

transcribed by Dr. Myung-Suk Chun (KIST), December 2001

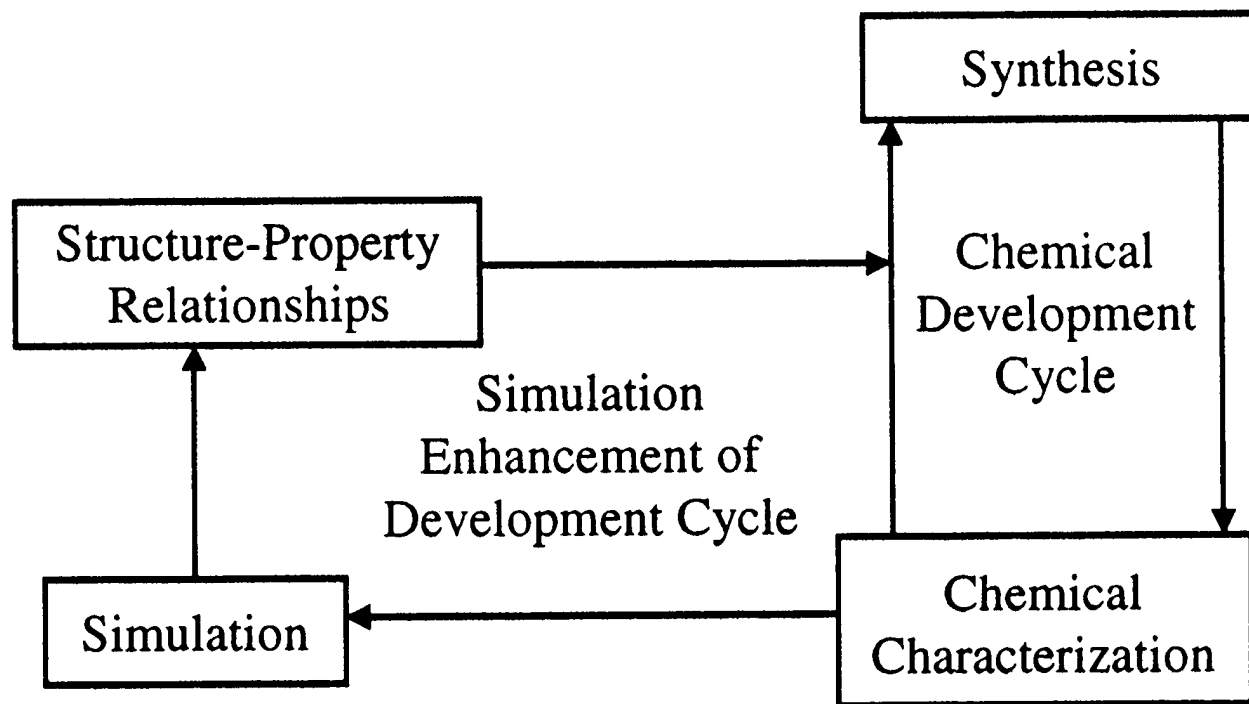
Molecular Simulations: Introductory Tutorial

“Molecularly-Based Modeling for Materials and Chemicals Applications”
presented at the topical conference on *AIChE Annual Meeting*, Reno, Nevada 2001.

