

CHEM 4010

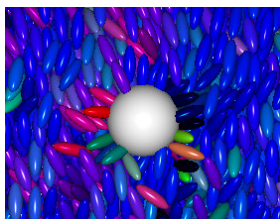
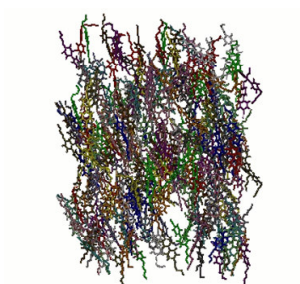
Computer simulation of polymeric systems: An overview

Francisco R. Hung

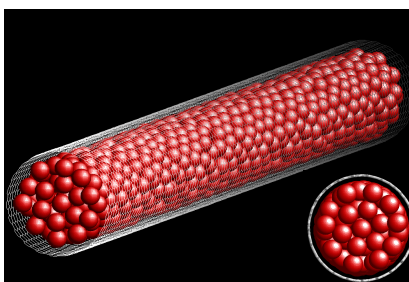
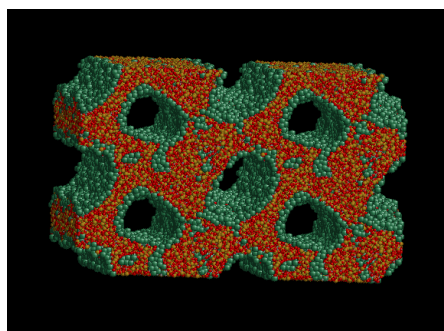
**Cain Department of Chemical Engineering
Louisiana State University**

<http://www.che.lsu.edu/faculty/hung/>

Disclaimer



Modeling polymeric systems is *not*
my main area of expertise (however I
am trying to get into that area)



Outline

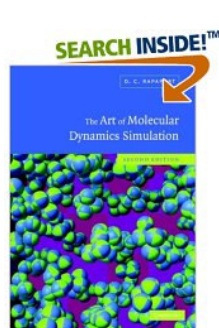
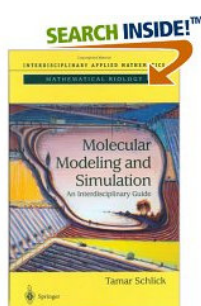
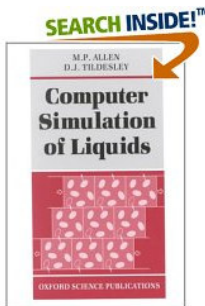
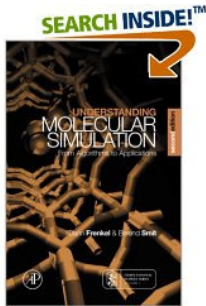
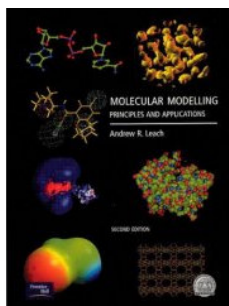
- UPDATE!
- Today's material adapted from:
 - Keith Gubbins' lecture notes on Advanced Chemical Engineering Thermodynamics, North Carolina State University
 - David Kofke's lectures on Molecular Simulation, SUNY Buffalo
<http://www.eng.buffalo.edu/~kofke/ce530/index.html>
 - Sharon Glotzer's lectures on Computational Nanoscience of Soft Materials, University of Michigan
 - Doros' paper; de Pablo et al paper

3

Simulation Methods - General Features

References:

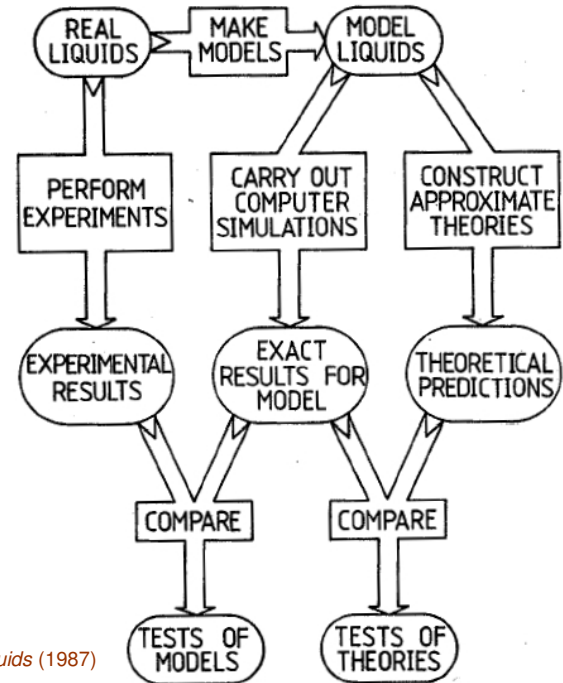
- A. R. Leach, *Molecular Modelling*, 2nd ed., Ch. 6, 8, Prentice Hall (2001)
- D. Frenkel and B. Smit, *Understanding Molecular Simulation*, 2nd ed., Academic Press (2002)
- M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Clarendon Press, (1987)
- T. Schlick, *Molecular Modeling and Simulation*, Springer-Verlag, (2002)
- D. C. Rapaport, *The Art of Molecular Dynamics Simulation*, 2nd ed., Cambridge University Press (2004)



