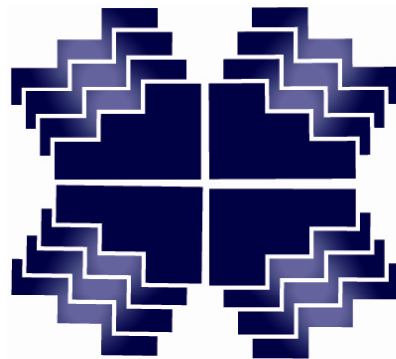


Multiscale Materials Modeling

Lecture 03

Capabilities of Mesoscale Modeling



STAIR

Sustainable Technology through
Advanced Interdisciplinary Research

Capabilities of Mesoscale Modeling

- I. What is Mesoscale Modeling?
 - I.A. Degrees of Coarse Graining
 - I.B. Mesoscale Modeling
- II. Techniques, Challenges and Applications
 - II.A. Potential Generation
 - II.B. Brownian Dynamics
 - II.C. Random Walks
 - II.D. Polymer Models
- III. Strengths and Weaknesses
 - III.A. Theoretical Limitations
 - III.B. Computational Limitations
- IV. References

What is coarse-graining?

Coarse-graining is the reduction in the degrees of freedom of a system. The purpose of coarse-graining is to simplify the system so that a theoretical or computational solution is more tractable. The goal of coarse-graining is to eliminate/replace/consolidate many degrees of freedom with just enough to capture the essential physics of interest.

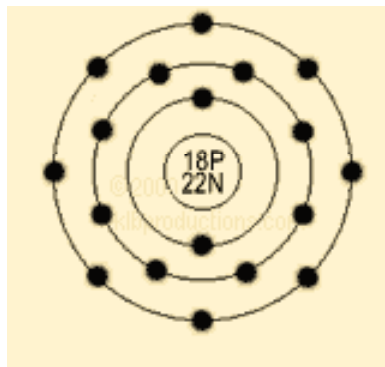
Coarse-graining requires knowledge and creativity. One needs knowledge to understand which degrees of freedom are essential for observing certain physical phenomena. One needs creativity in imagining an approximate model that can replace the lost degrees of freedom.

Examples of coarse-graining

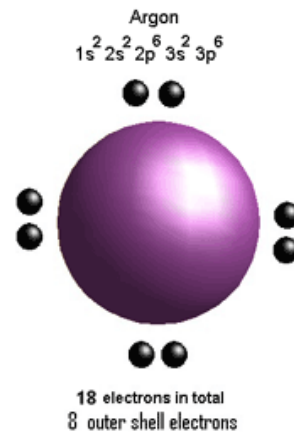


the argon atom

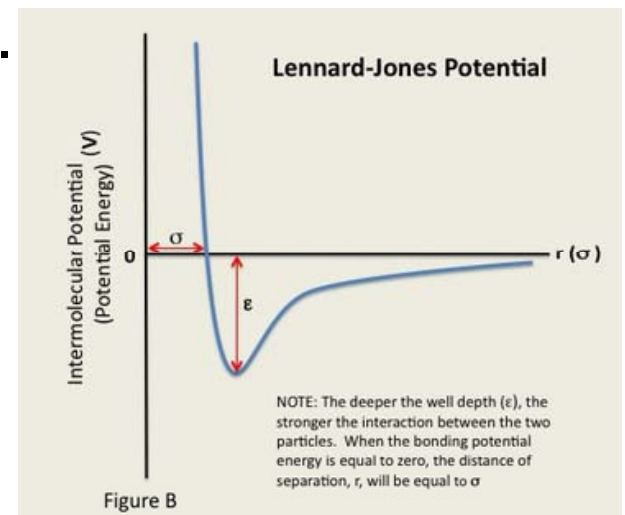
Quantum mechanics treats the argon atom as being composed of a nucleus with a positive charge and electrons each with a negative charge. Classical molecular simulation treats the argon atom as a neutral sphere, with no internal degrees of freedom.



Quantum models of argon treat it as a nucleus and 18 electrons.



Pseudopotentials can empirically represent non-reactive core electrons.