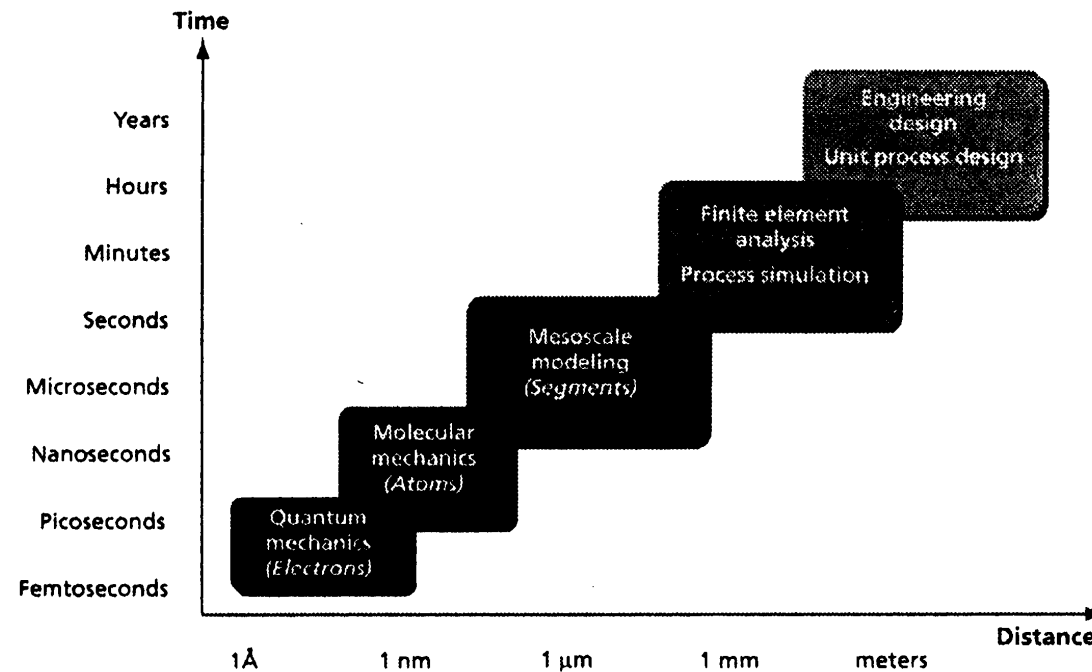
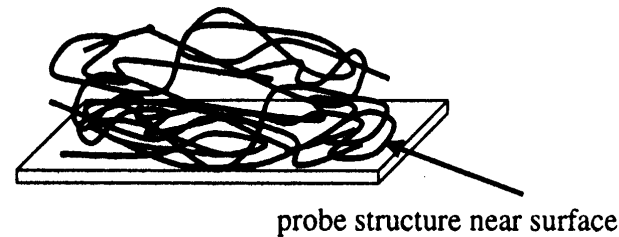
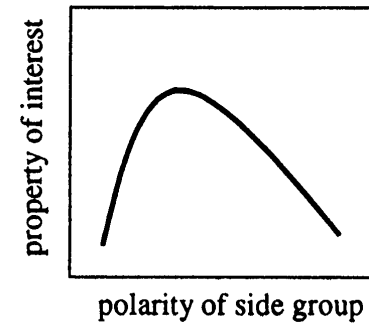
Sponsored by Accelrys, Gaussian Inc. and the CAChe Group, Fujitsu

Introduction to Molecular Simulation

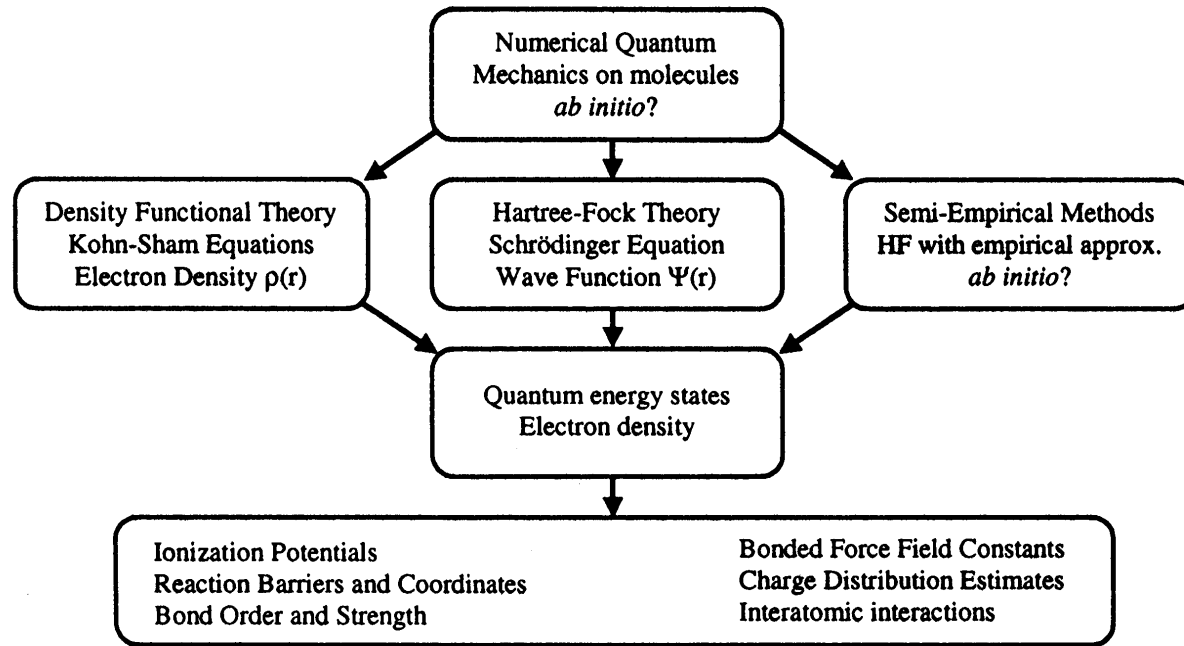
Molecular Modeling Paradigm



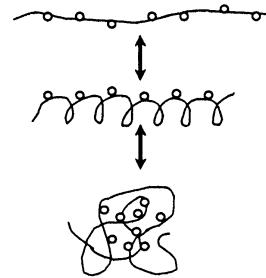
- Structure Property Trends are often sufficient
- Modeling can probe structural details that are difficult to access using experiment
- Modeling is another analytical technique like spectroscopy



