Lecture 8

Mesoscale Methods for Soft Materials and Complex Fluids
Dissipative Particle Dynamics

Reading:
Wiki pages & related articles
Frenkel and Smit (pp 465-473)
So far we’ve learned about MD methods, MC methods, and Brownian dynamics methods for simulating soft materials.

**With all these methods**, we’ve seen how atomistic force fields are used to model different types of systems with as much detail as needed. And, we’ve seen how “coarse-grained” or mesoscopic models are used when:
- the details of the chemistry are unimportant, or
- the system or phenomenon or process we want to study requires more atoms than we can handle with our computers.

There are many problems in soft matter where atomistic models are simply out of the question due to the slowness of computers, or to the size of the problem, or where the phenomena of interest occurs on the mesoscale.
Mesoscale Models and Methods

- Molecular dynamics simulations using atomistic force fields typically reach time scales of nanoseconds.

- Many processes occur over longer times scales; thus alternative methods are required.

- For solute-solvent system, we saw how Brownian dynamics can be used to include solvent implicitly, allowing us to put our cpu effort into modeling the solute.
  - Brownian dynamics is an example of a “mesoscale” method, although individual solute particles may still be modeled atomistically.
Dissipative particle dynamics is a method used for simulating fluid phenomena and processes on the mesoscale.

The mesoscale refers to scales larger than individual molecules or small groups of molecules, but smaller than “macroscopic” scales on which structure can no longer be discerned.

Complex fluids and soft materials are rich with structure and dynamics that occur on mesoscopic length scales (tens of nanometers to tens of microns) and mesoscopic time scales (hundreds of nanoseconds and up).

- Surfactants, emulsions, polymer melts and blends, block copolymers, colloidal suspensions, lipid bilayers, etc.
DPD: A Mesoscale Method


  - **Note:** Example 27 makes incorrect claims regarding BD.
In DPD, the fast motion of the atoms or molecules is integrated out, leaving as the fundamental “unit” particles representing a small droplet of fluid, which interact with each other via an appropriate force field.
The total force on each particle is due to a combination of three types of forces:

- conservative interactions with other particles
- random forces accounting for thermal motion
- dissipative forces accounting for frictional drag force between fluid elements (particles)

The trajectory of the system through phase space is calculated by integrating Newton’s laws of motion in the usual way.
The model used in DPD is usually developed in terms of mass, length and time units that are all set to unity.

- Similar to reduced units for Lennard-Jones potential
- With this scaling, a single simulation can often be mapped onto several different systems simultaneously.

The force acting on any particle is equal to:

$$ \mathbf{f}_i = \sum_{j=1, j\neq i}^{N} \left( \mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R \right) $$

The sum is performed over all other particles $j$ that are within a certain cutoff radius $r_c$ of particle $i$. It’s common to use this cutoff radius as the unit of length in DPD.
DPD: The Forces

The conservative force $F_{ij}^C$ is modeled as a soft repulsion that acts along the line connecting $i$ and $j$:

$$F_{ij}^C = \begin{cases} a_{ij} (1 - r_{ij}) \hat{r}_{ij} & r_{ij} < 1 \\ 0 & r_{ij} \geq 1 \end{cases}$$

This force is “soft” because it has no hard-core repulsion between particles. Thus in DPD, particles can actually move through each other.

This soft force will allow us to take much larger steps in time, which will allow us to simulate systems on much longer time scales than MD.
DPD: The Forces

- The **dissipative force** or **drag force** $F_{ij}^D$ is proportional to the relative velocity of the two particles and acts so as to reduce their relative momentum:

$$F_{ij}^D = \begin{cases} -\gamma \omega^D(r_{ij})(\hat{r}_{ij} \cdot \mathbf{v}_{ij})\hat{r}_{ij} & r_{ij} < 1 \\ 0 & r_{ij} \geq 1 \end{cases}$$

- Here $r_{ij}$ is a unit vector in the direction of $\mathbf{r}_{ij}$, $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ is the relative velocity, $\gamma$ is the **friction coefficient**, and $\omega^D(r_{ij})$ is a **weight function** that depends on the distance $r_{ij}$ and disappears for inter-particle distances greater than $r_c$ (unity).
DPD: The Forces

- The **random force** $\mathbf{F}_{ij}^R$ between any pair of particles acts along the line connecting the pair:

$$F_{ij}^R = \sigma \omega^R (r_{ij}) \theta_{ij} \hat{r}_{ij}$$

where $r_{ij} < 1$.