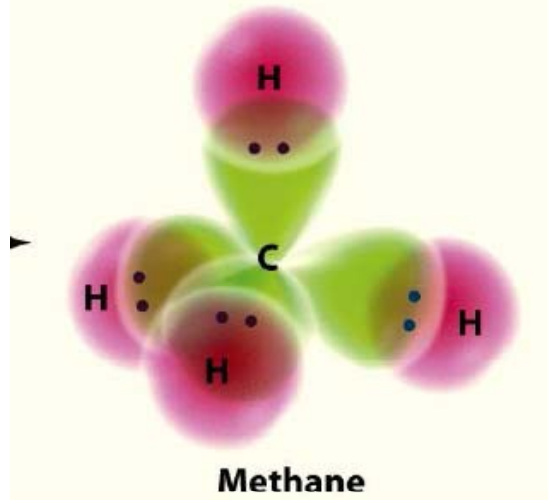


Classical simulations model treat Argon as a Lennard-Jones sphere.

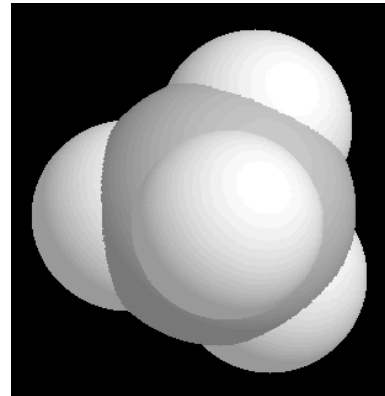
Examples of coarse-graining

the methane molecule

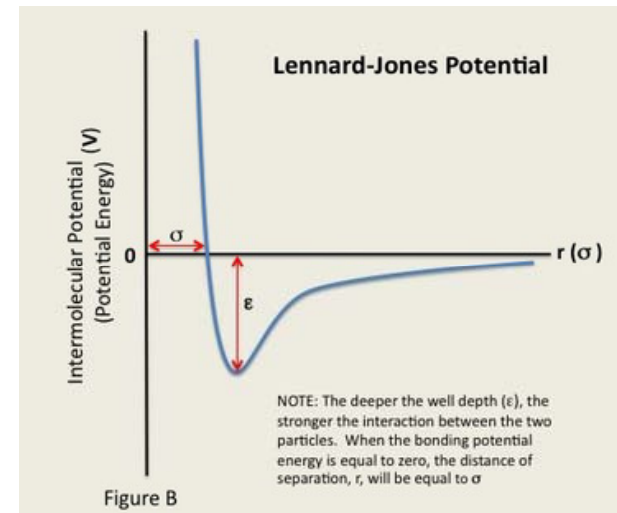
Simulations treat methane as one carbon atom bonded to four hydrogen atoms. Many classical molecular simulations treat the methane molecule as a neutral sphere, with no internal degrees of freedom (a pseudo-atom).



Quantum models of methane treat it as five nuclei and eight valence electrons.



All-atom models of methane treat it as five Lennard-Jones particles bound together by springs.



United-atom models of methane treat it as a Lennard-Jones fluid.

Examples of coarse-graining

A polymer chain

Linear polyethylene can be modeled as

- a chain of CH_2 units in which each C & H atom is distinct
- a chain of CH_2 pseudo-atoms
- bead/spring & bead rod models, where groups of CH_2 units are collected into beads
- entanglement networks, where all that is important to the ultimate behavior of the system is creation, destruction and movement of entanglements between chains

Each of these models is a further degree of coarse-graining.

What is Mesoscale Modeling?

In today's parlance, mesoscale modeling has come to mean a model in which the coarse-graining employed results is coarser than the molecular level but is finer than the continuum level.

A rule of thumb:

quantum mechanics – electron distributions

molecular simulation – atom and molecule distributions

mesoscale simulation – coarse-grained “beads” or “super-atoms”

macroscopic simulation – continuum models

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Potential Generation

In quantum mechanical calculations, we have a well established set of physical rules and a set of well-tested approximations to describe how electrons and nuclei interact with each other.

