Scale Bridging Simulations of Soft Matter

College Park 17-04-2007

K. Kremer

Max Planck Institute for Polymer Research, Mainz

Max-Planck Institute for Polymer Research Mainz

THEORY GROUP

Central Topics of the Theory Group

⇒Method Development,
Scientific Open Source Software (ESPResSo)

⇒Multiscale Modeling

⇒Analytic Theory of disordered Systems
⇒Long Range Interactions, Hydrodynamics
⇒Charged Systems, Polyelectrolytes, Gels
⇒Membranes….Biophysics
⇒Complex Fluids
⇒Computational Chemistry of Solvent-Solute Systems
⇒Melts, Networks – Relaxation, NEMD …
⇒Soft Matter and Electronic Properties

COWORKERS:

L. Delle Site
N. Van der Vegt
D. Andrienko,
M. Praprotnik, B. Hess, X. Zhou (Los Alamaos Nat. Lab.)
W. Schravendijk, V. Harmandaris
D. Reith (Fraunhofer Institute, Bonn)

N. Adhikari (Univ. Katmandu)
F. Müller-Plathe (TU Darmstadt)
R. Everears (ENS Lyon)
O. Hahn (Würzburger Druckmaschinen)
D. Mooney (Univ. College Dublin)
H. Schmitz (Bayer AG)
W. Tschöp (DG Bank)
S. Leon (UPM Madrid)
C. F. Abrams (Drexel)
H. J. Limbach (Nestle)

BMBF Center for Materials Simulation, EU FP6,
Bayer, BASF, DSM, Rhodia, Freudenberg, Nestle

- **Structure Property Relations for Soft Matter => Linking Scales**
  - **Interplay universal - system specific aspects**
  - **Truly quantitative information**

Soft Matter??

Thermal energy of particles/ per degree of freedom

E=kT

$\Rightarrow$ Room temperature 300K:

$$E = 1.38 \cdot 10^{-23}\ J/K \cdot 300\ K$$

$$\approx 4.1 \cdot 10^{-21}\ J = kT$$

Chemical Bond $E \approx 3 \cdot 10^{-19}\ J \approx 80\ kT$

Hydrogen Bond $E \approx 6\,kT - 10\ kT$

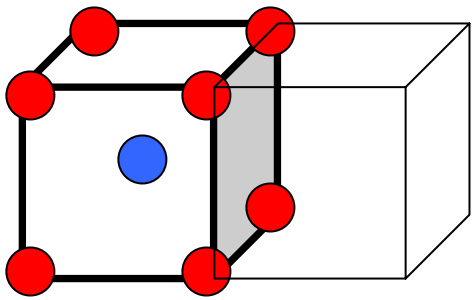
Soft Matter: Thermal Energy dominates properties

Soft Matter I: Energy Density

"Normal" crystal: NN Energy $E \approx 1..2\ kT$ to $\leq 100kT$

noble gas … covalent x-tal

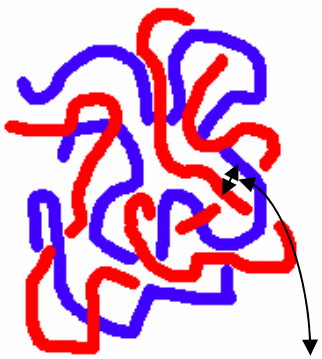
# of Neighbors ≈ 10



< 1 – 2 Å >

$E/V \approx 5 .. 100\ kT/Å^3$

Polymer Glas (Plastics,Rubber):



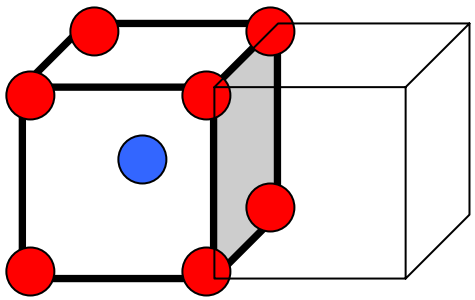
strand-strand distance 3-6 Å

$E/V \approx 10^{-2}...10^{-1} kT/Å^3$

100 to 10000 times "softer" than "normal" crystals

Soft Matter I: Elastic Constant *E*

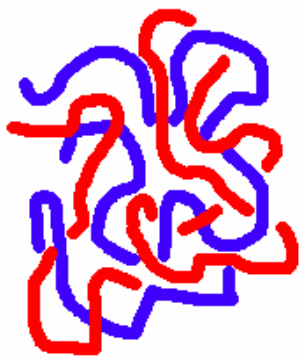
"Normal" crystal



< 1 – 2 Å >

$$E \approx 100GPa = 10^{11} Nm/m^3$$
$$\approx 25kT / \mathring{A}^3$$

Polymer Glas (Plastics,Rubber):



$$E \approx 10..10^3 MPa = 10^7..10^9 Nm/m^3$$
$$\approx 0.0025..0.25kT / \mathring{A}^3$$

100 to 10000 times "softer" than "normal" crystals

Soft Matter

"Soft" means:

- **low energy density**
- **nanoscopic length scales (10Å …1000Å)**
- **large fluctuations**
- **<u>thermal energy k_BT</u>**

<u>relevant energy scale</u>

100 to 100000 times softer than normal crystals

Energy Scale kT for T=300K

$$E = 1.38 \cdot 10^{-23}\ J/K \cdot 300\ K$$

$$kT \approx 4.1 \cdot 10^{-21}\ J$$

$$kT \approx 2.5 \cdot 10^{-2}\ eV$$

Electronic structure, CPMD

$$kT \approx 9.5 \cdot 10^{-4}\ E_H$$

Quantum Chemistry

$$kT \approx 4.1\ pNnm$$

Biophysics Membranes, AFM

$$kT \Rightarrow 200\ cm^{-1}$$

Spectroscopy

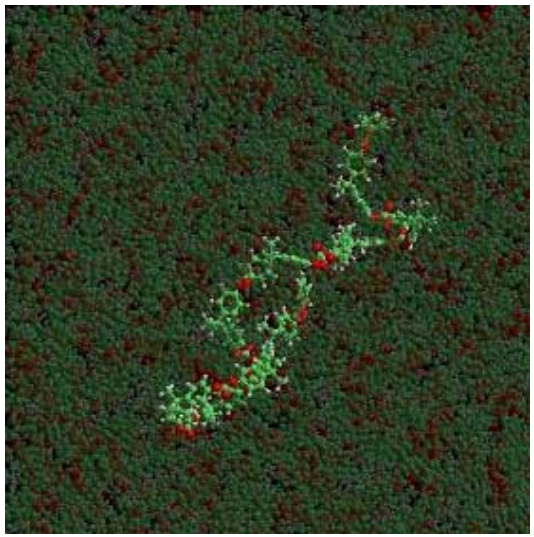
$$kT \Rightarrow 0.6\ kcal/mol$$

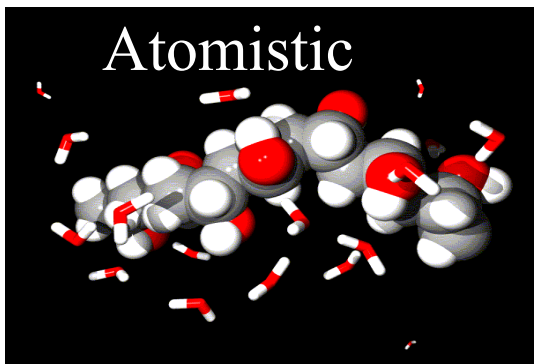
$$kT \Rightarrow 2.5\ kJ/mol$$

Polymers

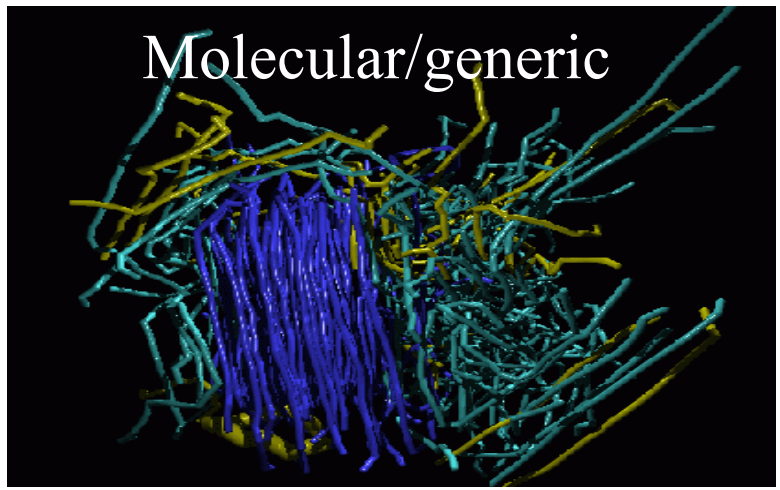
Structure Property Relations

...





versus

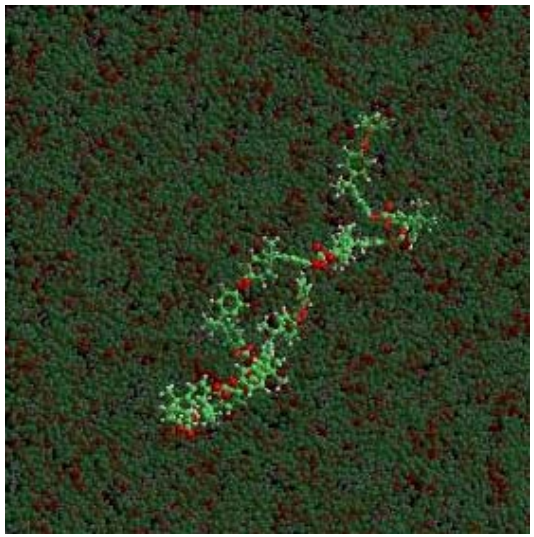


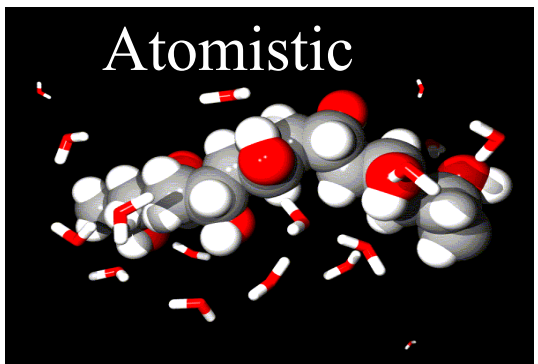
...

Polymers

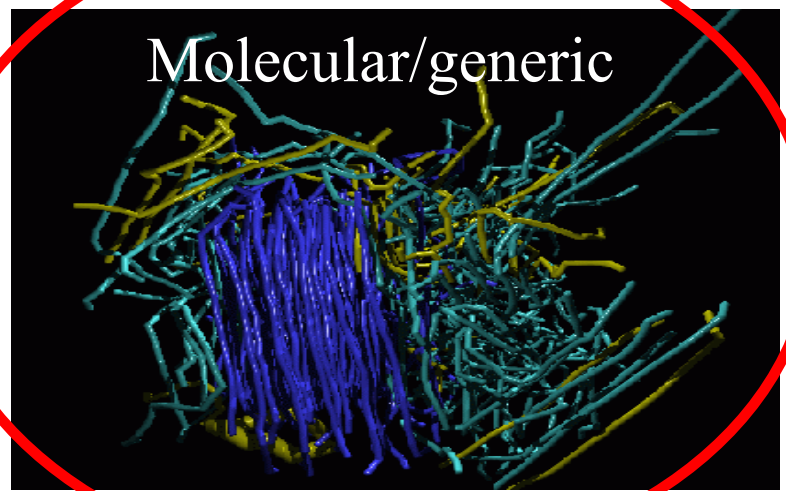
Structure Property Relations

...





versus

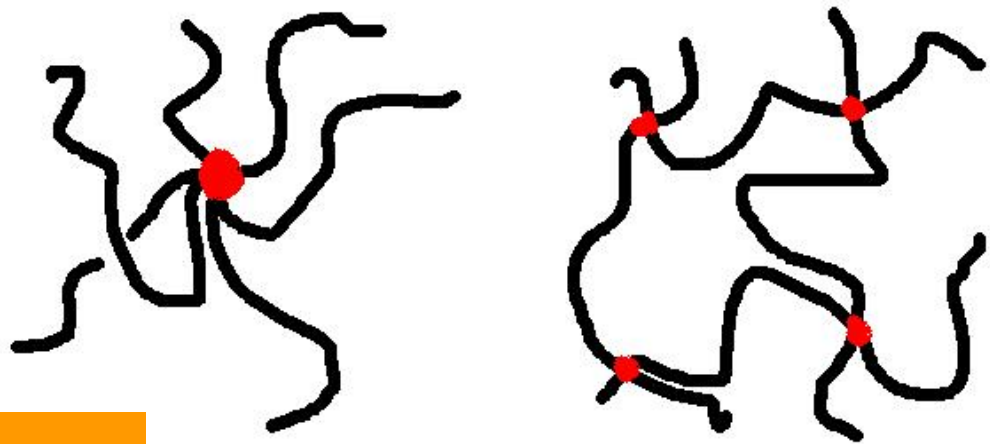


...

Architectures I:

Linear polymers:

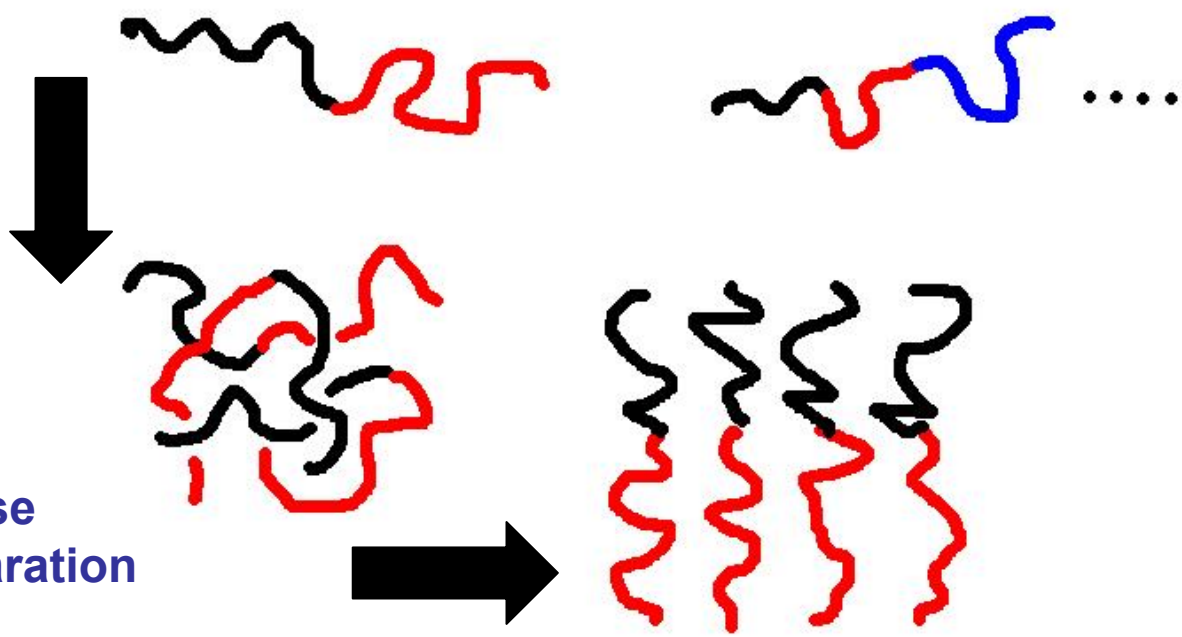
Branched polymers



Intramolecular entropy :
S = kT O(N)

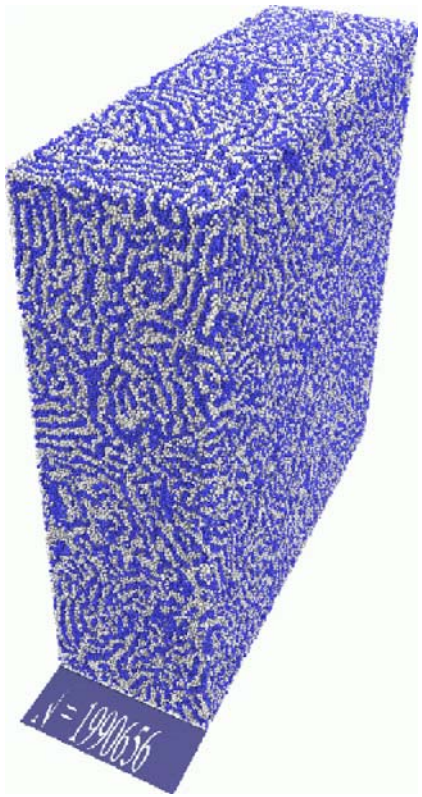
Architectures II:

Block Copolymers

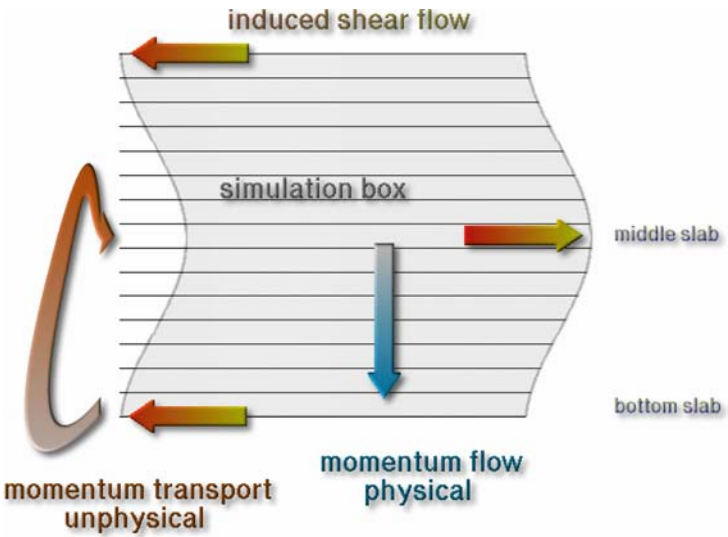


(Shearing) Lamellar Systems -Block Copolymers, Smectics, ...

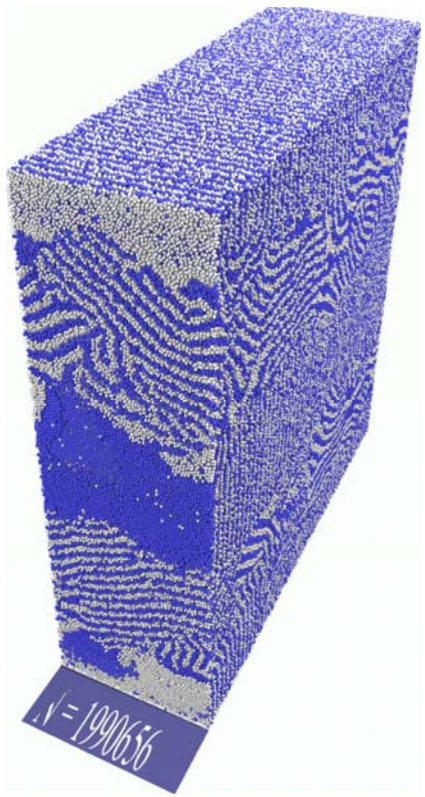
T. Soddemann, H. X. Guo, B. Dünweg, K. K.



Multidomain lamellar



Reverse NEMD Shear algorithm

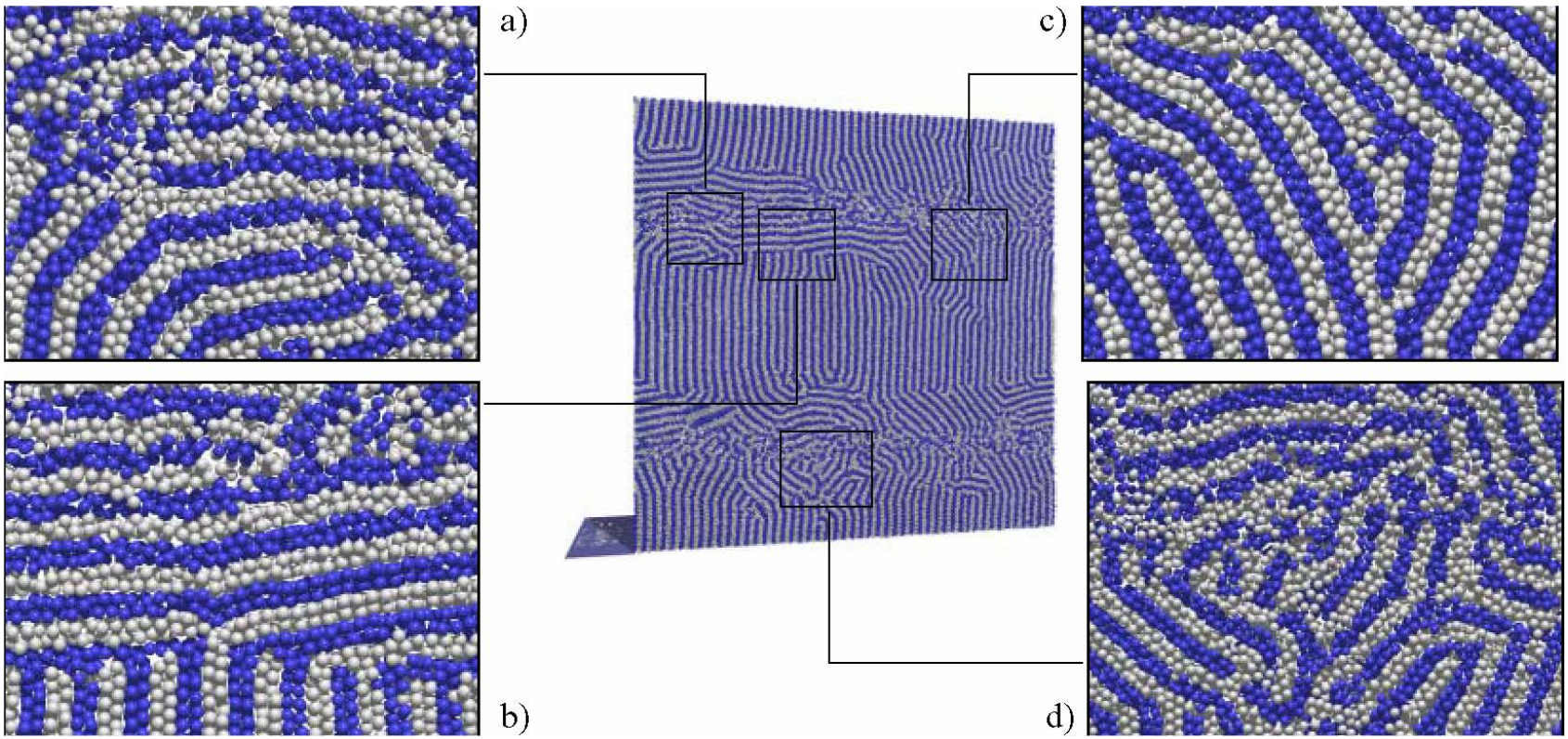


Partially ordered shear bands

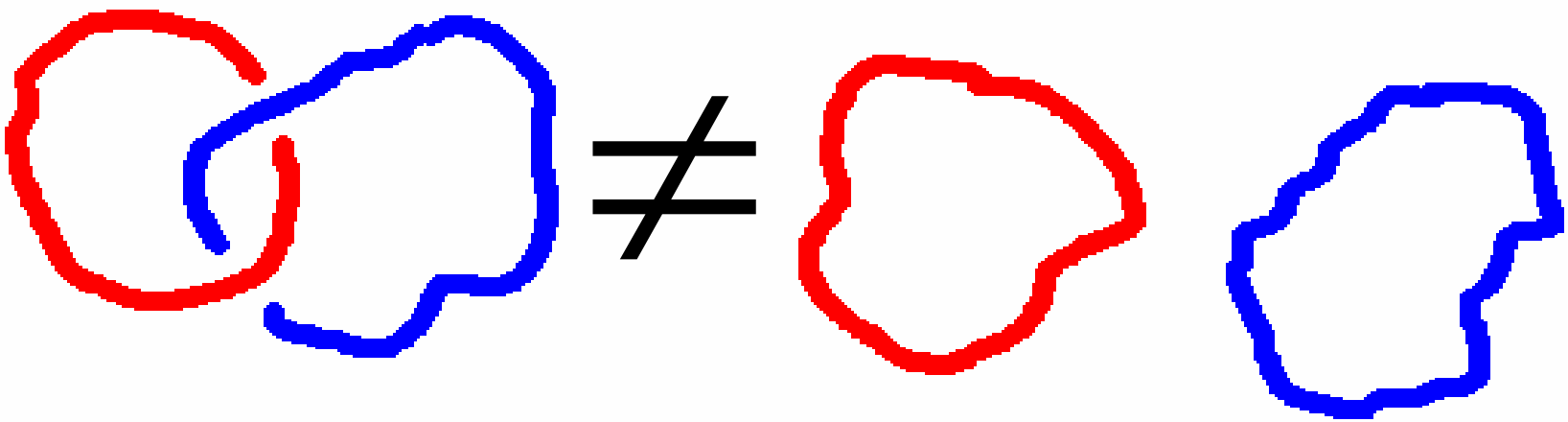
...

Shearing Lamellar Systems: Dimers

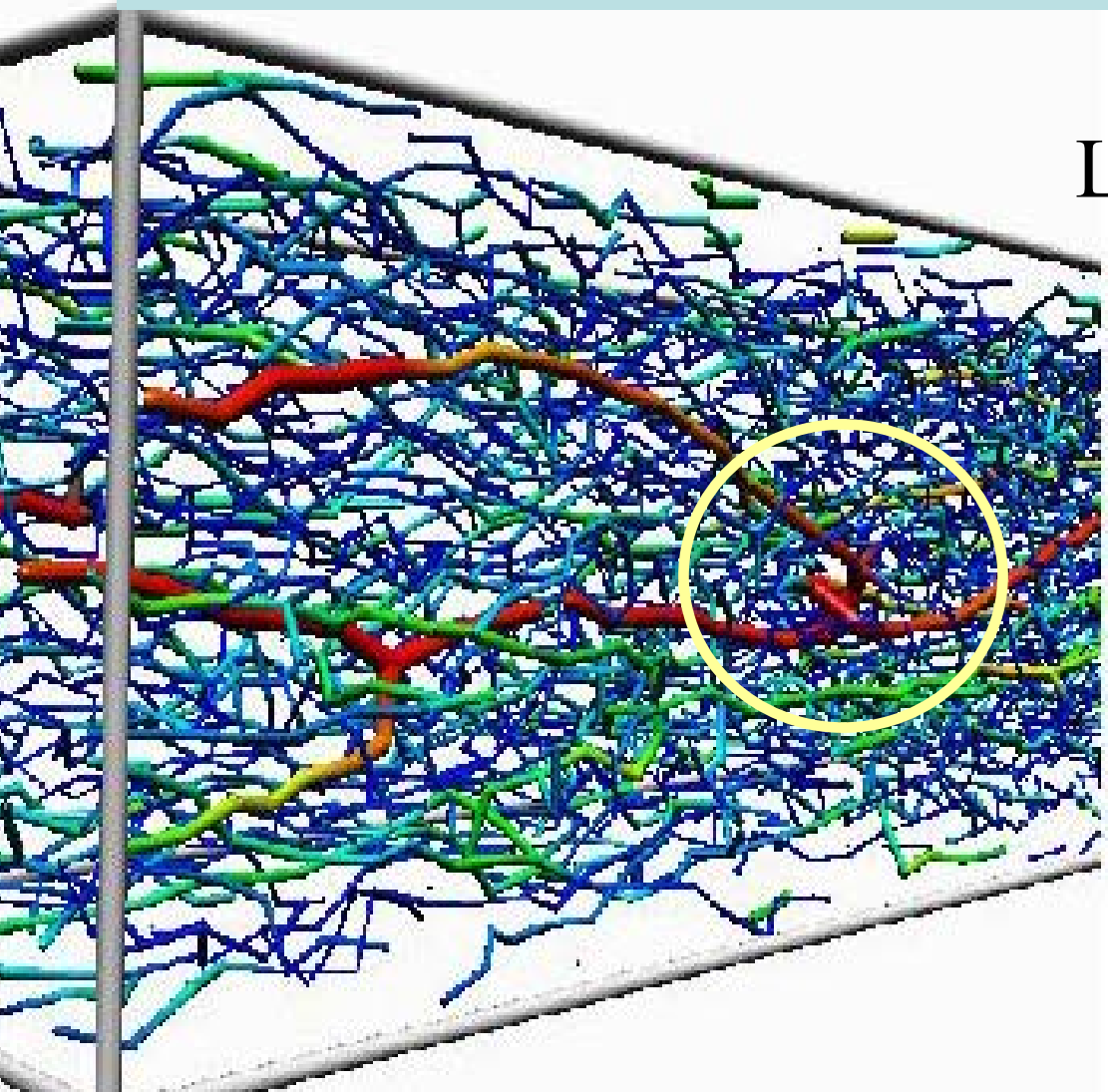
T. Soddemann, H. X. Guo, B. Dünweg, K. K.



