Computer simulation of complex fluids

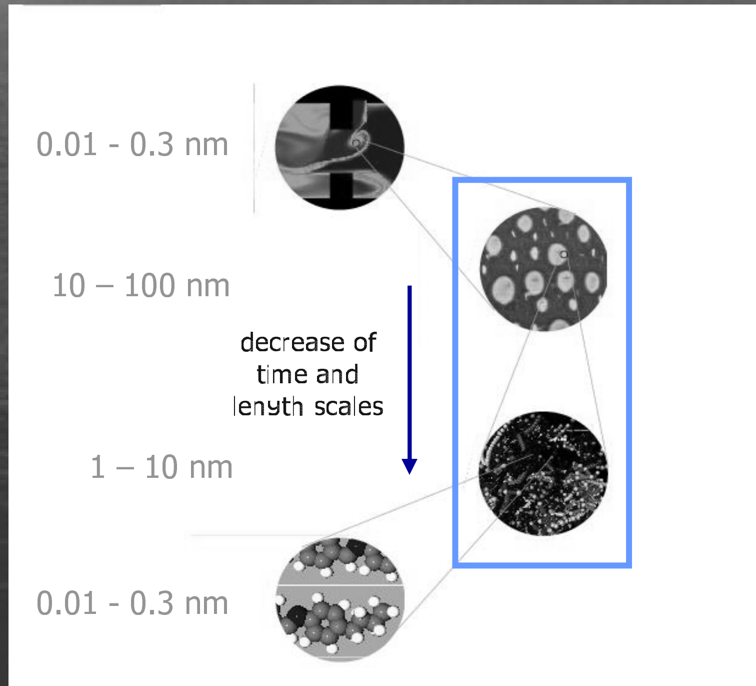
Materials Day 2003

Martin Kröger

ETH Materials

basic consideration

- Time and length scales of relevance for material design are out of reach for first principles calculations

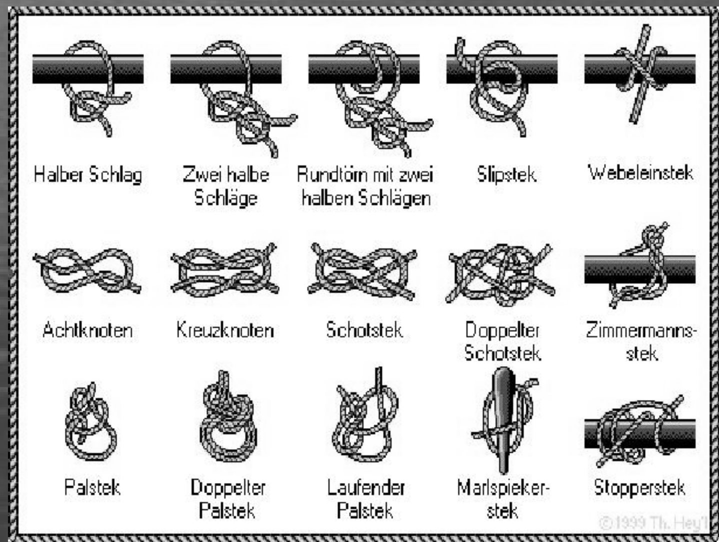


ETH Bulletin 274 (1999) 16-19

mesoscopic modelling
multiscale modelling

simplifying feature

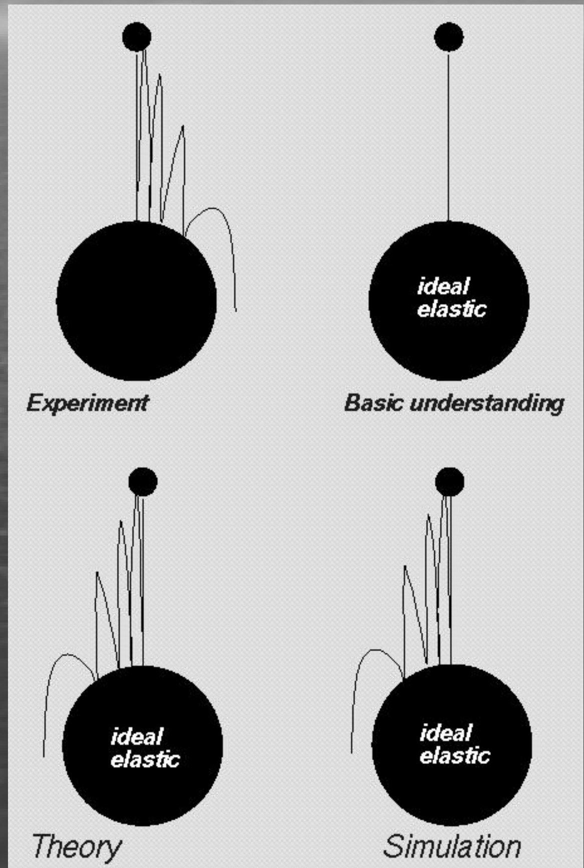
- Material properties are insensitive to chemical details