Simulation Methods - General Features

- Role of computer simulations

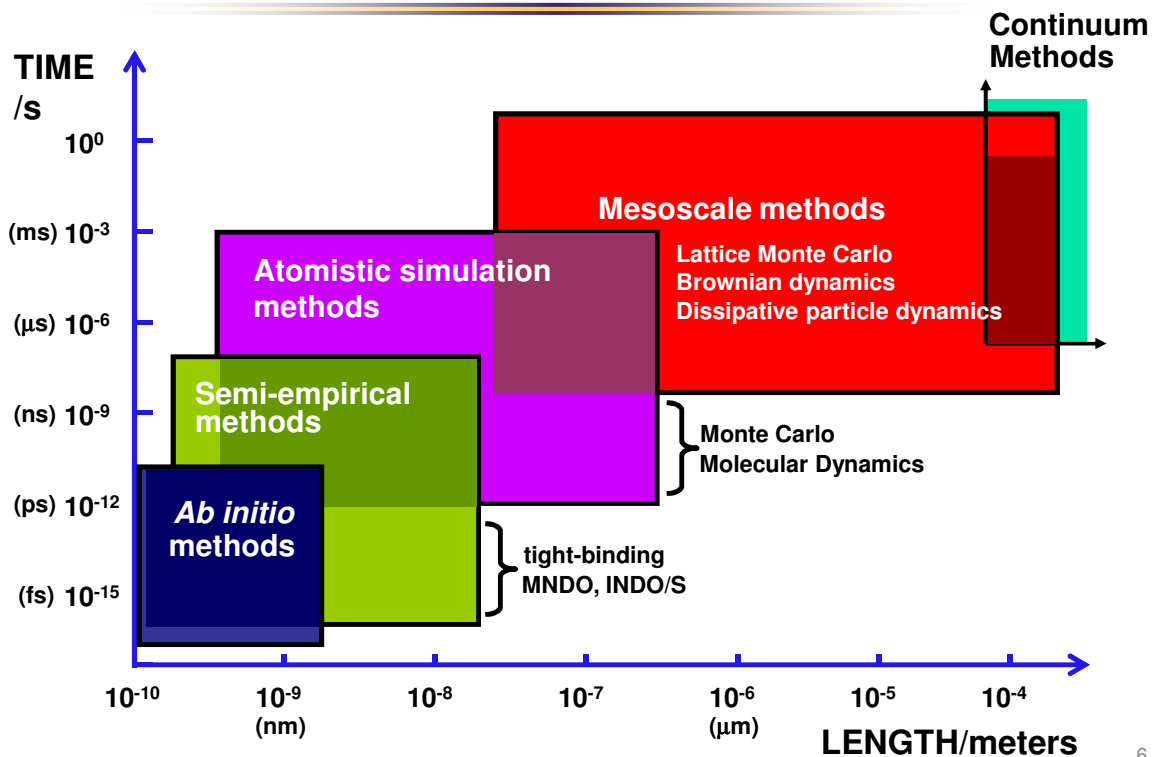
- Assist in interpretation of experimental results
 - e.g., capture subtle details of molecular motion, structure, other phenomena difficult / expensive to probe with experiments
- Predict / explore effect of variables
 - e.g., explore conditions for which experiments would be impossible / expensive
- Give insights / complement experimental work; influence experimental efforts
- Test validity of theories (which are computationally less expensive than simulations)



From Allen and Tildesley, *Computer Simulation of Liquids* (1987)

5

Simulation methods



6

Molecular Dynamics: Introduction

- Molecular Dynamics (MD) simulates the “real” dynamics of a collection of atoms, molecules, particles, or other extended objects. MD is one of the most commonly used methods for materials simulations.
- Positions and velocities of each molecule are followed in time by solving Newton’s equations of motion:

$$\mathbf{F}_i = m_i \mathbf{a}_i = m_i \frac{d^2 \mathbf{r}_i}{dt^2} = - \frac{\partial U}{\partial \mathbf{r}_i} \quad i=1,2,3,\dots N$$

U = inter/intra-molecular potential (i.e., interactions between atoms)

\mathbf{r}_i = position vector of atom i

\mathbf{F}_i = force acting over atom i

m_i = mass of atom i

Thus MD is a deterministic method: the state of the system at any future time can be predicted from its current state (in principle, at least).