Topology



Universal Confinement: Links &Stress



Local stress distribution

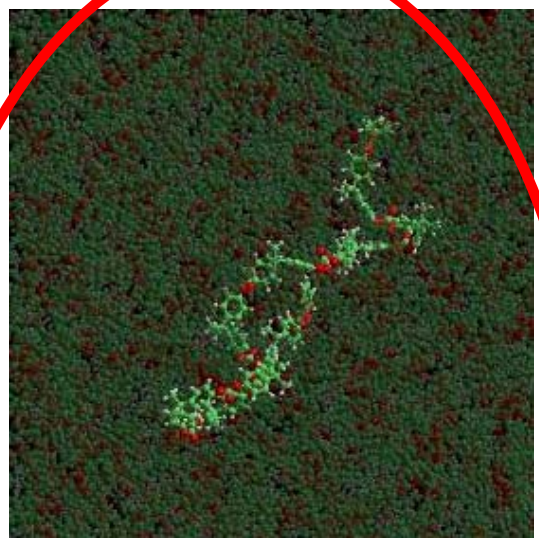
- SMALL STRESS
- **LARGE STRESS**

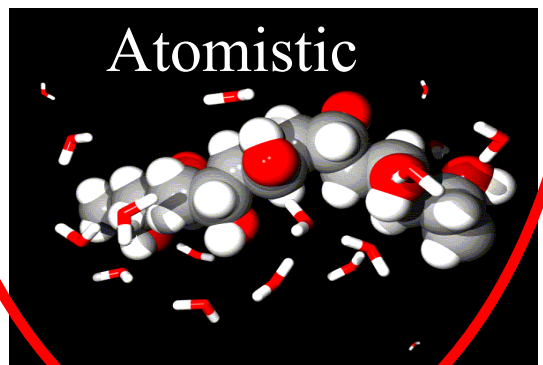
R Everaers&K. K (1996), RE (1999)

Polymers

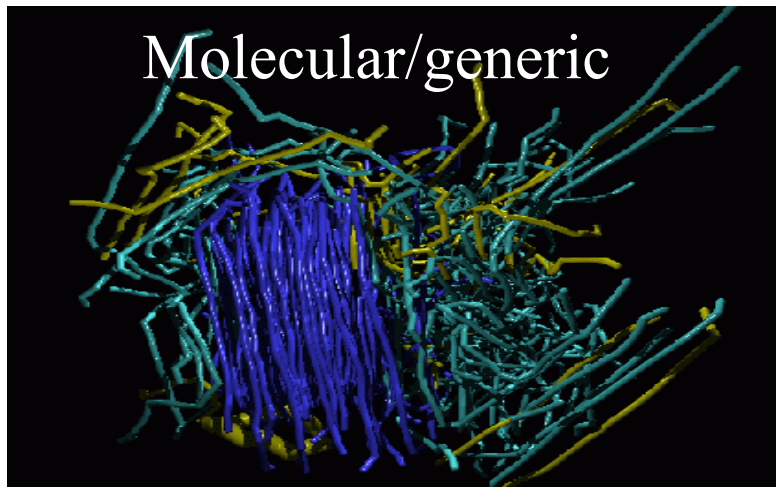
Structure Property Relations

...





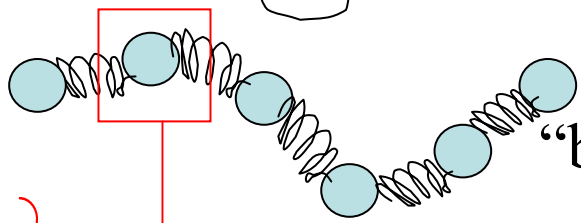
versus



...

Polymers
"oil soluble"

"path" in space

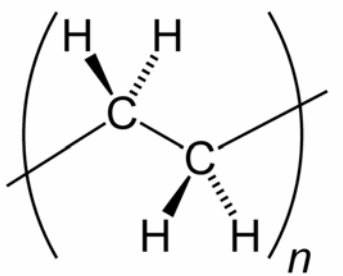


"bead spring" chain

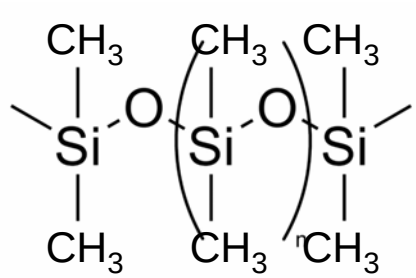
PE

$N_e \approx 100$

$M_e \approx 1400$



PDMS



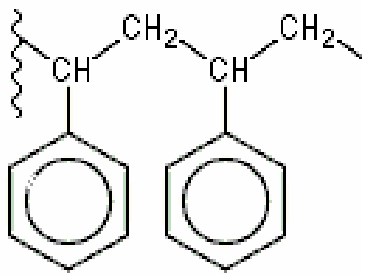
$M_e \approx 9000$

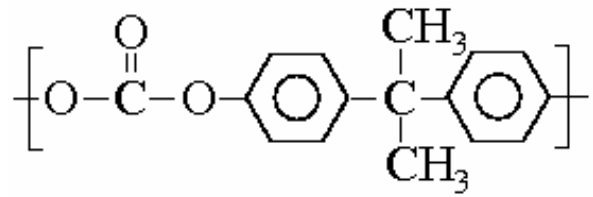
$N_e \approx 120$

PS

$M_e \approx 18000$

$N_e \approx 170$





BPAPC

$N_e \approx 5\text{-}6 \quad M_e \approx 1500$

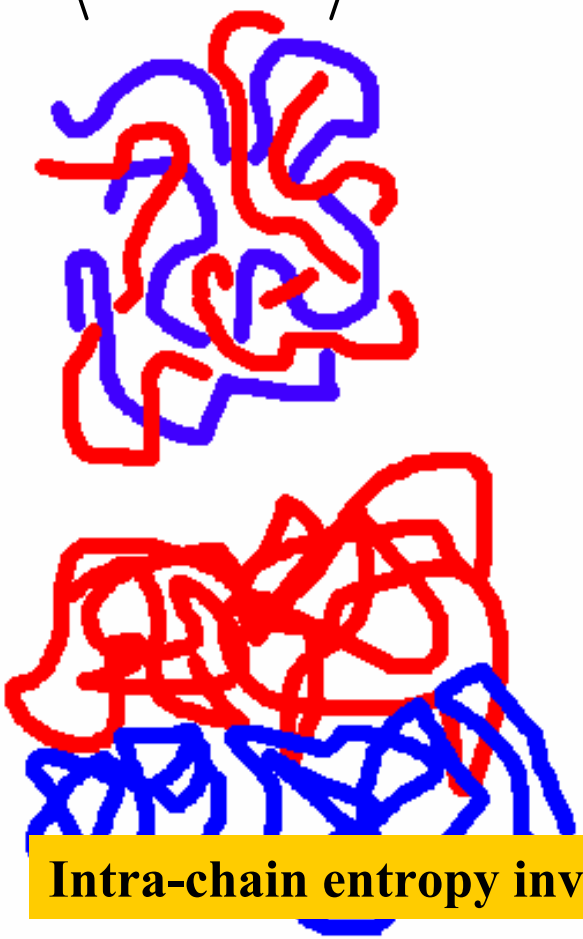
Glass transition temperature T_G of polymers

Polymer	T_G (K)
Polyethylene (LDPE)	150K
Polypropylene (PP, atactic)	250K
Poly(vinyl acetate) (PVAc)	300K
Polyethylene terephthalate (PET)	350K
Poly(vinyl alcohol) (PVA)	360K
Poly(vinyl chloride) (PVC)	355K
Polystyrene (PS)	370K
Polypropylene (PP, isotactic)	273K
Poly(3-hydroxybutyrate) (PHB)	273K
Poly(methylmethacrylate) (PMMA, atactic)	380K
Polycarbonate (BPA –PC)	420K
HIP(TMC)- Polycarbonate	$\approx$ 520K

Mixtures Polymer A, B

#*AA*, #*BB*, #*AB* contacts =*O(N)*

$$\left\langle R^2(N)\right\rangle \propto N$$



$$U_{AB} \propto N\varepsilon_{AB}$$

$$U_{AA} \approx U_{BB} \propto N\varepsilon$$

$$\varepsilon_{eff} = \varepsilon_{AB} - \varepsilon$$

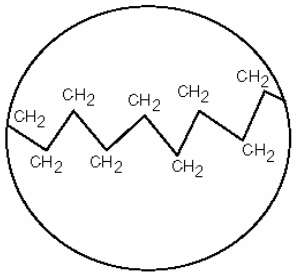
Phase separation, critical interaction

$$\varepsilon_{eff}^{c} = const \cdot N^{-1}$$

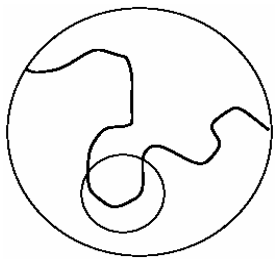
"chemistry" **"generic"**

Intra-chain entropy invariant => small energy differences => phase separation

Example Viscosity η of a polymer melt (extrusion processes ....)



↕



Microscopic — **materials/ chemistry specific Prefactor**

$L \cong 1Å - 3Å$

$T \cong 10^{-13}$ sec

(e.g. function of T_G, glass transition)

$\eta = A\, M^X$

"Energy dominated"

Mesoscopic — **generic/universal Properties**

$L \cong 10Å - 50Å$

$T \cong 10^{-8} - 10^{-4}$ sec

$\eta = A\, M^X$ $\quad X = 3.4$

M molecular weight

"Entropy dominated"

$\eta = A\, M^X$

varies for many decades

varies for many decades

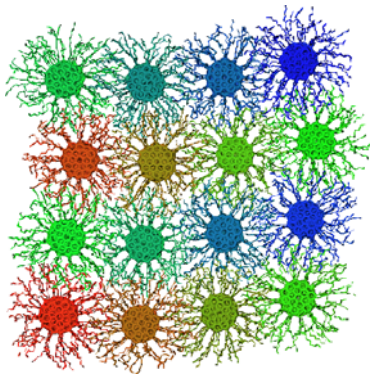
e.g.: M → 2M $\quad \eta(2M) \approx 10\eta(M)$

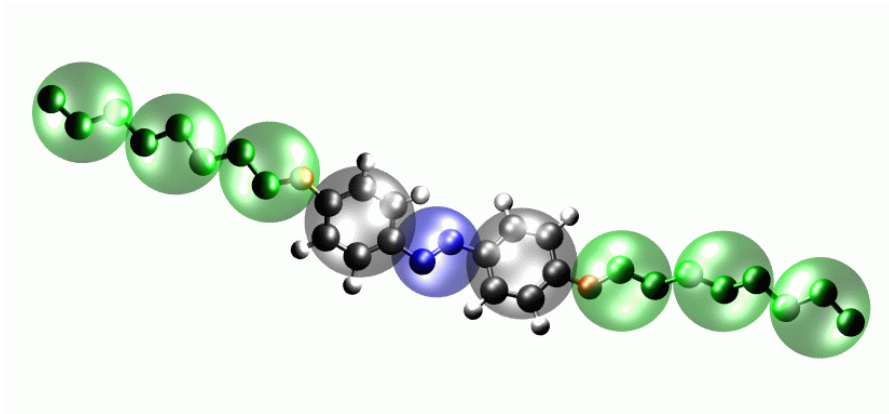
T =500 K → 470K

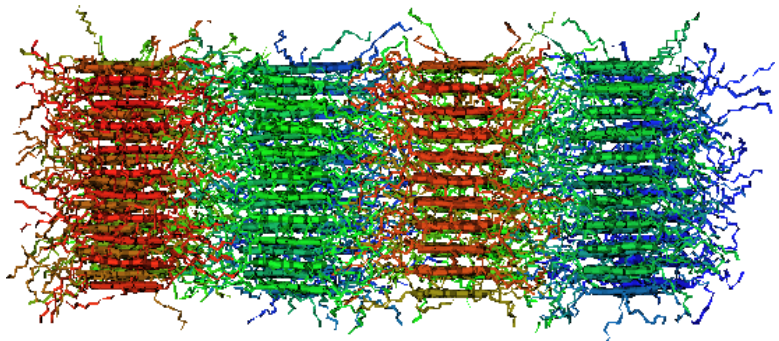
$\eta(T = 470\ K) \approx 10\ \eta(T = 500\ K)$

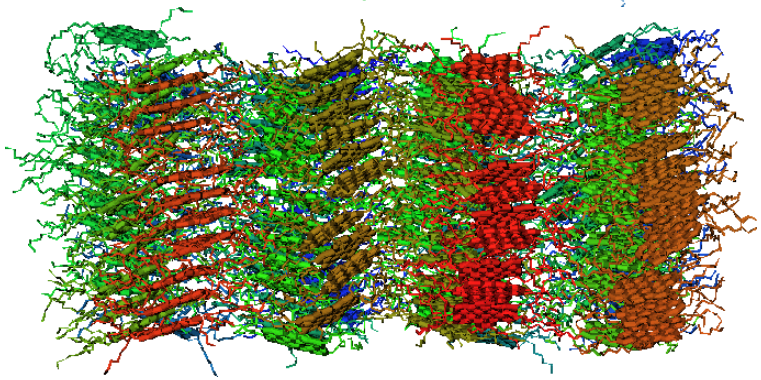
(typical values for BPA-PC)

Polymers II:

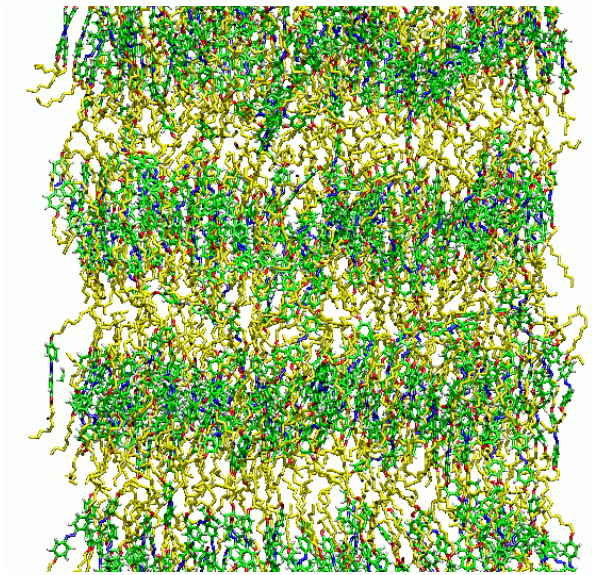






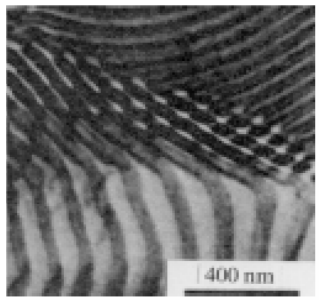


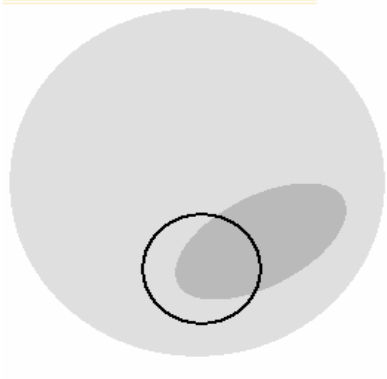
D. Andrienko et al

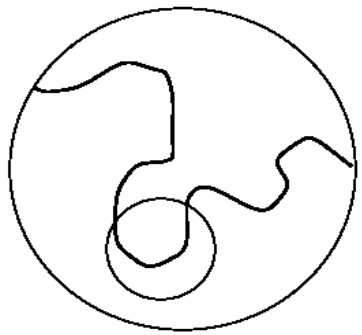


C. Peter

Time and length scales





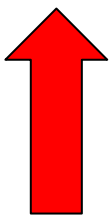


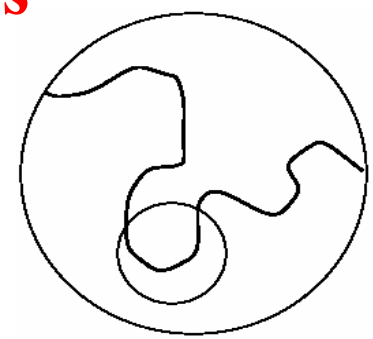
Macroscopic domains etc.

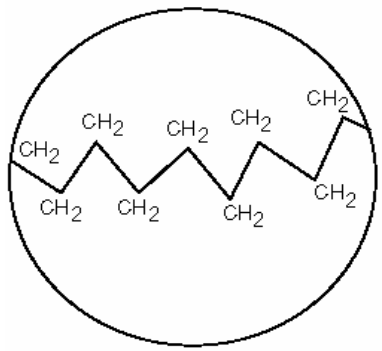
Semi macroscopic
L ≈ 100Å - 1000Å
T ≈ 0 (1 sec)

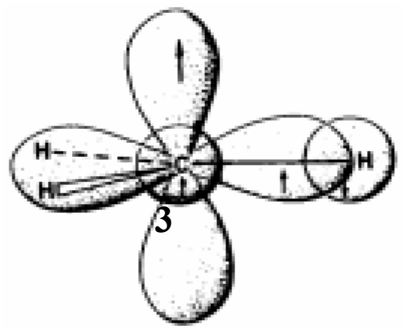
Mesoscopic
L ≈ 10Å - 50Å
T ≈ 10^{-8} - 10^{-4} sec
Entropy dominates

Properties









Mesoscopic
L ≈ 10Å - 50Å
T ≈ 10^{-8} - 10^{-4} sec
Entropy dominates

Microscopic
L ≈ 1Å - 3Å
T ≈ 10^{-13} sec
Energy dominates

(Sub)atomic
electronic structure
chemical reactions
excited states

generic/universal *** **chemistry specific**

Micro-Meso-Macro Simulation

Interplay Energy ⇔ Entropy

Free Energy Scale: $k_B T$

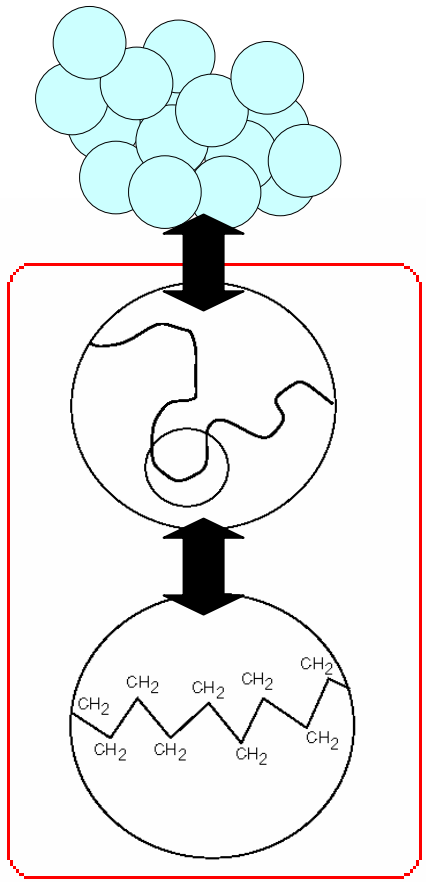
(SEMI-)MACROSCOPIC

"Coarse Graining"
Inverse Mapping

MESOSCOPIC
Simpler Models

"Coarse Graining"
Inverse Mapping

ATOMISTIC-MOLECULAR



Examples

- Polycarbonate
- (Polystyrene)

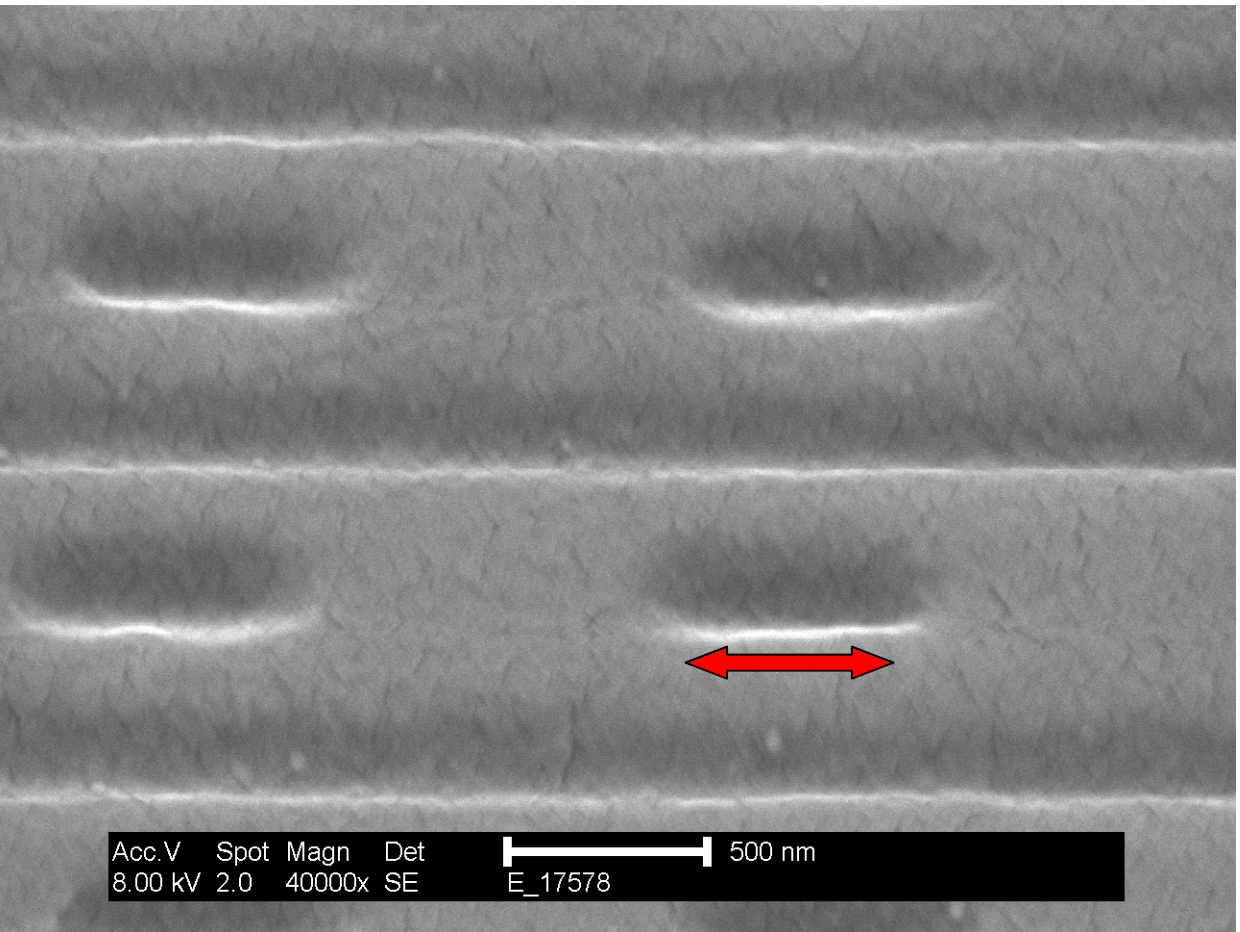
- Melt Dynamics (Rheology)
- (Membranes)

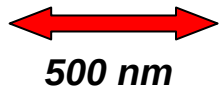
- Challenges - Outlook

  AdResS: Adaptive Resolution Scheme

Polycarbonate (PC) and the PC/Ni interface

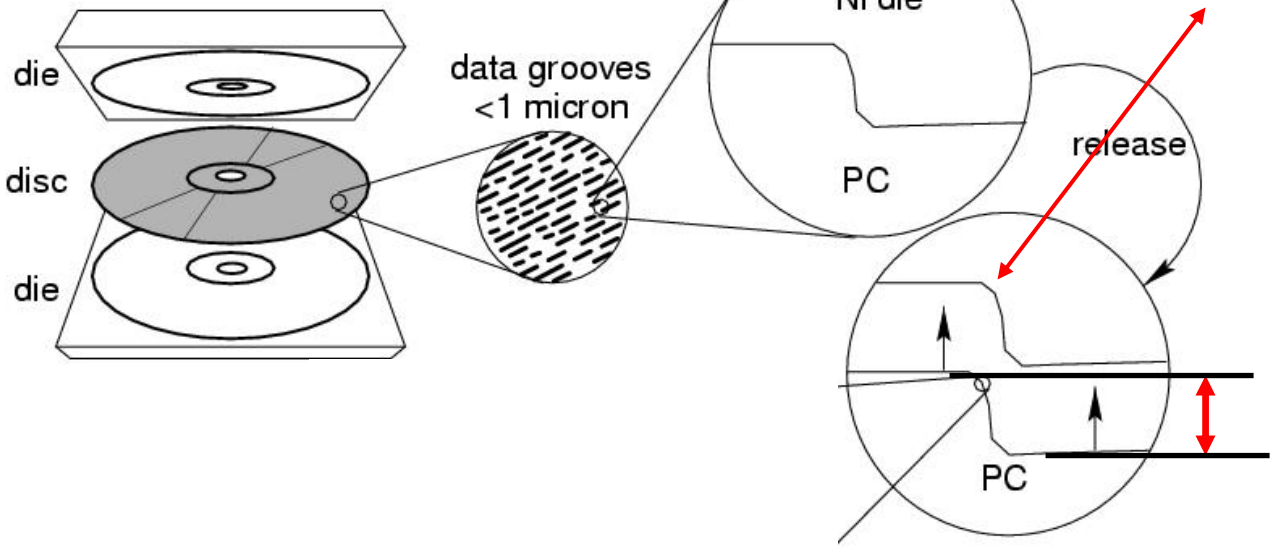
Grooves and address pits of a die cast sample of polycarbonate for a high storage density (**blue laser**) optical disc





Bayer Materials

Why study Polycarbonate and the PC/Ni interface?

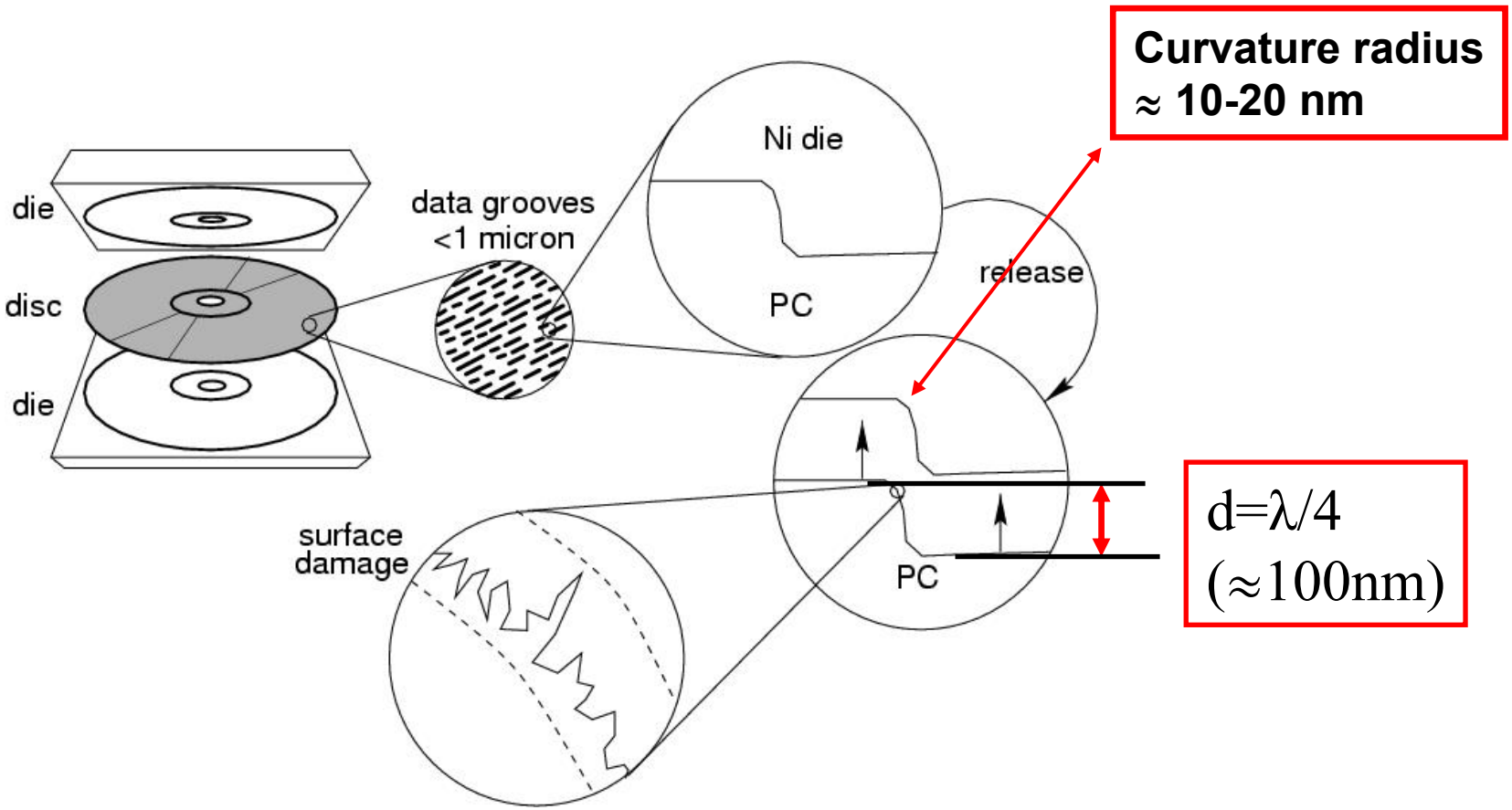


Curvature radius
≈ 10-20 nm

d=λ/4
(≈100nm)

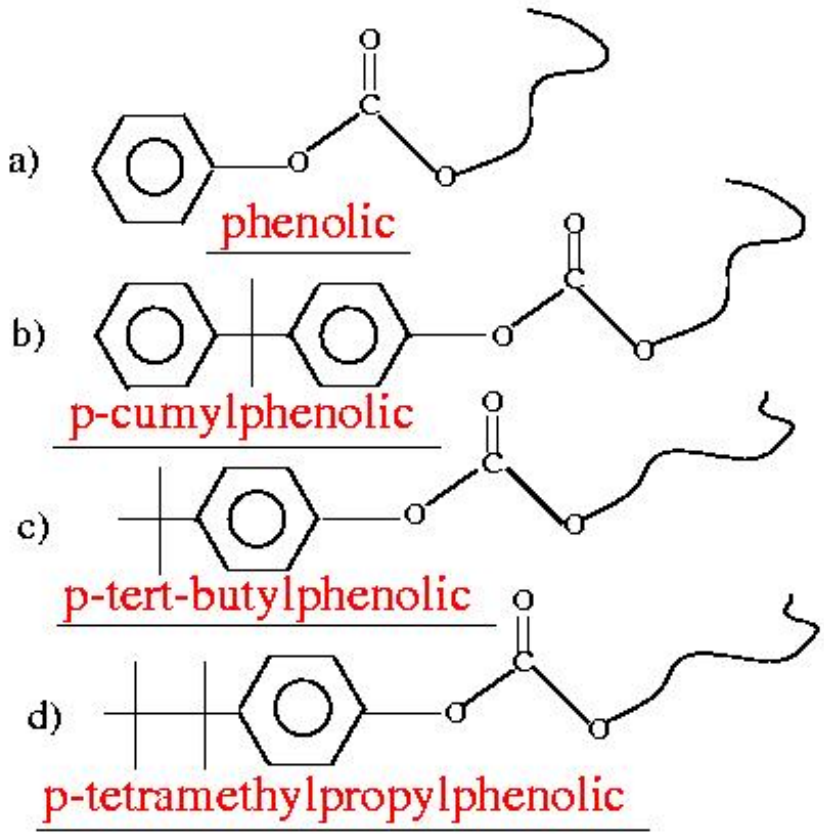
"only" high tech commodity polymer

Why study Polycarbonate and the PC/Ni interface?