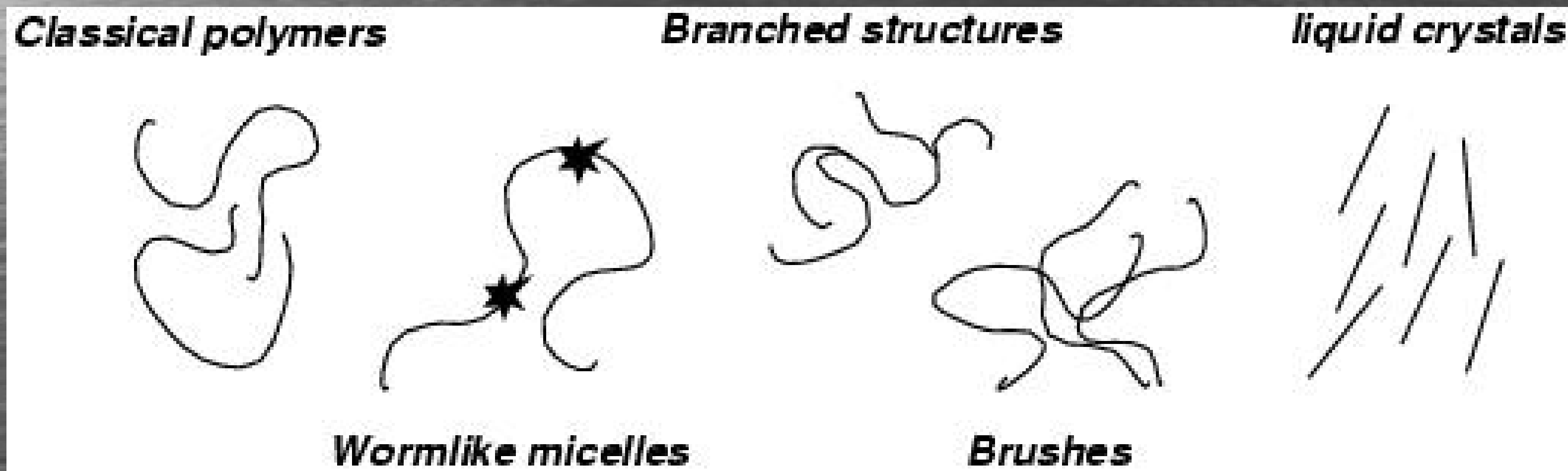
consider:
polymeric shapes

- Chemistry is responsible for important prefactors

Models should be simple ...

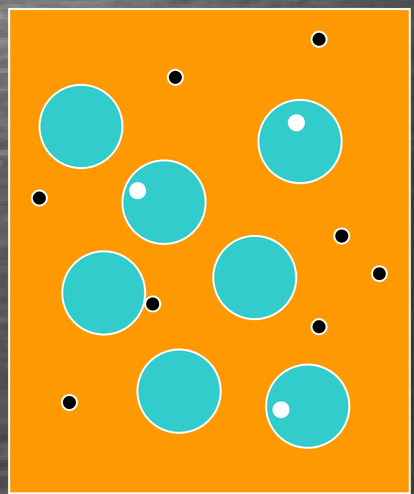


.. but not simpler

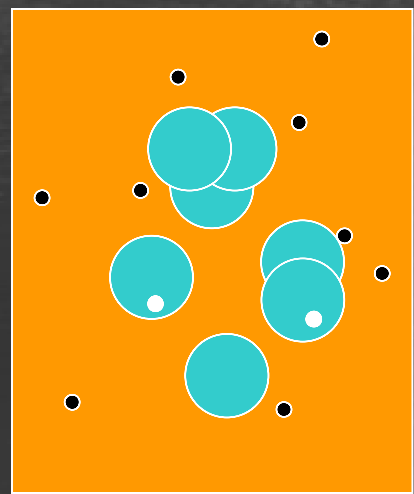


Equilibrium Monte Carlo

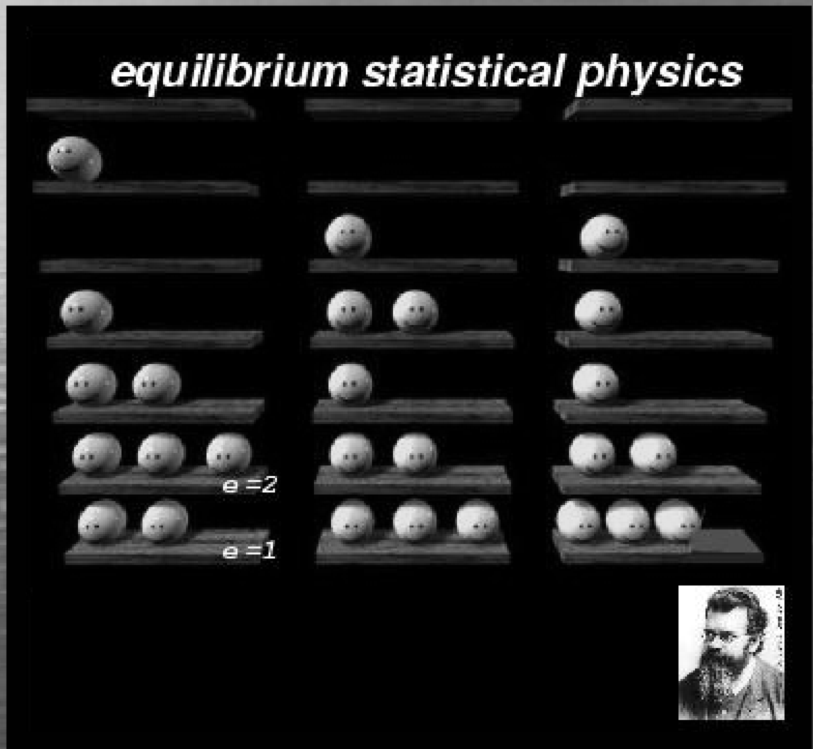
- Efficient calculation of high dim. Integrals
- Realization of ensembles
- Using random numbers

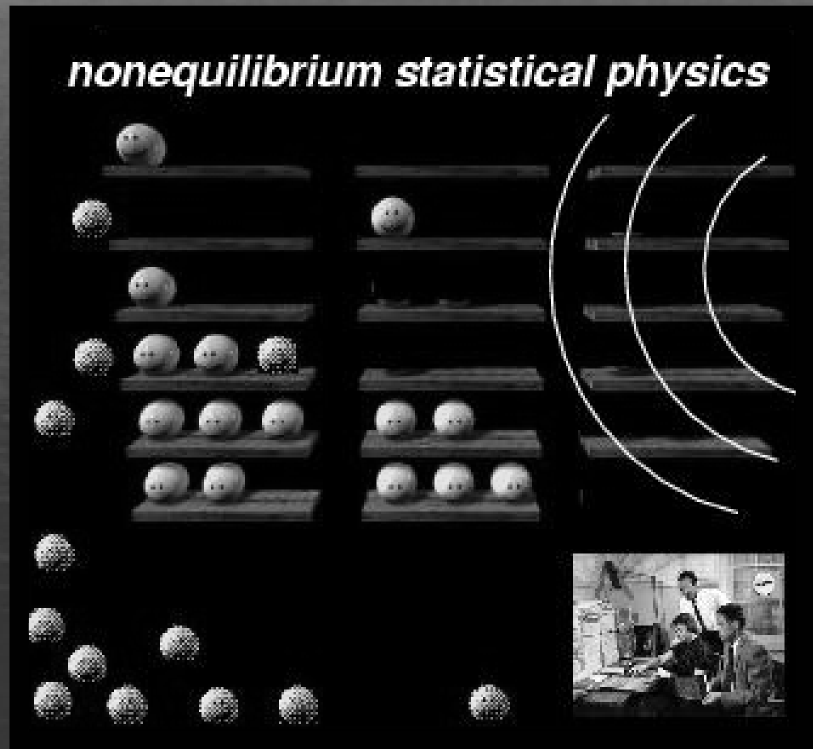


occupied
volume
ratio: 3/2



Nonequilibrium systems – concurrent mechanisms





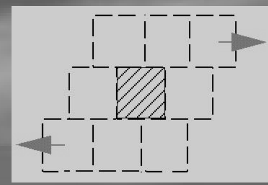
Outline

- Simple models for complex fluids
  - to be checked against experiment
  - being consistent with current theoretical frameworks
- FENE-chain models for polymers
- Stochastic differential equations
- GENERIC