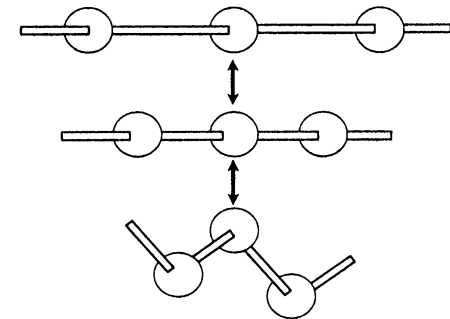
Quantum Mechanics Modeling



Mesoscale Model Problems



Interactions can be quite conformationally dependent with polar polymers



Intersegment potentials in mesoscale models should depend on conformation

Force Field Components

- Bonded Interactions

- ◆ Bonding parameters
- ◆ Bond angle parameters
- ◆ Torsion angle parameters
- ◆ Inversion parameters

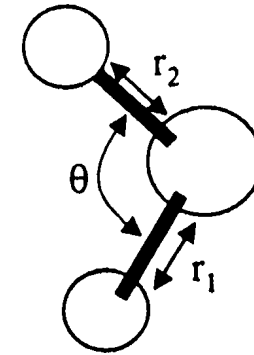
$$\frac{\hbar}{\sqrt{2mkT}} \left(\frac{N}{V} \right)^{1/3} \ll 1$$

Classical Force Fields
are justified when De Broglie
wavelength is low

- Dispersion Interactions (Lennard Jones etc.)
- Polar Interactions
- Other (hydrogen bonding...)

Bonded Interactions

$$\text{Hessian Matrix} = \begin{bmatrix} \frac{\partial^2 E}{\partial r_1^2} & \frac{\partial^2 E}{\partial r_1 \partial r_2} & \frac{\partial^2 E}{\partial r_1 \partial \theta} \\ \frac{\partial^2 E}{\partial r_2 \partial r_1} & \frac{\partial^2 E}{\partial r_2^2} & \frac{\partial^2 E}{\partial r_2 \partial \theta} \\ \frac{\partial^2 E}{\partial \theta \partial r_1} & \frac{\partial^2 E}{\partial \theta \partial r_2} & \frac{\partial^2 E}{\partial \theta^2} \end{bmatrix} = \begin{bmatrix} k_1 & k_{12} & k_{1\theta} \\ k_{12} & k_2 & k_{2\theta} \\ k_{1\theta} & k_{2\theta} & k_\theta \end{bmatrix}$$



angle potentials

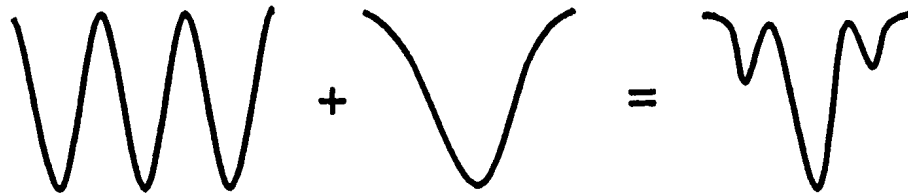
$$E_\theta = \frac{1}{2} k_\theta (\theta - \theta_o)$$