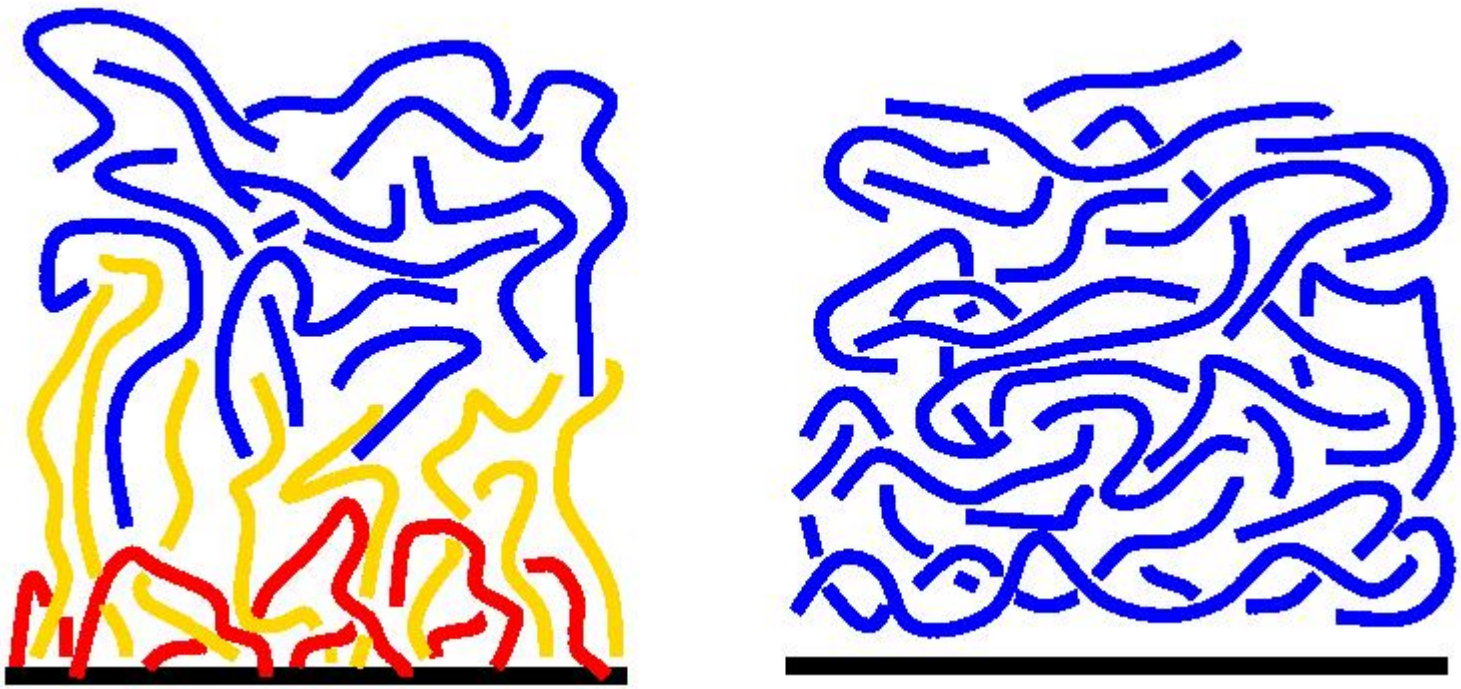


"only" high tech commodity polymer

Typical Chain Ends



Specific Adsorption



Two extreme cases

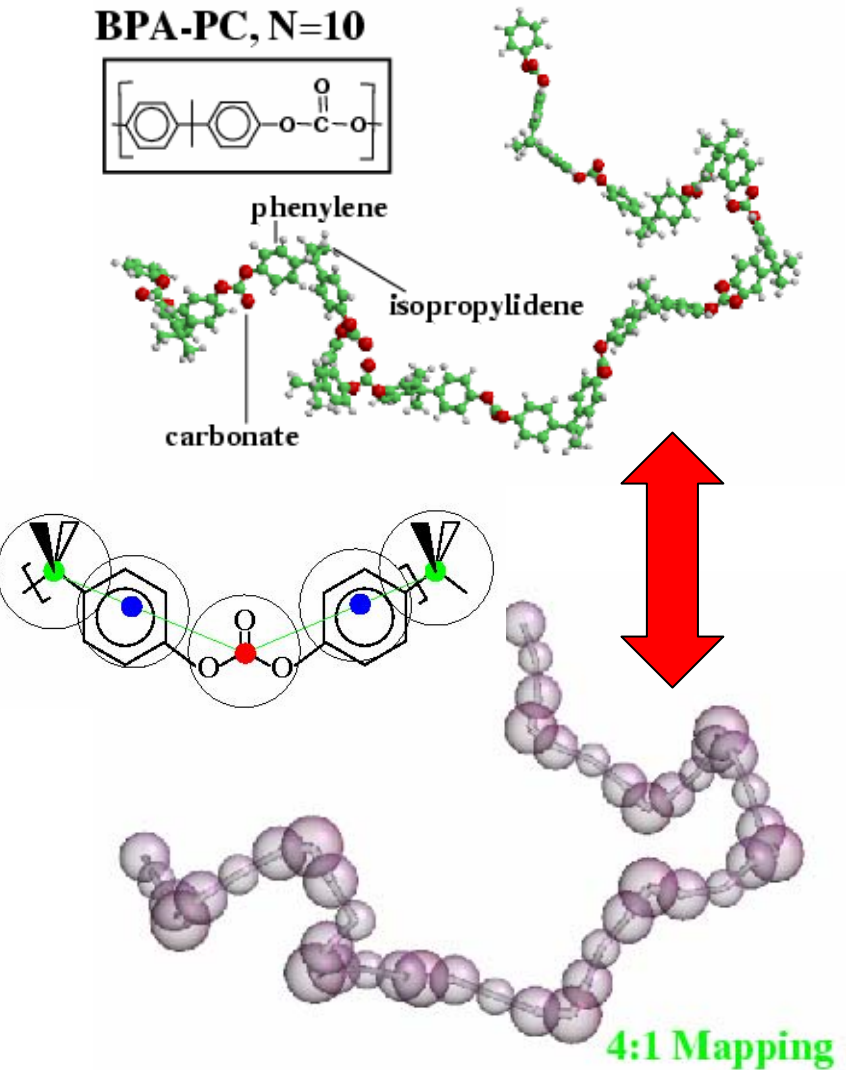
end adsorption only
energy dominated

"inert" surface
entropy dominated

Polycarbonate on Metal Surface

- **Linking Scales for Bisphenol-A-Polycarbonate (BPA-PC)**
  - **Molecular Coarse-Graining (=> Polymer melts, bulk)**
  - **Inverse Mapping, (Phenol Diffusion => F. Müller-Plathe)**
- BPA-PC Melts near Nickel Surfaces
  - *Ab initio* calculations: Surface/molecule energetics
  - Multiscale simulation: Molecular orientation at liquid/metal interface
  - Adsorption at a step
  - Shearing a melt

Molecular Coarse-Graining of Bisphenol-A-Polycarbonate

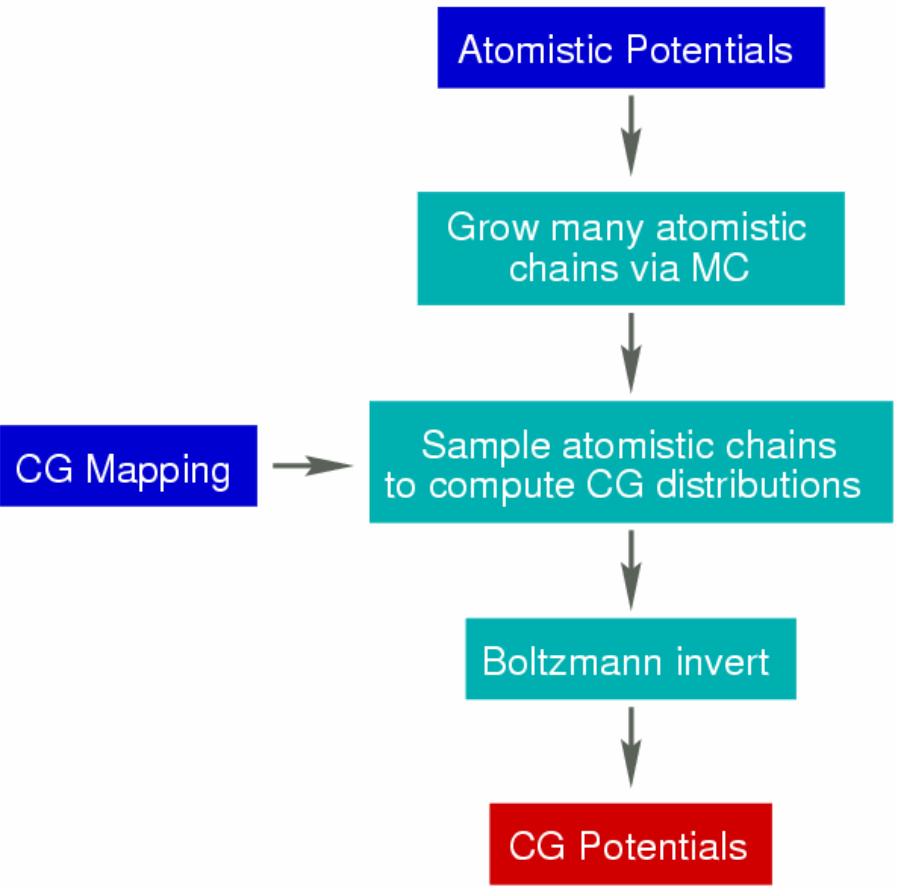


Coarse-graining:
map bead-spring chain over molecular structure.
=> Many fewer degrees of freedom

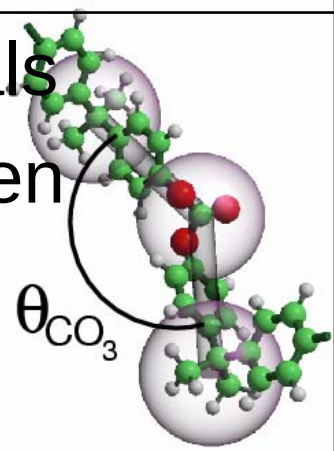
Inverse mapping: grow atomic structure on top of coarse-grained backbone
=>Large length-scale equilibration in an atomically resolved polymer

Mapping Scheme

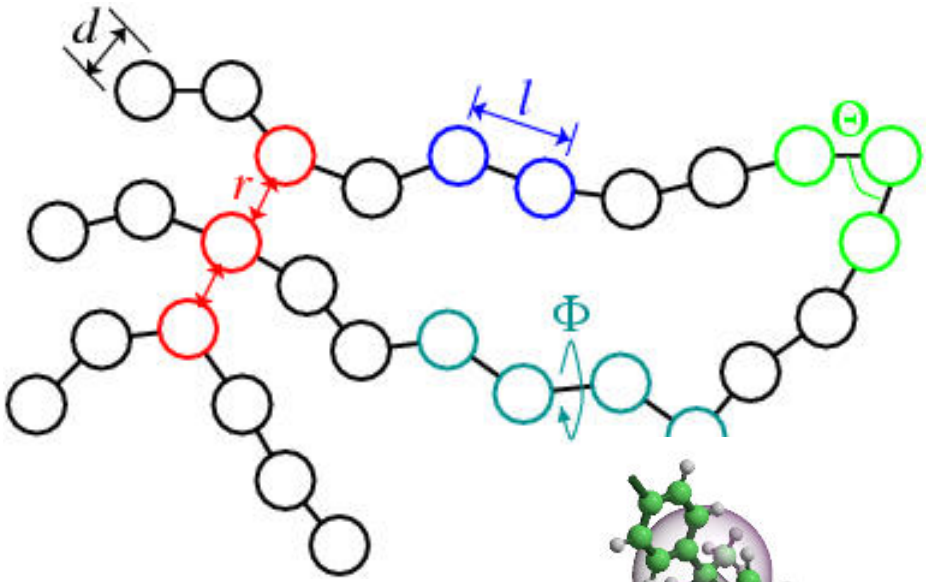
W. Tschöp, K. Kremer, J. Batoulis, T. Bürger, O. Hahn, Acta Polym. *49*, 61 (1998); ibid. *49*, 75



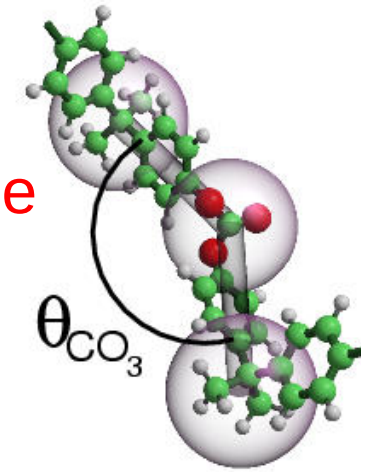
Quantum Chemistry
Monte Carlo, isolated all atom chain
sample CG distributions on basis of all atom chain
Intra-chain potentials for CG melts at given temperature



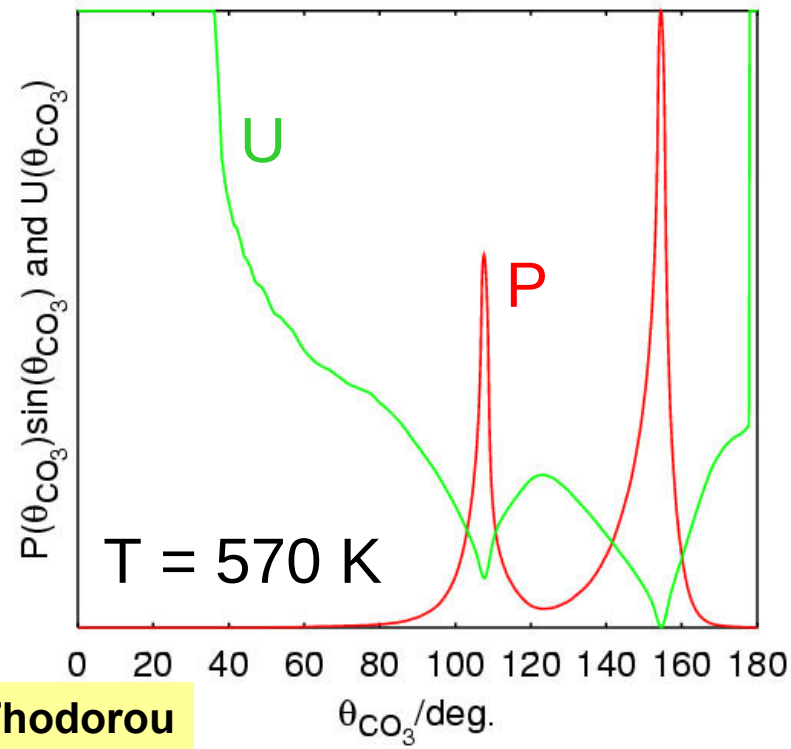
Interaction Energies in the Coarse-Grained Model



- Excluded volume
- Bonds
- Angles
- Torsions



Angle potentials are T-dependent Boltzmann inversions; *e.g.,* at carbonate:

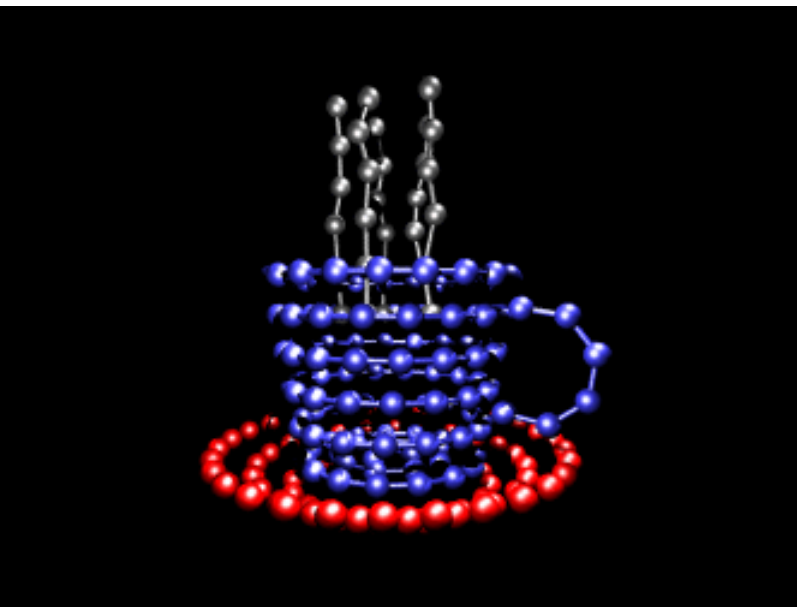


Alternative approaches e.g. F. Müller-Plathe, D. Thodorou

Software: ESPResSo

Open Source Modular Simulation Package
by C. Holm et al

Extensible Simulation Package for Research on Soft matter



Level	Module	Content	

Script Level	`blockfile`
	`part`
	`inter`
	`setmd`
	`integrate`
	`analyze`
		Tcl commands for	structured file I/O
			setting particle properties
			defining interactions
			setting simulation parameters
			integration
			analysis, measuring observables

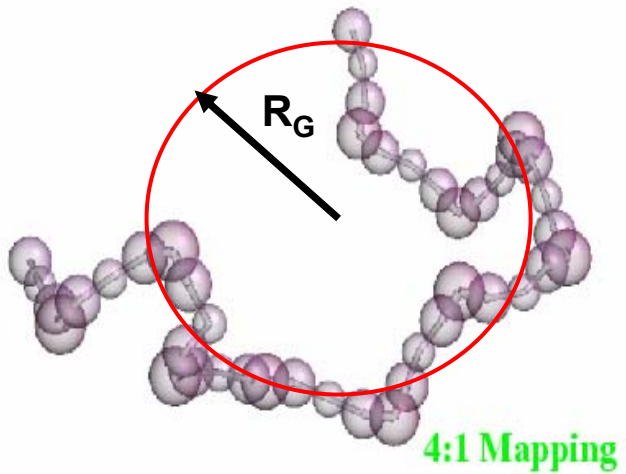
Simulation Level	Molecular Dynamics Forces Thermostat Monte Carlo Energy Pressure	Integration by Newton's equation F=ma Calculation of the forces from all interactions Temperature control for constant temperature MD Integration using Boltzmann-Factors Calculation of the energies from all interactions Pressure is needed for e. g. constant pressure simulaions	
Special Task Level	Communication	Data exchange in parallel runs outside integration	
	Linked cell Verlet lists Ghost particles	Algorithms for	sorting particles spatially short-ranged interactions calculation data exchange in parallel integrations
	P3M MMM1D/2D L.-J., Debye-Hückel FENE, bond-angle	Potentials for	electrostatic in periodic b.c. using FFT electrostatics in partially periodic b.c. short-ranged interacions bonded interactions
	IMD	Realtime visualization using VMD	

Local contact: Thorsten Stühn
http://www.espresso.mpg.de/

Results for Melts, N=20….120

- Molecular Coarse-Grained Melt

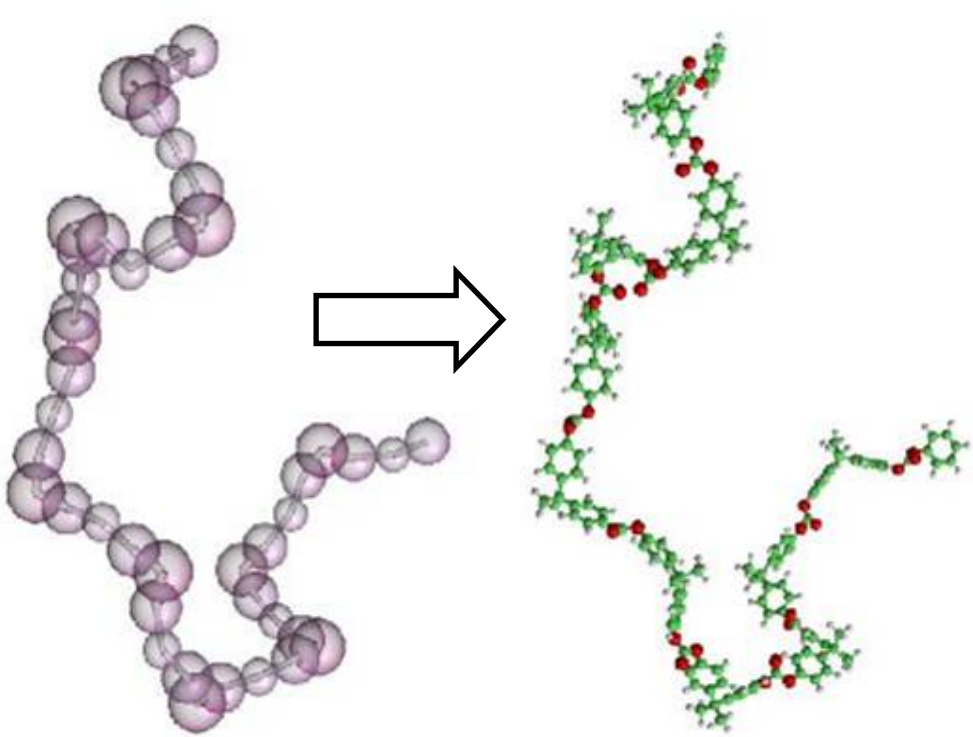
$$\left\langle R_G^2(N)\right\rangle / N \cong 37\ \text{Å}^2$$



R_G of coarse grained simulations agrees to n-scattering experiments!

- Reintroduce Details: Inverse Mapping

Bisphenol-A Polycarbonate: Inverse Mapping Control of Approach vs Experiment

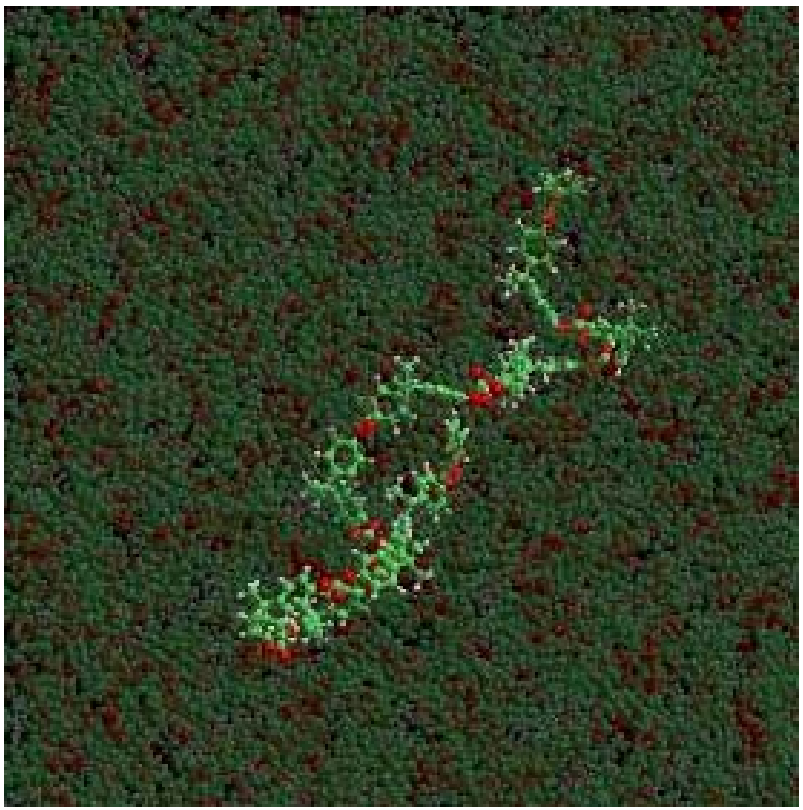


For each CG Chain

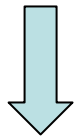
Create corresponding atomic chain

Vary $\boldsymbol{r}_{CM}$, Θ, Φ, Ψ, $\{\varphi_i\}$ to minimize distance between respective mapping points and CG beads

Inverse Mapping



Slowly introduce excluded volume



Short relaxation run
for 1-2 ps!

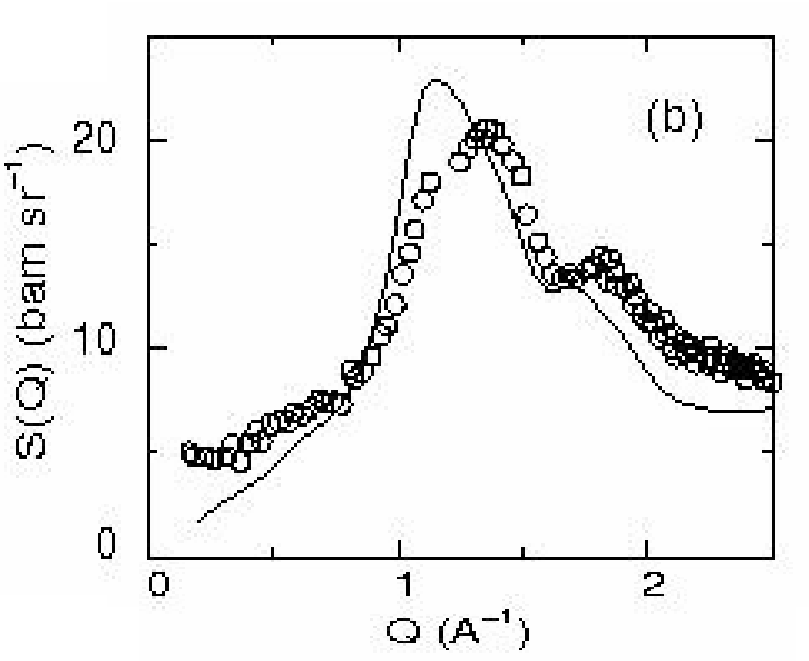
$$\left\langle \Delta r^2 \right\rangle^{1/2} \leq 1.5 \text{Å}$$

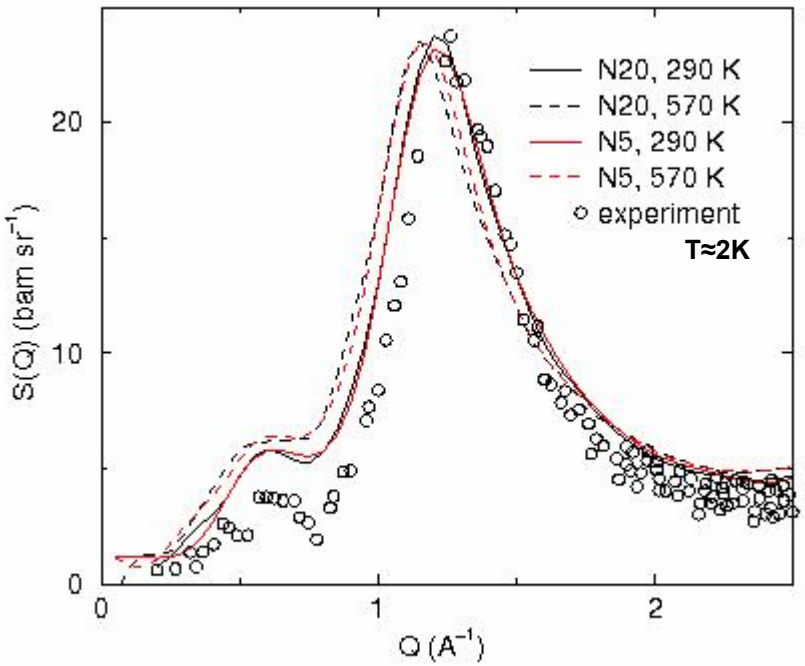
How good are the conformations?
Dynamics?