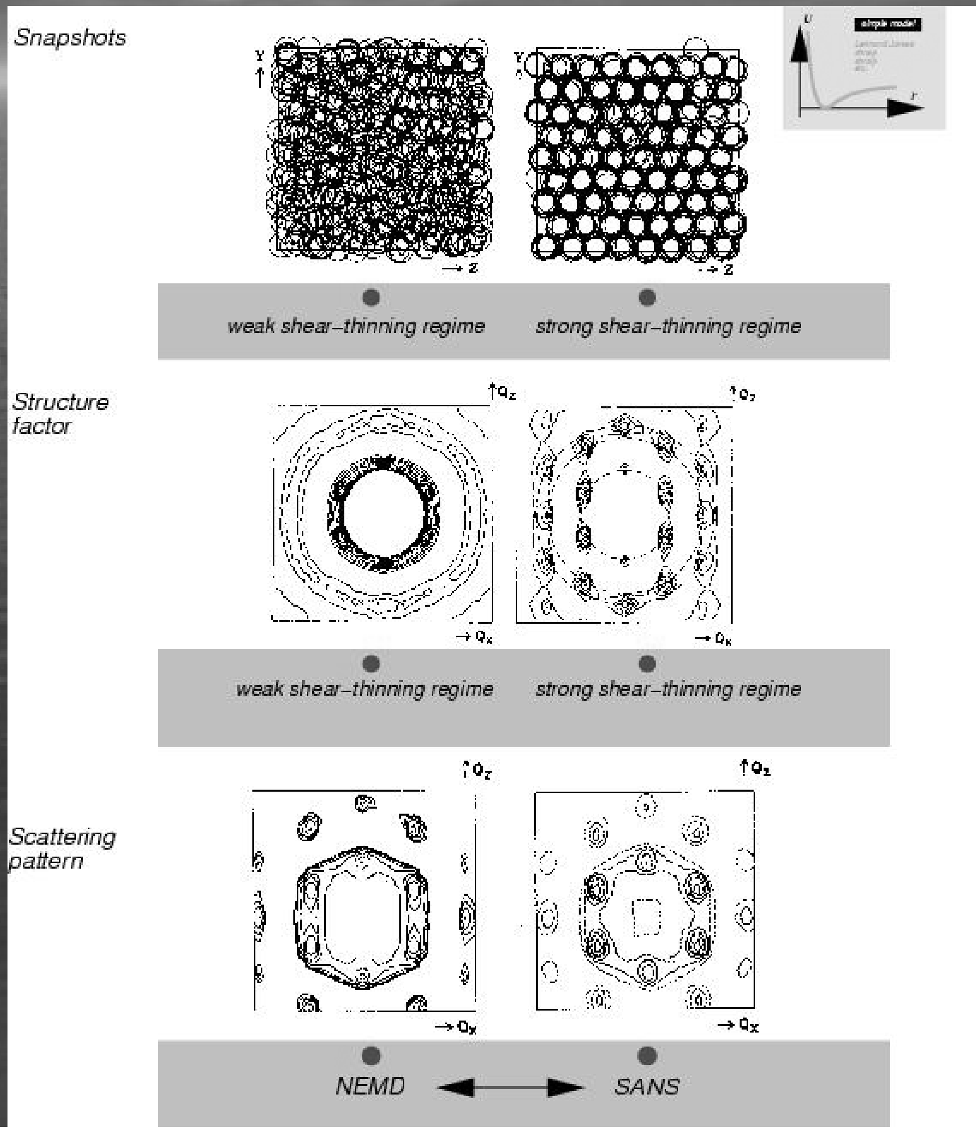
ETH Beowulf

Colloidal Latex suspensions

subjected to a shear flow



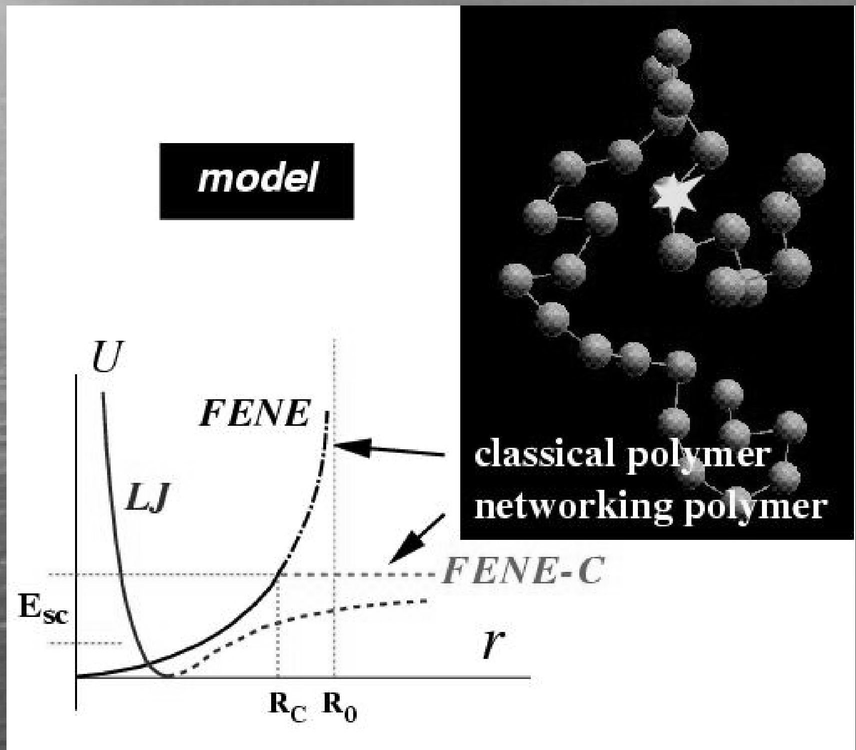
- shear thickening
- string formation
- ordering transition