bonding potentials

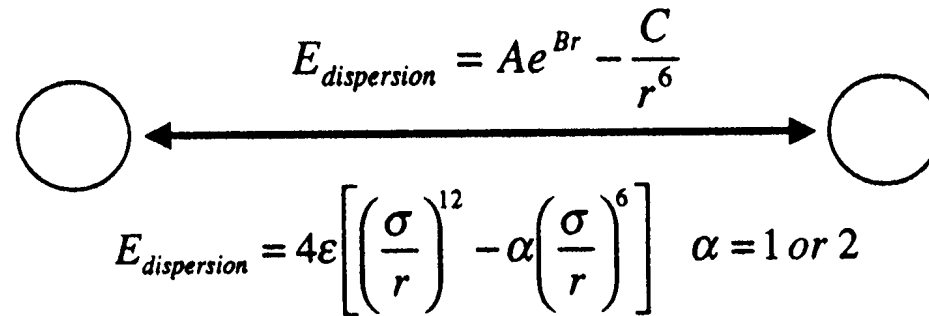
$$E_b = \frac{1}{2} k_1 (r_1 - r_1^o)$$

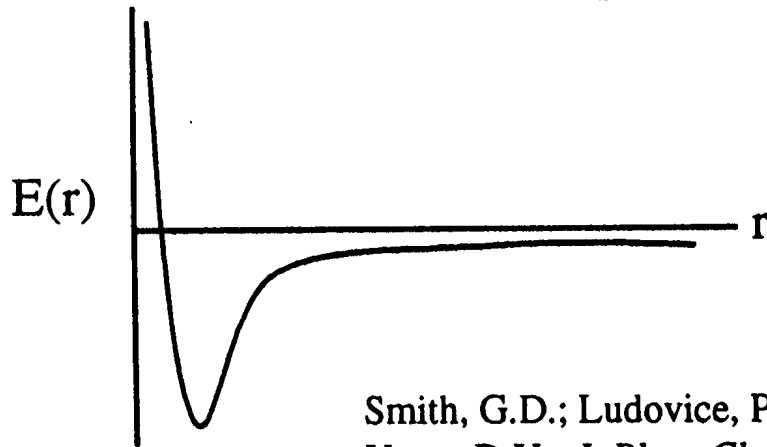
“Intrinsic” torsional potentials

$$E_\phi = \sum_{n=1}^6 k_n (1 + \cos(n\phi))$$



Dispersion Interactions

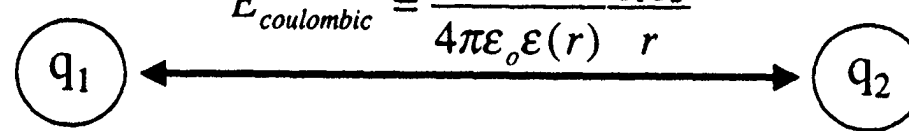

$$E_{dispersion} = Ae^{Br} - \frac{C}{r^6}$$
$$E_{dispersion} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \alpha \left(\frac{\sigma}{r} \right)^6 \right] \quad \alpha = 1 \text{ or } 2$$



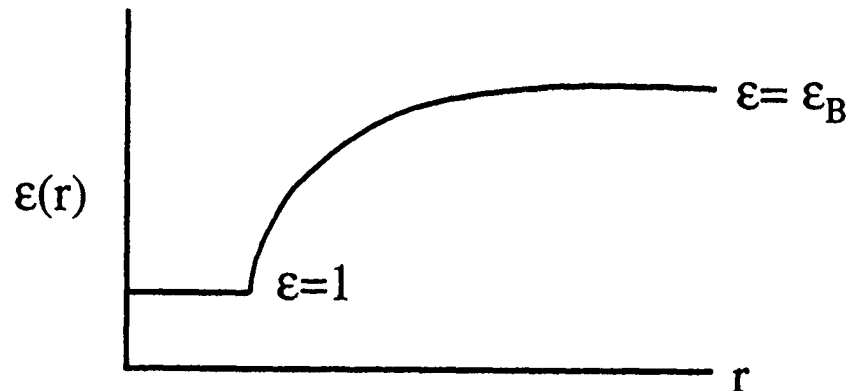
Origin of energy is electron correlation. Therefore this is difficult to fit from quantum calculations due to problems with correlation and overlap.

Smith, G.D.; Ludovice, P.J.; Jaffe, R.L.;
Yoon, D.Y.; *J. Phys. Chem.*, **99**, 164-172
(1995).