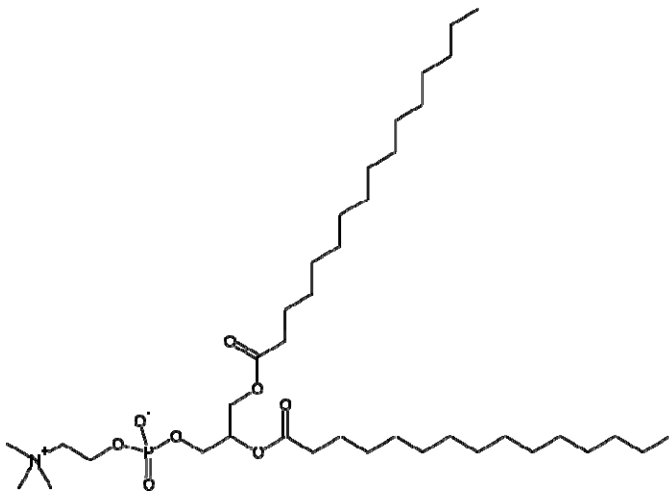
In classical simulation, we are at a state today where there are transferrable force fields (aka interaction potentials) that can be pulled from the literature to describe how atoms interact with each other.

However, if you arbitrary group a set of atoms together to make a new mesoscale super-atom, you don't have an interaction potential that states how these super-atoms interact with each other. You must generate the potential.

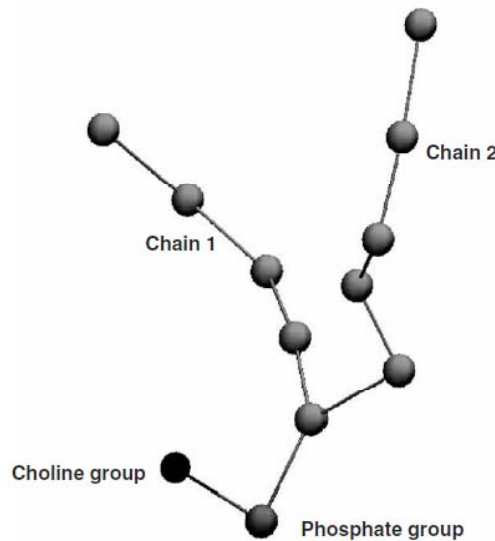
In a subsequent lecture on multiscale modeling, we will explore potential generation for mesoscale models in greater detail. Here we simply make the point that the potentials don't exist and must be generated before any mesoscale simulations can be performed.

Potential Generation

Some mesoscale models (Gromacs) simply use a few “types of super-atoms”, such as polar, non-polar, charged, etc.



atomistic model of surfactant,
DPPC
(dipalmitoylphosphatidylcholine)



Mesoscale model of DPPC
(Adhangale et al. Mol. Phys. 2006)

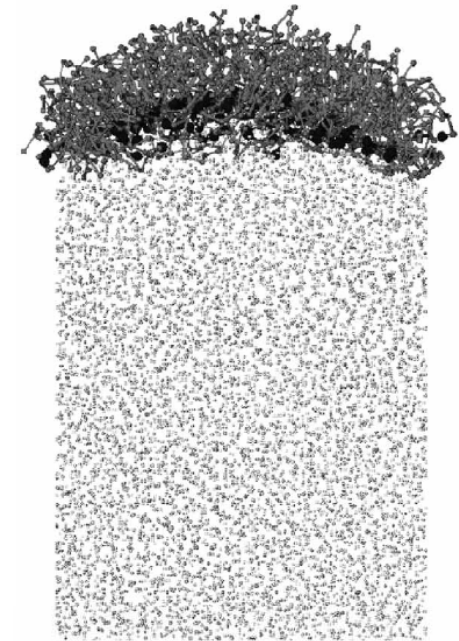


Figure 3. Snapshot of the coarse-grained DPPC monolayer at the air/water interface.

This mesoscale model retained sufficient information to describe surface tension at the air/water interface.

Brownian Dynamics

Frequently the dynamics of mesoscale models are evaluated using Brownian Dynamics simulations.

The approach is characterized by the use of simplified models while accounting for omitted degrees of freedom by the use of stochastic differential equations.

In Brownian Dynamics simulations,

$$\dot{X}(t) = -\nabla U(X)/\zeta + \sqrt{2D}R(t)$$

where t is time,

X is a particle position

\dot{X} is the particle velocity

U is the particle-particle interaction potential

D is an effective particle diffusivity

R is a random number generated from a Gaussian distribution

ζ is a measure of the inertial mass

Brownian Dynamics

Brownian Dynamics simulations are used to model many processes on many levels.