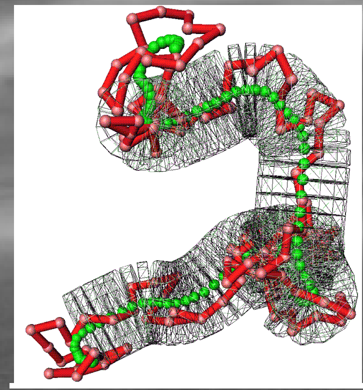


Physica A 240 (1997) 126-144

J. Rheology 36 (1992) 742-787

FENE chain models for polymers



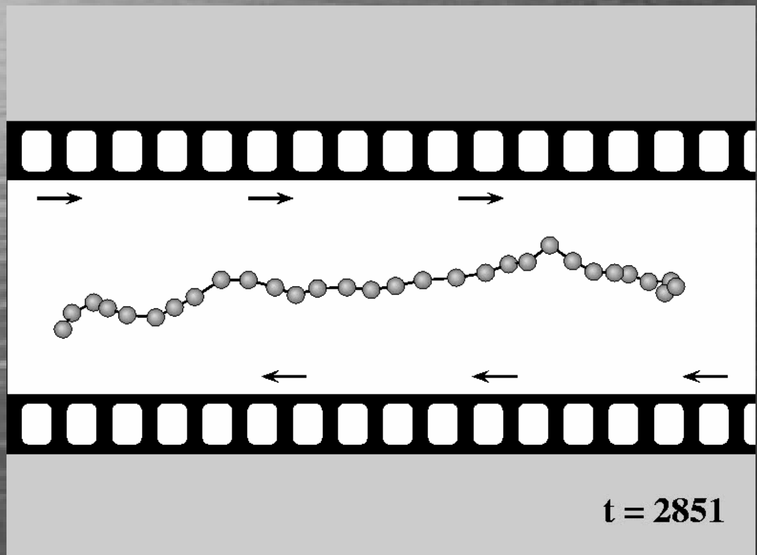


Phenomena

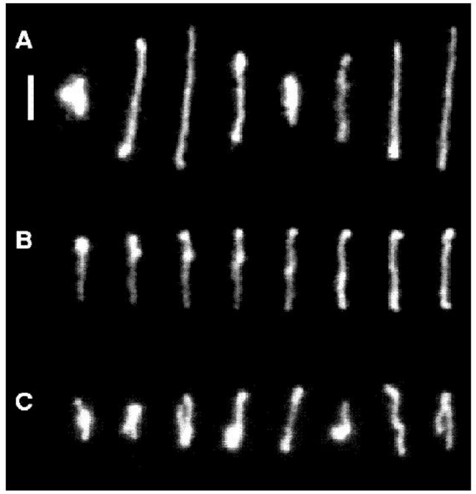
- Flow birefringence, scattering patterns
- Shear thinning, anisotropic viscosities, drag reduction
- Viscoplastic and –elastic behaviors
- Dynamics of single molecules, rheochaos
- Friction on the nanometer scale

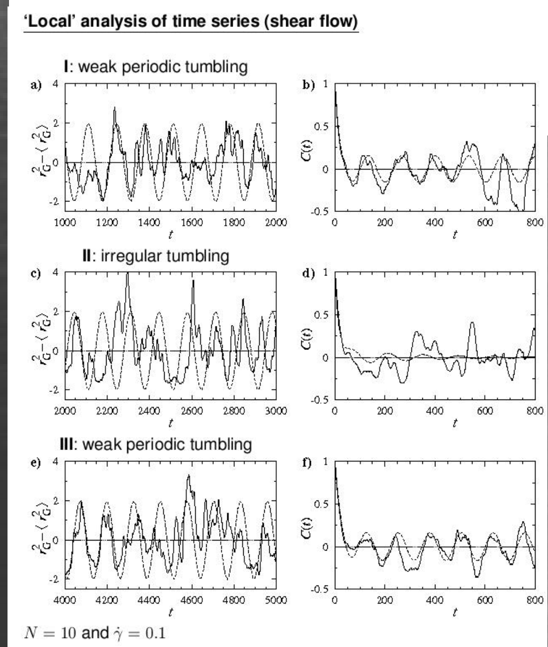
Dynamics of single molecules

Hydrodynamic drag forces overcome entropic forces which tend to coil the chain



Macromolecules 32 (1999) 5660-5672

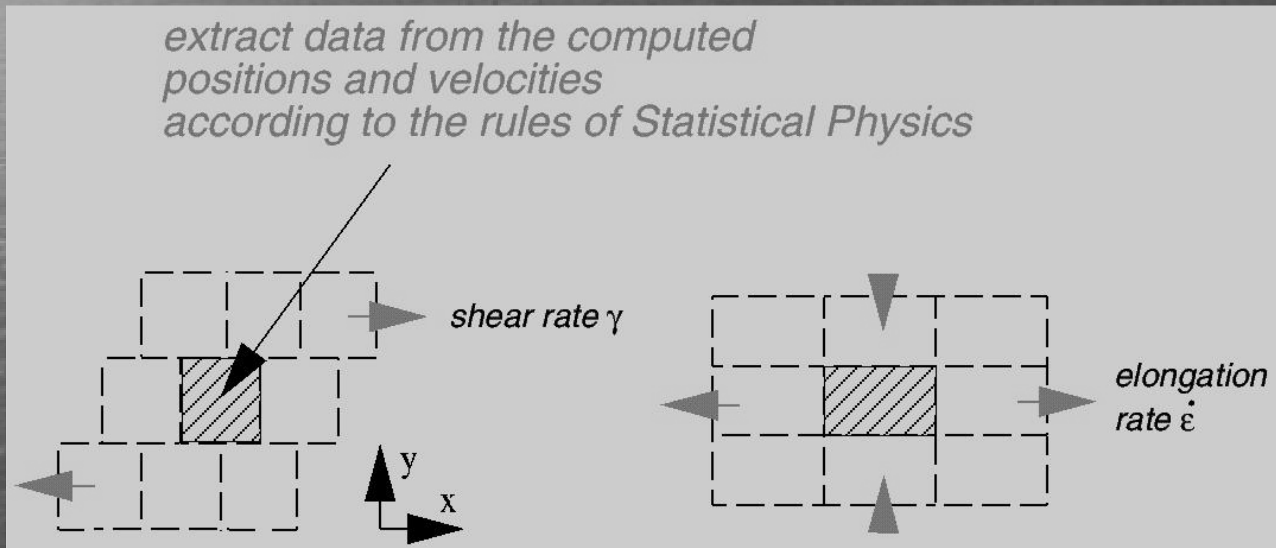




Unstable and tumbling orbits are observed

NonEquilibrium Molecular Dynamics (NEMD)