Conformation: Simulation n-Scattering

Structure factors of (deuterated) BPA-PC

Right: standard BPA-PC
Bottom: fully deuterated BPA-PC





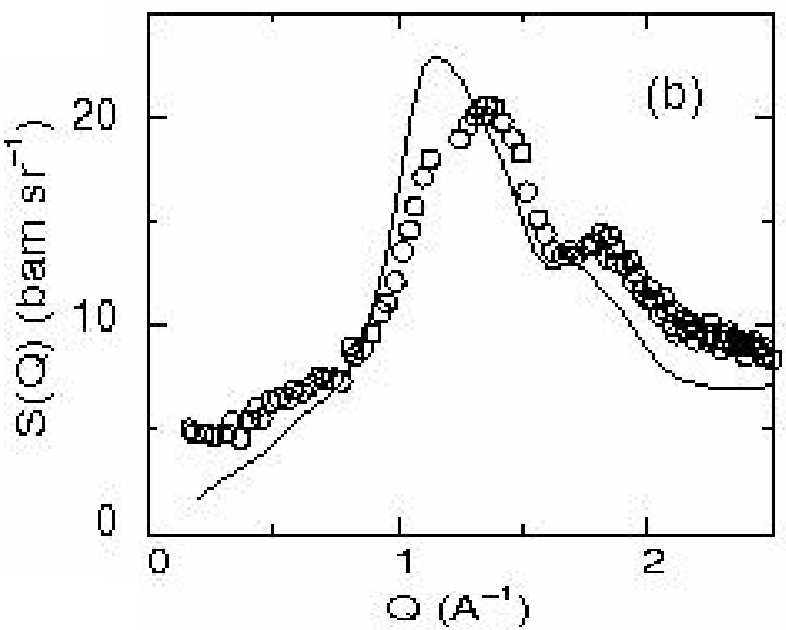
J. Eilhard et al,
J. Chem. Phys. **110**, 1819 (1999)
B. Hess et al, Soft Matter 2006

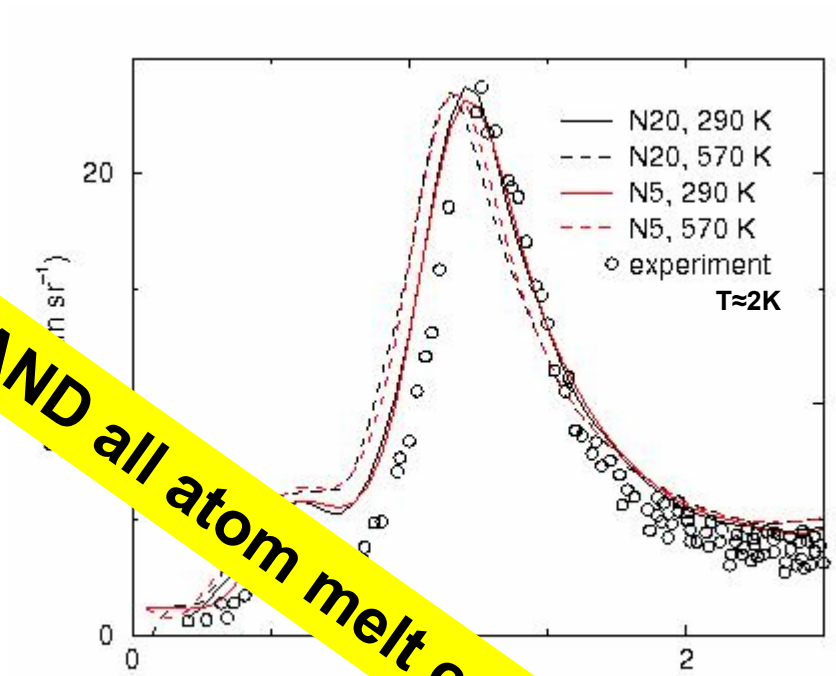
Conformation: Simulation n-Scattering

Well equilibrated coarse grained AND all atom melt configurations

Structure factor
(deuterated) BPA-PC

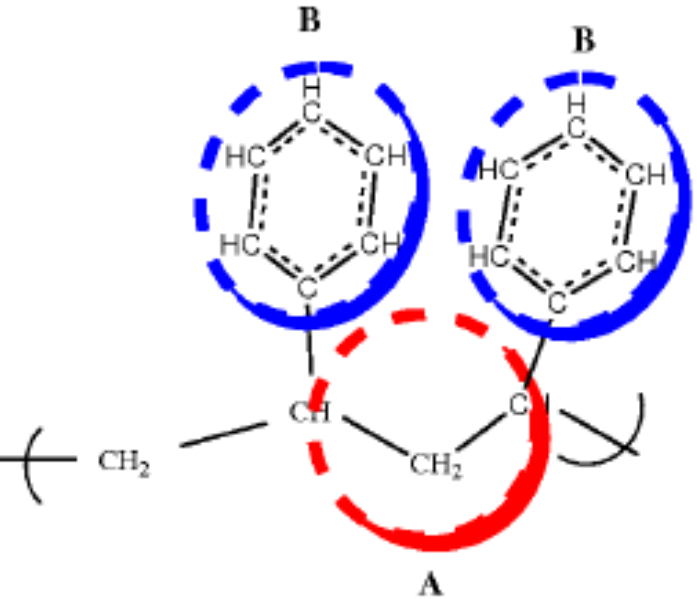
Right: standard BPA-PC
Bottom: fully deuterated BPA-P

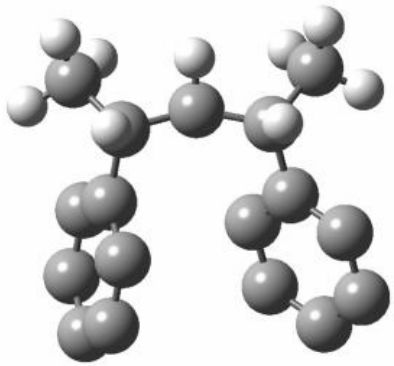


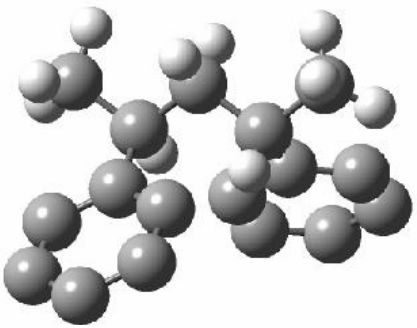


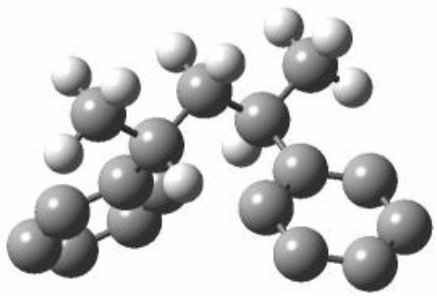
J. Eilhard et al,
J. Chem. Phys. **110**, 181 (1999)
B. Hess et al, Soft Matter 2006

DETOUR Polystyrene









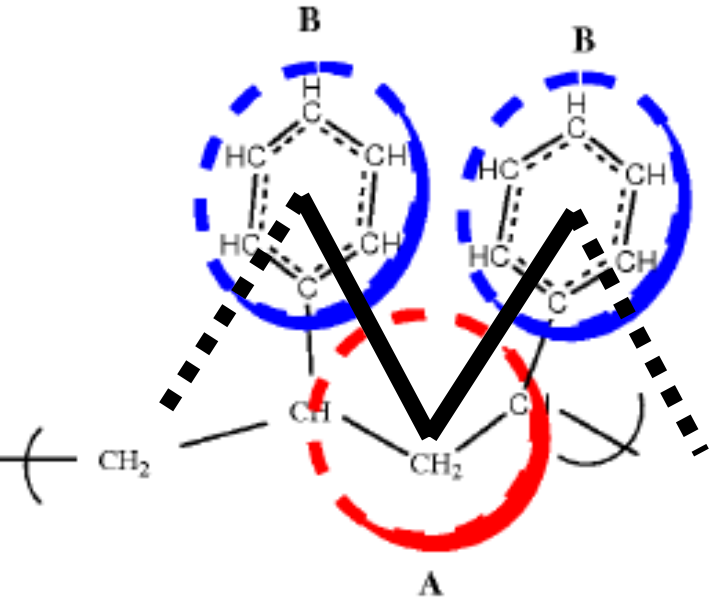
Orientation along backbone
For sampling

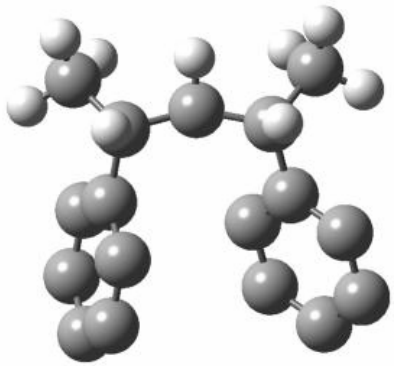
Iso

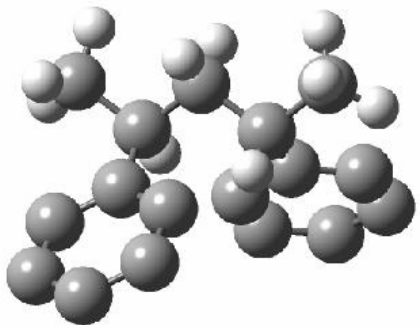
Syndio I

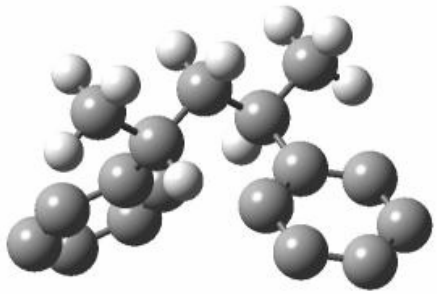
Syndio II

DETOUR Polystyrene









Orientation along backbone
For sampling

Iso

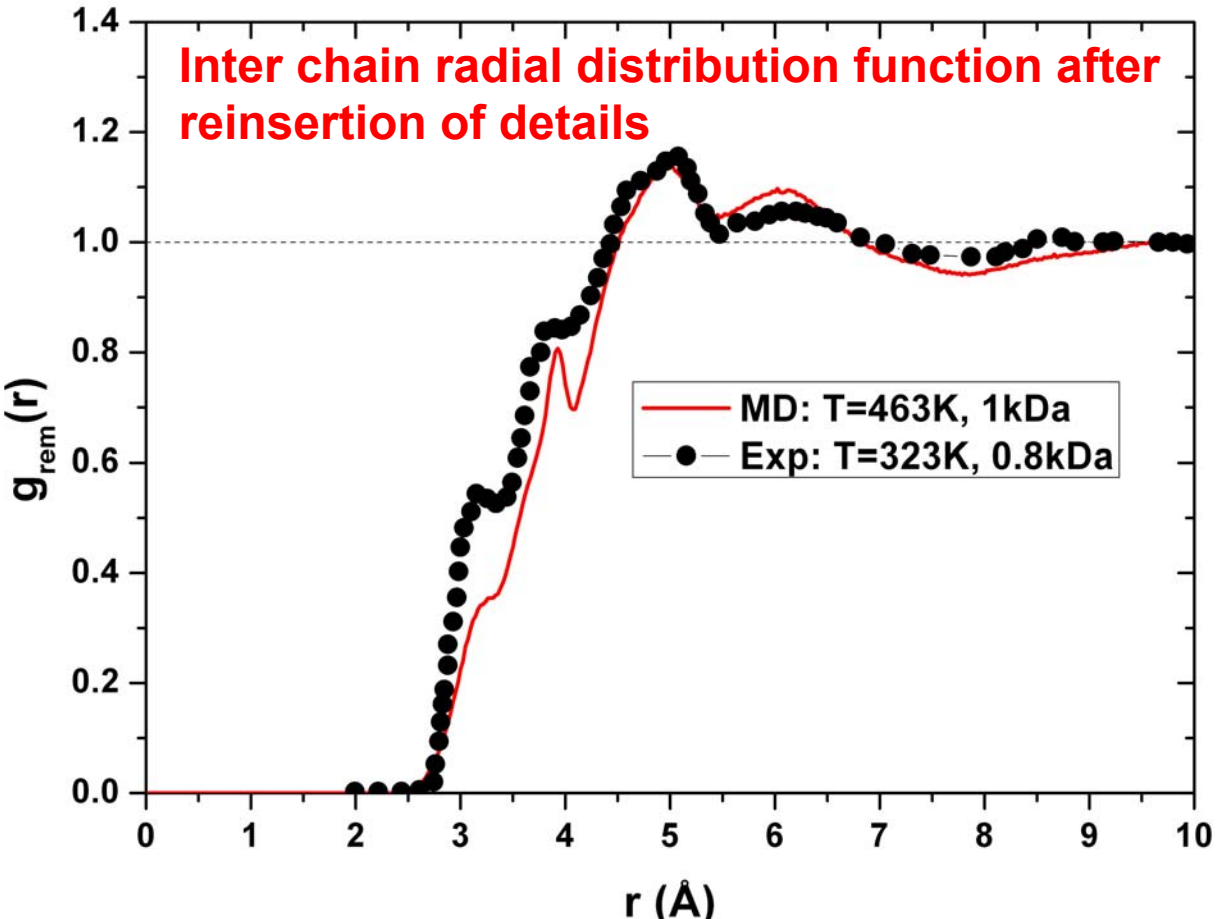
Syndio I

Syndio II

DETOUR Polystyrene

- **Direct comparison simulation vs x-ray scattering**

V. Harmandaris et al, MM 2006



Simulation: united atom, reintroduced details

Experiment:

Londono et al.

J. Polym. Sc. B, 1996.

Polycarbonate Melt Dynamics coarse grained - atomistic

- Linking Scales for Bisphenol-A-Polycarbonate (BPA-PC)
  - Molecular Coarse-Graining
    => Long chain melt dynamics
  - Inverse Mapping
    => long chain atomistic trajectories

Polycarbonate Melt Dynamics coarse grained - atomistic

- Linking Scales for Bisphenol-A-Polycarbonate (BPA-PC)
  - Molecular Coarse-Graining

    => Long chain melt dynamics

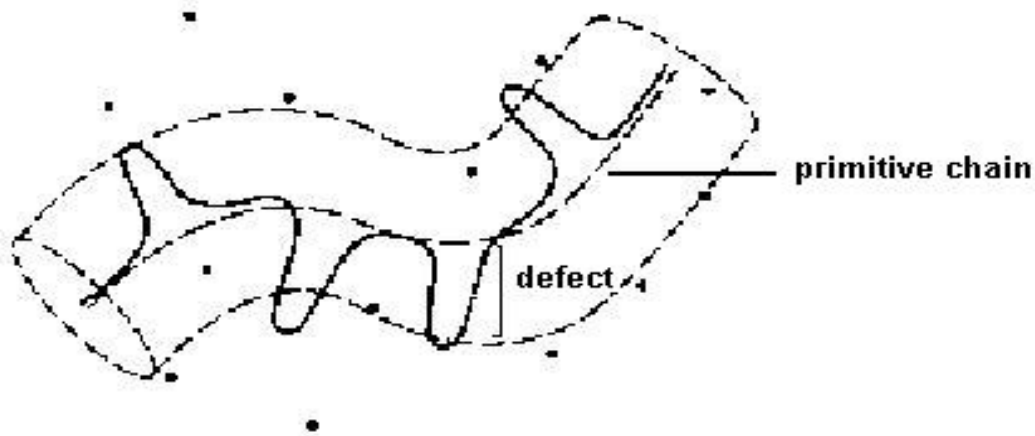
    Entanglement analysis

  - Inverse Mapping

    => long chain atomistic trajectories

Primitive Path Analysis
for equilibrated long chain polymer melts

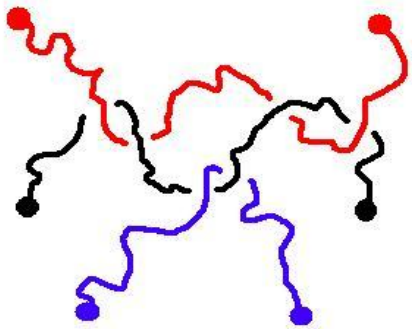
- Length of primitive path
- ↔
- tube diameter

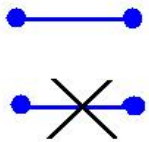


(Doi & Edwards)

Problem: "Obstacles" are not fixed in space
→primitive path determination needs to be consistent:
→Simultaneously for all chains!

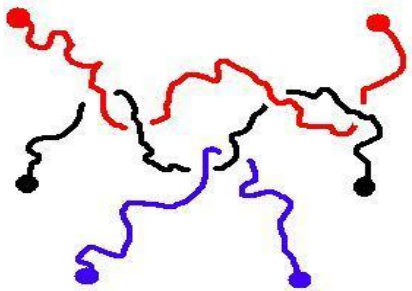
Constraints: Multi-Chain Effects
Constraints red-black

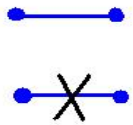




2 Constraints (links)

0 Constraints

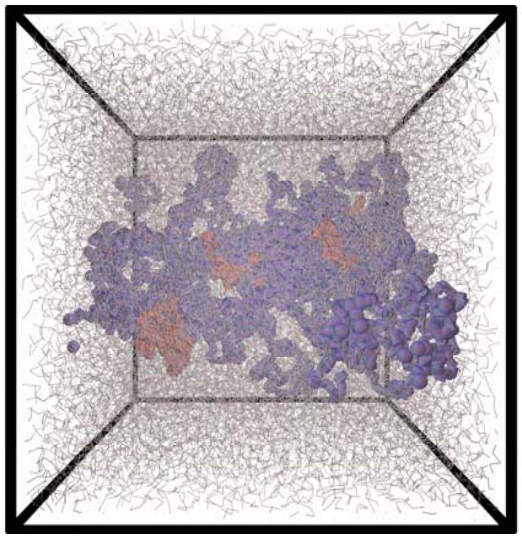


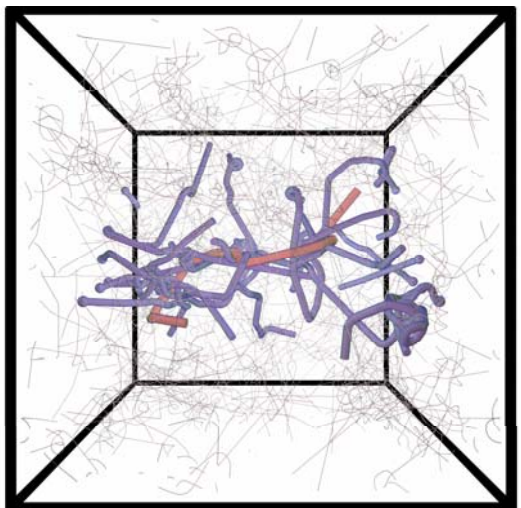


2 Constraints

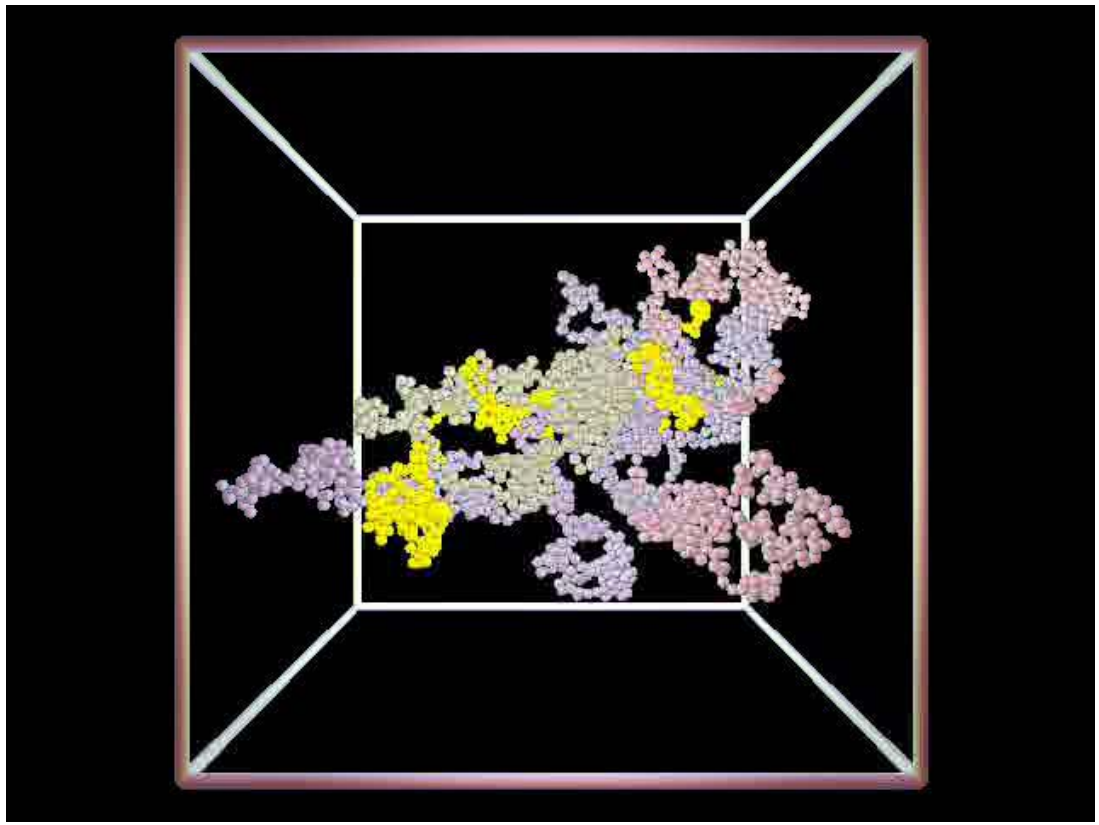
1 Constraint

Entanglements: Primitive Path Analysis



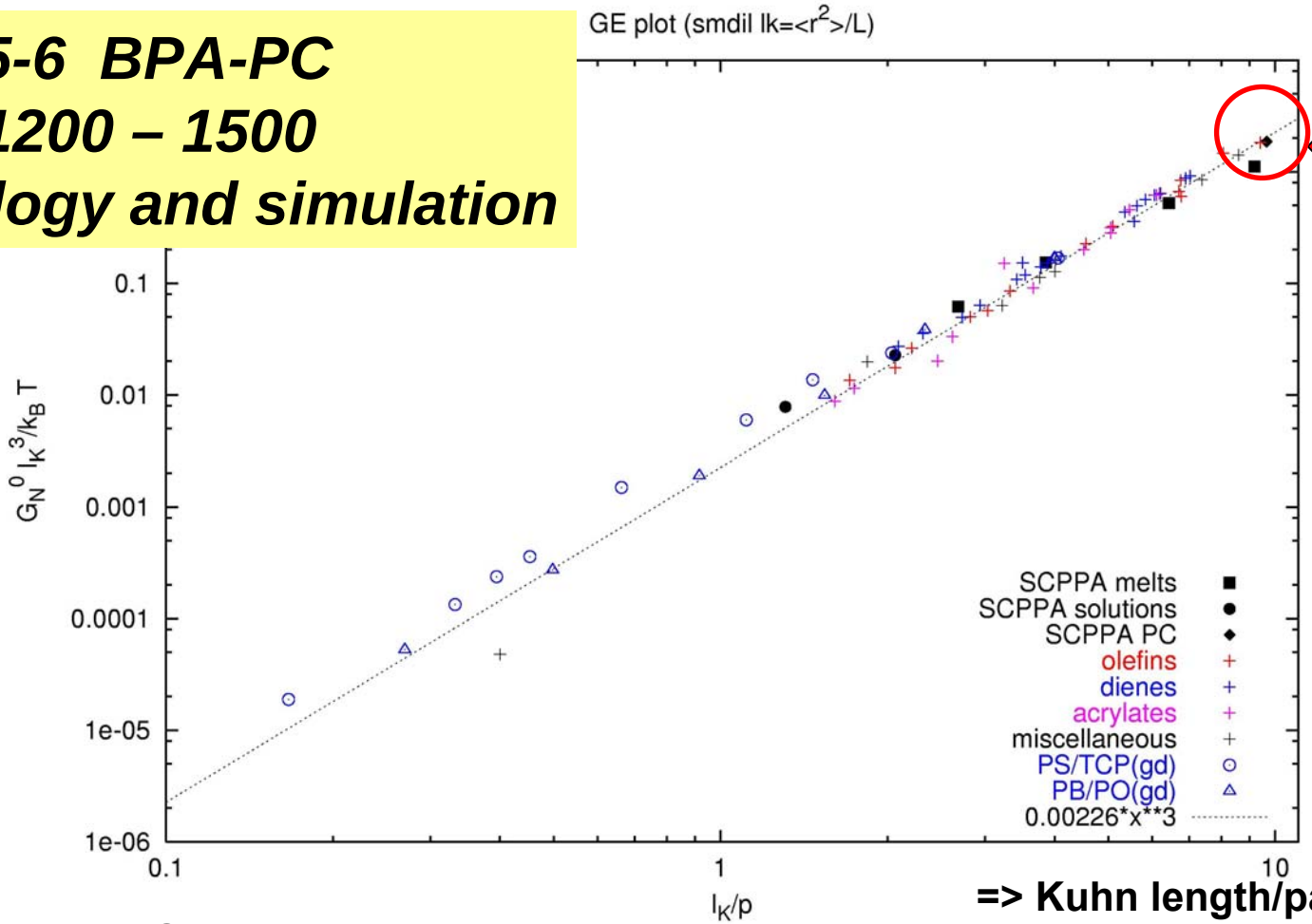


- Evolution of entangled chain cluster (Everaers et al , Science 2004)



Plateau Modulus Different Polymers
Melts and Solutions: Tological analysis and experiment

N_e = 5-6 BPA-PC
M_e = 1200 – 1500
Rheology and simulation



BPA-PC

=> Kuhn length/packing length

Everaers et al Science 2004, Leon et al Macrom. 2005

Polycarbonate Melt Dynamics coarse grained - atomistic

- Linking Scales for Bisphenol-A-Polycarbonate (BPA-PC)
  - Molecular Coarse-Graining

    => Long chain melt dynamics

    Entanglement analysis

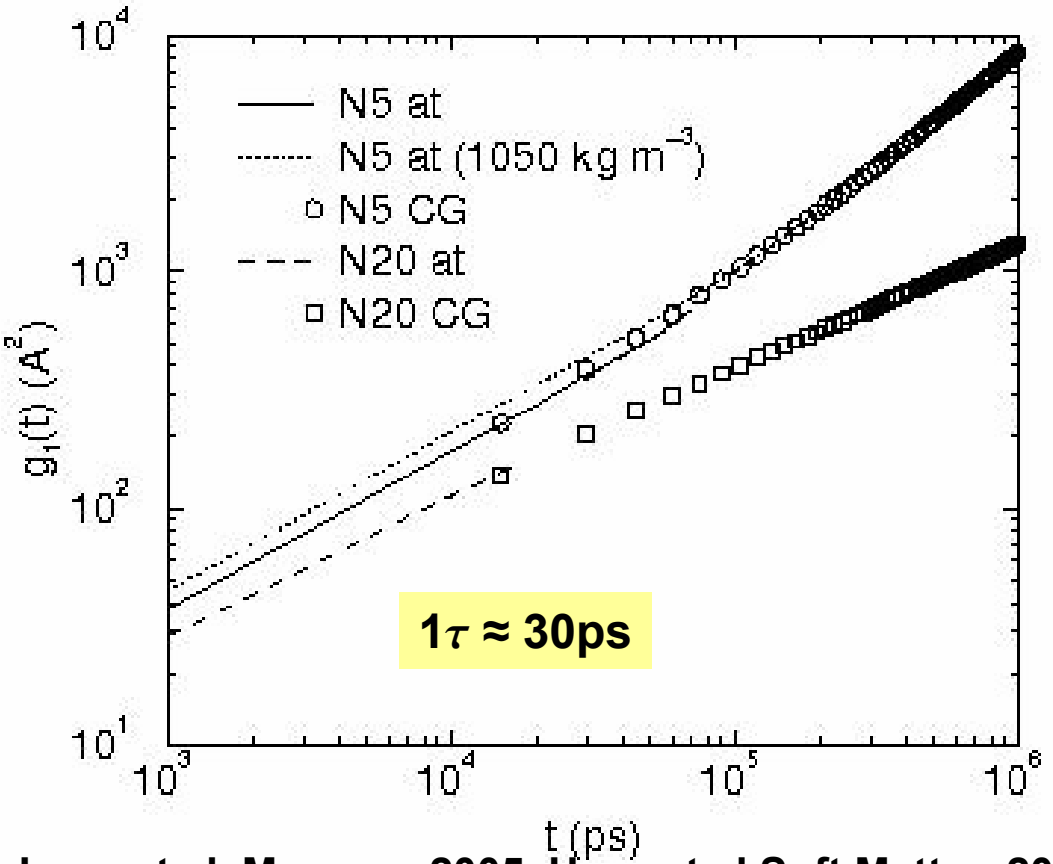
  - Inverse Mapping

    => long chain atomistic trajectories

    from coarse grained trajectories

Atomistic vs cg Simulation: Time Mapping

mean square displacements atomistic vs coarse grained



Leon et al, Macrom. 2005, Hess et al Soft Matter, 2006

Largest atomistic systems generated by this approach:

Box of
200 chains of N=120 (≈ 20 Ne)

$$L \cong 100 \times 100 \times 100 nm^3$$

$$t_{\max} \cong 4 \times 10^{-5} \sec$$

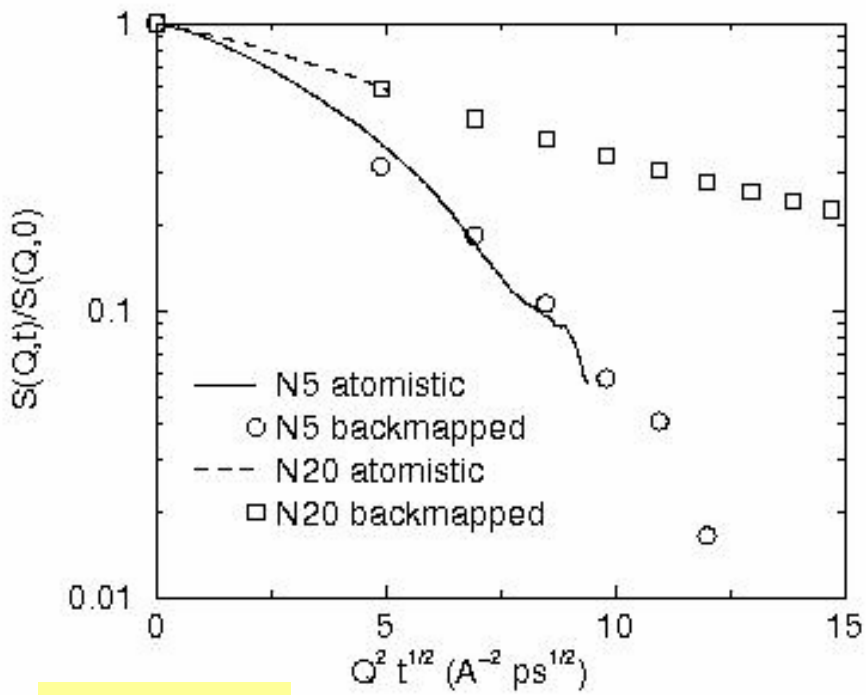
100 chains of N=60

$$L \cong 60 \times 60 \times 60 nm^3$$

$$t_{\max} \cong 6 \times 10^{-5} \sec$$

Atomistic vs cg Simulation: Time Mapping

Dynamic scattering function atomistic vs coarse grained
NO ADJUSTABLE PARAMETER!