Polar Interactions

$$E_{coulombic} = \frac{1}{4\pi\epsilon_0\epsilon(r)} \frac{q_1q_2}{r}$$


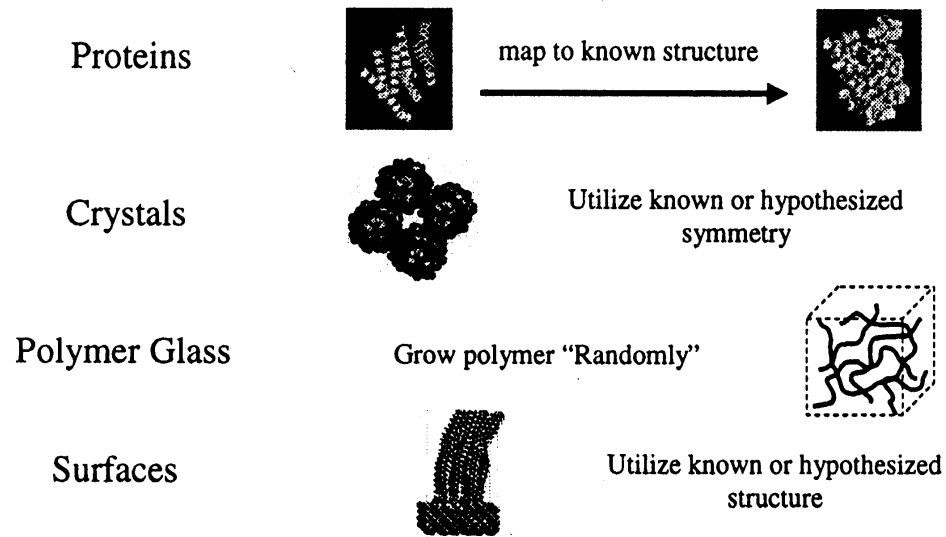
Some charge distribution must be used to mimic polar molecules.
Atom-centered point charges (q_1, q_2) are commonly used.



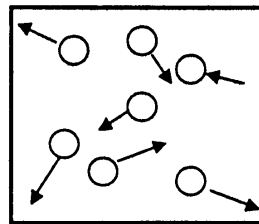
Distance dependent dielectrics $\epsilon(r)$ are used to account for shielding due to polarizable material.

Ludovice, P.J. and Suter, U.W.; from Computational Modeling of Polymers, pages 401-435, (J. Bicerano, Ed.), New York: Marcel Dekker (1992).

Initial Conformation Generation

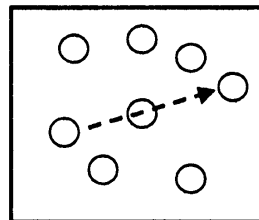
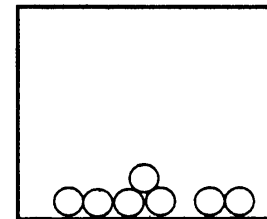


Equilibration Methods



Molecular Dynamics (MD)
Integrate Newton's 2nd Law
 $F=ma$,
most accurate, least efficient

Molecular Mechanics (MM)
Energy Minimization, motion
is a perturbation about a mean
position (MD at 0 K)



Monte Carlo (MC)
random perturbations replace
differential equation, algorithms
assure correct distribution of states

Statistical Mechanics

- Thermodynamics is observed to be true
- Thermodynamics can be derived from statistical mechanics
- MC models numerically reproduce statistical mechanical ensembles
- MD reproduces MC models at long times (ergodic hypothesis)
- Energy Minimization is MD at 0K for systems where entropy is not important (crystals)

An ensemble is the distribution of molecular states for a given set of constant properties.

NVE, NVT,
NPT, μ VT

There is a function (partition function) that governs the distribution of these states.

$$Q(N, V, T) = \sum_j e^{-E_j / kT} = \sum_{E_j} \Omega(N, V, E) e^{-E_j / kT}$$


$$Z(N, P, T) = \sum_j e^{-PV_j / kT} = \sum_V Q(N, V, T) e^{-PV / kT}$$

$$A(N, V, T) = -kT \ln(Q(N, V, T))$$

$$\mu = -kT \left(\frac{\partial \ln(Q)}{\partial N} \right)_{V, T} \quad E = kT^2 \left(\frac{\partial \ln(Q)}{\partial T} \right)_{N, V} \quad \text{Properties can be derived from these functions.}$$

Statistical Mechanics

Analytical solution of these equations for realistic systems is very difficult. Molecular simulation is the numerical solution of these equations.

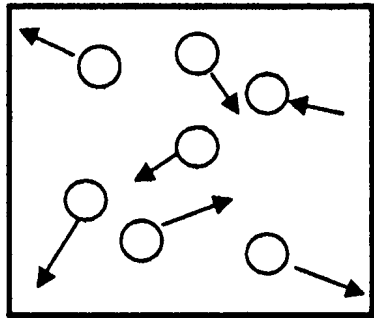
$$K_{NVT} = \sum_j P_j(NVT) K(NVT) = \sum_j \frac{e^{-E_j/kT}}{Q(NVT)} K(NVT)$$


Metropolis-Monte Carlo method stochastically samples according to this distribution so properties can be averaged from MC results to calculate any property K .

$$\langle K \rangle_{ensemble} = \langle K \rangle_{time}$$

The ergodic hypothesis equates the results of MC and MD in the thermodynamic limit

Molecular Dynamics (MD)



$$m_i \ddot{x}_i = F_i = -\nabla_i E_p$$

2nd order ODE is integrated
using 2nd order algorithm
(Verlet class algorithms) and
 $\Delta t \approx 1 \text{ fs}$.