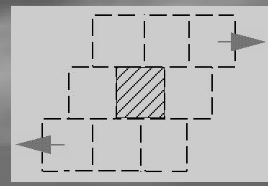
a many particle simulation method



J. Rheology 37 (1993) 1057

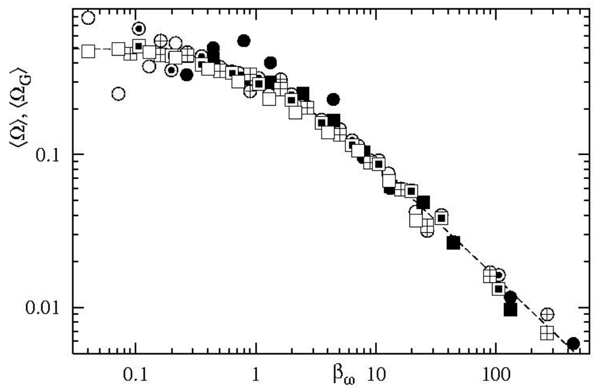
dynamics & structure

subjected to a shear flow



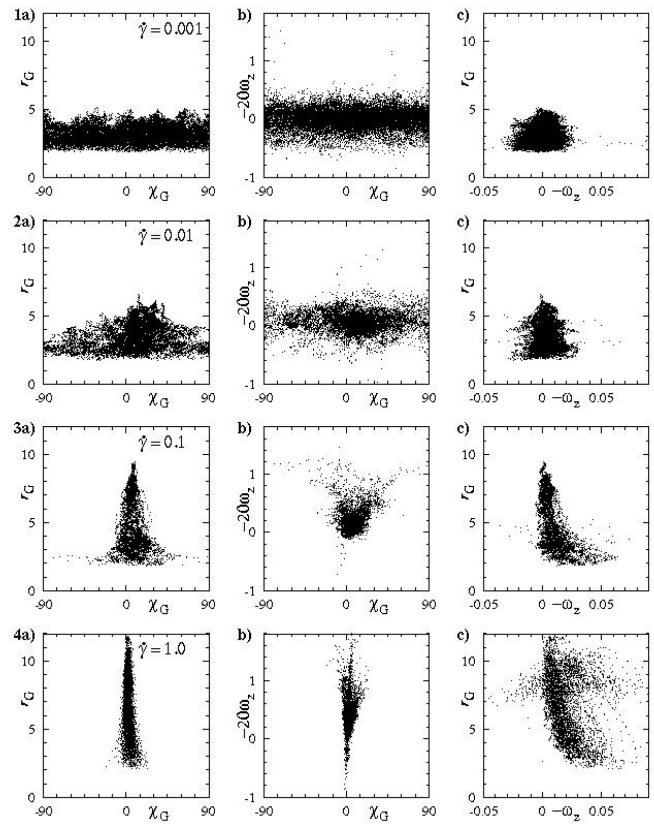
of single molecules

Angular momentum optic rule $\langle\Omega\rangle \stackrel{?}{=} \langle\Omega_G\rangle$



power law: $\mu = -0.75$

Cross correlations (shear flow)



Improving on basic rules for complex behavior

Macromolecules 35 (2002) 8621-8630

Universal results

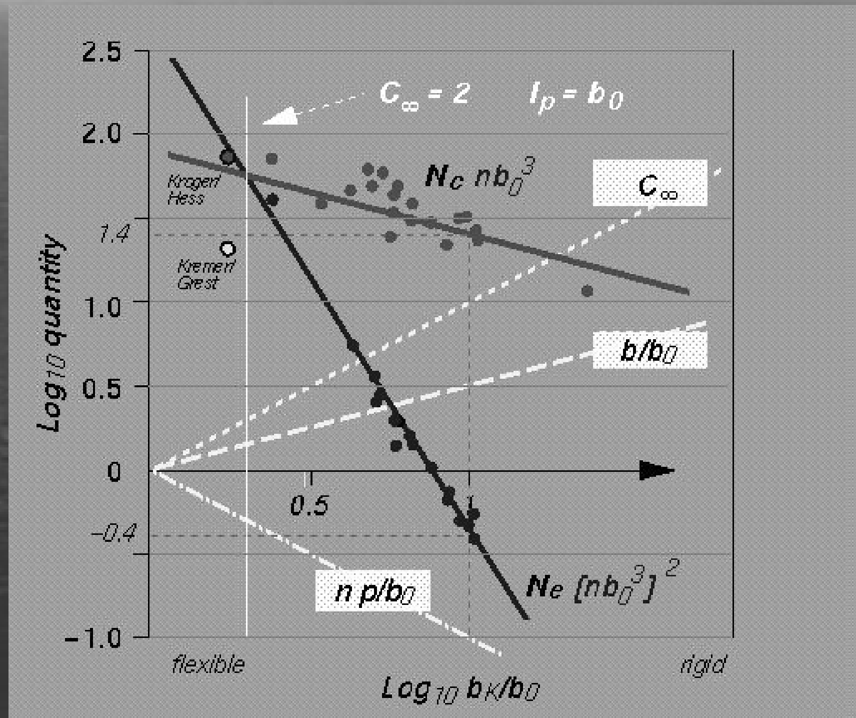
for polymer melts

Phys. Rev. Lett. 85 (2000) 1128-1131.

for polymer solutions

J. Chem. Phys. 113 (2000) 4767

obtained via NEMD / NEBD



reduced critical molecular weights vs stiffness of linear polymers

Substances

- Polymer solutions and melts
- Self-organizing, amphiphilic systems, micelles
- Dipolar, magneto- and electrorheological fluids
- Polymeric networks
- Solids, metals, foams

Methods from Statistical Physics

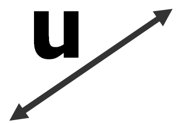
- Nonequilibrium Molecular and Brownian dynamics
- Embedded atoms
- Smooth particle dynamics
- GENERIC Monte Carlo
- Structure recognition