- Here $\omega^R(r_{ij})$ is a **distance-dependent weight function** similar to that for the dissipative force.

- The quantity $\theta_{ij}$ is a function that ensures the random force between each pair of particles **averages to zero** over time and is **independent of the force** between every other pair of particles.
DPD: The Forces

- The random force is often expressed in terms of the *timestep* in the integration scheme:

\[ F_{ij}^R = \frac{\sigma \omega_R(r_{ij}) \xi_{ij} \hat{r}_{ij}}{\sqrt{\delta t}} \]

- Here \( \xi_{ij} \) is a random number with zero mean and unit variance, chosen independently for each pair of particles and at each time step in the integration.

- Both the random force and the dissipative force conserve linear and angular momentum because the forces act pairwise.
  - Contrast that with BD as presented in class.
DPD: The Weight Functions

There are two unknown functions $\omega^D(r_{ij})$ and $\omega^R(r_{ij})$ and two unknown constants $\gamma$ and $\sigma$ (friction coefficient and amplitude of random force).

- Only one of the two weight functions can be chosen arbitrarily.

\[
\omega^D(r_{ij}) = \left| \omega^R(r_{ij}) \right|^2 = \begin{cases} 
(1 - r_{ij})^2 & r < 1 \\
0 & r \geq 1 
\end{cases}
\]

Form is usually chosen so that the random force has the same form as the conservative force.

- The two constants $\sigma$ and $\gamma$ are related by the temperature:

\[
\sigma^2 = 2\gamma k_B T
\]
Force expressions in DPD

\[ F_{ij}^C = a_{ij} (1 - r_{ij}) \hat{r}_{ij} \]

\[ F_{ij}^D = -\frac{\sigma^2}{2k_B T} (1 - r_{ij})^2 (\hat{r}_{ij} \cdot \mathbf{v}_{ij}) \hat{r}_{ij} \]

\[ F_{ij}^R = \sigma \frac{\varsigma_{ij}}{\sqrt{\delta t}} (1 - r_{ij}) \hat{r}_{ij} \]

Set values of parameters \( \sigma, \delta t, \) and either \( a_{ij} \) or \( T \), using other as control variable.

\[ F_{ij}^C = F_{ij}^D = F_{ij}^R = 0 \quad \text{if} \quad r_{ij} \geq 1 \]

\[ r_{ij} < 1 \]
DPD: Integrating the equations

The equations of motion are integrated using a modified velocity Verlet algorithm with a predictor-corrector step.

- The modification is required because the force depends on the velocity.
Solving the DPD equations of motion

Modified velocity-Verlet

\[ \mathbf{r}_i(t + \delta t) = \mathbf{r}_i(t) + \delta t \mathbf{v}_i(t) + \frac{1}{2} (\delta t)^2 \mathbf{f}_i(t) \]

\[ \tilde{\mathbf{v}}_i(t + \delta t) = \mathbf{v}_i(t) + \lambda \delta t \mathbf{f}_i(t) \quad \text{--- Predicted velocity} \]

\[ \mathbf{f}_i(t + \delta t) = \mathbf{f}_i(\mathbf{r}(t + \delta t), \tilde{\mathbf{v}}(t + \delta t)) \]

\[ \mathbf{v}_i(t + \delta t) = \mathbf{v}_i(t) + \frac{1}{2} \delta t \left( \mathbf{f}_i(t) + \mathbf{f}_i(t + \delta t) \right) \quad \text{--- Corrected velocity} \]

\[ \lambda \in \left( \frac{1}{2}, 0.65 \right) \text{ chosen for stability} \]

\[ m = 1 \]

\[ \mathbf{f}_i = \sum_{j \neq i} \left( \mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R \right) \]
DPD: Integrating the equations

- The unit of time used in DPD simulations is

\[
[\tau] = r_c \sqrt{m / k_B T}
\]

- If the units of mass, length, and energy \([k_B T]\) are set to one, then the unit of time is also one.
DPD: Setting parameters

- We still need to assign values to the noise amplitude $\sigma$, the time step for integration $\delta t$, and the repulsion parameter $a_{ij}$.

