Molecular Simulations (2): Application Issues

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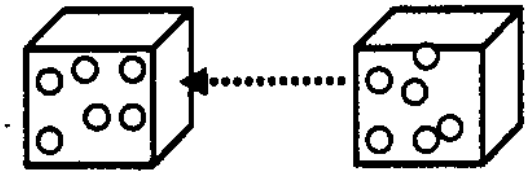
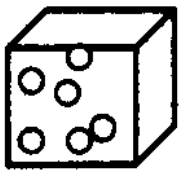
Conformation Space Sampling Techniques

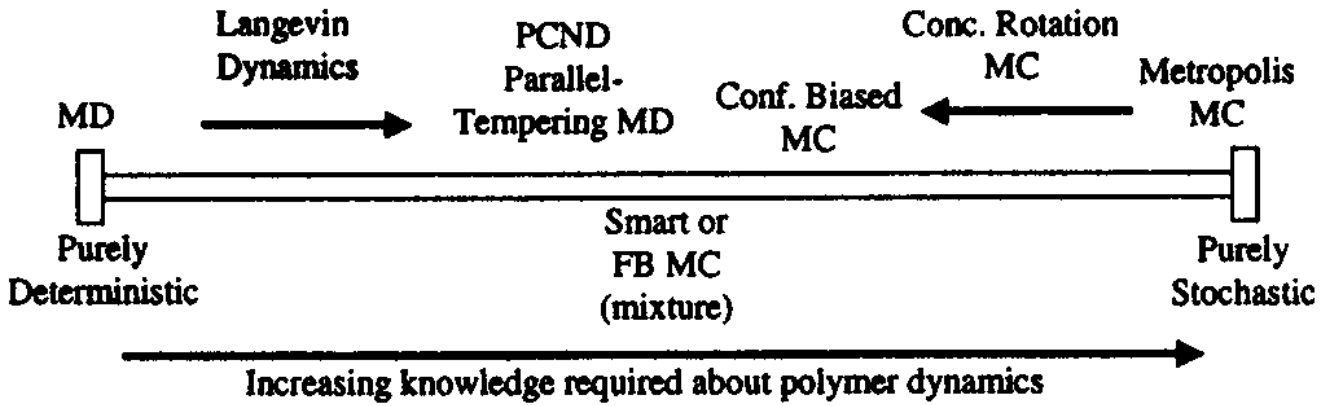


Low Temp High Temp

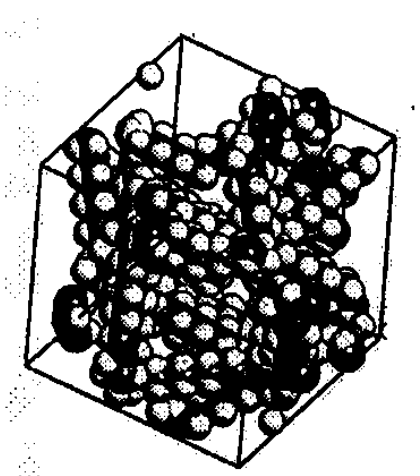
Parallel Tempering Dynamics

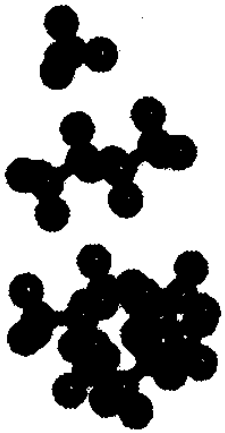


Protracted Colored-Noise Dynamics



Dealing with Molecule Insertion





Widom Insertion

Continuum Configurational Bias

Expanded Ensemble

Equation of Motion

$$M\frac{\partial^2 X(t)}{\partial t^2} = -\nabla E(X(t)), \qquad \frac{\partial X(t)}{\partial t}(t) = V(t)$$