NE Brownian dynamics (NEBD) Fokker-Planck / relaxation equations

describing molecular orientations

Modeling the motion of a system of rods

Nonlinear relaxation equation for molecular alignment



$$\mathbf{a} = \langle \overline{\mathbf{u}\,\mathbf{u}} \rangle\,, \quad a_{\mu\nu} = \langle \overline{u_\mu u_\nu} \rangle$$

$$\tau_a \frac{\partial a_{\mu\nu}}{\partial t} + \zeta^2 \triangle a_{\mu\nu} + \Phi_{\mu\nu}(\mathbf{a}) + F_{\mu\nu}(\mathbf{a}) = 0$$

damping term — *dynamics thermodynamics*

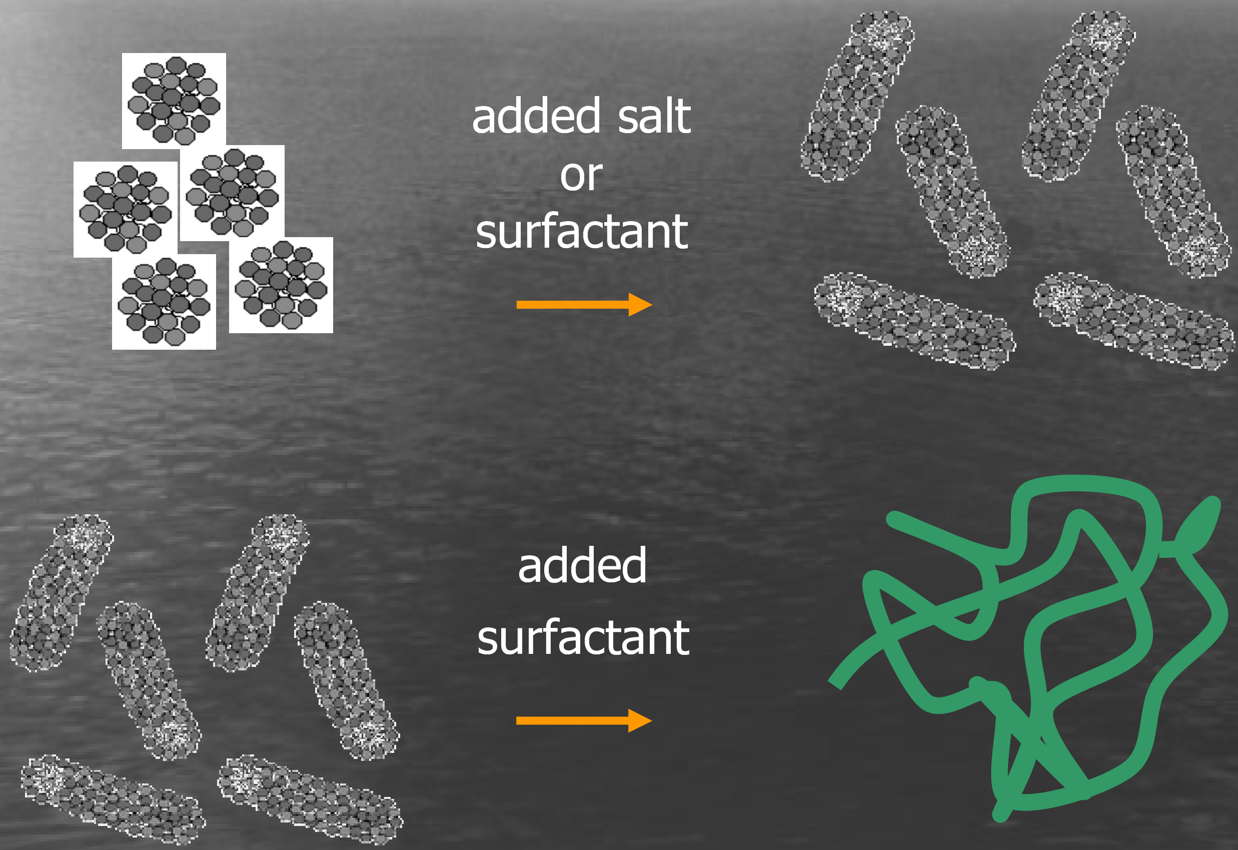
Frank elasticity

derivative of a Landau–de Gennes potential — *phase transitions*

external fields — *field–induced phase transitions*, *field–induced alignment*, *birefringence stress tensor*