7

MD: How does it work?

- Newton’s equations of motion for the N -particle system:

where: $\mathbf{F}_i = m_i \ddot{\mathbf{r}}_i \quad (1)$

$$\mathbf{F}_i = - \frac{\partial U}{\partial \mathbf{r}_i} = \text{Force acting on particle } i \quad m_i = \text{Mass of particle } i$$

$$\ddot{\mathbf{r}}_i = \frac{d^2 \mathbf{r}_i}{dt^2} = \text{Acceleration of particle } i$$

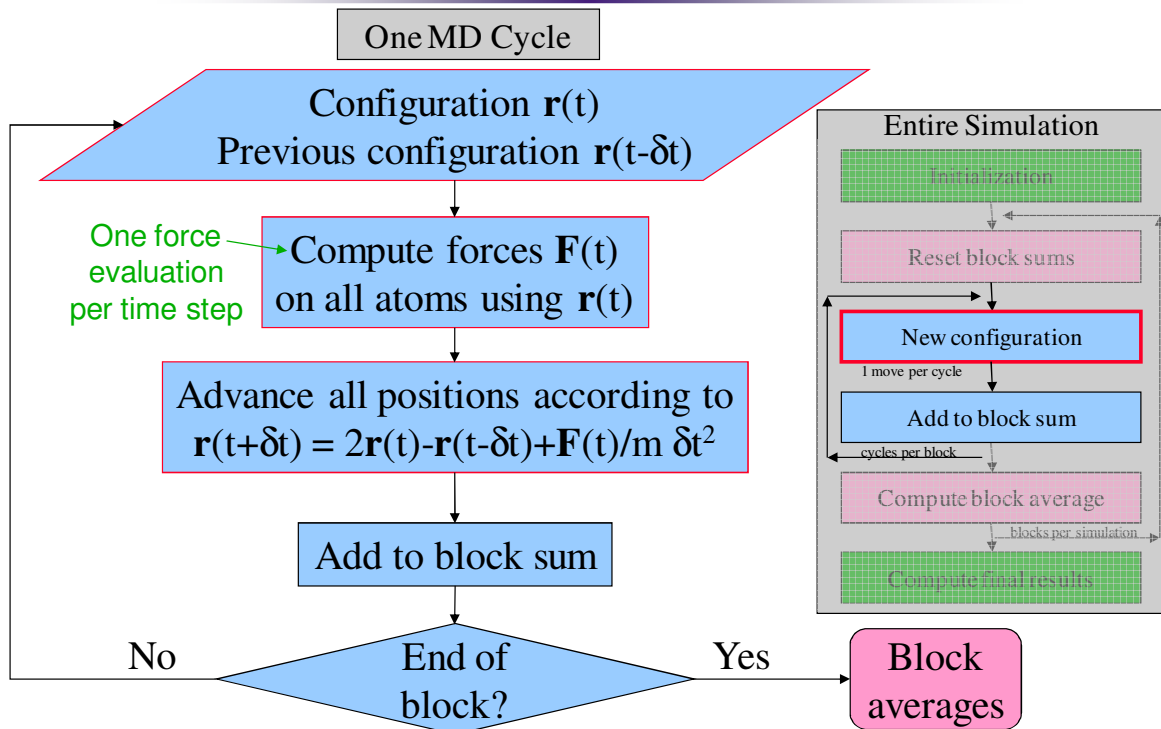
- In MD these equations are integrated numerically to obtain the time evolution of the system under the given potential.
- There are several approximate methods to numerically solve this system of equations.

Each method has trade-offs:

- Accuracy
- Stability
- Time reversibility
- Memory requirements
- Complexity

8

Verlet Algorithm 2. Flow diagram



9

Pair Potentials: Large, Flexible Mols.