$1\tau \approx 30$ps

Largest atomistic systems generated by this approach:

Box of
200 chains of N=120 (≈ 20 Ne)

$$L \cong 100 \times 100 \times 100 nm^3$$

$$t_{\max} \cong 4 \times 10^{-5} \sec$$

100 chains of N=60

$$L \cong 60 \times 60 \times 60 nm^3$$

$$t_{\max} \cong 6 \times 10^{-5} \sec$$

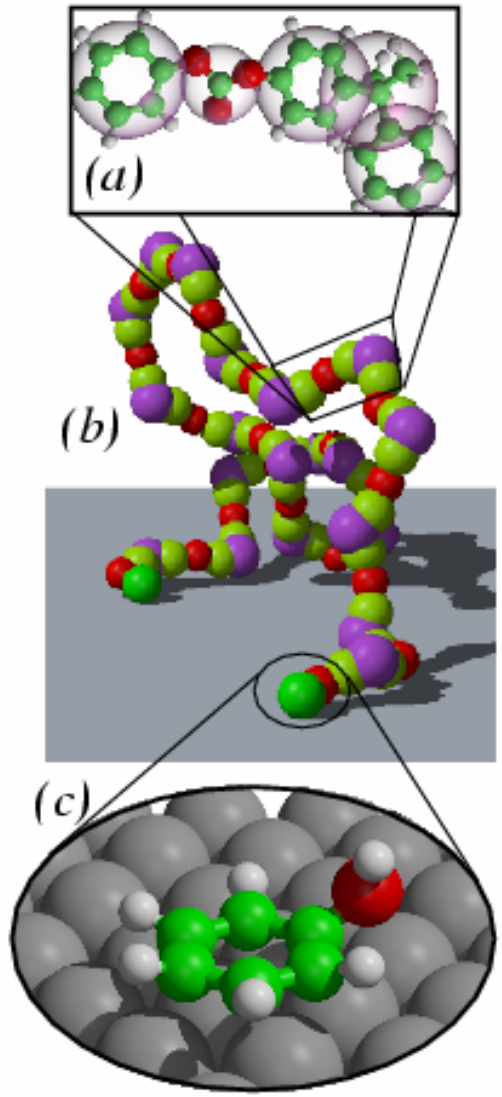
Leon et al, Macrom. 2005, Hess et al Soft Matter, 2006

Polycarbonate on Metal Surface

- Linking Scales for Bisphenol-A-Polycarbonate (BPA-PC)
  - Molecular Coarse-Graining
  - Inverse Mapping, (atomistic trajectories for entangled melts for up to almost 10^{-4}sec!)

- **BPA-PC Melts near Nickel Surfaces**
  - **Ab initio calculations: Surface/molecule energetics**
  - **Multiscale simulation: Molecular orientation at liquid/metal interface**

Simulating BPA-PC/Metal Interfaces



Molecular structure coarse-grained onto bead-spring chain

↓

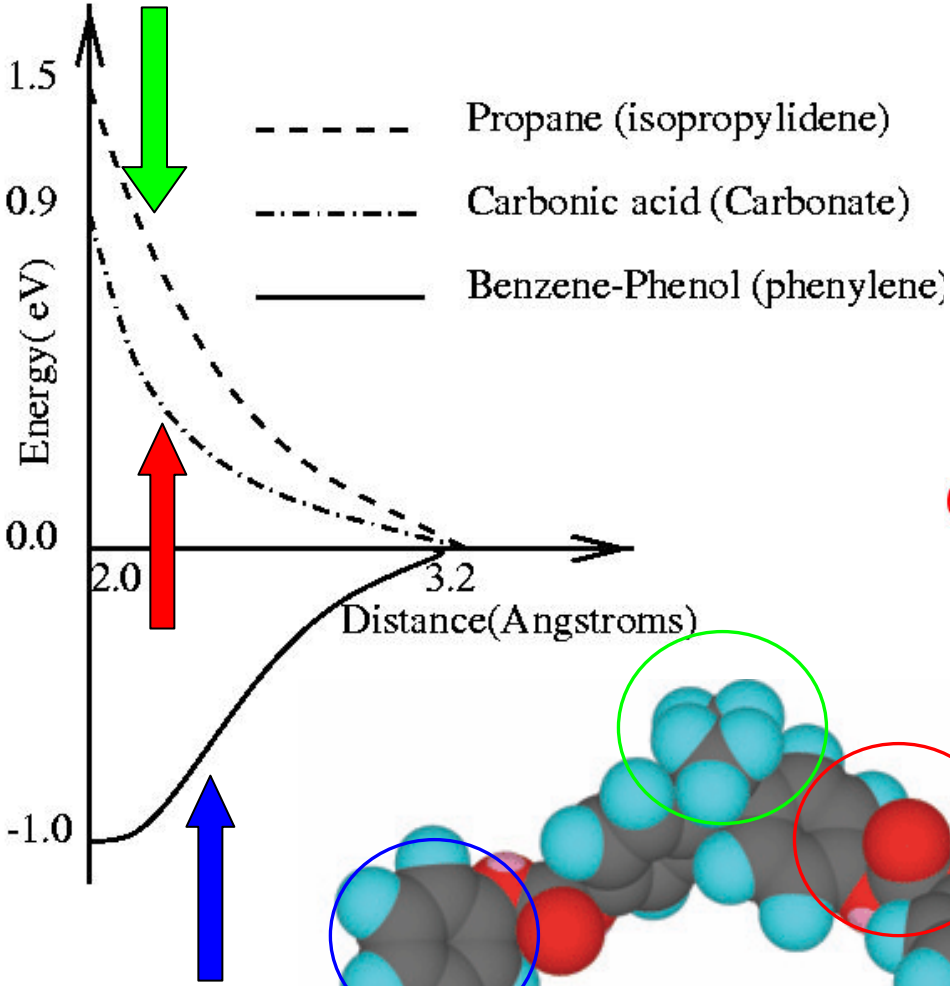
Simulation of coarse-grained BPA-PC liquids (T = 570K) next to metal surface

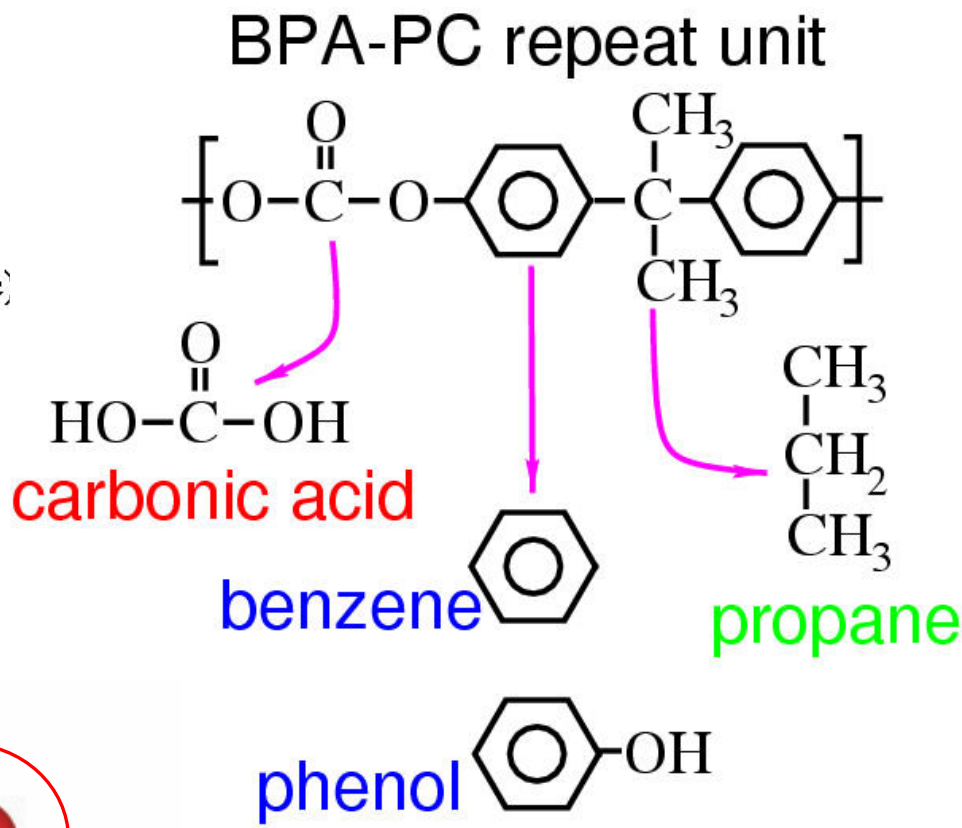
↑

Specific surface interactions investigated via *ab initio* calculations

C.F. Abrams, et al. PRE 021807 (2003); L. DelleSite, et al. PRL 156103 (2002); BMBF Zentrum MatSim

Ab initio Investigations of Comonomeric Analogues on Nickel





CPMD: Conclusions

- Strong repulsion of propane and carbonic acid
  + the strong orientational dependence
  + short interaction range of phenol

  with Ni {111}

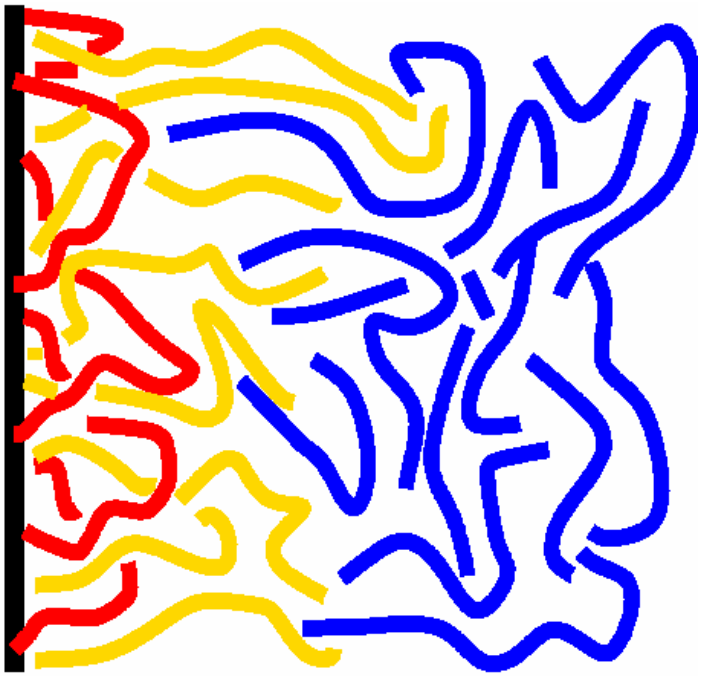
➔

Internal phenylene comonomers in BPA-PC are sterically hindered from adsorbing on Ni {111}.

➔

Torsional freedom in carbonate group allows for terminal phenoxy groups to adsorb

Schematic structure of "End-Sticky" Melts



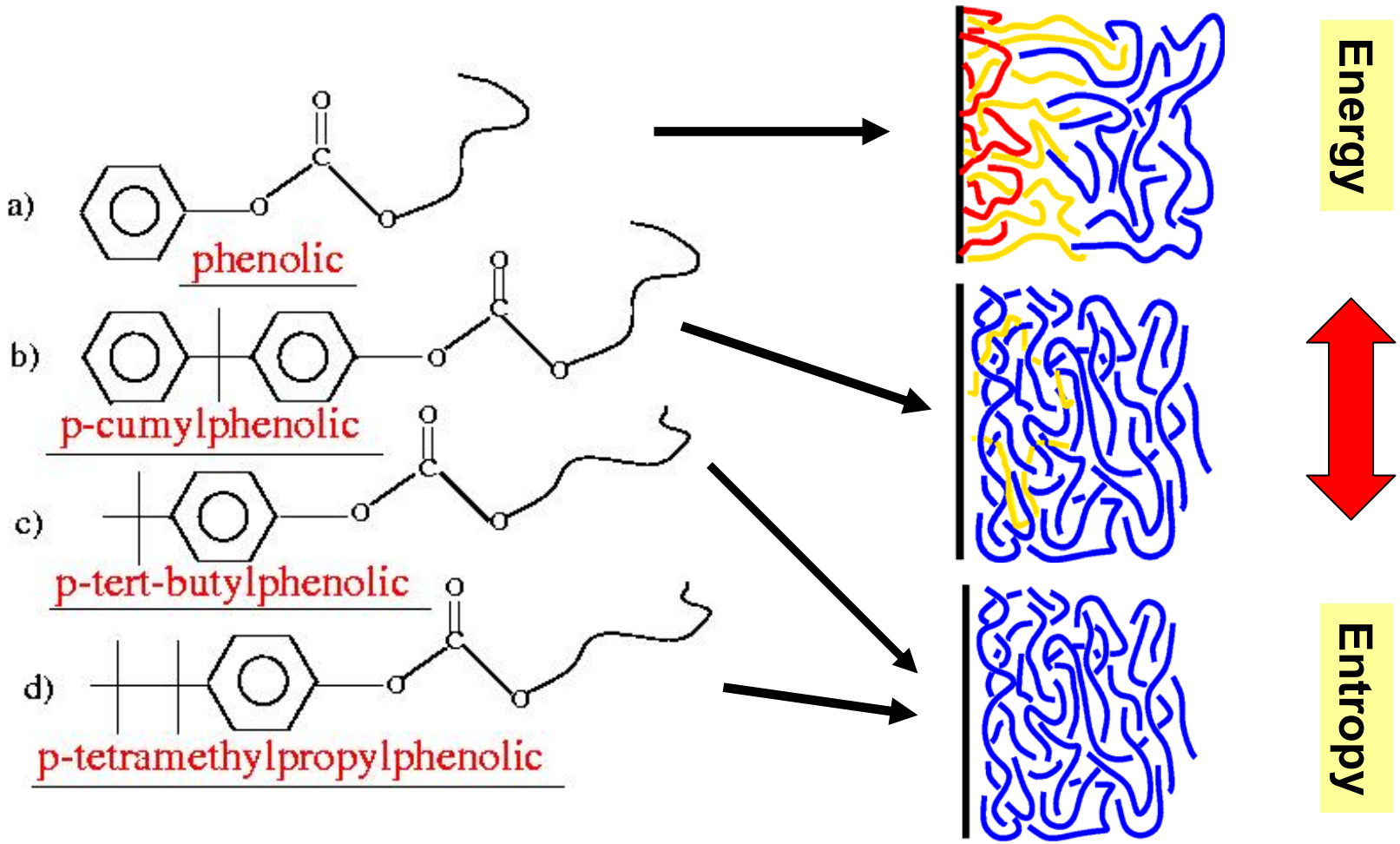
Chains "compressed"

Chains "elongated"

Normal Bulk conformations

➔ Coupling Surface ←→ Bulk?

Other Chain Ends
Energy - Entropy Competition



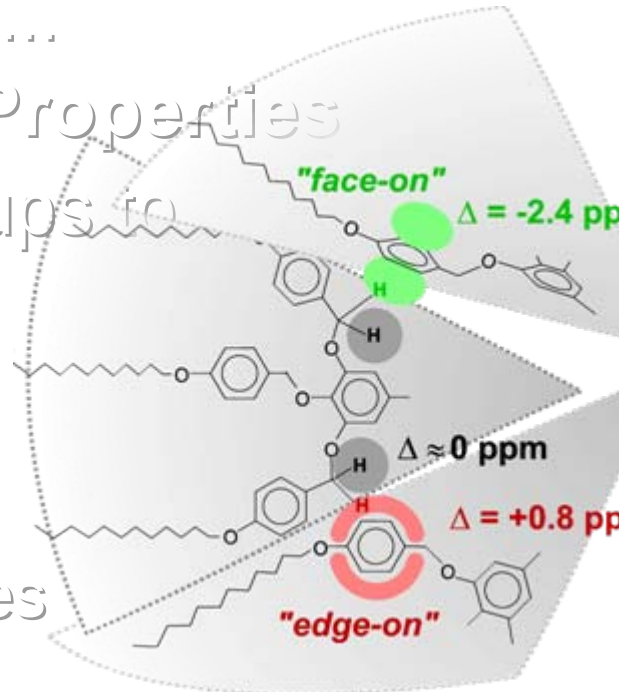
Polycarbonate on Metal Surface

- Linking Scales for Bisphenol-A-Polycarbonate (BPA-PC)
  - Molecular Coarse-Graining
  - Inverse Mapping

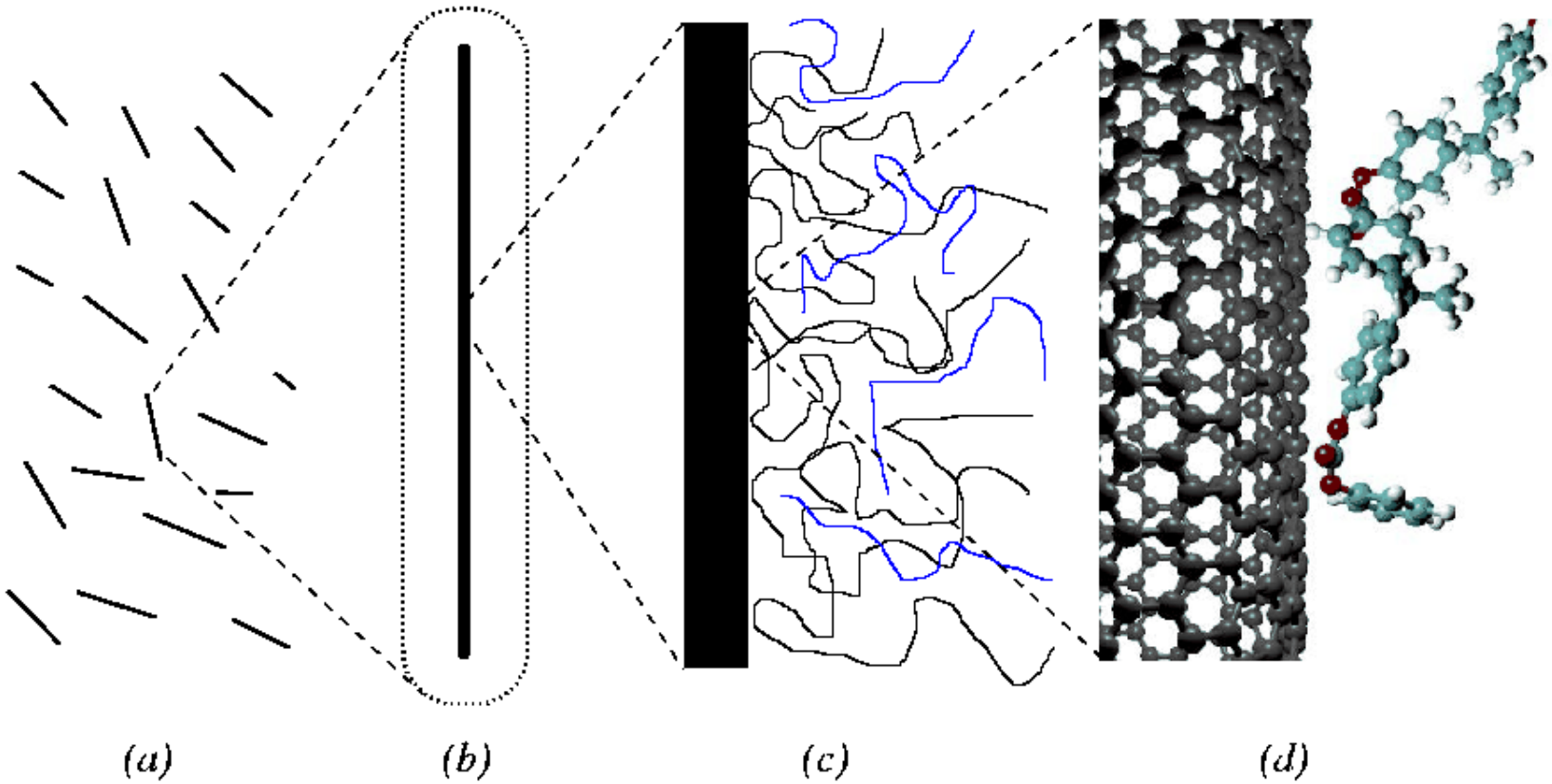
- **BPA-PC Melts near Nickel Surfaces**
  - **Ab initio calculations: Surface/molecule energetics**
  - **Multiscale simulation: Molecular orientation at liquid/metal interface**

A few Challenges

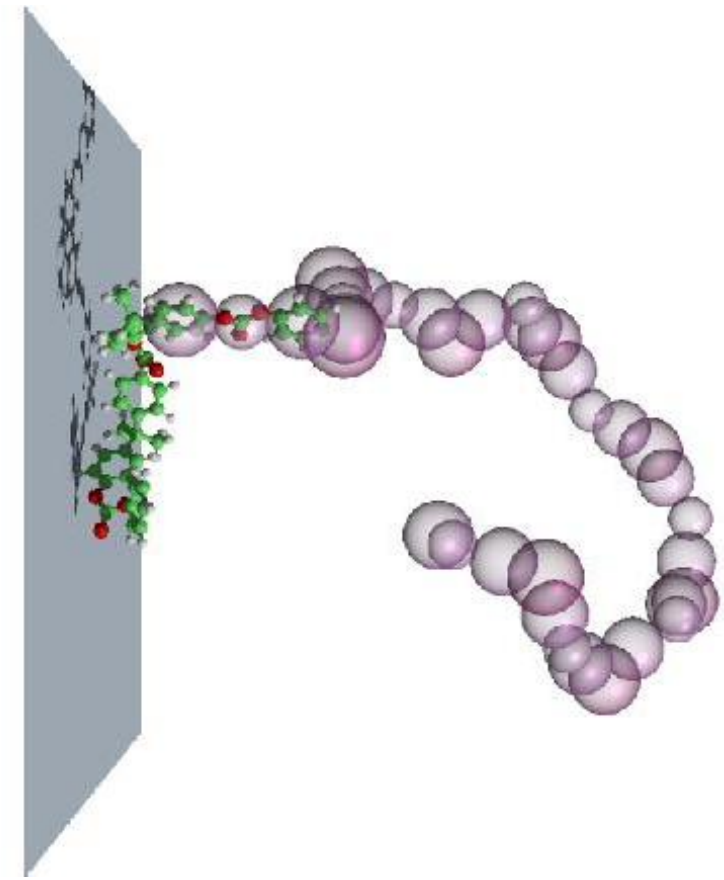
- **Dual-Triple… Scale Simulations/Theory**
  - **Adaptive** quantum⇔**force field⇔coarse grained …**
- Nonbonded Interactions:
  - Morphology, Solvation, Adsorption…
- Conformations ⇏ Electronic Properties
  - E.g. coupling of aromatic groups to backbone conformation, or to other chains
- Online Experiments:
  - Nanoscale Experiments, long Times



Application: Multiscale Simulation of Polymer/Nanotube Composites



Adaptive Inhomogenous Coarse-Graining



Specific atomic-scale energetics dominant at surface

Molecule-scale entropy dominant in bulk

Coarsened fragments provide equilibrated “boundary conditions” for full-blown embedded atomistic simulation

Motivation/Considerations

All-Atom Simulation

- **study (classical) processes on atomistic level**
- **short times and small system sizes**

Mesoscopic MD Simulation

- **reduced set of degrees of freedom (DOFs) => longer times, larger systems**
- **chemical details usually lost**

Hybrid Simulation

- **combine adaptively atomistic and more coarse grained simulations**
- **changing DOFs on the fly:**

AdResS – Adaptive Resolution Scheme

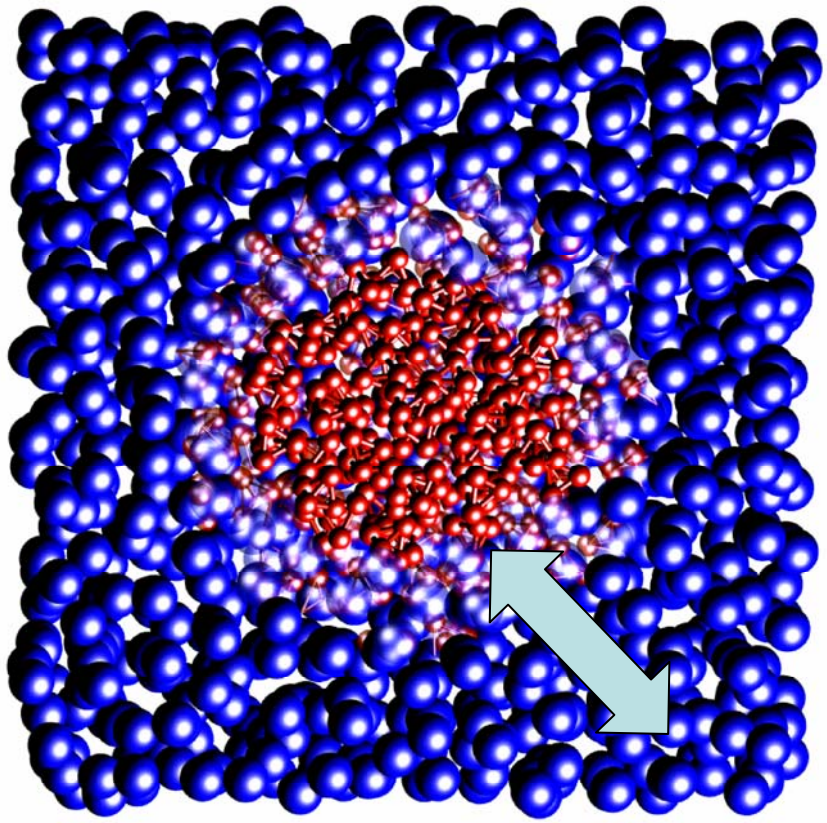
M. Praprotnik, L. Delle Site, KK, 2005ff

Adaptive Methods: Changing degrees of freedom on the fly

Requirements

- Same center-center g(r)
- Same mass density
- Same Pressure (=>Eq. of state)
- Same temperature
- Free exchange between regimes

- Simple two body potential



⇒ Some analogies to 1st order phase transition
⇒ Phase equilibrium
⇒ Thermostat has to provide/take out latent heat due to change in degrees of freedom

VW Foundation Project
M. Praprotnik, L. DelleSite, KK, JCP2005, PRE 2006,2007, JCP2007,

AdResS: Adaptive Resolution Simulations
Changing degrees of freedom on the fly

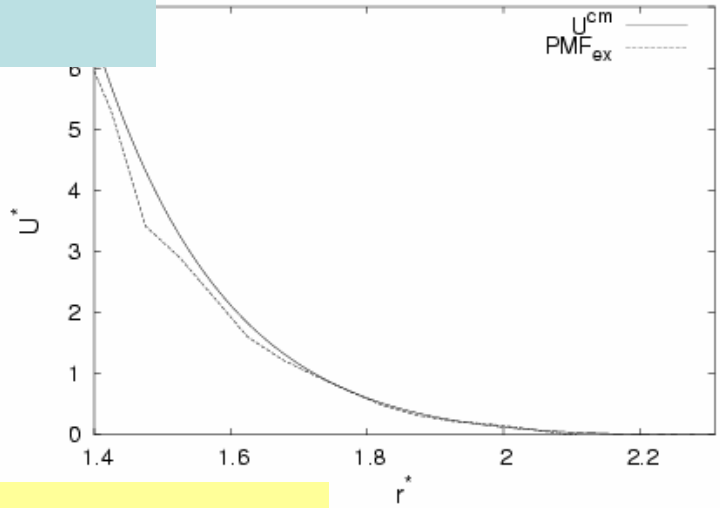
- A tetrahedral molecule has a defined spatial orientation and $3N = 12$ DOFs:
  - 3 translational
  - 3 rotational
  - $3N - 6 = 6$ vibrational
- One particle mesoscopic molecule has no defined spatial orientation and only 3 translational DOFs.