∇E : *the collective gradient vector of the potential energy E*

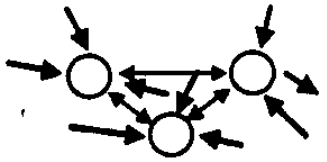
M : *diagonal mass matrix*

X, V : *position and velocity vectors*

Stochastic Molecular Dynamics

Langevin Dynamics

$$m\ddot{x}_i = -\nabla_i U + R_i - \gamma\dot{x}$$



$$\langle R_i(t)\rangle = 0 \quad \langle R_i(t)\cdot R_i(t')\rangle = 2mkT\gamma\delta(t-t') \quad \gamma = kT/mD$$

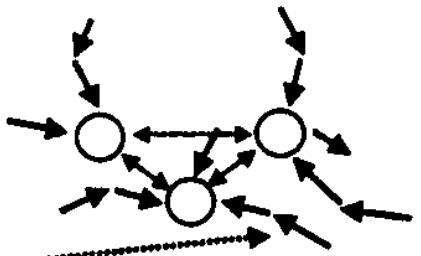
Langevin Eqn: Frictional and Random-force terms are added to mimic molecular collisions

$$M\frac{\partial^2 X(t)}{\partial t^2} = -\nabla E(X(t)) - gMV(t) + R(t), \quad \frac{\partial X(t)}{\partial t}(t) = V(t)$$

$$< R(t) >= 0, \qquad < R(t)R(t')^T > = 2gk_BTMd(t-t')$$

Colored Noise Dynamics

$$m\ddot{x}_i = -\nabla_i U + R_i - \gamma\dot{x}$$



$$\langle R_i(t)\rangle = 0 \qquad \langle R_i(t)\cdot R_i(t')\rangle = f(\gamma)e^{-|t-t'|/\tau}$$

Colored Noise Forces decay exponentially in time so they "push" on the atoms longer.

Interatomic Forces

Stochastic Forces

Damping Forces

Colored Noise Samples Wider Regions of Phase Space

P. Hanggi, *Journal of Statistical Physics*, v. 54, p.1367 (1989)

Protracted Colored Noise Dynamics

- Equations of Motion:

$$m\ddot{x}_i = -\nabla_i U + R_i - \gamma\dot{x}$$

$$\dot{\gamma} = \frac{1}{Q}\left(\frac{T_{System}}{T_{Bath}} - 1\right)$$

Nosé-Hoover thermostat constrains temperature

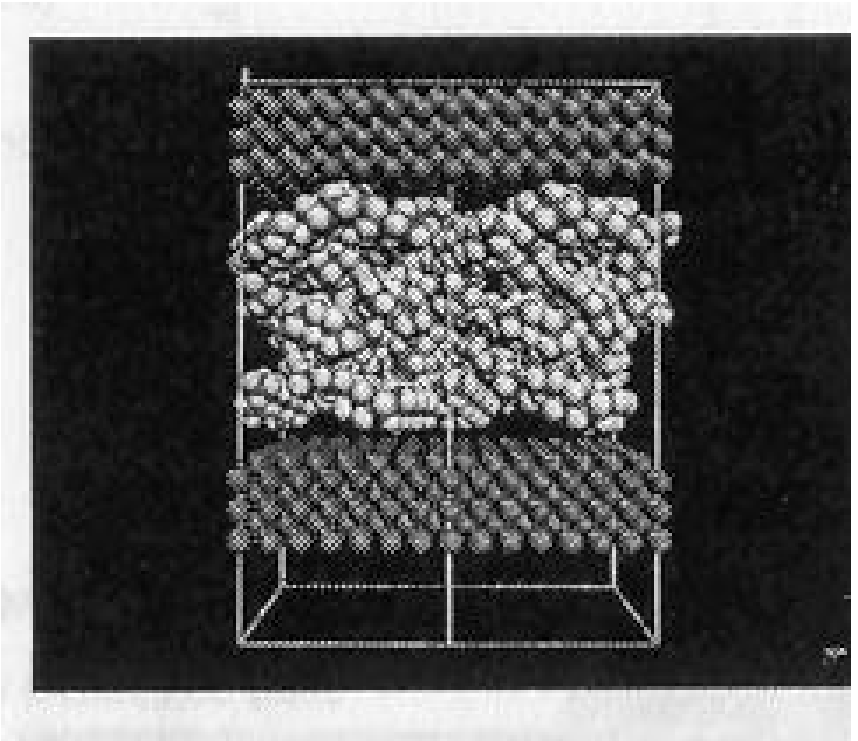
Decoupling of the damping term and random noise allows for large fluctuations, but violates the Fluctuation Dissipation Theorem (FDT).