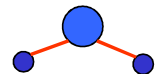
- Total pair energy breaks into a sum of terms:

$$U(\mathbf{r}^N) = U_{str} + U_{bend} + U_{tors} + U_{disp} + U_{elec} + U_{pol}$$

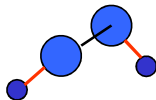
- U_{str} - stretch



- U_{bend} - bend



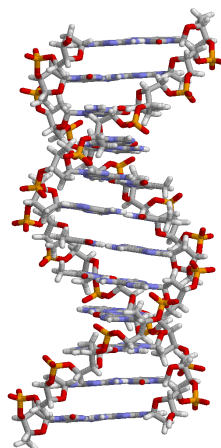
- U_{tors} - torsion



- U_{disp} - dispersion (van der Waals)

- U_{elec} - electrostatic

- U_{pol} - polarization



DNA

A Typical Force Field

$$\begin{aligned}
 U(\{\mathbf{r}_i\}) = & \underbrace{\sum_j \frac{k_j^l}{2} (l_j - l_j^0)^2}_{\text{Bond stretch}} + \underbrace{\sum_j \frac{k_j^\theta}{2} (\vartheta_j - \vartheta_j^0)^2}_{\text{Valence angle bend}} \\
 & + \sum_{\text{torsions}} \frac{V_n}{2} (1 + \cos(n\varphi - \gamma)) \quad \text{torsional} \\
 & + \underbrace{\sum_{i,j=1}^N \frac{q_i q_j}{r_{ij}}}_{\text{Electrostatic (Coulomb)}} + \underbrace{\sum_{i,j=1}^N 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]}_{\text{van der Waals (Lennard-Jones)}}
 \end{aligned}$$

Intra-Molecular

Intra- and Inter-molecular

11

Atomistic MD and polymeric systems

The time step, Δt , for numerical integration of Newton's equations of motion in atomistic MD is determined by the fastest modes.

$$\Delta t \sim 1 \text{ fs} = 10^{-15} \text{ s} \quad (\text{Bond vibrations})$$

However, for **polymer melts** the longest relaxation times are on the order of milliseconds – seconds (for typical molecular weights under processing conditions)

$$t_{\text{total}} \sim 1 \text{ s} = 10^{15} \text{ fs}$$

A very optimized MD package (Gromacs v. 4) dealing with a system of an ion channel placed in a model membrane solvated with water and ions (totaling **121,449 atoms**), running on **128 cores (32 nodes) in parallel** ~ **66 ns/day** = $66 \times 10^{-9} \text{ s/day}$ (Hess et al., *J. Chem. Theory Comput.* **2008**, 4, 435)

→ **A ballpark estimate**: to simulate 1 s of real time would take

$$\text{Computing time} \sim \frac{1 \text{ s}}{66 \times 10^{-9} \text{ s/day}} \sim 15,151,515 \text{ days} \sim 41,483 \text{ years!!!!}$$

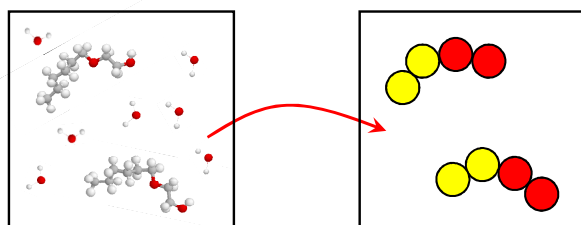
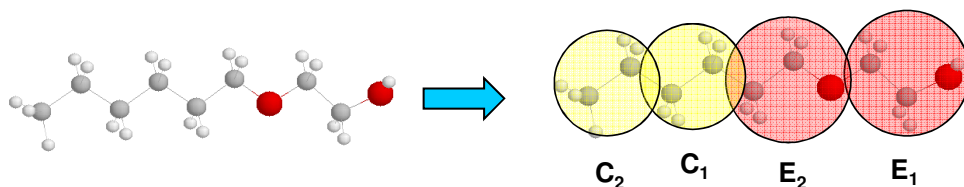
With current computers, we can model a few microseconds (at most)

→ **Atomistic MD is unable to equilibrate a long-chain polymer melt**

12

Modeling polymeric systems

First, introduce simplifications to atomistic methods to remove the faster degrees of freedom, and/or treat groups of atoms ('blobs of matter') as individual entities interacting through effective potentials → **coarse-graining the system**.



Although it might appear simple, properly coarse-graining a system is difficult...