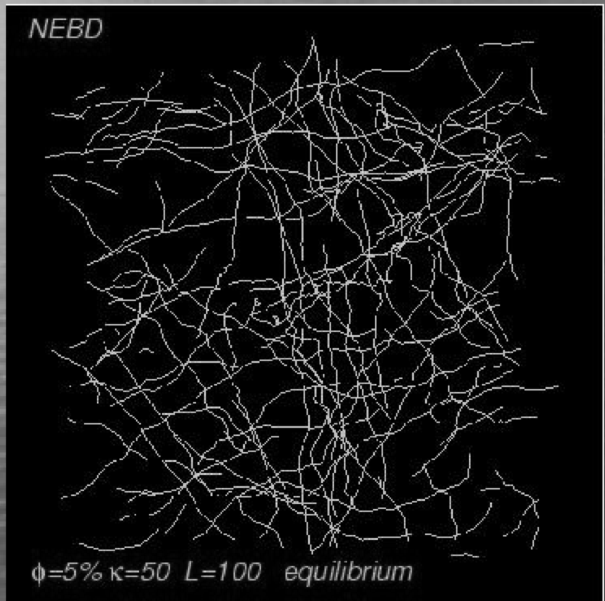
1/26/2003

Amphiphilic systems



Actin filaments, liquid crystals, semiflexible polymers

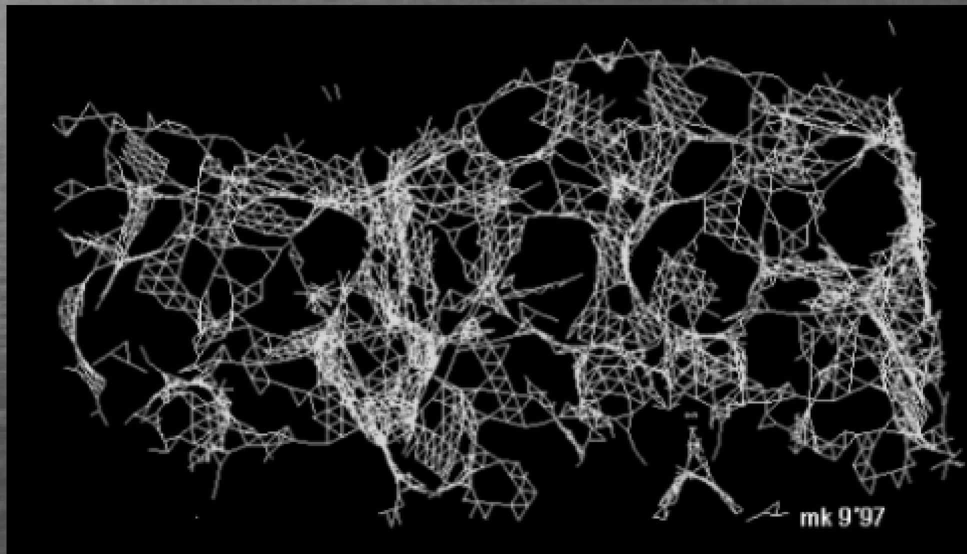
Part of the human sceleton



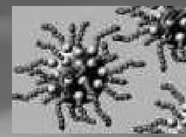
Phys. Rep. (2003) to appear

Polymeric branched networks

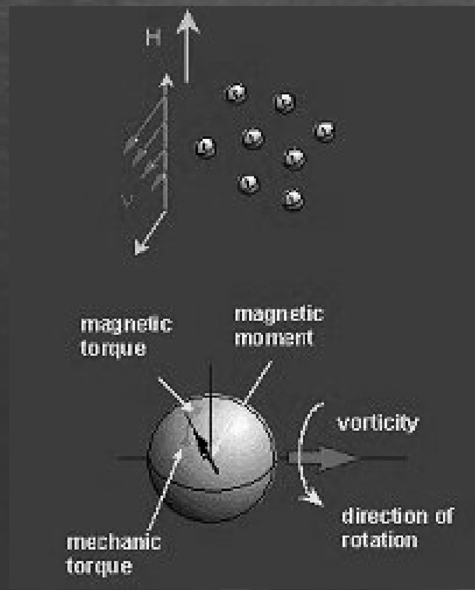
- Viscoelasticity, tracer diffusion

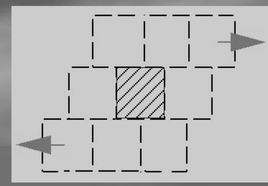


Ferro/magnetorheological fluids



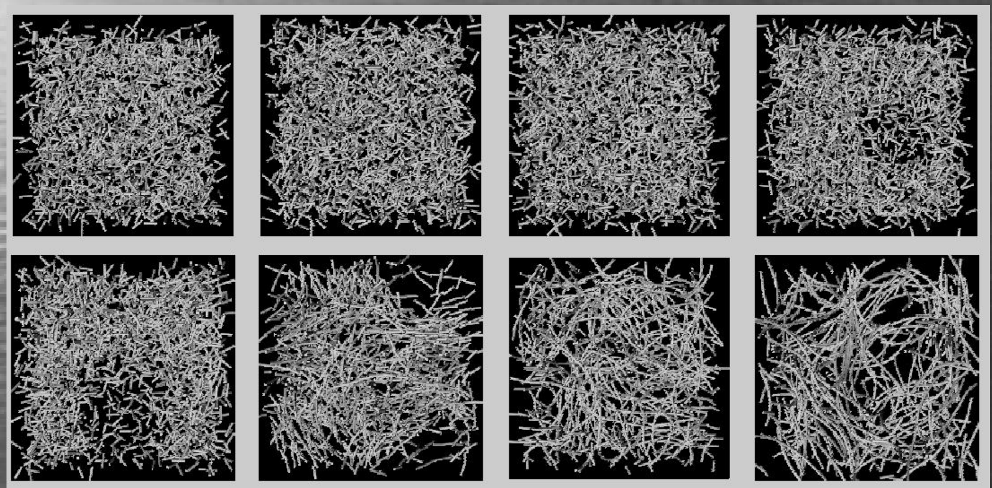
- Liquid with a solid touch
- Tune viscosity by magnetic field
- `Negative viscosity´effects





Ferro/magnetorheological fluids

- Formation of chains and clusters
- Antiferromagnetic phases

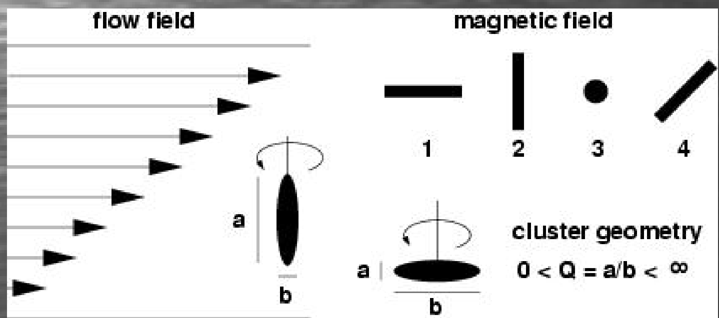


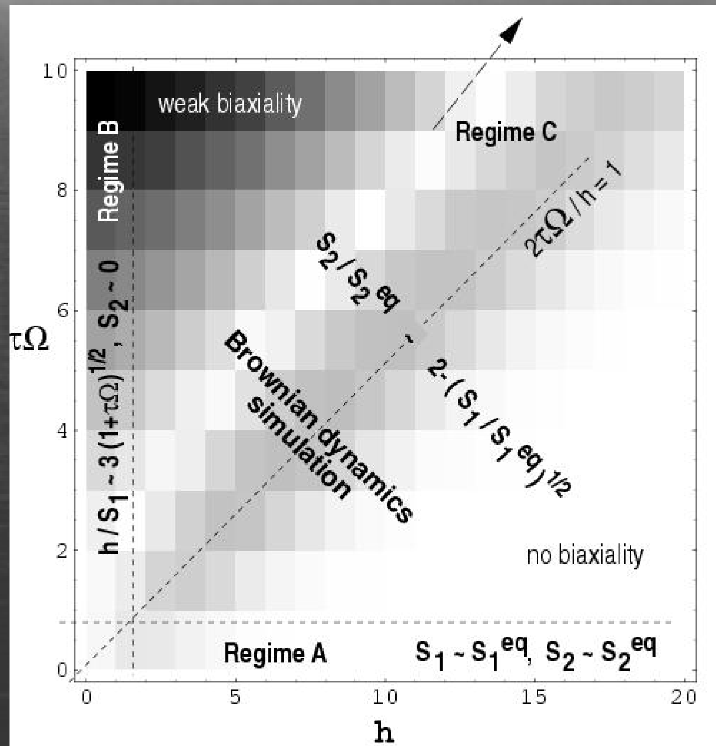
J. Chem. Phys. 116 (2002) 9078-9088
Phys. Rev. E 66 (2002) 021501