- Colored Stochastic Force:

$$\langle R_i(t)\rangle = 0 \qquad \left\{\langle R_i(t)\cdot R_i(t')\rangle\right\} = \frac{\Omega}{\tau}e^{-|t-t'|/\tau}$$

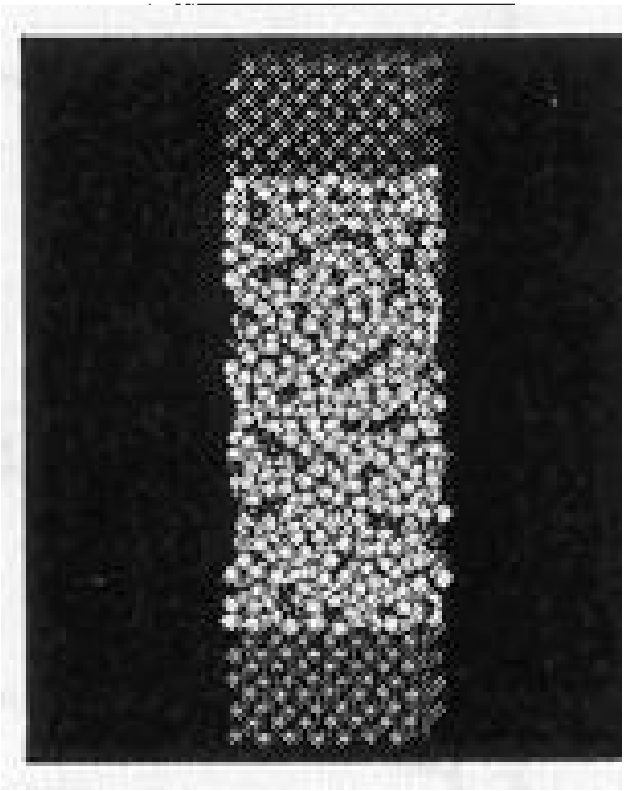
Simulation of Shear Behavior for Polymers

- A confined shear cell simulation of Fe - PE - Fe
- The Layer builder is used to construct the cell.
- Applications include lubrication, and microdevice fabrication



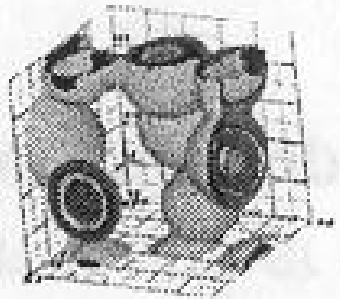
Rheology of confined polymeric liquids

- Discover dynamics simulations and analysis
- Relevant factors are
  - chain length and topology
  - fluid-wall and fluid-fluid interactions
- Atomistically defined walls
- Planar Couette flow:
- Maintain wall atoms at constant T (NVT)
- Fluid at constant energy (NVE)
- Properties: density, velocity and temperature profiles, stress