- The first two are chosen for stability of the integration, and are thus related to the choice of integration method.
  - Groot and Warren found that $3 < \sigma < 8$ worked well for modified velocity Verlet. For larger values, the integration became unstable.
  - They also found that $0.04 < \delta t < 0.06$ works well for modified velocity Verlet. Any larger and $T$ increases artificially during the simulation.
The parameter $a_{ij}$ is the key parameter controlling the thermodynamics of the system.

For a single component fluid, $a_{ij} = a$. To choose its value, the DPD model can be related to bulk thermodynamic properties like compressibility.

- E.g. to model water at room temperature, $a$ is related to the density $\rho$ by: $a = 75k_B T/\rho$ since for water $1/k_B T \rho \kappa_T \approx 16$.

$$\kappa^{-1} \approx 1 + 0.2 a \rho / k_B T$$

- Note that density has different meaning than in MD, since no excluded volume. *Relate compressibilities to match systems in MD and DPD.*

For a binary mixture, $a_{ij} = a + \Delta a$,

where $\Delta a = a_{AB} - (a_{AA} + a_{BB})/2 > 0$, and $a = (a_{AA} + a_{BB})/2$.

Thus $\Delta a = a_{AB}$
The theory of phase separation is based on the Helmholtz free energy of mixing of an incompressible binary mixture:

\[
\frac{f(\phi)}{k_B T} = \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi)
\]

where

\[
\chi = \frac{z}{k_B T} \left( \varepsilon_{AB} - \frac{1}{2} (\varepsilon_{AA} + \varepsilon_{BB}) \right)
\]

The shape of \( f \) depends on temperature, and has distinctly different structure above and below a critical temperature \( T_c \), or equivalently, a critical chi, \( \chi_c \).
Free Energy

\[ f(\phi) \]

\[ \phi_1, \phi_2 \text{ defined by: } \frac{\partial f}{\partial \phi} = 0 \]

\[ \phi_{s1}, \phi_{s2} \text{ defined by: } \frac{\partial^2 f}{\partial \phi^2} = 0 \]

For every \( T < T_c \), there exists unique values of \( \phi_1, \phi_2, \phi_{s1}, \text{ and } \phi_{s2} \).
For each $T < T_c$, plot $\phi_1$, $\phi_2$, $\phi_{s1}$, and $\phi_{s2}$. This defines boundaries between (i) a miscible and immiscible region and (ii) a metastable and unstable immiscible region.
DPD may be used to simulate polymers as well as non-polymeric fluids.
To simulate a polymer, individual particles are connected to each other with an *additional conservative force* \(-kr_{ij}\) that comes from a Hookean spring potential.

For polymers that involve particles of different types, the repulsion \(a_{AB}\) between unlike particles is chosen larger than between like particles \((a_{AA} \text{ and } a_{BB})\), as in a binary fluid.
Free Energy of Polymer Blends

- Helmholtz free energy of mixing of an incompressible binary mixture:
  \[ \frac{f(\phi)}{k_B T} = \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \]

- Helmholtz free energy of mixing of an incompressible polymer blend from the Flory-Huggins lattice theory:
  \[ \frac{f(\phi)}{k_B T} = \frac{\phi}{N_A} \ln \phi + \frac{(1 - \phi)}{N_B} \ln(1 - \phi) + \chi \phi(1 - \phi) \]

- Entropic part of \( f \) for polymers is smaller by a factor of inverse chain length. Thus for long chains, even a slight attractive interaction between like polymers will induce phase separation since there is so little gain from entropy of mixing (enthalpy dominates).
The Flory-Huggins model has a critical point at

$$\phi_c = \frac{\sqrt{N_B}}{\left(\sqrt{N_A} + \sqrt{N_B}\right)}$$

$$\chi_c = \frac{\left(\sqrt{N_A} + \sqrt{N_B}\right)^2}{2N_A N_B}$$

Thus a blend will be miscible for $\chi < \chi_c$ and immiscible for $\chi > \chi_c$ at the critical concentration.