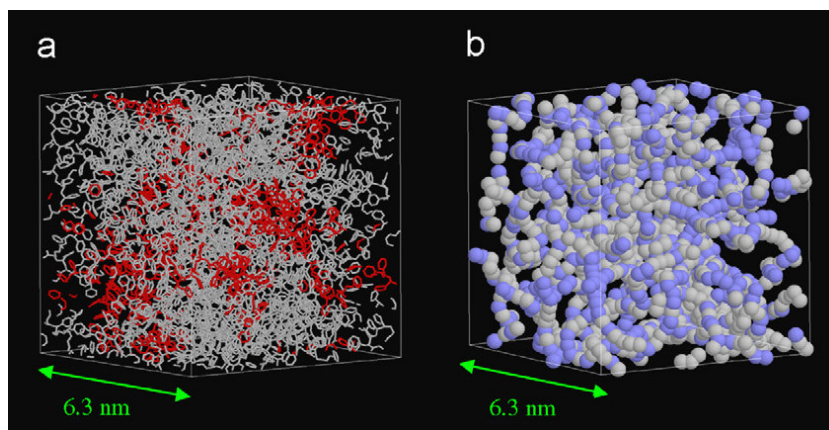
Application of coarse-graining to polymers has been reviewed:

J. Baschnagel et al., *Advances in Polymer Science* **2000**, 152, 41
 F. Muller-Plathe, *ChemPhysChem* 2002, 3, 754
 D. Reith et al., *J. Comp. Chem.* 2003, 24, 1624

13

Modeling polymeric systems

Coarse-graining polymeric systems



Three levels of representation of atactic polystyrene melt specimens at 500K and 1 bar:

- Detailed united-atom model formed from four 350 dyad-long parent chains (molar mass 36,500 g mol⁻¹). Segments coming from one of the parent chains are traced in red, for clarity.
- Coarse-grained model formed from four 350 dyad-long parent chains, wherein each dyad of monomers is represented as an interaction site (superatom). The two types of dyads (*m*, *r*) are shown in different colors.

D. N. Theodorou, *Chem. Eng. Sci.* **2007**, 62, 5697

14

Modeling polymeric systems

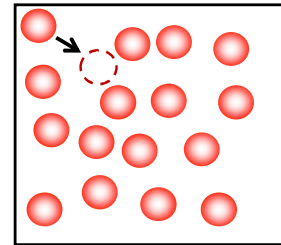
Monte Carlo method: generate configurations of a system by making random changes to positions/orientations/conformations of the atoms/molecules, over and over again

Differences between MD and MC:

- **MD:** generate successive configurations by calculating conservative forces derived from gradients in the potential energy and then solve deterministic equations of motion
- **MC:** generate random configurations with a probability that depends on the potential energy of a new configuration compared with the previous one.

- At each iteration of a MC simulation, a new configuration is generated.

- This is usually done by making a random change to the coordinates of a randomly chosen particle, using a random number generator. Moves are accepted with a probability $\sim \exp[-(U_{new} - U_{old})/(kT)]$

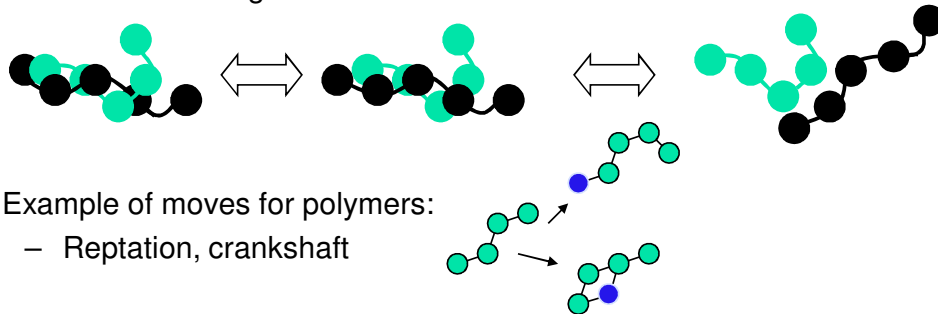


- A great variety of random moves can be attempted

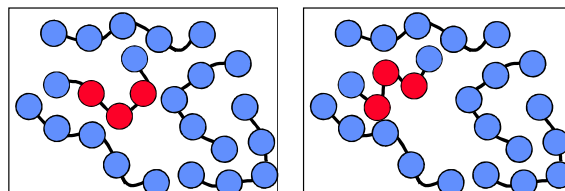
15

Trial Moves in MC simulation

- Significant increase in efficiency of algorithm can be achieved by the introduction of clever trial moves
 - Example: simulating chain molecules (e.g. polymers). Relaxation times are large, exploration of phase space is very slow, need concerted moves to disentangle chains

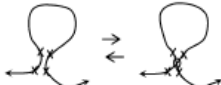
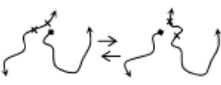


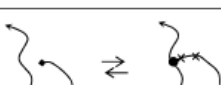

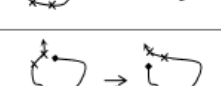
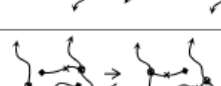
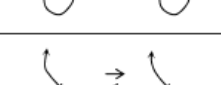
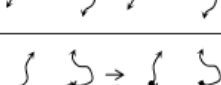


- Example of moves for polymers:
 - Reptation, crankshaft
 - Chain regrowth
 - and many more



Using these physically unrealistic moves, we can explore phase space faster than in MD!