More commonly expressed in
terms of the Hamiltonian
 $H = E_k + E_p$

$$\dot{p}_i = -\left(\frac{\partial H}{\partial x_i}\right) \quad \dot{x}_i = \left(\frac{\partial H}{\partial p_i}\right)$$

Other MD “Ensembles”

Common conditions of MD simulations include:

- NVT constant temperature and constant volume
- NPT constant pressure and constant temperature
- NVE constant energy and constant volume
- NPH constant pressure and constant enthalpy

$$\dot{p}_i = -\nabla_i E_p - \eta p_i \quad \text{Use constraint multiplier to control T}$$

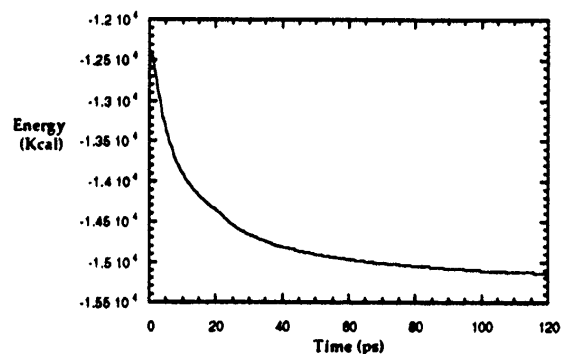
$$\dot{\eta} = \frac{3N}{Q} (kT - kT_{\text{desired}}) \quad \text{“Integral Controller” of Nosé \& Hoover}$$

$$\dot{\eta} = \frac{3N}{Q} (kT - kT_{\text{desired}}) \quad \text{Where does Q come from?}$$

Q controls the rate of response of the controller and therefore the fluctuations around the average. Q can be adjusted to match fluctuations predicted by statistical mechanics.

$$\langle E_k^2 \rangle - \langle E_k \rangle^2 = \frac{3N}{2} (kT)^2 \quad \langle V^2 \rangle - \langle V \rangle^2 = V kT \left(-\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{NT} \right)$$

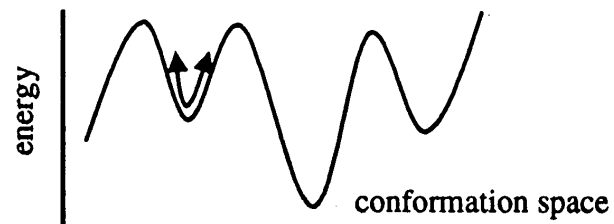
Molecular Dynamics (MD)



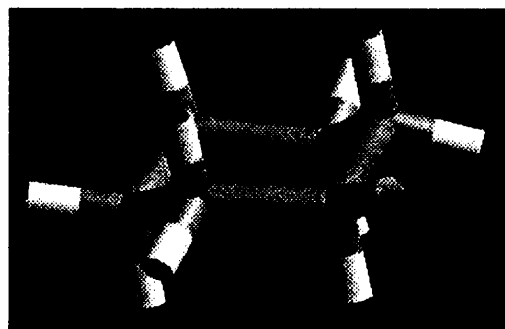
When is MD done?

Properties approaching steady state is a necessary but not sufficient condition for equilibration.

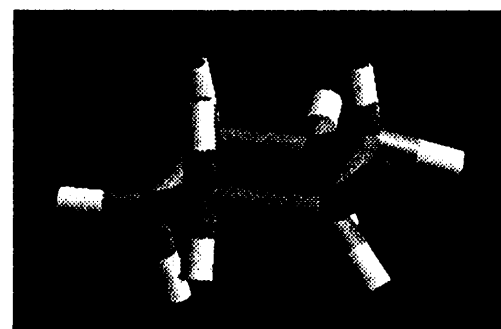
May be stuck in a local minimum, so comparison to experiment is important.