M. Praprotnik, L. DelleSite, KK, JCP2005

Tetrahedron, repulsive LJ Particles, FENE bonds ⇔ **Hybrids** ⇔ **"Softer" Sphere**

Explicit Atom regime ⇔ **Transition regime** ⇔ **Coarse Grained regime**

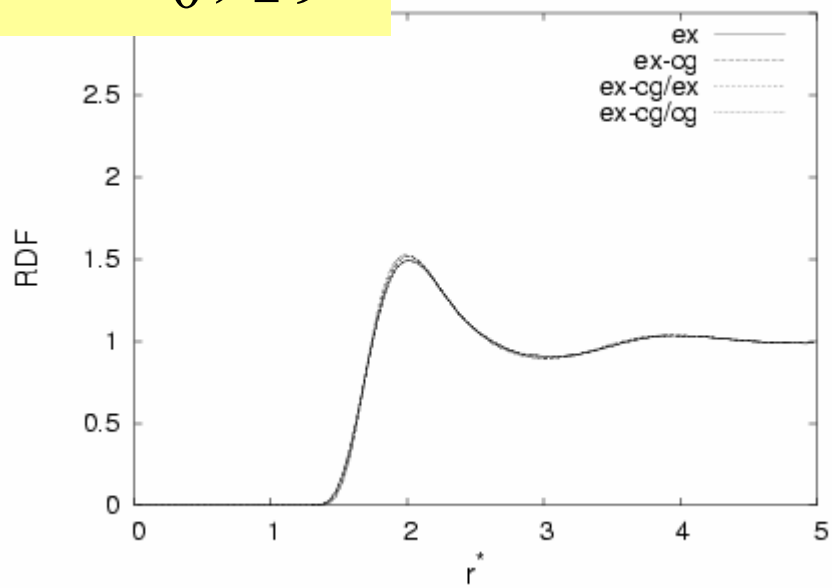
1st step: Coarse Grained Model



Study explicite atom and CG system seperately
=> fit CG Interaction Potential:

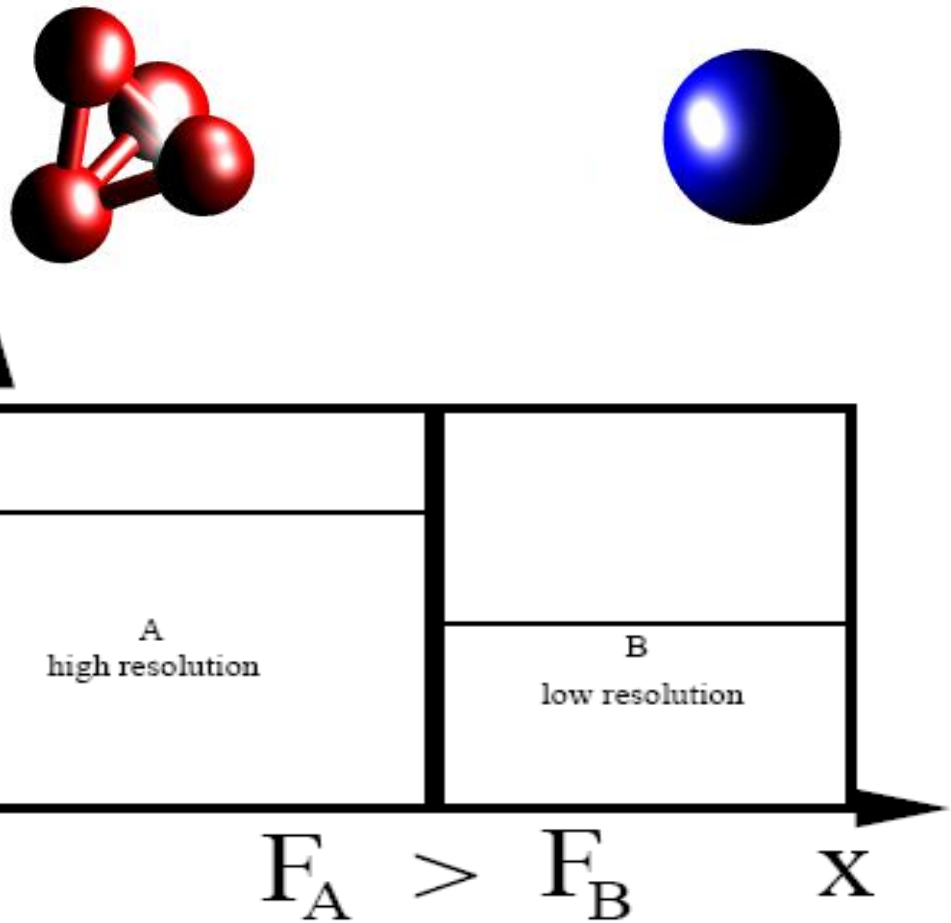
$$U^{cm}(r) = \gamma\{1 - \exp[-\kappa(r - r_0)]\}^2$$

$\mu_{ex} = \mu_{cg}$, $p_{ex}=p_{cg}$, $T_{ex}=T_{cg}$

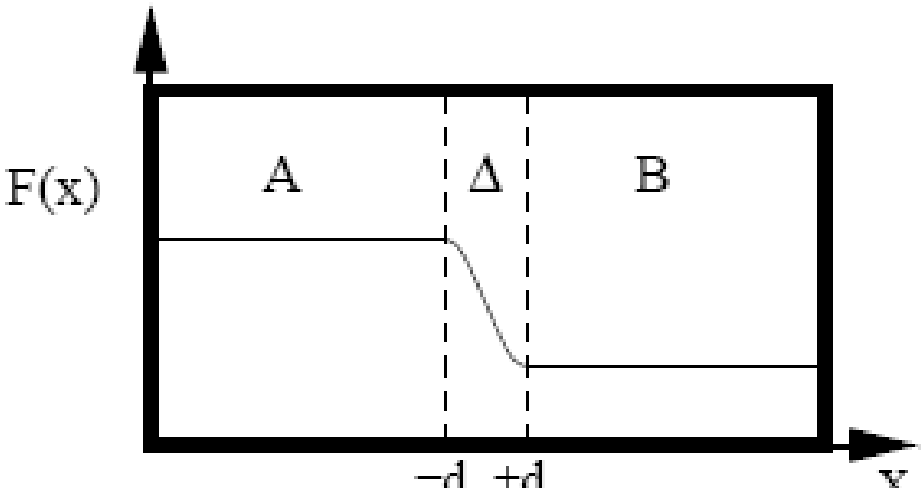


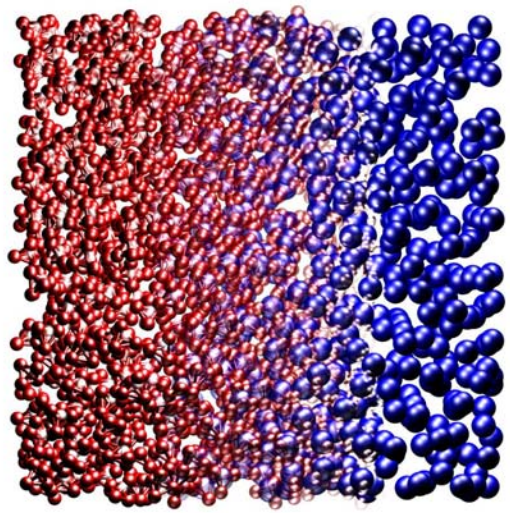
General Considerations

$$\mu_{ex} = \mu_{cg}, \qquad p_{ex} = p_{cg}, \qquad T_{ex} = T_{cg}$$



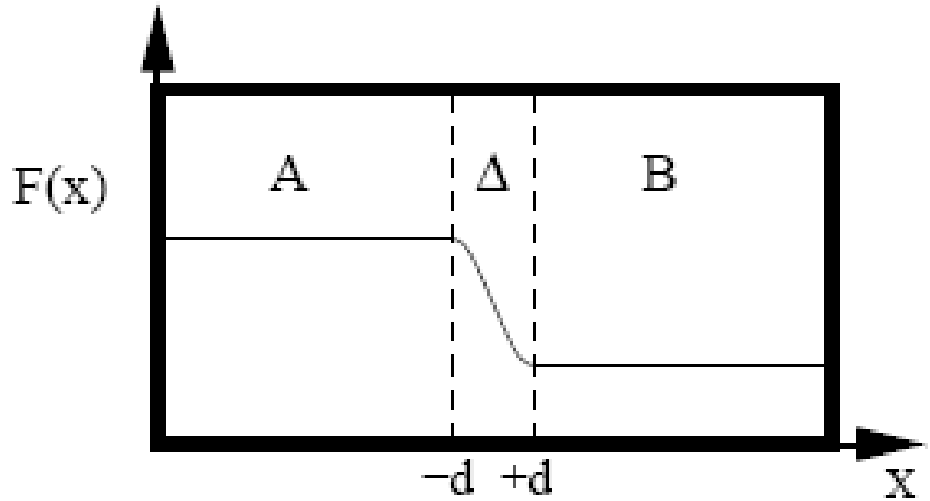
Transition Regime: Changing Degrees of Freedom (DOF)





- The number of DOF is $n = n(x)$ with ; $n_A = const_A$; $n_B = const_B$; and $n_\Delta = n(x)$
- The system is in equilibrium which implies: $\lim_{x \to d-} \frac{\partial F_A(x)}{\partial x} = \lim_{x \to d+} \frac{\partial F_B(x)}{\partial x} = 0$

Temperature: Changing Degrees of Freedom (DOF)



Definition of Temperature in transitions regime:
Fractional degrees of freedom
=> generalization of equipartition theorem
=> Defines thermostat to take out/in "latent heat of the DOFs"

$$H(q) = q^n$$

$$\langle H(q) \rangle_\alpha = \frac{\alpha}{n} k_B T$$

α is the fractionality of DOF *q*

α=1 and n=2 standard case

Temperature: Noninteger Degrees of Freedom (DOF)

- For the fractional quadratic DOF Θ with the weight $w = \alpha$ we can write the partition function as:

$$\exp(-\beta F_\alpha) = C \int \exp(-\beta f(\alpha) p_\Theta^2/2)\, dV_\alpha =$$

$$= 2C \int_0^\infty \exp(-\beta f(\alpha) p_\Theta^2/2)\, |p_\Theta|^{\alpha-1} \frac{dp_\Theta}{\Gamma(\alpha)} =$$

$$= \frac{2^{\alpha/2} C \Gamma(\alpha/2)}{\Gamma(\alpha)} f(\alpha)^{-\alpha/2} \beta^{-\alpha/2} \sim \beta^{-\alpha/2}.$$

- $\langle K_\alpha \rangle = \frac{d(\beta F_\alpha)}{d\beta} = \frac{\alpha}{2\beta} = \frac{\alpha T}{2}$.
- In equilibrium $T_A = T_B = T_\Delta = T$ and thus: $n_\alpha \sim \alpha$.

M. Praprotnik, K. Kremer, L. Delle Site, Phys. Rev. E 75, 017701 (2007).

AdResS: Main Steps

AdResS consists of two main steps:

1. Derive the effective pair potential U^{cm} between coarse-grained molecules on the basis of the reference all-atom system.
2. Couple the atomistic and mesoscopic scales:

$$\mathbf{F}_{\alpha\beta} = w(X_\alpha)w(X_\beta)\mathbf{F}^{atom}_{\alpha\beta} + [1 - w(X_\alpha)w(X_\beta)]\mathbf{F}^{cm}_{\alpha\beta},$$

where

$$\mathbf{F}^{atom}_{\alpha\beta} = \sum_{i\alpha, j\beta} \mathbf{F}^{atom}_{i\alpha j\beta}$$

is the sum of all pair interactions between explicit atoms of molecules α and β and

$$\mathbf{F}^{atom}_{i\alpha j\beta} = -\frac{\partial U^{atom}}{\partial \mathbf{r}_{i\alpha j\beta}},$$

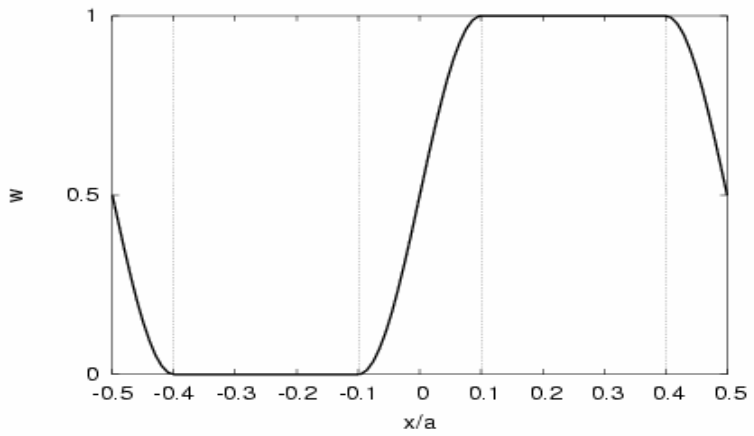
$$\mathbf{F}^{cm}_{\alpha\beta} = -\frac{\partial U^{cm}}{\partial \mathbf{R}_{\alpha\beta}}.$$

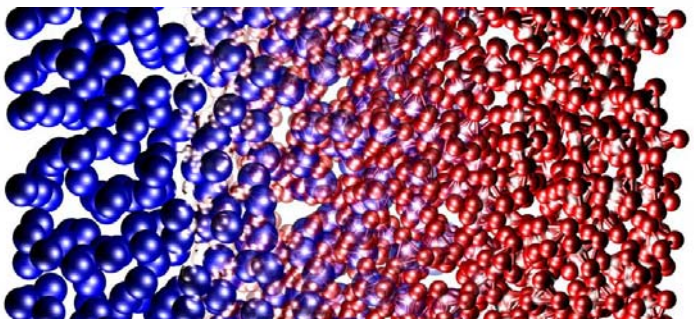
Transition Regime: Force Interpolation

$$F_{\alpha\beta} = w(X_\alpha)w(X_\beta)F_{\alpha\beta}^{atom} + [1 - w(X_\alpha)W(X_\beta)]F_{\alpha\beta}^{cm}$$

Full atomistic force

Full coarse grained force



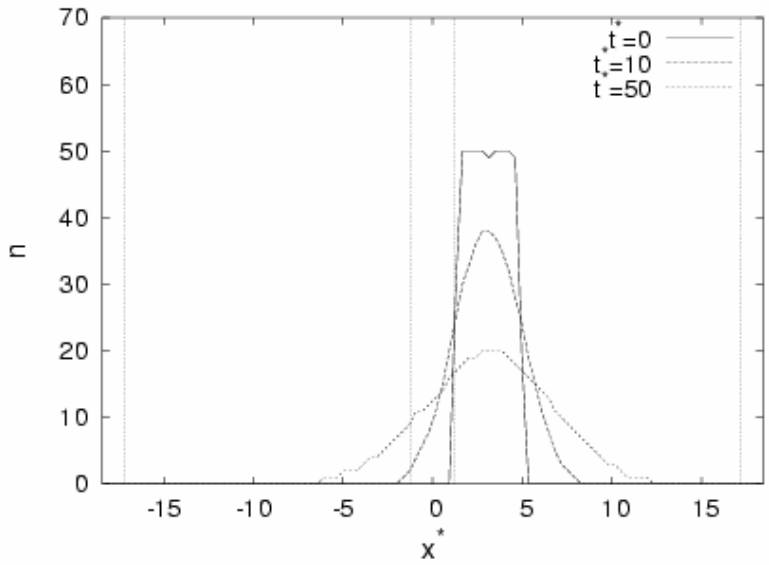


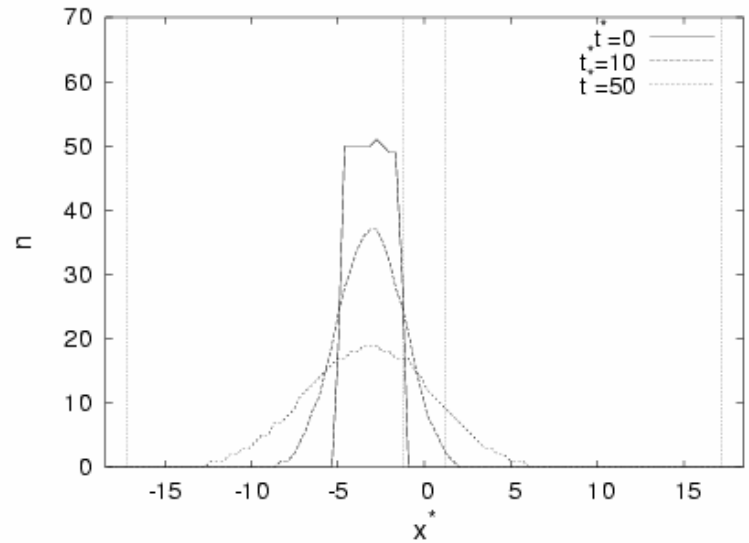
Interactions

explicit-explicit
CG-CG
hybrid-hybrid

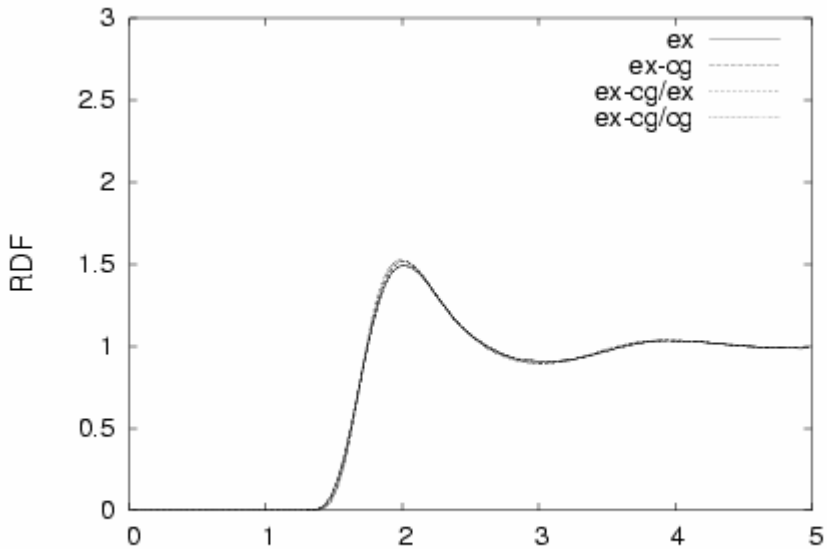
CG- hybrid: CG-CG
explicit-hybrid: explicit-explicit

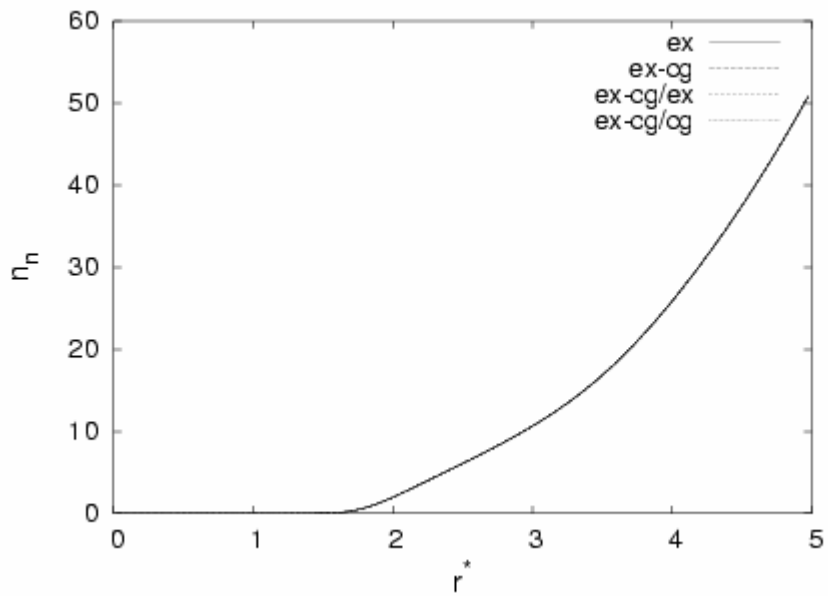
Particle Exchange



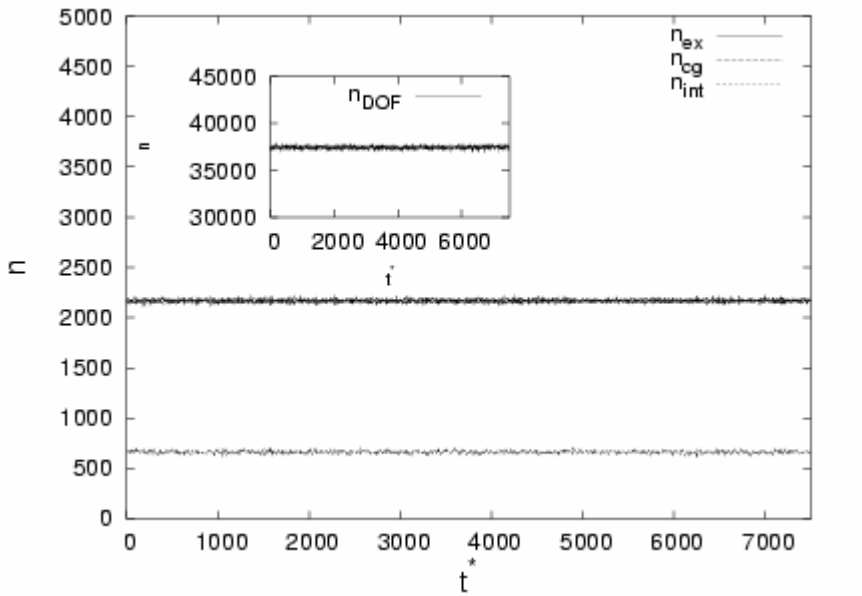


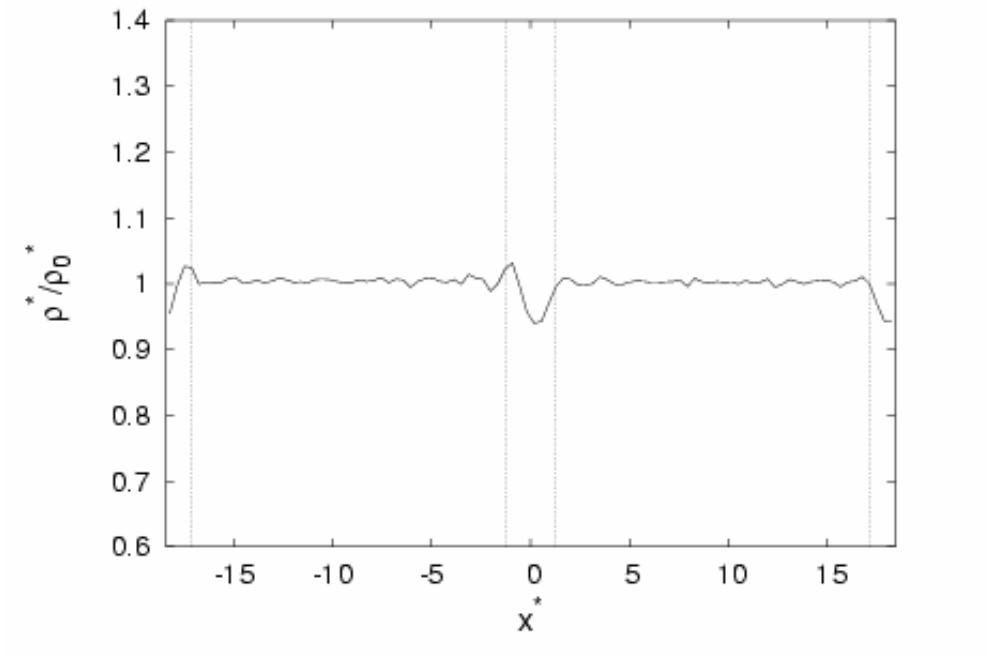
Radial Distributions, Number of neighbours



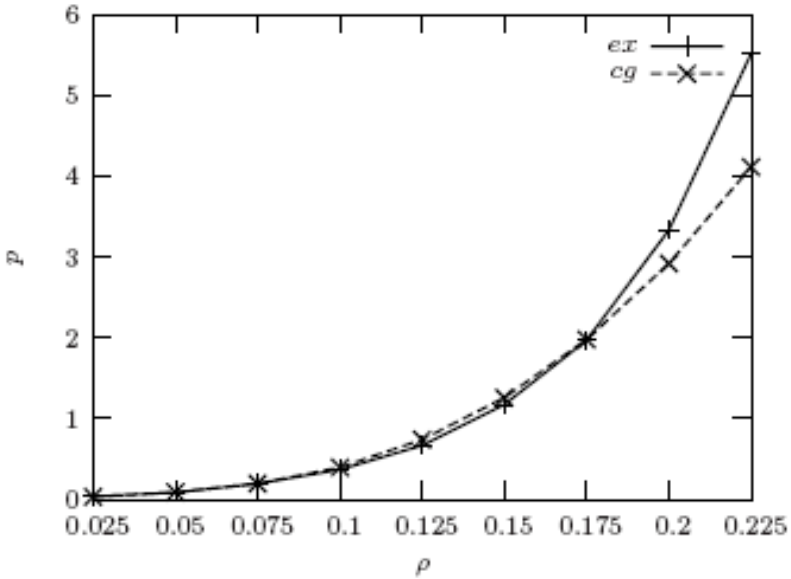


Particle Numbers, Density

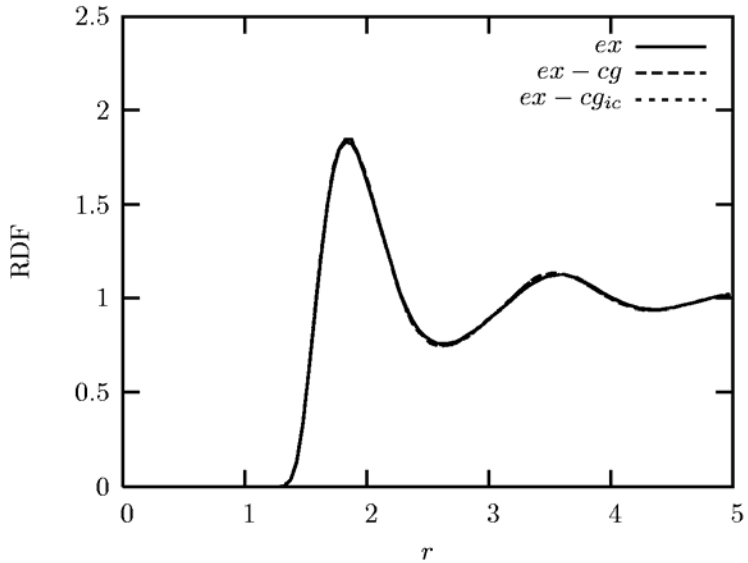


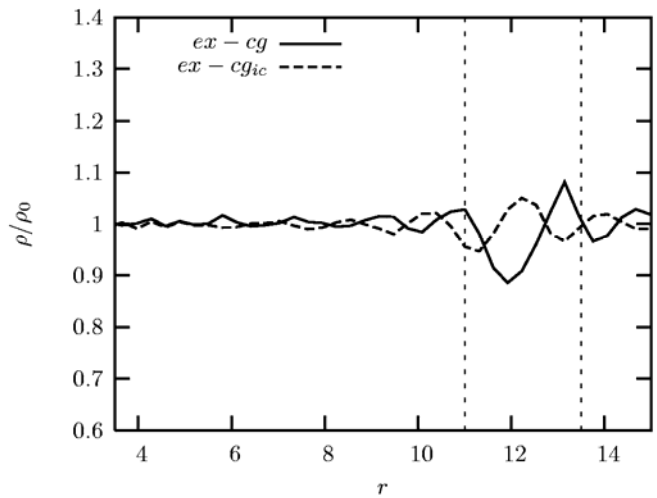


Radial Distributions, Densities, high density

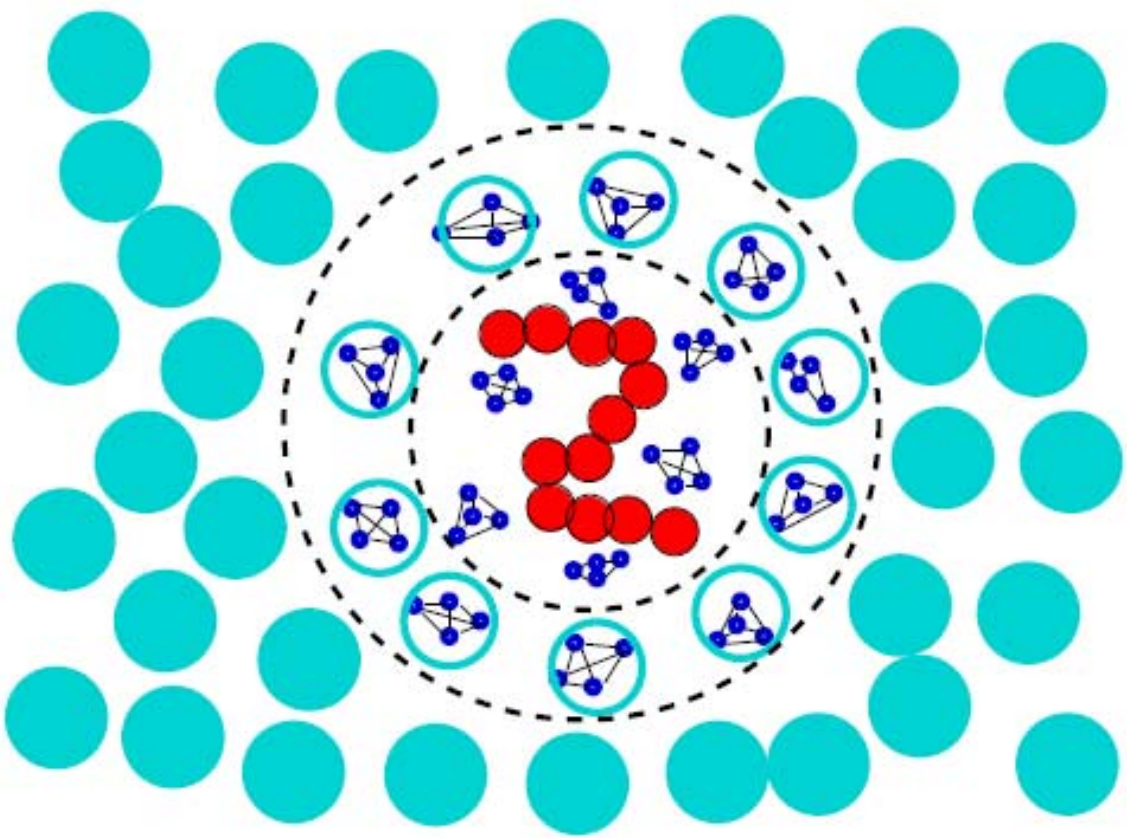


(m) Equation of state for $\rho = 0.175$ and $T = 1$.





