R_i = \begin{cases} 
    \sum_{j}^{(i \neq j)} \left[ \sigma \xi_{ij} dt^{-0.5} \left( 1 - \frac{r_{ij}}{r_c} \right) \right] & r_{ij} < r_c \\
    0 & r_{ij} \geq r_c 
    \end{cases}$$

- Brownian motion
Dissipative force, $F^D$

- Dissipative force
  - This is a drag force on the beads

$$F^D_{ij} = \begin{cases} 
- \sum_{(i \neq j)} \left[ \gamma \left( 1 - \frac{r_{ij}}{r_c} \right)^2 \mathbf{v}_{ij} \cdot \hat{r}_{ij} \right] \\
0 & \text{if } r_{ij} < r_c \\
 & \text{if } r_{ij} \geq r_c
\end{cases}$$
Potential Shape

\[ F_i^R = \begin{cases} 
(i\neq j) \sum_j \left[ \sigma \xi_{ij} d t^{-0.5} \left( 1 - \frac{r_{ij}}{r_c} \right) \right] & r_{ij} < r_c \\
0 & r_{ij} \geq r_c 
\end{cases} \]

\[ F_i^C = \begin{cases} 
(i\neq j) \sum_j \left[ a_{ij} \left( 1 - \frac{r_{ij}}{r_c} \right) \right] & r_{ij} < r_c \\
0 & r_{ij} \geq r_c 
\end{cases} \]

\[ F_i^D = \begin{cases} 
(i\neq j) \sum_j \left[ \gamma \left( 1 - \frac{r_{ij}}{r_c} \right)^2 \mathbf{v}_{ij} \cdot \hat{r}_{ij} \right] & r_{ij} < r_c \\
0 & r_{ij} \geq r_c 
\end{cases} \]

□ Can be varied, so long as they are all the same
DPD Intramolecular Terms

- **Bonds**

1. Harmonic (Hookean/Fraenkel) bond:

   \[ U(r_{ij}) = \frac{k}{2} (r_{ij} - r_0)^2 \]

2. Finitely Extendible Non-linear Elastic (FENE) bond:

   \[
   U(r_{ij}) = \begin{cases} 
   -\frac{1}{2}k r_{max}^2 \ln \left[ 1 - \frac{(r_{ij} - r_0)^2}{r_{max}^2} \right] & r_{ij} < r_0 + r_{max} \\
   \infty & r_{ij} \geq r_0 + r_{max}
   \end{cases}
   \]

3. Marko-Siggia Worm-Like Chain (WLC):

   \[
   U(r_{ij}) = \begin{cases} 
   \frac{k_B T}{2A_p} \left[ \frac{1}{2} - \frac{1}{r_{ij} r_{max}} \right] \frac{1}{2} + \frac{1}{1 + \frac{r_{ij}}{r_{max}}} + \frac{r_{ij}^2}{2r_{max}^2} & r_{ij} < r_{max} \\
   \infty & r_{ij} \geq r_{max}
   \end{cases}
   \]

4. Morse potential bond:

   \[ U(r_{ij}) = D_e \left[ 1 - \exp \left( -\beta (r_{ij} - r_0) \right) \right] \]
DPD Intramolecular Terms

- Angles

1. Harmonic:

   \[ U(\theta_{ijk}) = \frac{\kappa}{2} (\theta_{ijk} - \theta_0)^2 \]

2. Harmonic cosine:

   \[ U(\theta_{ijk}) = \frac{\kappa}{2} (\cos \theta_{ijk} - \cos \theta_0)^2 \]
DPD Intramolecular Terms

1. Cosine torsion:

\[ U(\phi_{ijkl}) = A \left[ 1 + \cos(m\phi_{ijkl} - \delta) \right] \]

2. Harmonic:

\[ U(\phi_{ijkl}) = \frac{\kappa}{2} (\phi_{ijkl} - \phi_0)^2 \]

3. Harmonic cosine:

\[ \overline{U}(\phi_{ijkl}) = \frac{\kappa}{2} (\cos \phi_{ijkl} - \cos \phi_0)^2 \]
The self repulsion parameter is set to fix the compressibility of the system to the real system

\[
F_i^C = \begin{cases} 
(i \neq j) \sum_j \left[ a_{ij} \left( 1 - \frac{r_{ij}}{r_c} \right) \right] & r_{ij} < r_c \\
0 & r_{ij} \geq r_c 
\end{cases}
\]