A Sample Molecular Dynamics simulation



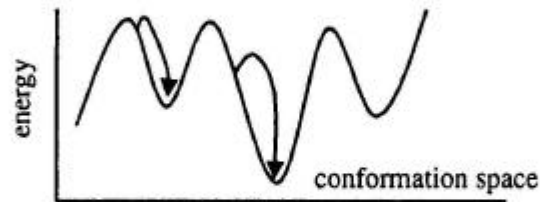
At 300K



At 3000K

Energy Minimization

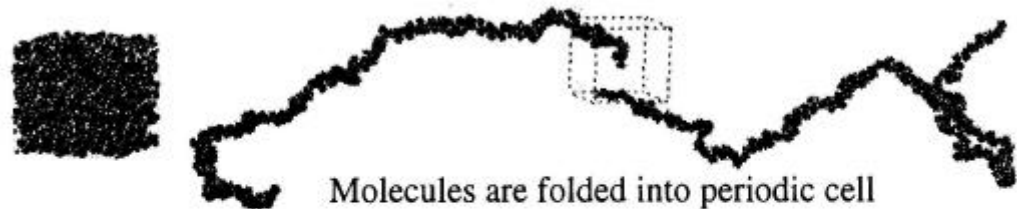
Energy minimization is MD at 0K! This is useful for systems where entropy is not important.



$$A = -RT \ln Z = -RT \ln(e^{-E_i / RT}) = E_i$$

$$Z = \sum_{i=1}^{\Omega} e^{-E_i / kT} \approx \sum_{i=1}^1 e^{-E_i / kT} = e^{-E_i / kT}$$

Periodic Boundary Conditions



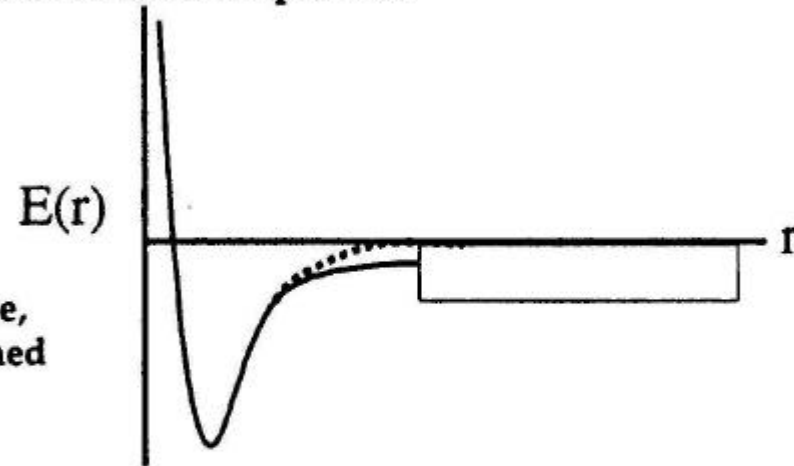
- Eliminates end effects in bulk simulations
- Creates artificial symmetry for non-crystalline systems
- Most simulations use macrocells in P1 symmetry
- Truncates long range interactions which may require correction (coulombic interactions)

Periodic Energy Corrections

Very computationally expensive therefore calculation times improve if you use cut-offs

Direct Cut-Off : Ignores all interactions after a certain cut-off limit

Spline Cut-Off : In the specified spline zone, gradually decreases the interactions examined

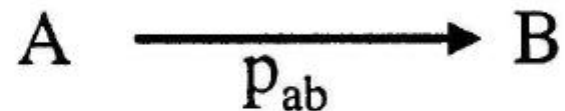


➤ **Ewald** : The summation of the non-bonded terms is carried out in reciprocal space. (summation is conditionally convergent)

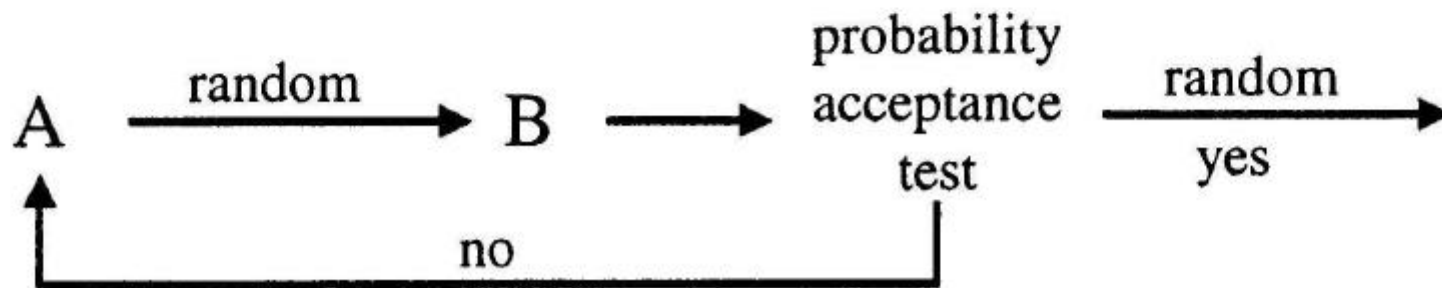
Cell Multipole : The simulation space is divided into uniform cubic cells and cells are approximated by a combination of multipoles. Multipole summations converge more rapidly than monopole summations