- particles in solution
(Heyes and Melrose, J. Non-Newtonian Fluid Mechanics, 2002)
- DNA
(Hur, Shaqfeh, Larson, J. Rheology, 2000)
- bacteria
(Frymier, Ford, Cummings, Chemical Engineering Science, 1993)
- animal swarms
(Ebeling and Schimansky-Geier, European Physical Journal, 2008)

Random Walks

Many natural processes obey Random Walk Theory, which describes the evolution of a process based on statistical laws rather than on physical forces.

Random walks have been used in many fields: ecology, economics, psychology, computer science, physics, chemistry, and biology. Random walks explain the observed behaviors of processes in these fields, and thus serve as a fundamental model for the recorded stochastic activity.

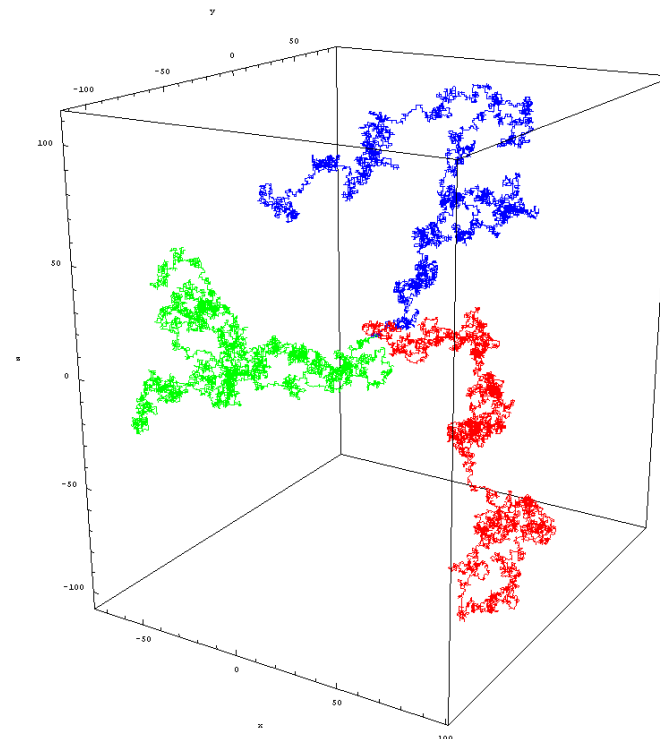
In materials modeling, particle trajectories can be modeled as independent particles (neglecting all particle-particle interactions and thus simplifying the problem tremendously) in an effective field. Some parameter describing the effective field is optimized to capture all of the interactions present in a more refined model.

Random Walks

In a random walk process, you select a velocity from the Maxwell-Boltzmann distribution and a random direction. You move in that direction at that velocity for a time step, Δt . Then you repeat the process, generating trajectories of the particle.



Random Walk trajectories in 2-D.



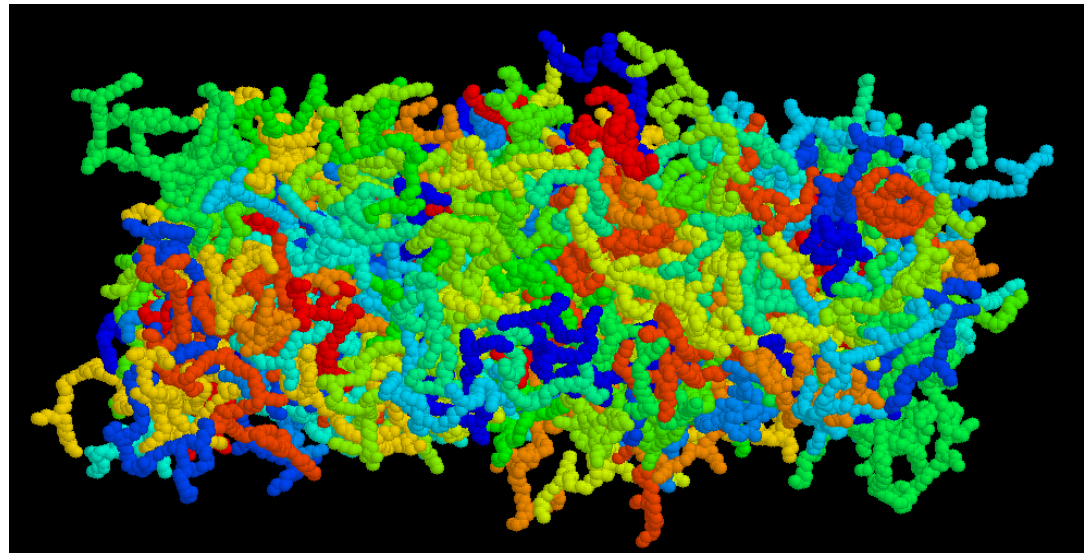
Random Walk trajectories in 3-D.