Observation of symmetries in sheared ferrofluids

Biaxiality vs
magnetic field (horizontal)
and shear rate (vertical)

Observed via NEBD,
implemented into kinetic theory

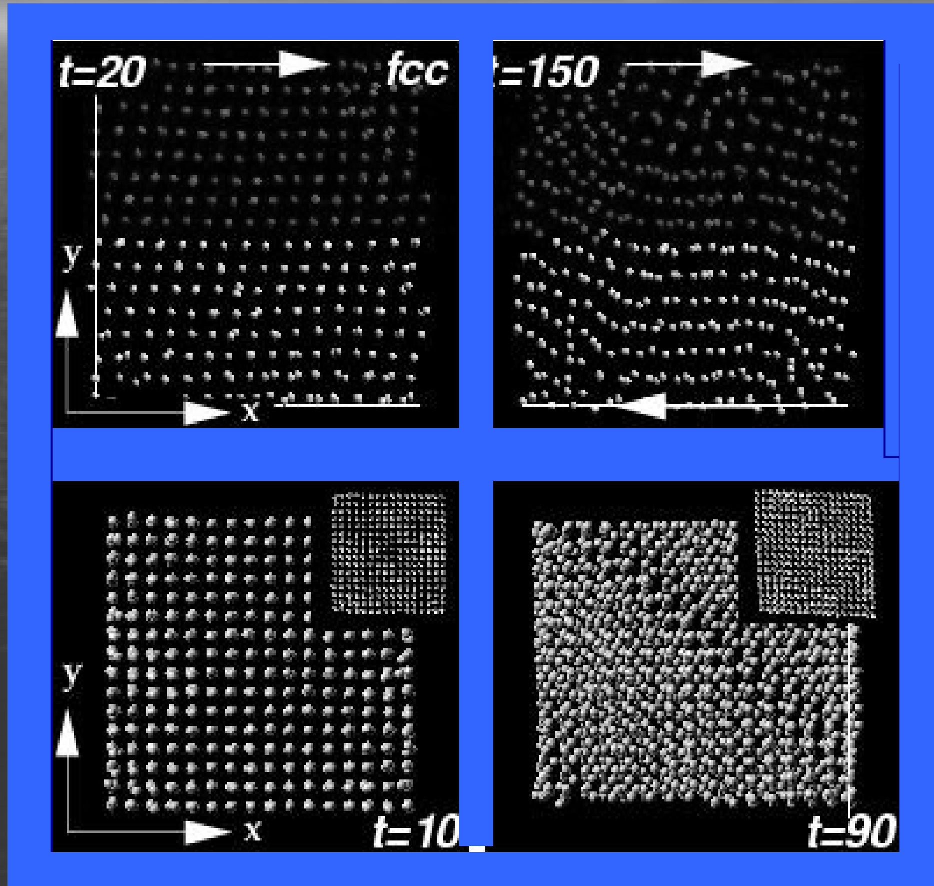




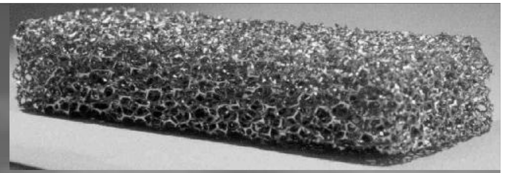
J. Chem. Phys. 116 (2002) 9078-9088

Embedded atoms method for metals

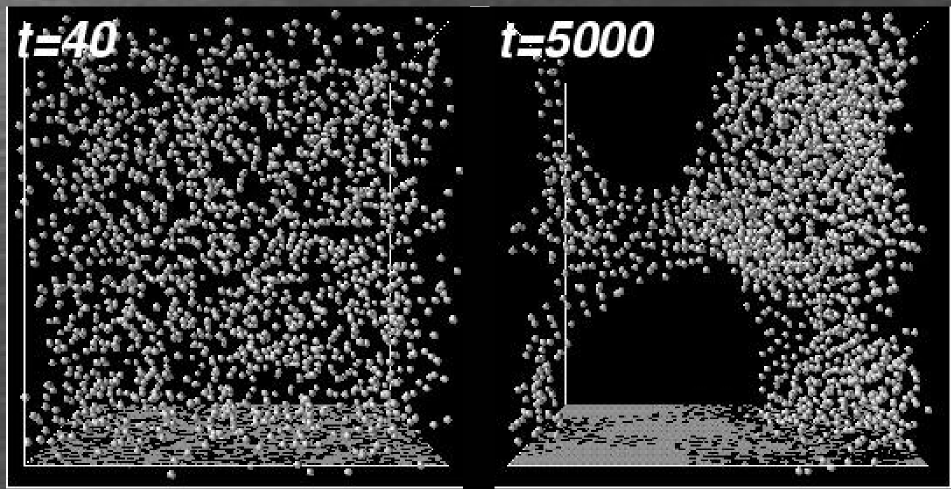
- Sold friction
- Single asperites
- Instabilities
- Friction reduction
- Polymer coating



Metal sponges and foams



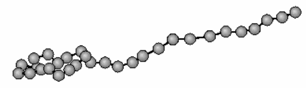
- Mismatch between local and global embedding densities
- Self-healing surfaces, new materials



Multiscale Modeling Simul. 1 (2003) in press

mesoscopic modeling

- These types of models allow to
  - resolve microscopic origins for material behavior
    - dynamics of molecules, flow-alignment, entanglements …
  - test the validity of analytic theories and their assumptions
    - symmetries …
  - predict material properties on large scales
    - rheology, tribology, friction, birefringence, diffusion …
  - handle multi-scale phenomena in cooperation



outlook

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- some conceptual and computational challenges
  - Hybrid methods
  - Closure relationships in kinetic theory
  - Reduced description, relevant variables
  - Implementation of nonequilibrium ensembles and identification of parameters through GENERIC