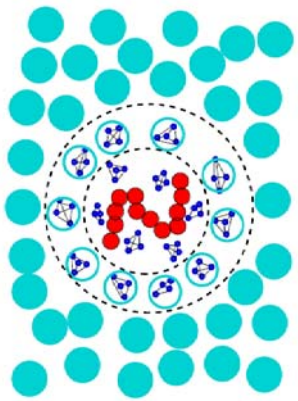
1st "Application": Chain in solvent

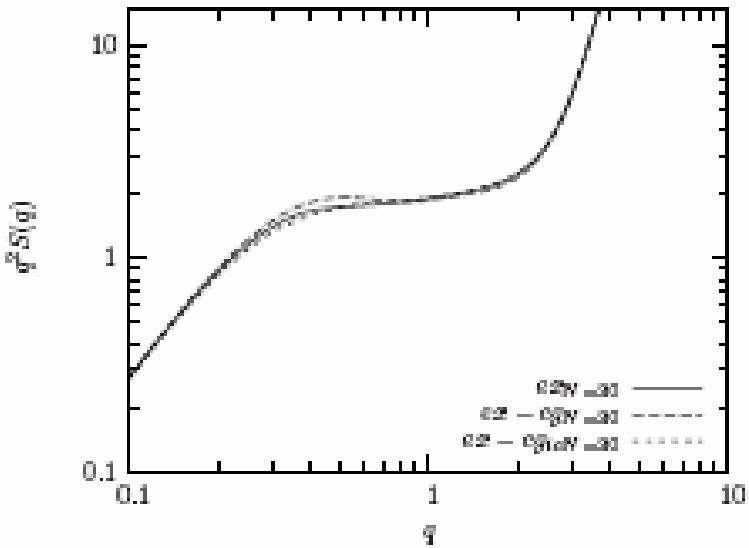


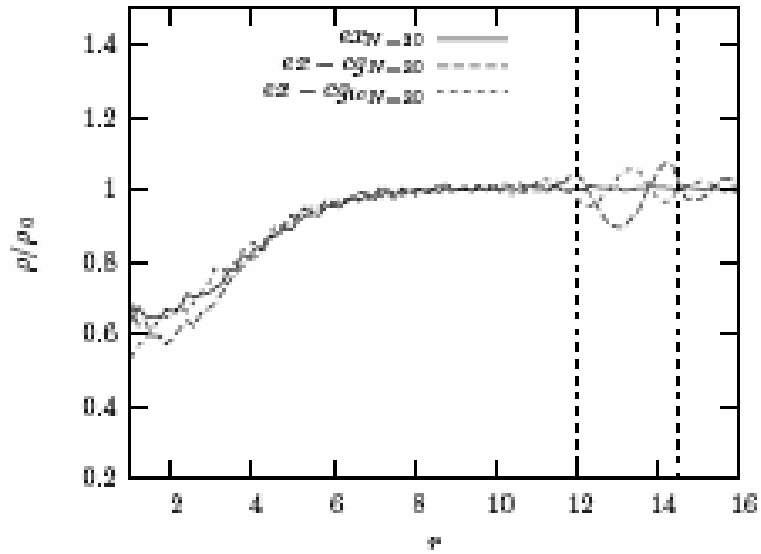
Explicit resolution regime moves with the polymer

M. Praprotnik, L. Delle Site, KK, JCP (2007)

1st Application: Chain in solvent



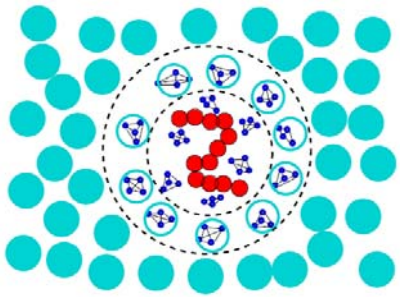




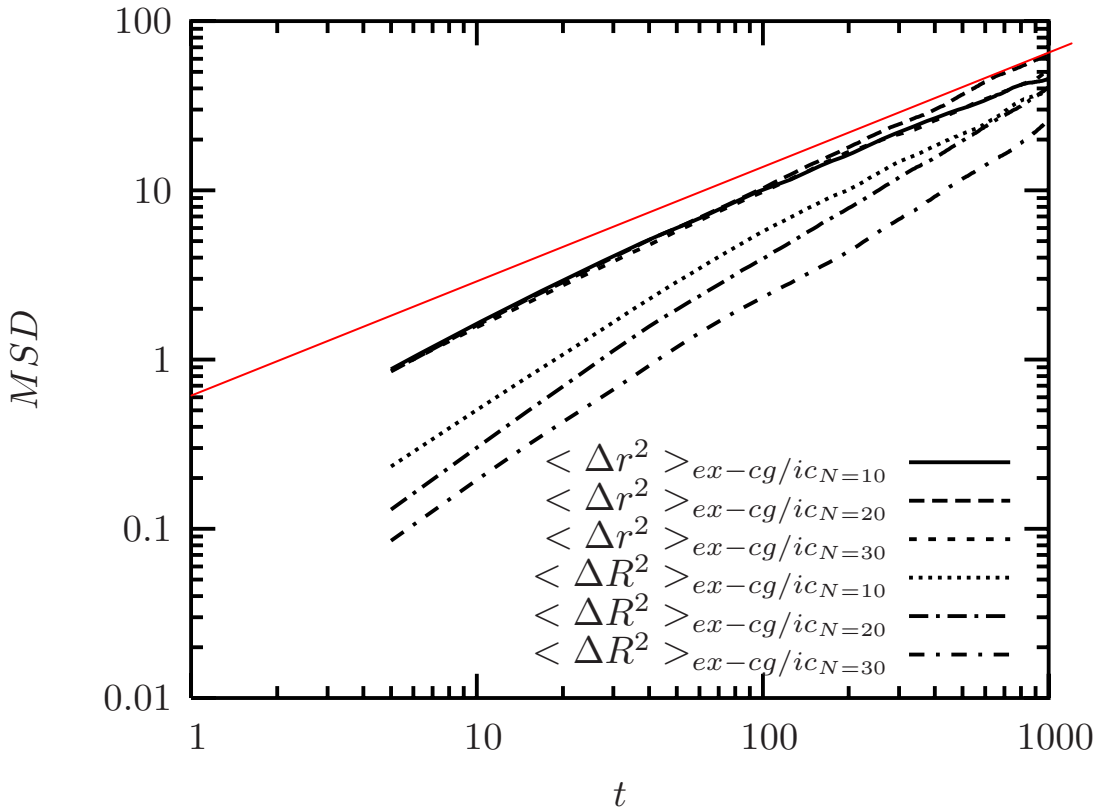
Explicit resolution regime moves with the polymer

powered by ESPResSo

1st Application: Chain in solvent

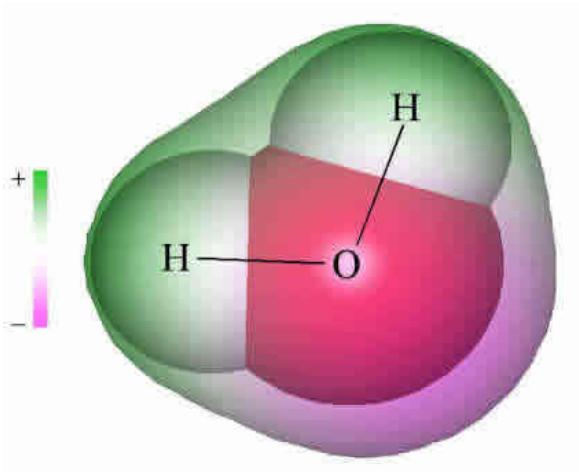


Zimm scaling

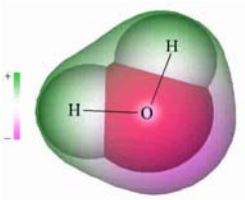


Explicit resolution regime moves with the polymer

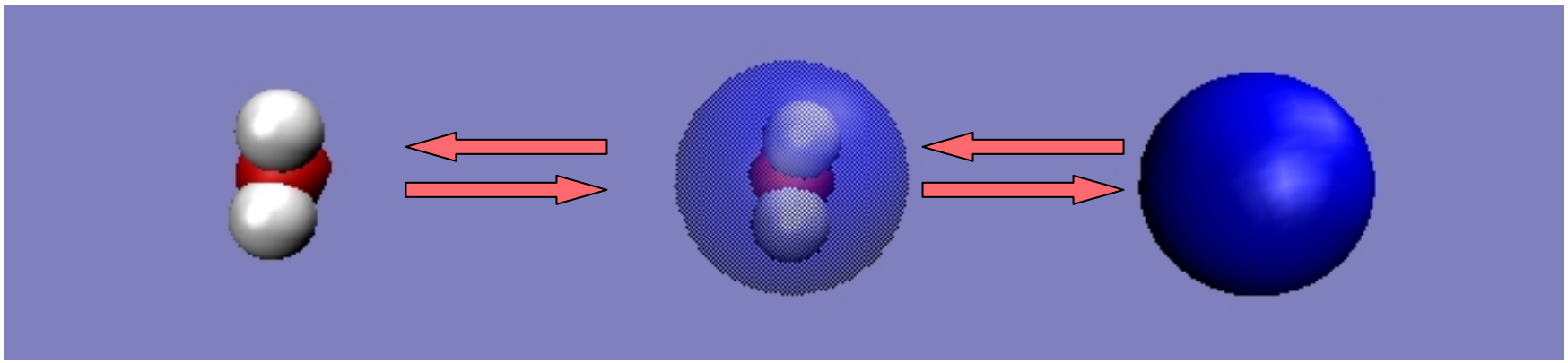
2nd Application TIP3P Water



Collaboration with Cecilia Clementi, Silvina Matysiak,
Department of Chemistry, Rice University, Houston, Texas



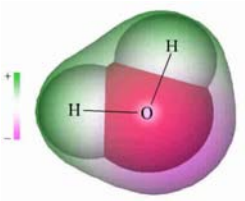
water plays a role at different length scales…



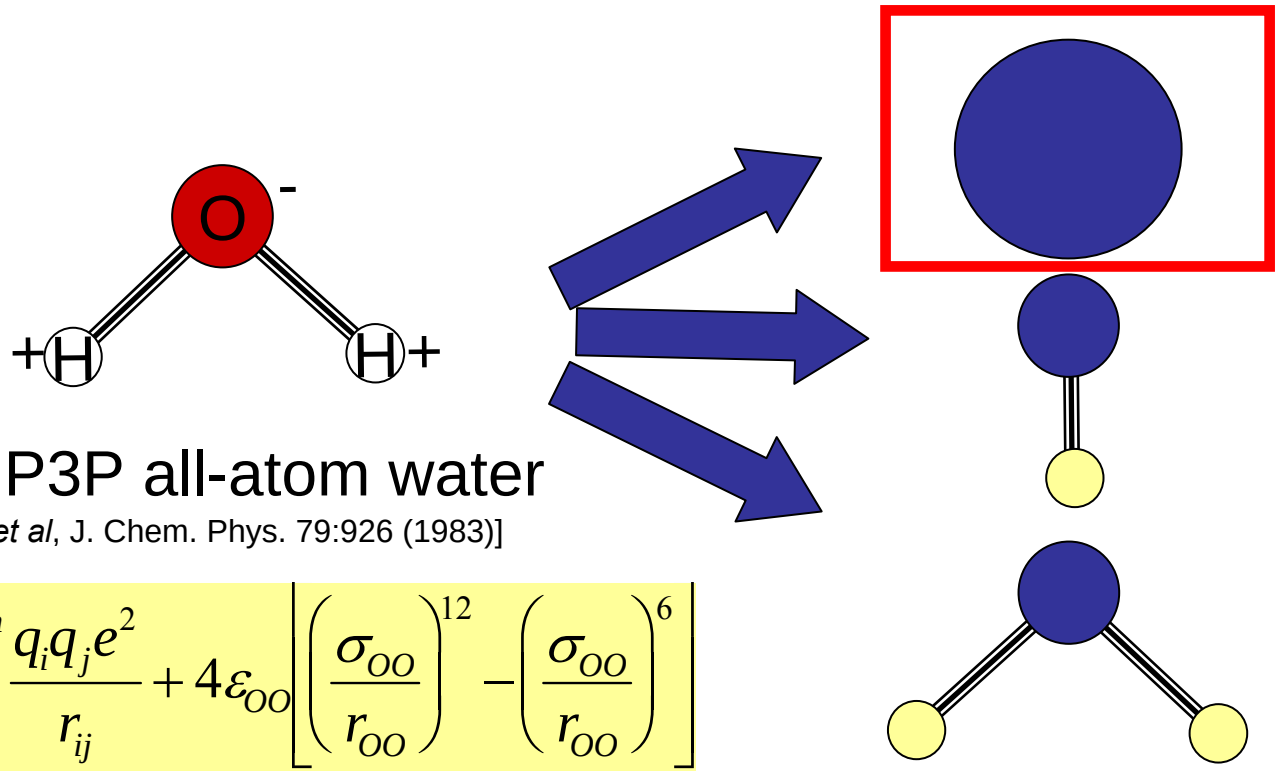
all-atom model,
physical force-field

adaptive, hybrid scheme
to switch from
one to the other “on-the-fly”

coarse-grained model,
effective interactions



First step: design a coarse-grained model of water (thermodynamically, dynamically and **structurally**)



Rigid TIP3P all-atom water

[Jorgensen *et al*, J. Chem. Phys. 79:926 (1983)]

$$U_{mn} = \sum_{i}^{On\_m} \sum_{j}^{Om\_n} \frac{q_i q_j e^2}{r_{ij}} + 4\varepsilon_{OO}\left[\left(\frac{\sigma_{OO}}{r_{OO}}\right)^{12} - \left(\frac{\sigma_{OO}}{r_{OO}}\right)^{6}\right]$$

Model

direct

inverse

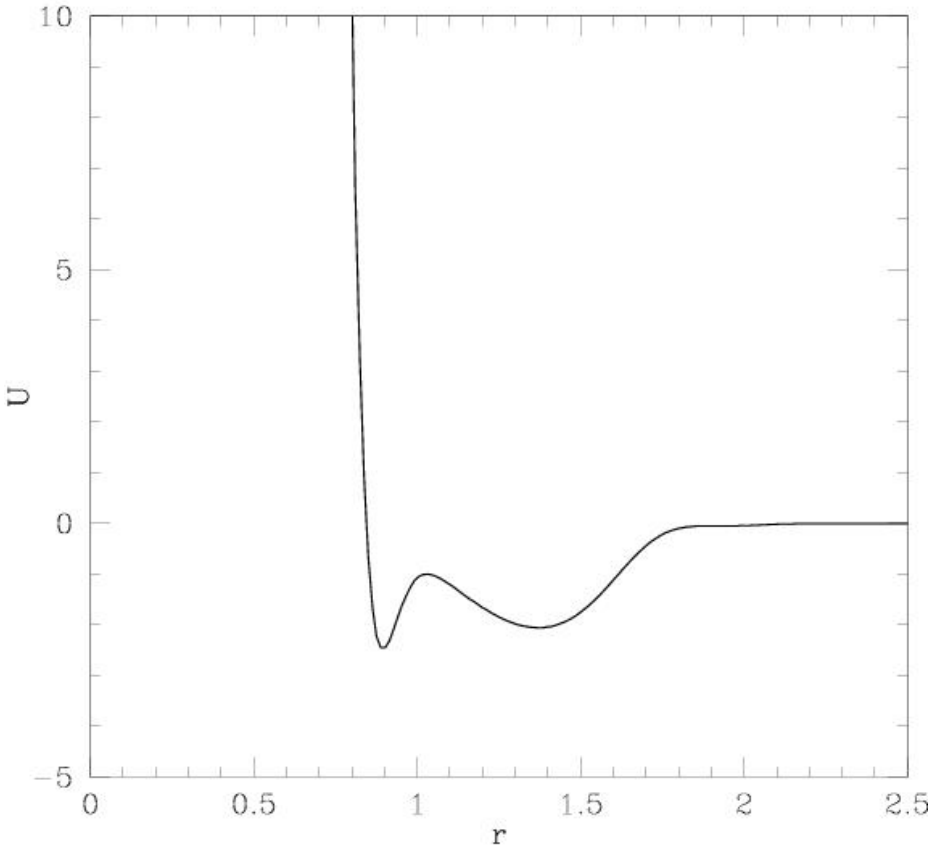
Properties

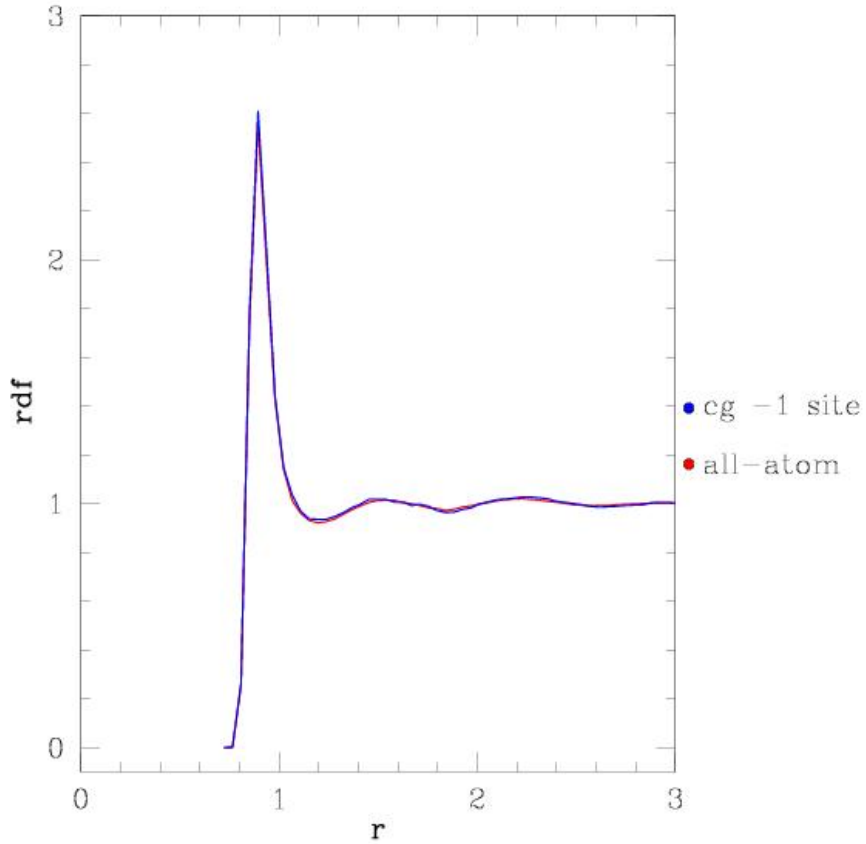
Interaction potential

Radial distribution functions

New Single-site model

(needed to match correlation functions!)

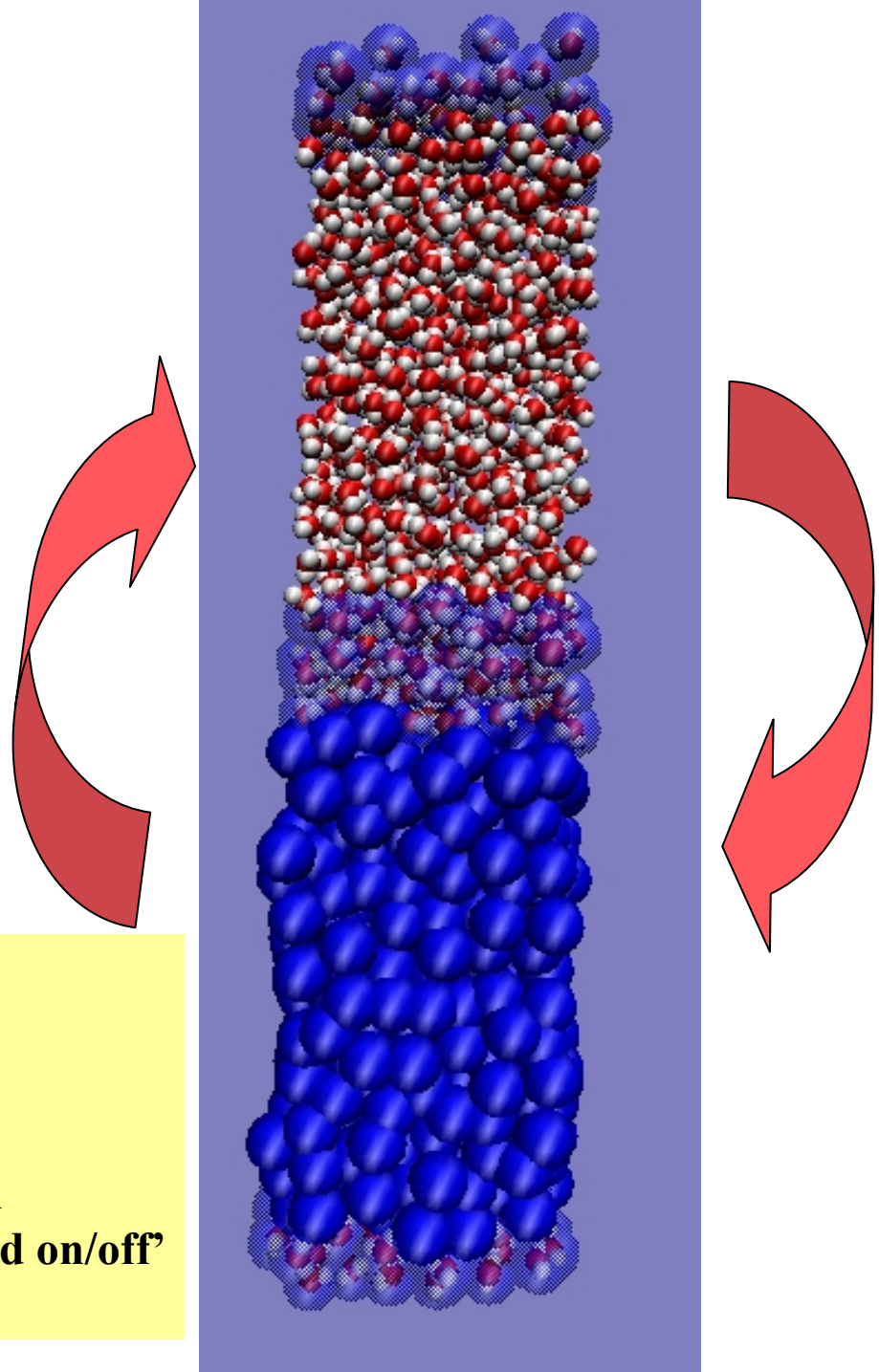




Thermodynamics (pressure, temperature) is also in excellent agreement, 4 nearest neighbors in first shell

Requirements

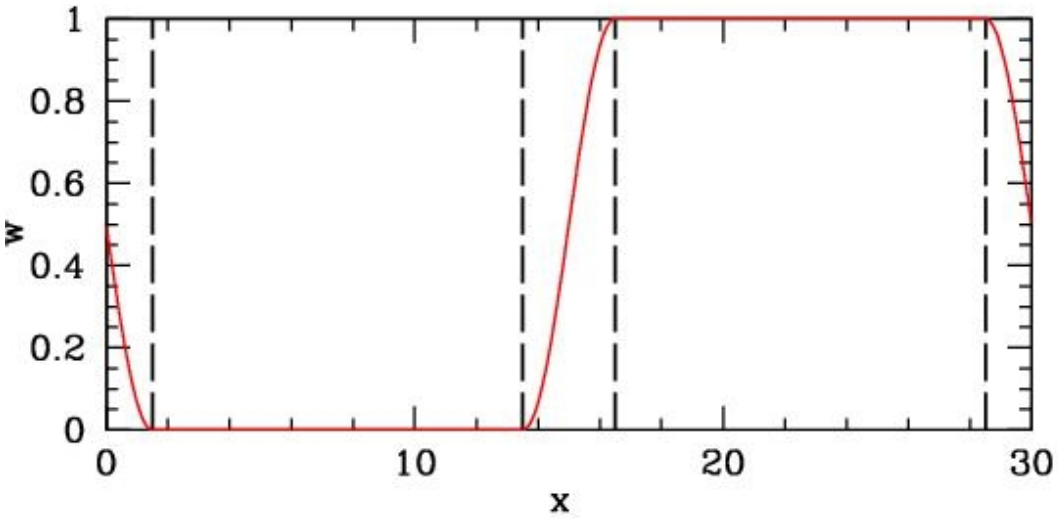
- Same center-center rdf
- Simple two-body potential
- Same mass density
- Same Pressure
- Same temperature
- Free exchange between regimes

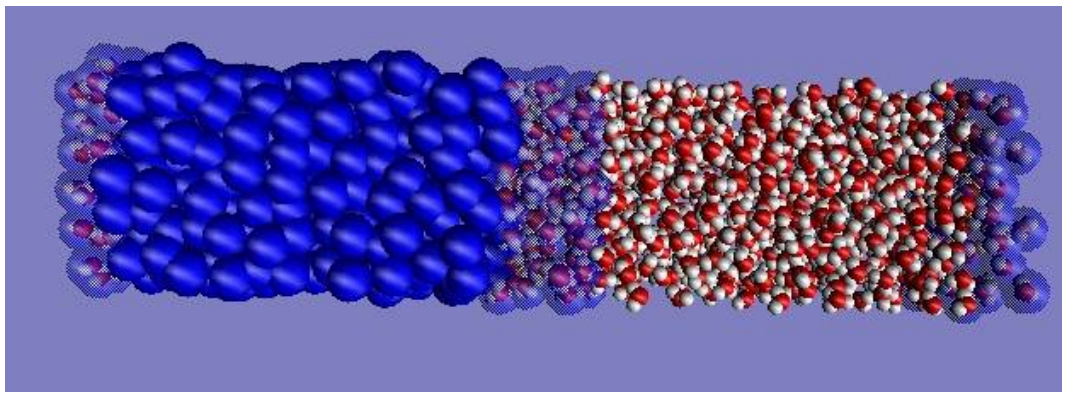


⇒ Phase equilibrium
⇒ Thermostat has to provide/take out
latent heat due to change in degrees
of freedom
⇒ Molecules adapt their level of resolution
⇒ Rotational DOFs are gradually ‘swichted on/off’
⇒ Same linear momentum

Transition Regime

coarse grained hybrid explicit





$$F_{\alpha\beta} =$$

$$w(X_\alpha)w(X_\beta)F_{\alpha\beta}^{atom} +$$

$$[1 - w(X_\alpha)w(X_\beta)]F_{\alpha\beta}^{cm}$$

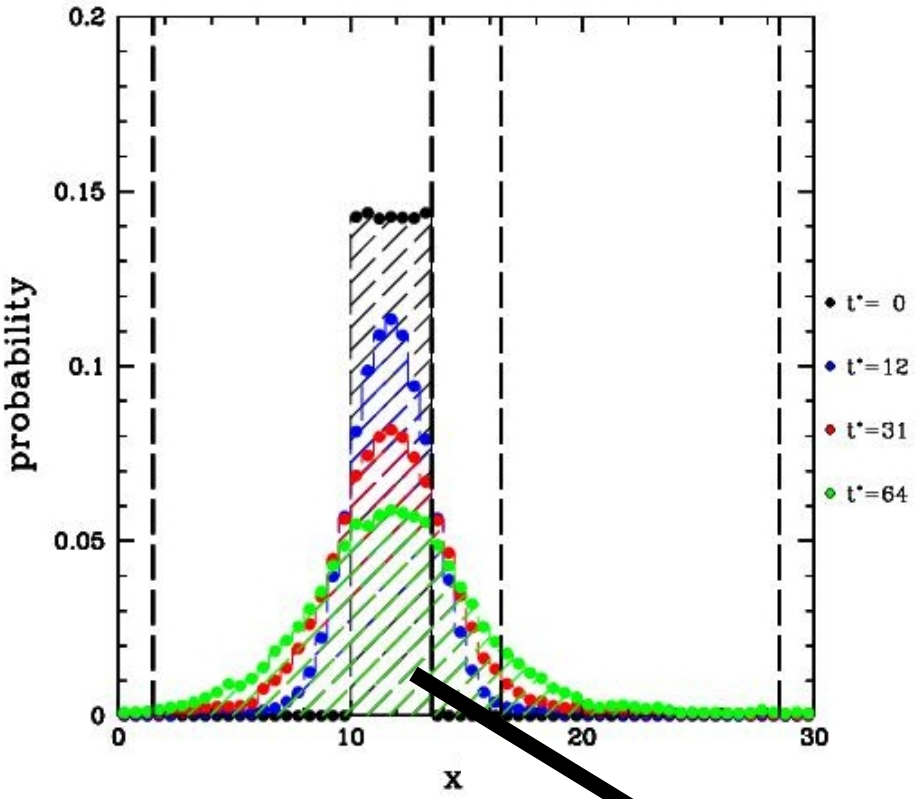
Interactions

explicit-explicit
CG-CG
hybrid-hybrid

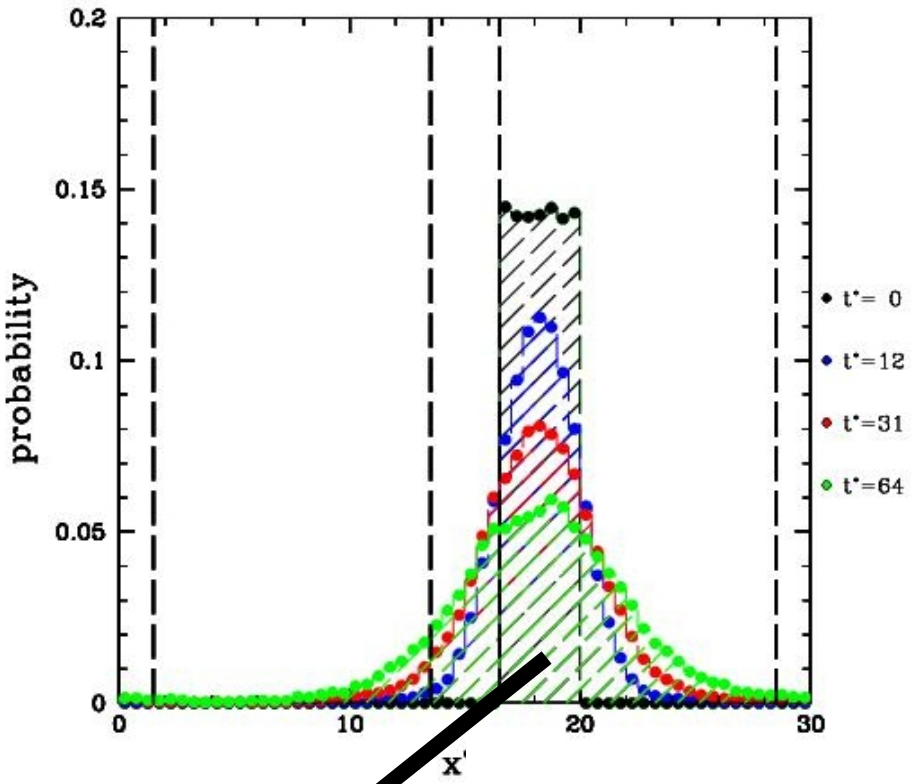
CG- hybrid: CG-CG
explicit-hybrid: explicit-explicit