From analysis of these trajectories dynamic properties can be obtained.

Polymer Mesoscale Models

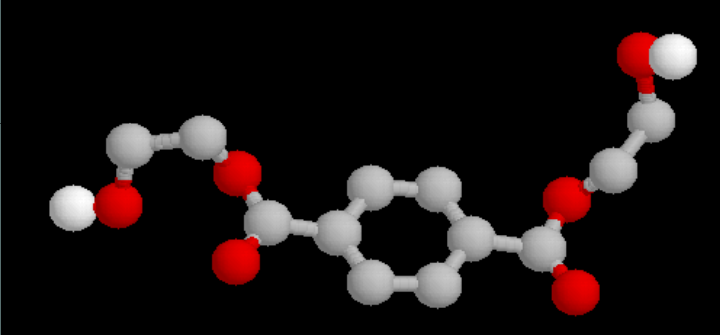
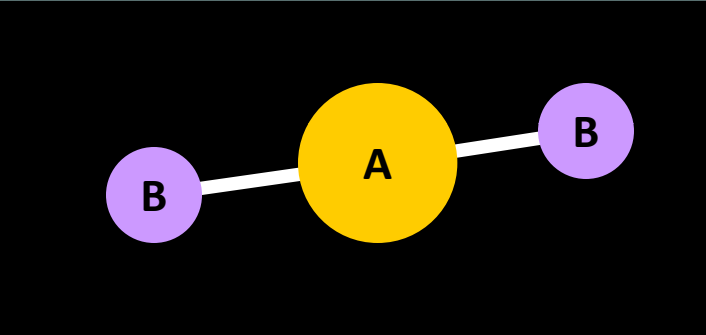
Atomistic Simulation of Polymers gives finely resolved description of chains but can't be used to describe long chains. Why?

The bond vibration between carbons requires time steps of about a femtosecond (10^{-15} s), but the relaxation time of polymers can be on the order of seconds. Therefore we would need 10^{15} (a quadrillion) MD time steps to solve this problem, which is not currently feasible. Some MD simulations of polymers have run for 100 ns, requiring 10^8 (a hundred million) MD time steps. We are still seven orders of magnitude (ten million times) too slow.