Trial Moves in MC simulation

	A. INTRA-MOLECULAR BRIDGING	B. INTER-MOLECULAR BRIDGING
I.		
II.		
III.		
IV.		
V.		

L. D. Peristeras
et al.,
Macromolecules
2005, 38, 386

Figure 1. Schematic representation of various intramolecular and intermolecular bridging moves.

“Connectivity-altering moves provide vigorous sampling of the long-range conformational features of chains (end-to-end distance, radius of gyration), and are thus extremely efficient in inducing equilibration in long-chain polymer systems” D. N. Theodorou, *Chem. Eng. Sci.* **2007**, 62, 5697

17

MC simulations: coarse-grained polymeric systems

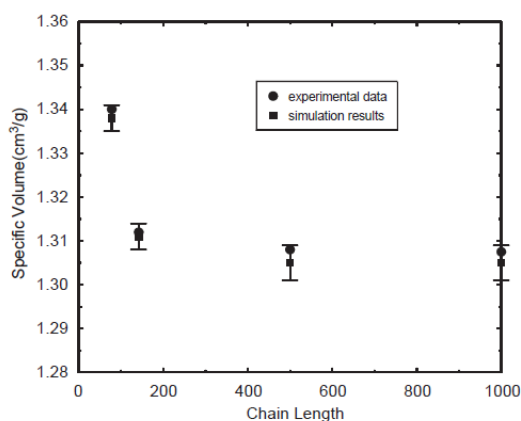


Fig. 1. Experimental (circles) and simulated (squares) specific volumes $1/\rho$ for a series of monodisperse polyethylene melts at 450 K and 1 atm (Karayiannis et al., 2002).

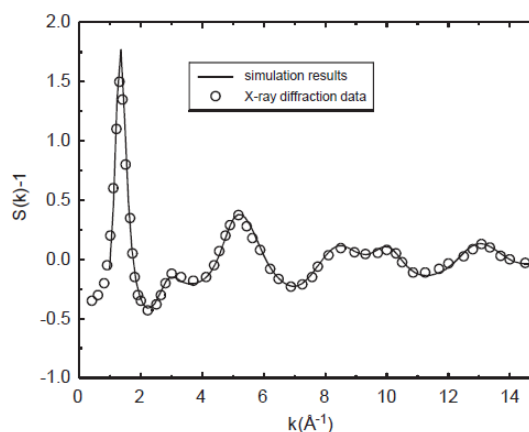


Fig. 2. Static structure factor $S(k)$ for a monodisperse linear C_{1000} polyethylene, as obtained from *NPT* MC simulations using DB and intramolecular double rebridging (IDR) moves, being compared to an experimental wide-angle X-ray diffraction pattern for PE. The simulation is at 450 K and 1 atm; the experimental data are at 430 K and 1 atm.

D. N. Theodorou, *Chem. Eng. Sci.* **2007**, 62, 5697

18

Rheology of coarse-grained polymeric systems

- Rheological properties important for polymer processing
- Atomistic MD not suitable (long relaxation times); MC not suited to measure time-dependent properties (only equilibrium properties)
- A hierarchical strategy can be used:
 1. Run MC simulations of model polymer systems. Properly equilibrate systems
 2. Run short MD simulations of systems previously equilibrated via MC simulations
 3. Map time-dependent results (time correlation functions, mean-square displacements) from short MD simulations onto mesoscopic theories of polymer dynamics (e.g., Rouse, reptation model)
 4. Use the mesoscopic theories (with parameters from MD simulations) to estimate rheological properties

Table 1

Friction factor per carbon atom, chain self-diffusivity, and zero shear rate viscosity of a melt of C₉₀ chains, as obtained by mapping united-atom MD simulations onto the Rouse model (from Harmandaris et al., 1998)