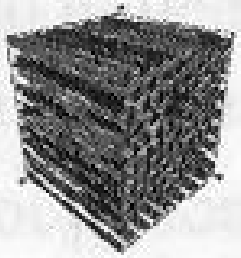


Mesoscale Simulations - focus areas

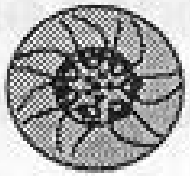
- Mesoscale chemical engineering



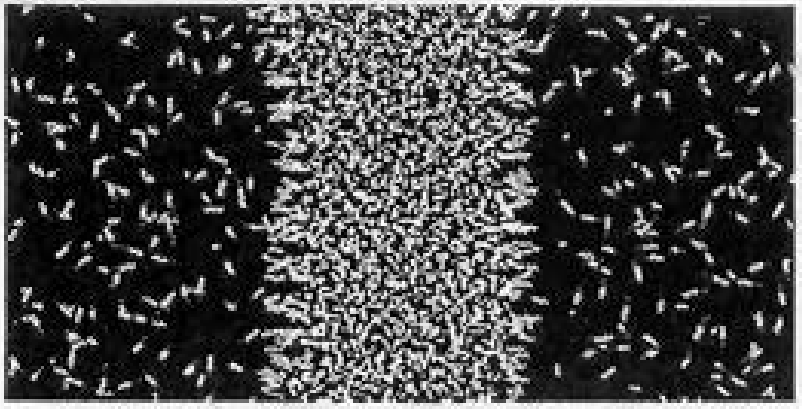
- Nanotechnology



- Biomedical materials and devices



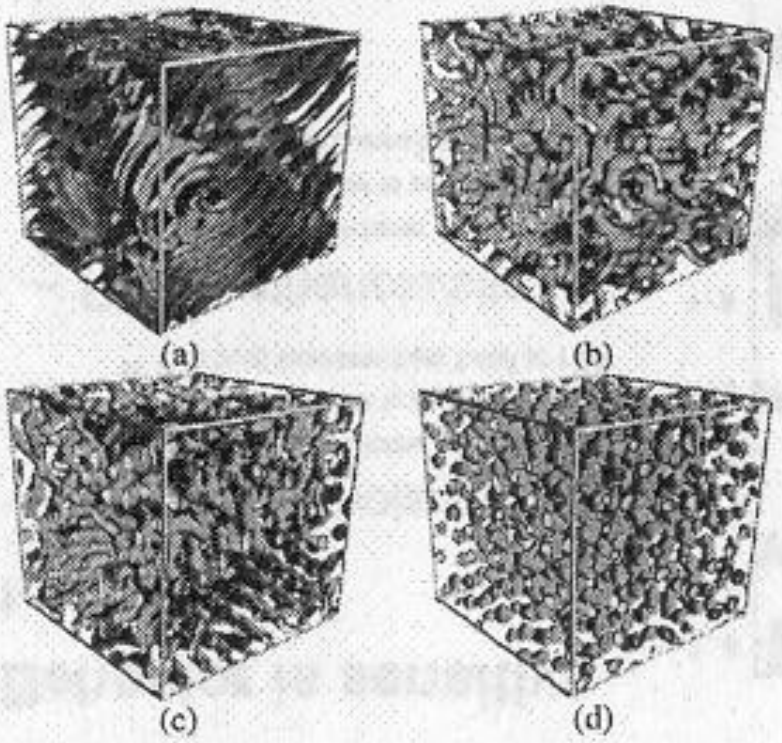
Mesoscale Modelling Tools



MesoDyn:
Mesoscale Dynamics
of
Polymer Ensembles

DPD:
Dissipative Particle Dynamics

Pluronic L64 structures as a function of concentration in aqueous solution:



- Predicted mesosphases:
  (a) (70%) lamellar
  (b) (60%) bicontinuous
  (c) (55%) hexagonal
  (d) (50%) micellar
- Excellent agreement with experiments.
- Same parameters also give correct predictions for other Pluronics.

B.A.C.van Vlimmeren, N.M.Maurits, A.V.Zvelindovsky, G.J.A.Sevink and J.G.E.M.Fraaije 1999 *Macromolecules 32: 646-656*