For symmetric blends, where $N_A = N_B = N$, $\chi_c = 2/N$.

Weak segregation limit (WSL): $\chi N \sim 2$

Strong segregation limit (SSL): $\chi N \gg 2$
Region of immiscibility expands for larger $N$

If we could sit at a given $T$ or $\chi$ and $\phi$ and polymerize monomers into chains, the phase boundary would move past us so that eventually we would sit in the immiscible region.
Mapping $\chi$ to DPD repulsion parameter

- The $\chi$-parameter is linearly proportional to $\Delta a$.
- For each density, there is a different slope.
- E.g. you can set density and $\Delta a$, which tells you $\chi$, and where you are on phase diagram by multiplying $\chi$ by $N$. 

Example: Block Copolymers

- **Diblock**
- **Triblock**

**Ordered** vs **Disordered**

Thermally Reversible

- ~50 nm
Mesoscale simulations of ordering in block copolymer melts

\[ \chi_N \]

- spheres
- cylinders (cyl)
- lamellae
- gyroid

S, C, G, L, G', C', S'
DPD Advantages

- Mesoscale method
- “Good” for complex fluid problems where microstructure development is of interest.
- Momentum conserving and thus exhibits correct hydrodynamics like MD (unlike BD).
- MD-like in implementation
  - Easy to modify MD code for DPD
  - Same ease of parallelization as MD
- Able to achieve long times.
DPD Issues

- Ratio of mass transport to momentum transport unusual, so dynamics “funny”.
  - Schmidt number roughly unity (measure of the momentum diffusion compared to the mass diffusion). Values of unity correspond to gas-like phases where the particles can move freely. For dense phases such as liquids, the Schmidt number is usually several orders of magnitude higher due to the relatively slow mass diffusion resulting from the restricted mobility of the particles.
  - This has been addressed in recent papers.
- Issues in mapping to specific systems.
- Advantages over MD and other methods not clear in all cases.

*Used widely in top chemical companies for insight.*
DPD: Available from Accelrys Cerius2

Oil, water, detergent

http://www.accelrys.com/mstudio/dpd.html
Studying models of real systems with DPD

- Surface: 3 to 10 nm dia gold nanoparticle
- Surface: Sphere of diameter 10σ

Chemical structures:
- HOOC-(CH₂)$_2$-SH
- CH₃-(CH₂)$_7$-SH
Equal length polymers on surfaces - comparison of results from DPD & atomistic MD simulations

**Spherical Surfaces**
- Sphere diameter = 10σ
- Sphere diameter = 7 nm

**Flat Surface**
- Surface: 35σ x 35σ
- Surface: 12.5 nm x 12.5 nm

DPD

Atomistic MD
Unequal length polymers on surfaces - comparison of results from DPD & atomistic MD simulations

**Spherical Surfaces**
- **Sphere diameter = 10σ**

**DPD**
- HOOC-(CH$_2$)$_5$-SH
- CH$_3$-(CH$_2$)$_8$-SH

**Atomistic MD**
- HOOC-(CH$_2$)$_5$-SH
- CH$_3$-(CH$_2$)$_8$-SH

**Flat Surface**
- **Surface: 35σ x 35σ**
  - Yellow:Red = 1:4

**DPD**
- CH$_3$-(CH$_2$)$_8$-SH

**Atomistic MD**
- HOOC-(CH$_2$)$_2$-SH
  - Surface: 12.5 nm x 12.5 nm
    - Yellow:Red = 1:4