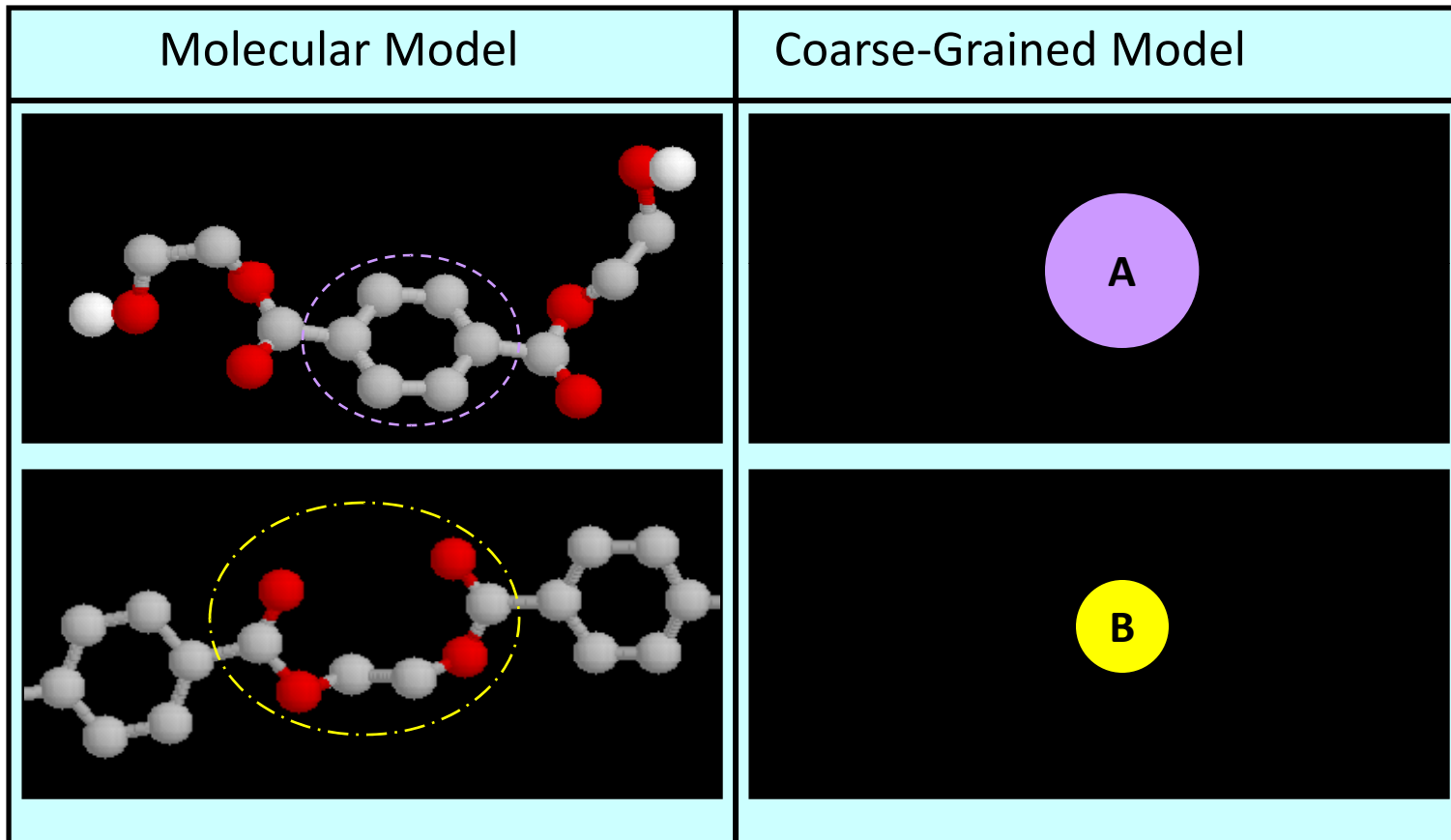
Polymer Mesoscale Models

What are the alternatives? Mesoscale models. Mesoscale models come in a huge variety of degrees of coarse-graining. The least coarse-grained is the introduction of super atoms.

Molecular Model	Coarse-Grained Model
	
<ul style="list-style-type: none">• atomistic detail• structure is known• interaction potentials known • many degrees of freedom• computationally expensive• limited to short chains	<ul style="list-style-type: none">• particles are molecular groups• grouping is based on intuition• interaction potentials unknown • fewer degrees of freedom• computationally modest• works for long chains