C ₉₀	Predicted	Experimental
ζ_D (10^{-9} dyn s cm ⁻¹)	0.47 ± 0.05	
ζ_τ (10^{-9} dyn s cm ⁻¹)	0.42 ± 0.04	
D_s (10^{-6} cm ² s ⁻¹)	1.46 ± 0.1	1.4
η_0 (cp)	8.6 ± 0.05	9.2

This mapping process can also:
(1) give insights about the ranges of applicability of the mesoscopic theories, (2) pinpoint inadequacies in the assumptions of the mesoscopic theories, which will help in the development of better theories

D. N. Theodorou, *Chem. Eng. Sci.* **2007**, *62*, 5697

19

CHEM 4010

Computer simulation of polymeric systems: An overview

Francisco R. Hung

Cain Department of Chemical Engineering
Louisiana State University

<http://www.che.lsu.edu/faculty/hung/>

Ab Initio Methods (including DFT)

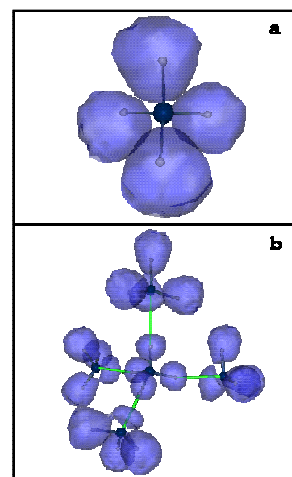
Calculate properties from first principles, solving the Schrödinger (or Dirac) equation numerically.

Pros:

- Can handle processes that involve bond breaking/formation, or electronic rearrangement (e.g. chemical reactions).
- Methods offer ways to systematically improve on the results, making it easy to assess their quality.
- Can (in principle) obtain essentially exact properties without any input but the atoms conforming the system.

Cons:

- Can handle only small systems, about $O(10^2)$ atoms.
- Can only study fast processes, usually $O(10)$ ps.
- Approximations are usually necessary to solve the eqns.



Electron localization function for (a) an isolated ammonium ion and (b) an ammonium ion with its first solvation shell, from *ab initio* molecular dynamics. From Y. Liu, M.E. Tuckerman, *J. Phys. Chem. B* 105, 6598 (2001)

Semi-empirical Methods

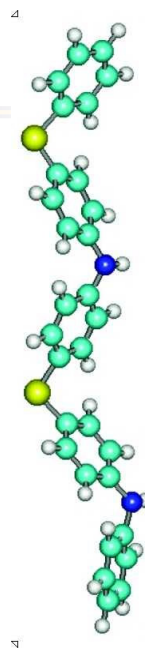
Use simplified versions of equations from *ab initio* methods, e.g. only treat valence electrons explicitly; include parameters fitted to experimental data.

Pros:

- Can also handle processes that involve bond breaking/formation, or electronic rearrangement.
- Can handle larger and more complex systems than *ab initio* methods, often of $O(10^3)$ atoms.
- Can be used to study processes on longer timescales than can be studied with *ab initio* methods, of about $O(10)$ ns.

Cons:

- Difficult to assess the quality of the results.
- Need experimental input and large parameter sets.



Structure of an oligomer of polyphenylene sulfide phenyleneamine obtained with the PM3 semiempirical method. From R. Giro, D.S. Galvão, *Int. J. Quant. Chem.* 95, 252 (2003)

Atomistic Simulation Methods

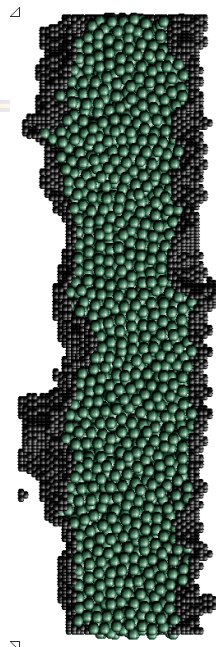
Use empirical or *ab initio* derived force fields, together with semi-classical statistical mechanics (SM), to determine thermodynamic (MC, MD) and transport (MD) properties of systems. SM solved ‘exactly’.

Pros:

- Can be used to determine the microscopic structure of more complex systems, $O(10^{5-6})$ atoms.
- Can study dynamical processes on longer timescales, up to $O(1)$ μ s

Cons:

- Results depend on the quality of the force field used to represent the system.
- Many physical processes happen on length- and timescales inaccessible by these methods, e.g. diffusion in solids, many chemical reactions, protein folding, micellization.