System pressure is calculated from virial theorem

\[
p = \rho kT + \frac{1}{3V} \left\langle \sum_{j>i} \left( \mathbf{r}_i - \mathbf{r}_j \right) \cdot \mathbf{F}_i \right\rangle
\]
Self Repulsion Parameter

- Pressure calculated with different repulsion parameters

\[ p = \rho k T + \alpha a \rho^2 \]

\[ \alpha \approx 0.1 \text{ when } \rho > 2.5 \]

Self Repulsion Parameter

- The dimensionless compressibility is

\[ \kappa^{-1} = \frac{1}{nkT \kappa_T} = \frac{1}{kT} \left( \frac{\partial \rho}{\partial n} \right)_T \]

- Therefore

\[ a = \frac{kT}{2\alpha \rho} (\kappa^{-1} - 1) \]

\[ \kappa_{\text{exp}}^{-1} = 15.98 \quad a = 75 \frac{kT}{\rho} \]
Non-like molecules need differences in the repulsion parameters otherwise they would mix

\[ a_{ij} = a_{ii} + \Delta a \]

How do we define ‘not mixing’?
Phase Separation

- Flory-Huggins theory

\[ \frac{G}{kT} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \chi \phi_A \phi_B \]
Phase Separation

- Minimum free energy is found at

\[
\mu = \frac{\partial G}{\partial \phi_A} = 0 \quad \Rightarrow \quad \chi N_A = \frac{\ln \left( \frac{1 - \phi_A}{\phi_A} \right)}{1 - 2\phi_A}
\]

- Though there is a correction for simulated short chains

\[
\frac{\ln \left( \frac{1 - \phi_A}{\phi_A} \right)}{1 - 2\phi_A} \approx 1 + 3.9 N^{-0.51} (\chi N)_{\text{eff}}^\dagger
\]

\dagger \text{Horsch et al., J. Chem.Phys., 2004}
Repulsion Parameter

- Flory-Huggins $\chi$–parameter calculated for different polymer lengths

\[ \frac{\chi N kT}{\Delta \alpha} = 0.306 N \]

\[ \overset{\dagger}{\text{Groot and Warren, J. Chem. Phys., 1997}} \]
Repulsion Parameter

Therefore,

\[
\frac{\Delta a}{kT} = \frac{1 + 3.9N^{-0.51}}{0.306N} (\chi N)_{\text{eff}}
\]

The effective Flory-Huggins parameter has to be large enough for phase separation

\[
(\chi N)_{\text{ODT}} = 10.5 + N^{-1/3}^\dagger
\]

\dagger\text{Fredrickson and Helfand, J. Chem. Phys., 1987}
Comparison with MD

- DPD has a very soft potential
- This allows longer time steps, $\delta t^*$, as beads don’t receive an infinite force
Timescales

- Simulation timescales are given by:

\[ t = \sigma \left( \frac{m}{kT} \right)^{1/2} \]

<table>
<thead>
<tr>
<th></th>
<th>MD</th>
<th>DPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma ) / Å</td>
<td>3.016</td>
<td>6.46(^{+})</td>
</tr>
<tr>
<td>(t) / ps</td>
<td>(~0.81)</td>
<td>(~3.02)</td>
</tr>
<tr>
<td>(\delta t^*)</td>
<td>&lt;0.002</td>
<td>~0.04</td>
</tr>
<tr>
<td>(\delta t) / fs</td>
<td>&lt;2</td>
<td>~120</td>
</tr>
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\(^{+}\)Groot and Rabone, Biophys. J., 2001
DPD
Interesting Variations

- Vapour-Liquid coexistence
  - Typical DPD interactions don’t allow this

- Particle clustering
  - Typical DPD interactions have no attractive potential

- On spheres
  - DPD chains attached on spheres
\[ F_{ij}^C = a_{ij} \left( 1 - \frac{r_{ij}}{r_c} \right) + b_{ij} (\rho_i + \rho_j) \left( 1 - \frac{r_{ij}}{r_d} \right) \]
Nano-clustering

Surfactant Nano-Patterning

Singh et al., PRL, 2007
DPD Software

- Gromacs-DPD
  - Free
- DPDmacs
  - Free
- HOOMD-blue
  - Free

Variations on Gromacs package and can use gromacs tools

- DL_MESO
  - Free
- LAMMPS
  - Free (simulates everything!!!)
- ESPResSo
  - Free