Polymer Mesoscale Models

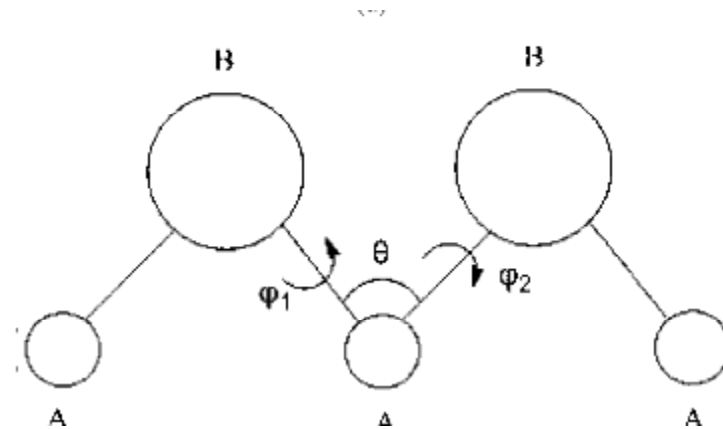
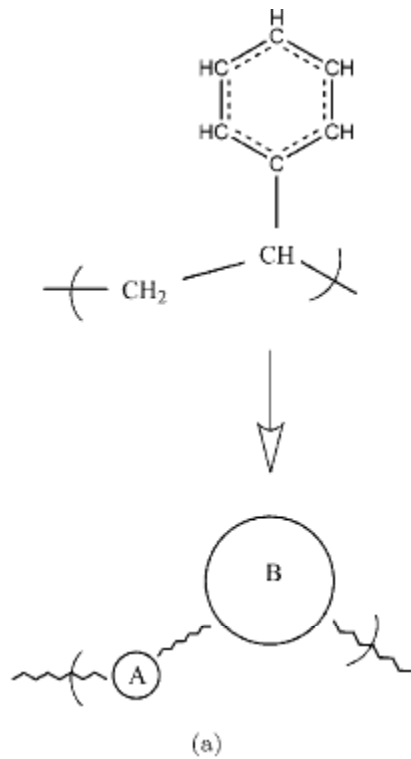
Example: PET



Wang, Q., Keffer, D.J., Petrovan, S., Thomas, J.B., in progress, 2009.