Metropolis MC Method

Monte Carlo methods find the states of a system by jumping from state to state using a known transition probability



Metropolis found a way to do this without the transition probability. He proved that this will sample the ensemble properly as long as the acceptance probability is chosen correctly



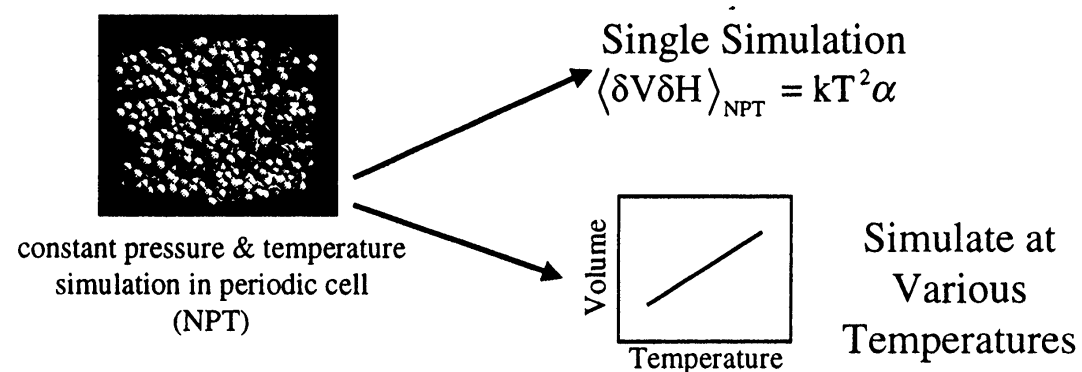
Extraction of Properties

Property	Method
Thermodynamic	Carry out multiple simulations at various states or use fluctuations
Transport	Integrate autocorrelation function of use Einstein relationship
Structural	Apply structural transform

Coefficient of Thermal Expansion α

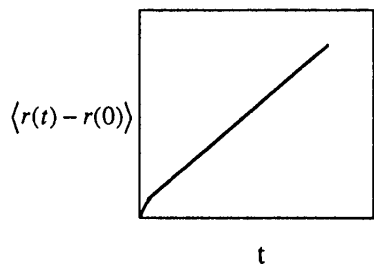
$$\alpha = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right)_P$$

For Poly(norbornene)
 $\alpha \approx 80 \text{ ppm}/^\circ\text{C}$



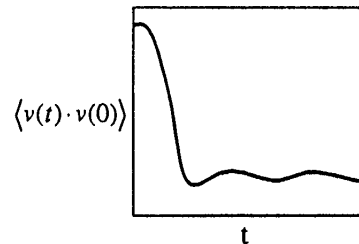
Diffusion Coefficient

After MD Simulation



Calculate slope of mean squared displacement

$$D = \text{slope} / 6$$



Integrate velocity autocorrelation function

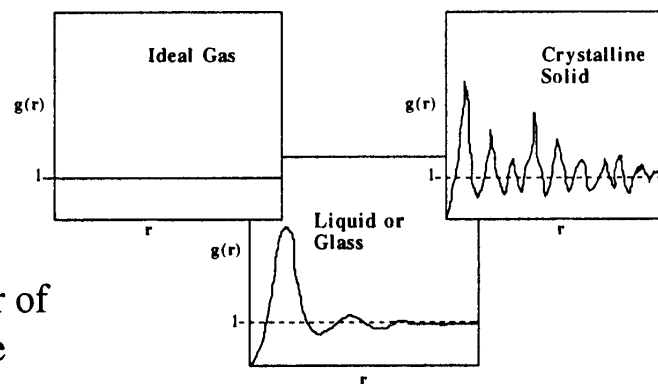
$$D = \frac{1}{3} \int_0^{\infty} \langle v(t) \cdot v(0) \rangle dt$$

Pair Distribution Function

$$g_{ij}(r) = \frac{dN_{ij}}{dV} \frac{V}{N_{ij}}$$

Normalized differential number of pairs per volume

$$E_{corr} = 2\pi N \rho \int_{r_c}^{\infty} g(r) U(r) r^2 dr$$



Can be used periodic energy correction and diffraction