Adsorption of Ar molecules in a model MCM-41 silica pore. From B. Coasne, F. R. Hung, R. J.-M. Pellenq, F. R. Siperstein and K. E. Gubbins, *Langmuir* 22, 194 (2006)

Mesoscale Methods

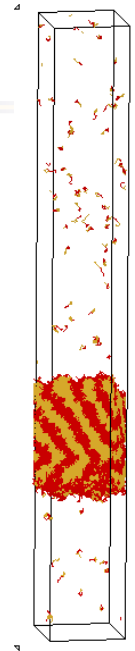
Introduce simplifications to atomistic methods to remove the faster degrees of freedom, and/or treat groups of atoms ('blobs of matter') as individual entities interacting through effective potentials.

Pros:

- Can be used to study structural features of complex systems with $O(10^8\text{-}9)$ atoms.
- Can study dynamical processes on timescales inaccessible to classical methods, even up to $O(1)$ s.

Cons:

- Can often describe only qualitative tendencies, the quality of quantitative results may be difficult to ascertain.
- In many cases, the approximations introduced limit the ability to physically interpret the results.



Phase equilibrium between a lamellar surfactant-rich phase and a continuous dilute surfactant phase in supercritical CO_2 , from a lattice MC simulation. From L.F. Scanu, C.K. Hall, K.E. Gubbins, *Langmuir*, 20, 514 (2004) .

Continuum Methods

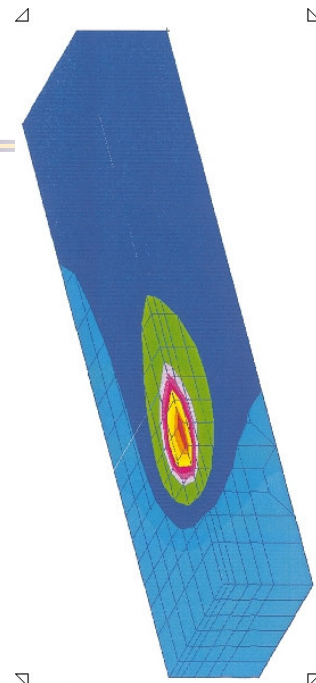
Assume that matter is continuous and treat the properties of the system as field quantities. Numerically solve balance equations coupled with phenomenological equations to predict the properties of the systems.

Pros:

- Can in principle handle systems of any (macroscopic) size and dynamic processes on long timescales.

Cons:

- Require input (viscosities, diffusion coeffs., eqn of state, etc.) from experiment or from a lower-scale method that can be difficult to obtain.
- Cannot explain results that depend on the electronic or molecular level of detail.



Temperature profile on a laser-heated surface obtained with the finite-element method. From S.M. Rajadhyaksha, P. Michaleris, *Int. J. Numer. Meth. Eng.* 47, 1807 (2000)

The Monte Carlo Method: procedure

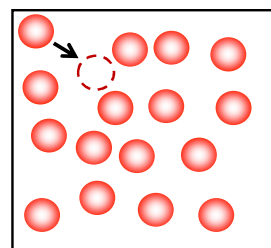
- At each iteration of the simulation, a new configuration is generated.
 - In a NVT simulation, this is usually done by making a random change to the coordinates of a randomly chosen particle, using a random number generator:

$$x_{new} = x_{old} + (2\xi_1 - 1)r_{max}$$

$$y_{new} = y_{old} + (2\xi_2 - 1)r_{max}$$

$$z_{new} = z_{old} + (2\xi_3 - 1)r_{max}$$

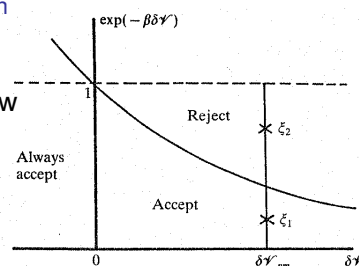
Where ξ_1, ξ_2, ξ_3 are random numbers in the range (0,1)
 r_{max} is the maximum allowed displacement in any direction



- The potential energy of the new configuration is calculated. We also calculate the difference in potential energy between the new and the old configuration, $\delta U = U(\mathbf{r}_{new}^N) - U(\mathbf{r}_{old}^N)$

- Calculate the Boltzmann factor, $\exp(-\delta U/kT)$

- If $\delta U < 0$, the new configuration is accepted
- If $\delta U \geq 0$, the Boltzmann factor is compared to a random number ξ in the range (0,1)
 - If $\xi \leq \exp(-\delta U/kT)$, the new configuration is accepted
 - If $\xi > \exp(-\delta U/kT)$, the new configuration is rejected. The old configuration is retained for the next iteration.



From Allen and Tildesley

For more details about the theory behind this algorithm, please consult any of the molecular simulation textbooks. 27