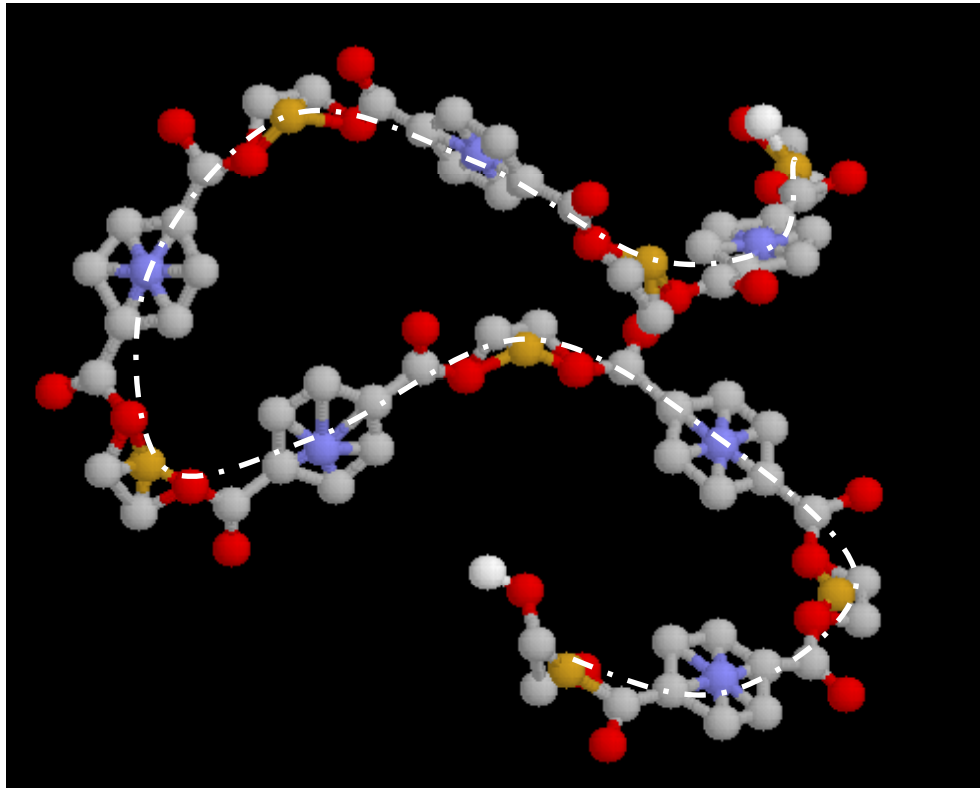
Polymer Mesoscale Models

Example: Polystyrene

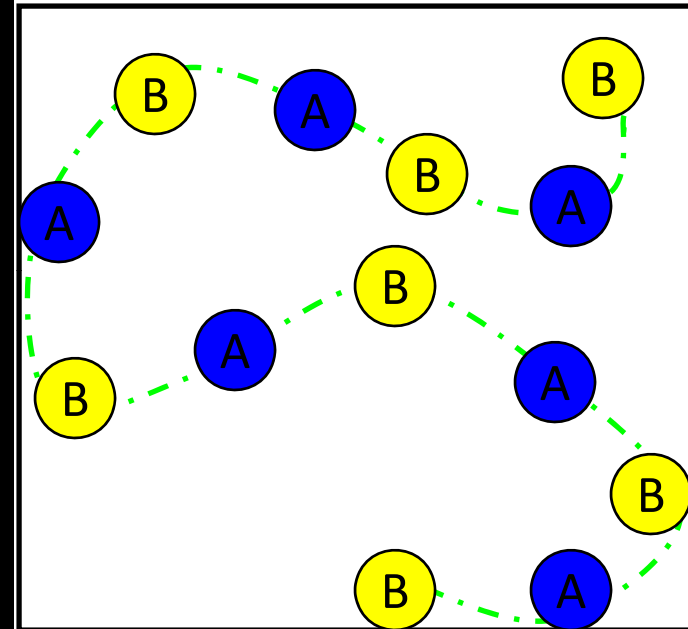


Harmandaris, Adhikari, van der Vegt, Kremer, *Macromolecules*, 2006.

Polymer Mesoscale Models



Coarse grained model on top of atomistic model for hexamer (DP=6)



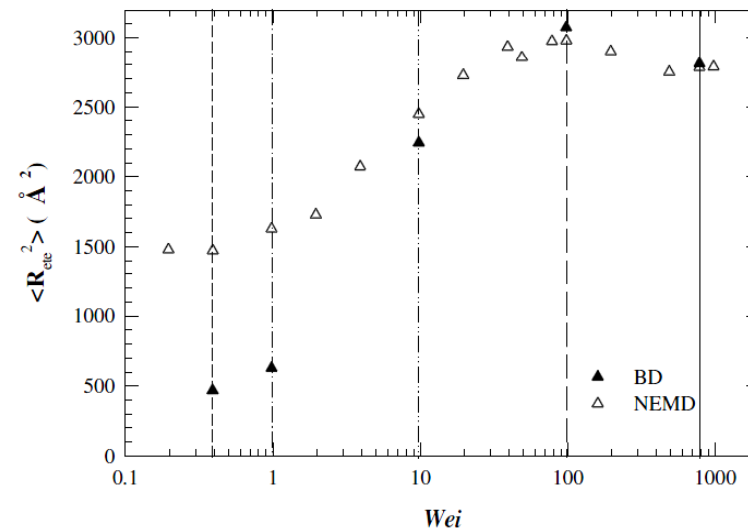
Coarse grained chain for hexamer, total interaction centers is 13 for each molecule (atomistic is 90).

Wang, Q., Keffer, D.J., Petrovan, S., Thomas, J.B., in progress, 2009.

Polymer Mesoscale Models

There are numerous more coarse-grained approaches to polymer modeling, including bead-rod and bead-spring models. The same concepts apply (grouping together more and more units) but the physics used to describe the polymer dynamics differs.

Example: polyethylene



Comparison of flow-induced extension based on molecular simulation of polymer melt and Brownian dynamics simulation of bead-rod model in dilute solution.

Kim, J.M., Edwards, B.J., Keffer, D.J., Khomami, B., under review, 2009.

Strengths and Weaknesses



Advantages:

Coarse-grained models provide the opportunity to capture behavior on large length and time scales. By integrating coarse-grained models with more finely resolved models, one can develop high-fidelity models with atomic details applied to macroscopic time and length scales.

Disadvantages:

- Coarse-grained models gain an advantage by dropping some physics. If you remove important physics, your model will not give accurate results.
- Coarse-grained models require parameterization from more finely resolved models.
- Multiscale Modeling algorithms are still an active research area. There remains great uncertainty in many aspects of the implementation and application.

References



There are numerous textbooks available on
Random Walk Theory
and
Brownian Dynamics

If you find one that you think is particularly insightful, please share it with me and I will list it here.