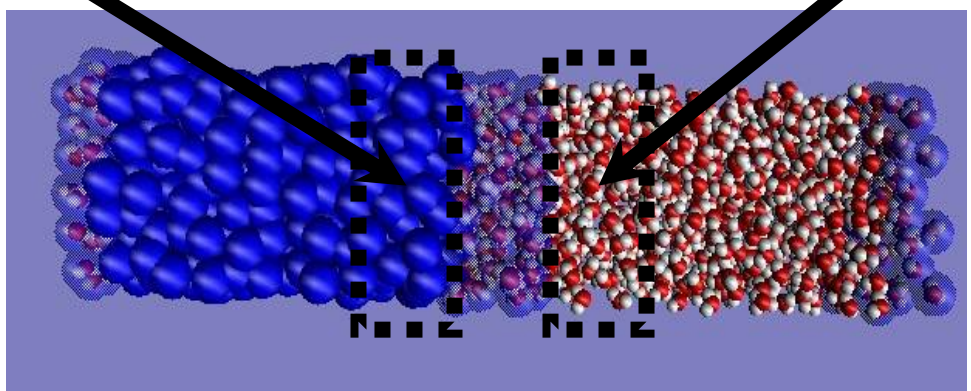
In explicit regime: Reaction field for electrostatics

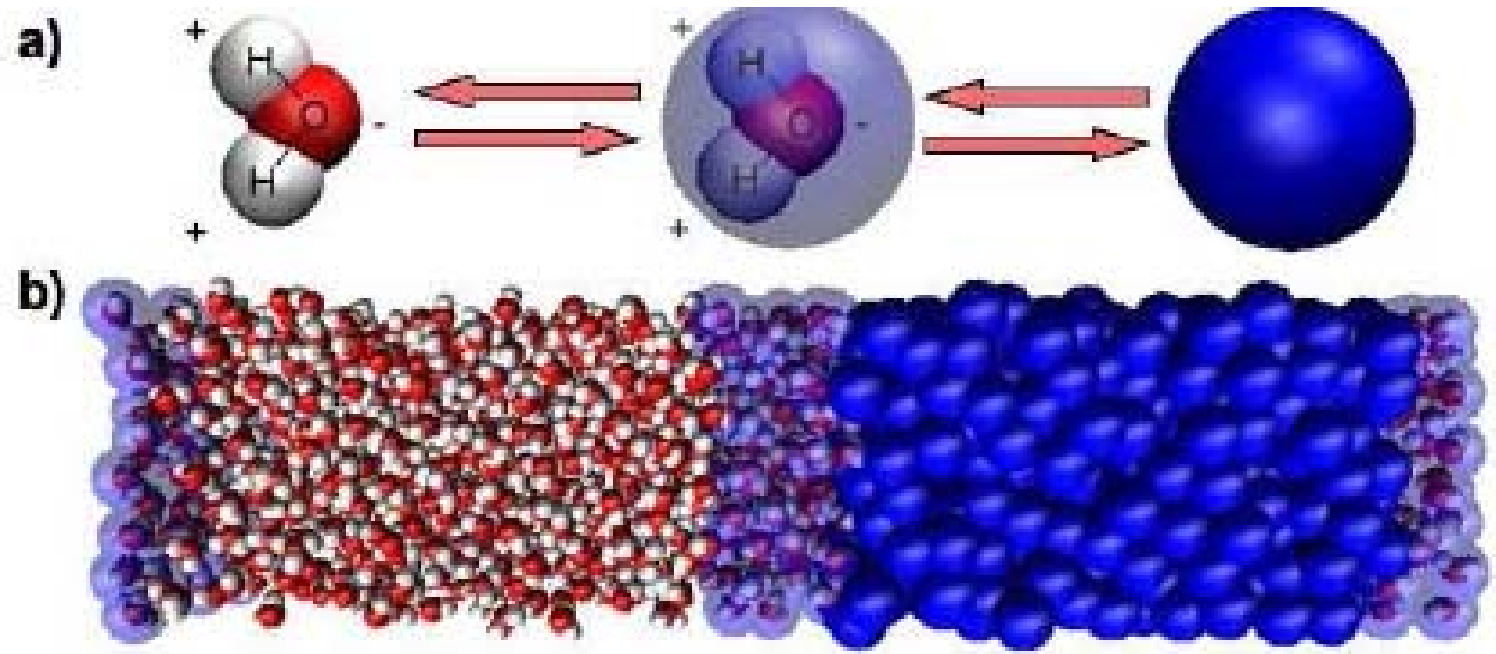
coarse grained hybrid explicit



coarse grained hybrid explicit

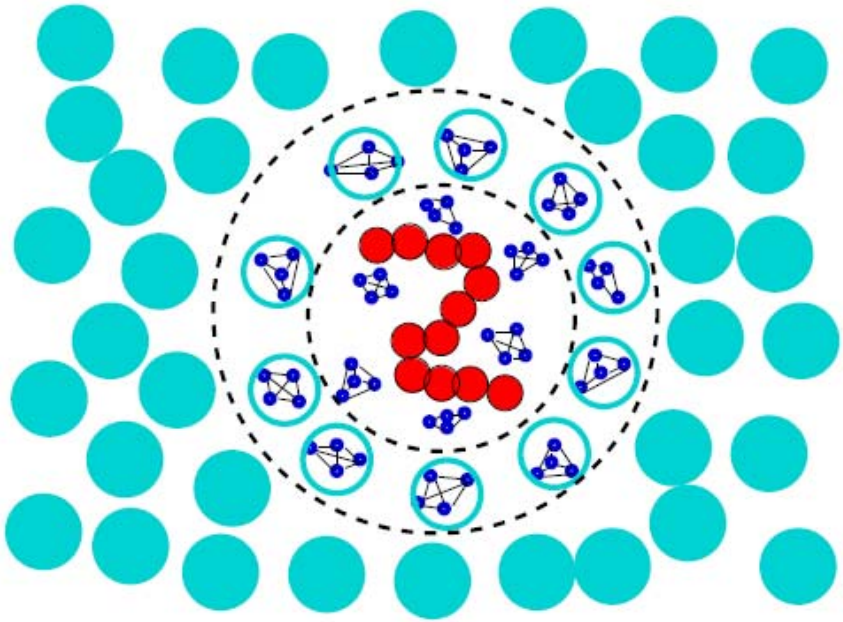






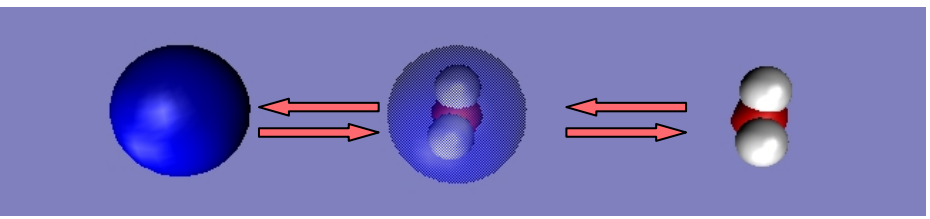
The simulation speed-up is $\sim 17 - 20$ compared to atomistic simulations.

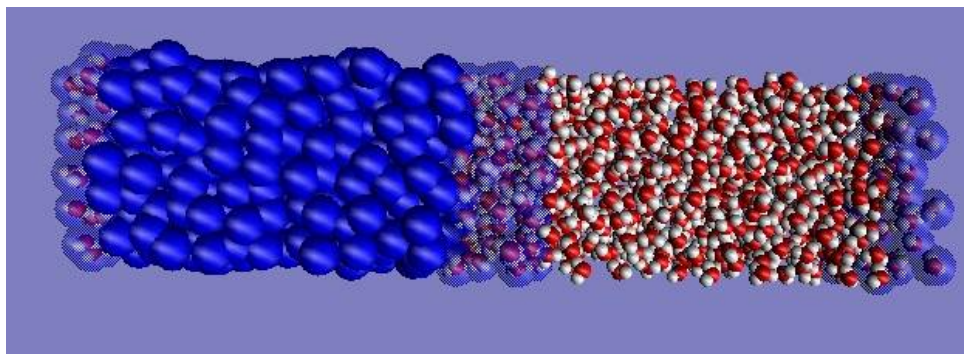
M. Praprotnik, L. Delle Site, K. Kremer, S. Matysiak, C. Clementi, cond-mat/0611544.



Explicit resolution regime moves with the polymer

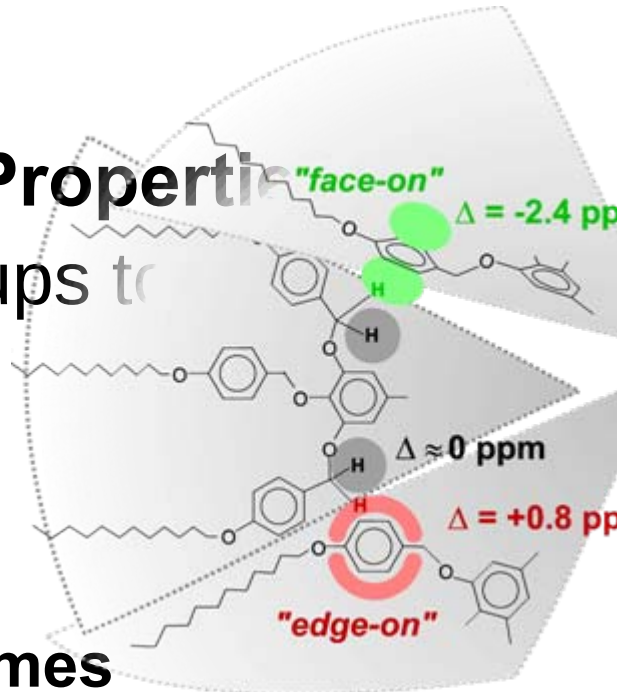
Adaptive Resolution Simulations of Water





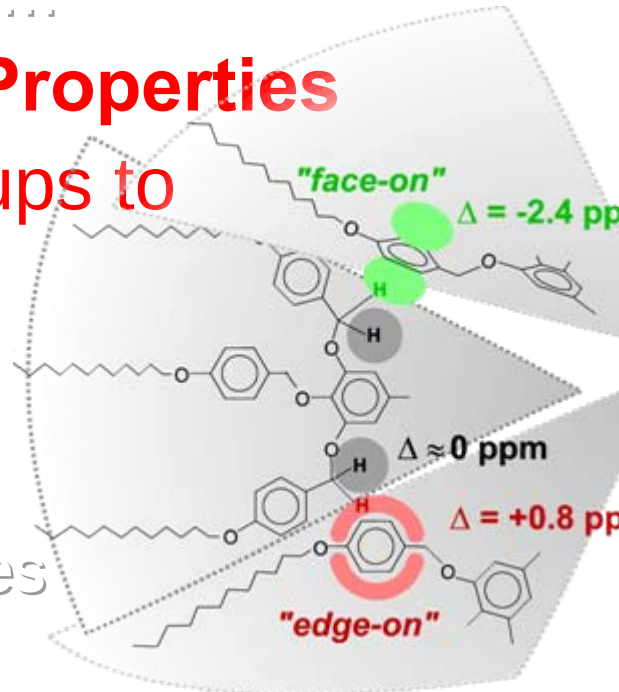
Conclusion: A few Challenges

- **Dual-Triple… Scale Simulations/Theory**
  - **Adaptive** quantum⇔force field⇔coarse grained …
- **Nonbonded Interactions: NEMD, Morphology…**
  - Accuracy k_BT***O(1/N)*** needed!
- **Conformations ⇔ Electronic Properti**
  - E.g. coupling of aromatic groups t backbone conformation, or to other chains
- **Online Experiments:**
  - **Nanoscale Experiments, long Times**

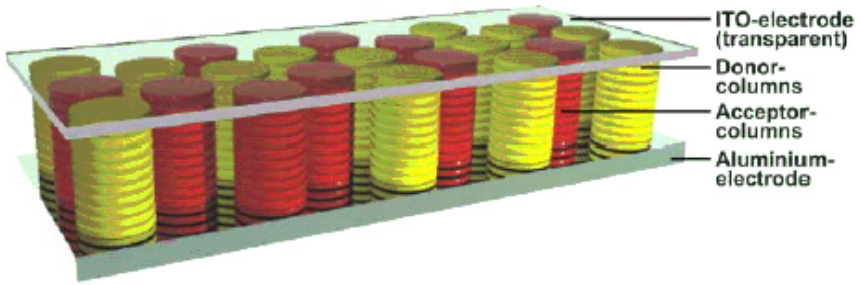


A few Challenges

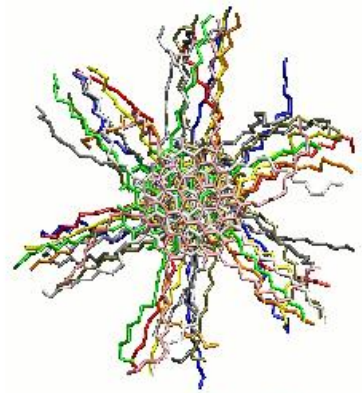
- Dual-Triple… Scale Simulations/Theory
  - Adaptive quantum⇏force field⇏coarse grained …
- Nonbonded Interactions:
  - Morphology, Solvation, Adsorption…
- **Conformations ⇔ Electronic Properties**
  - E.g. coupling of aromatic groups to backbone conformation, or to other chains
- Online Experiments:
  - Nanoscale Experiments, long Times

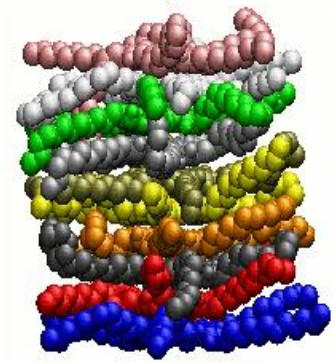


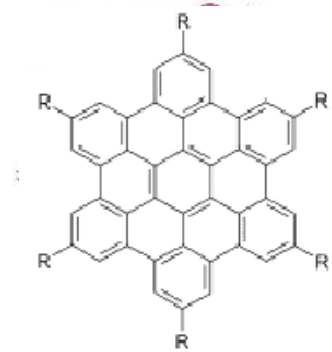
Columnar Phases of Hexabenzo-Coronene (D. Andrienko et al)



C. D. Simpson, J. Wu, M. D. Watson, K. Müllen
Journal of Materials Chemistry, 2003

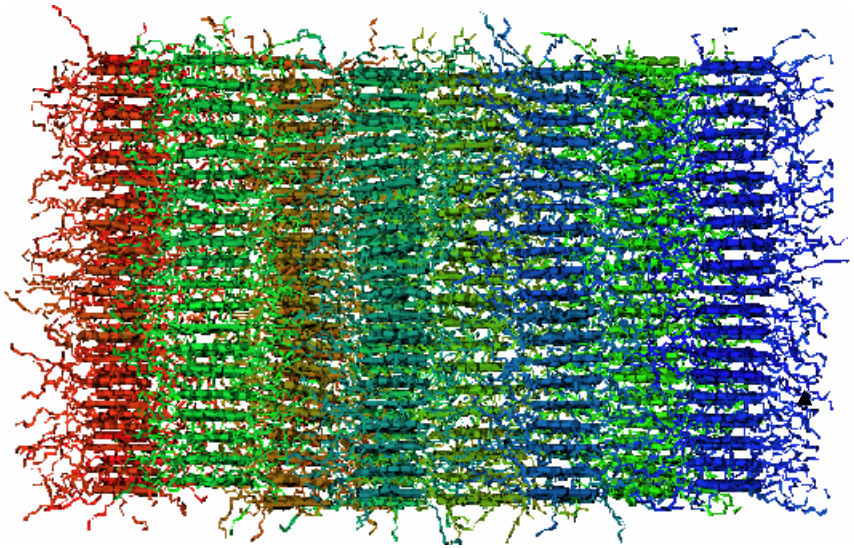


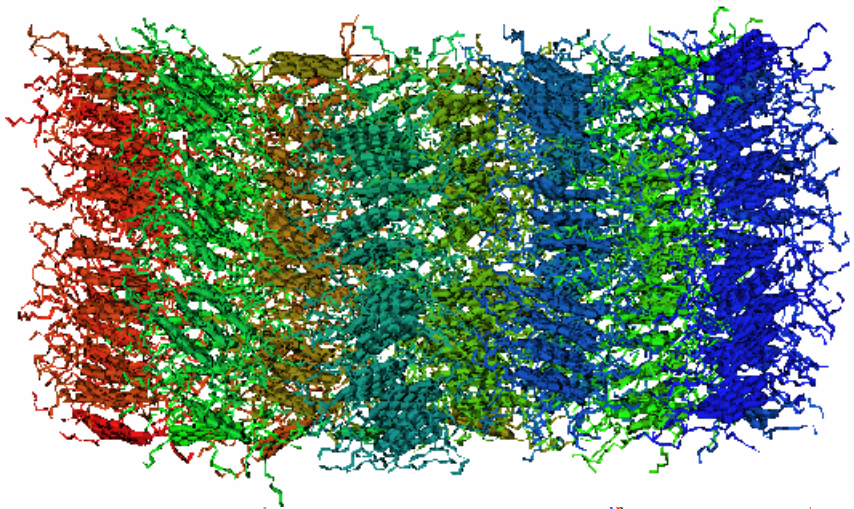


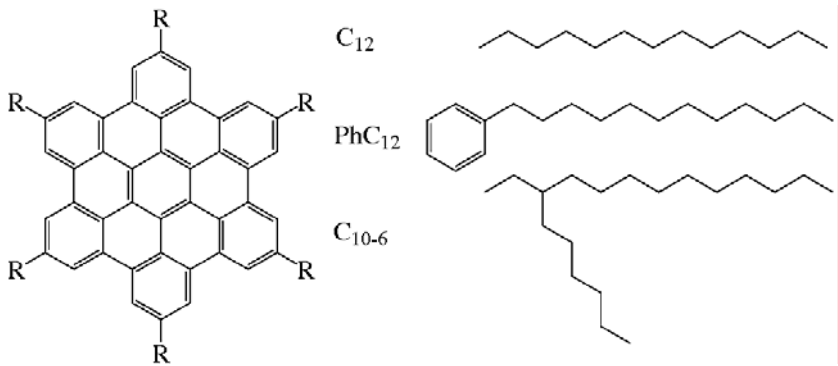


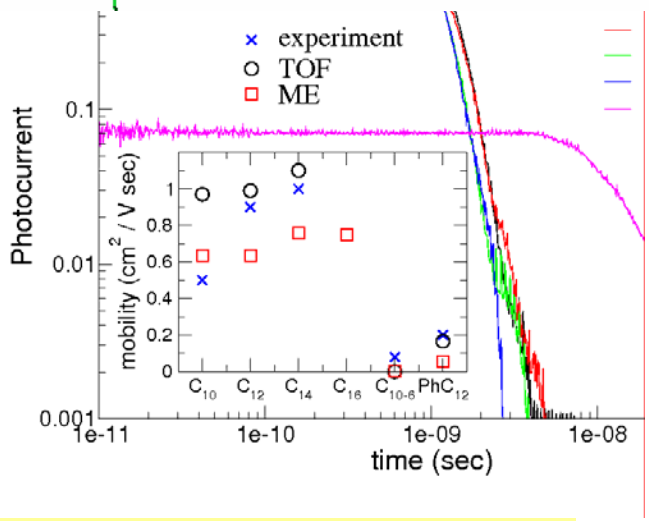
A. von Lilienfeld, D. Andrienko J. Chem. Phys. 2006
V. Marcon, D. Andrienko, KK, J. Chem. Phys. 2006

Columnar Phases of Hexabenzo-Coronene (D. Andrienko et al)



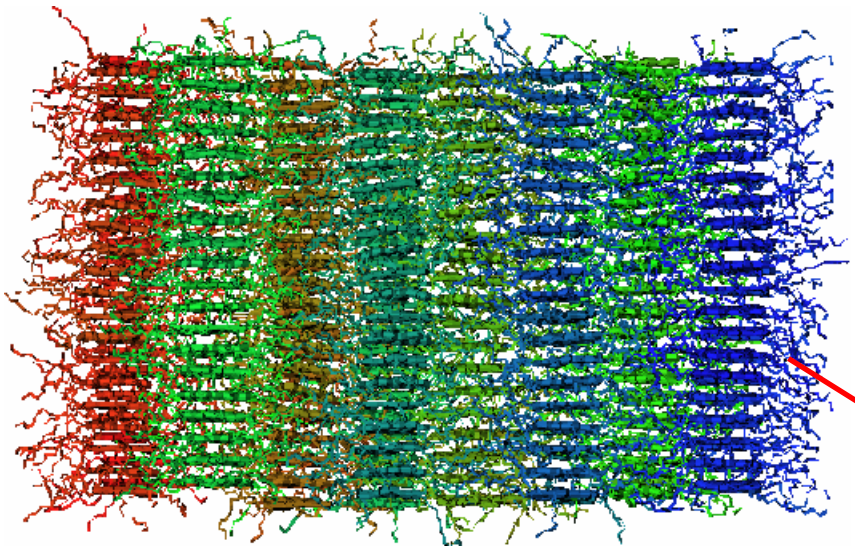


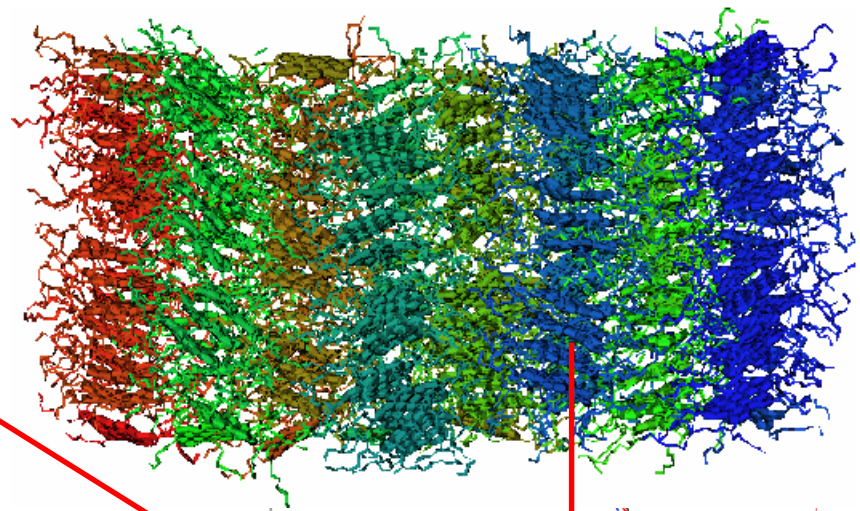


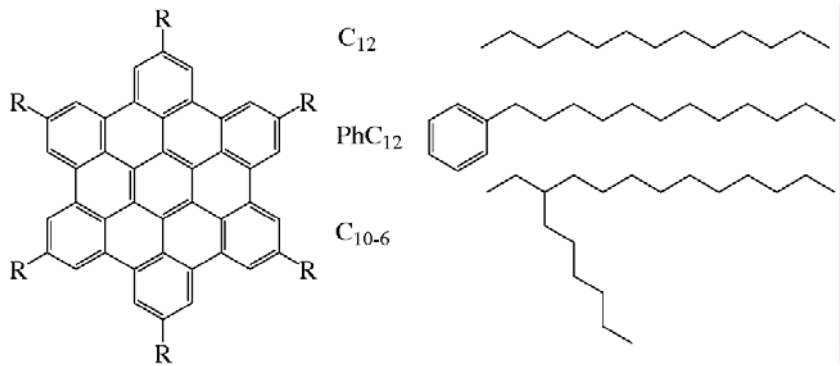


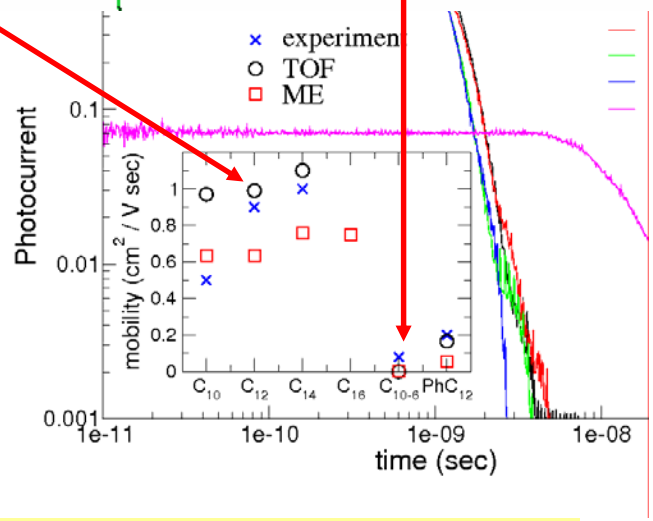
J. Kirckpatric, J. Nelson, V. Marcon, KK, D. Andrienko in prep. 2006

Columnar Phases of Hexabenzo-Coronene (D. Andrienko et al)







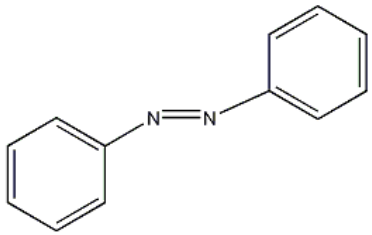


J. Kirckpatric, J. Nelson, V. Marcon, KK, D. Andrienko in prep. 2006

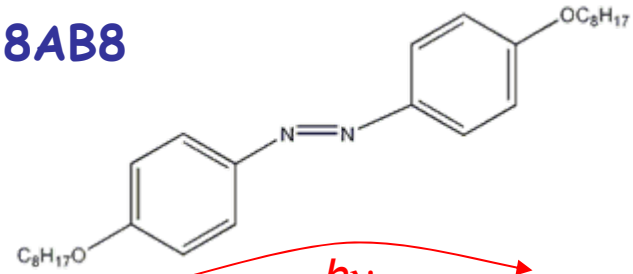
Photoswitchable Azobenzene

VW Stiftung, L. Delle Site, KK - D. Marx (Bochum)

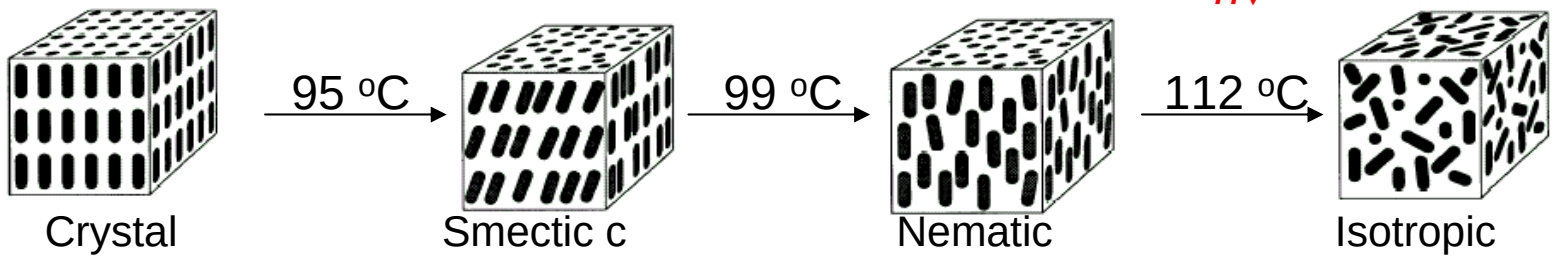
Azobenzene

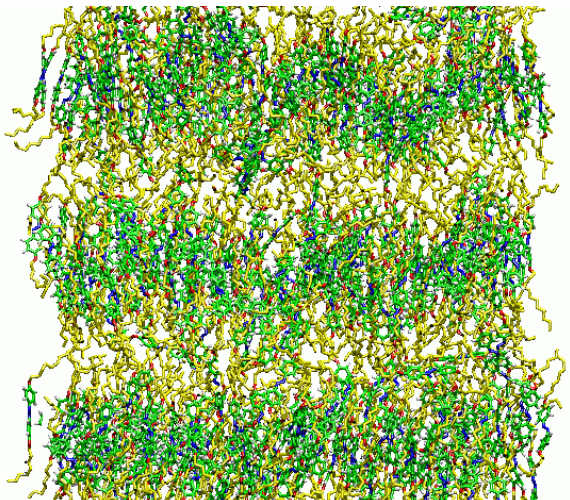


8AB8



Phases of 8AB8

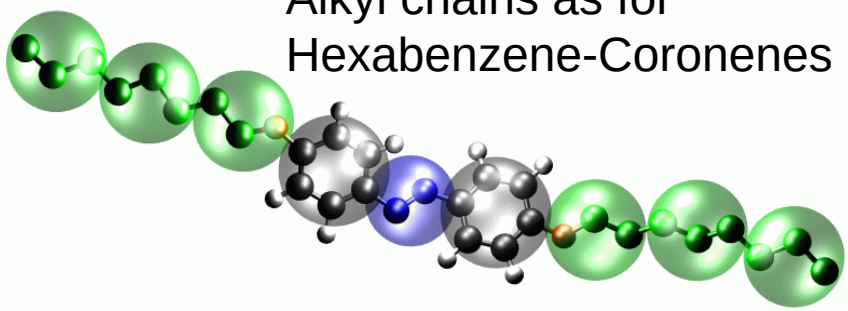




All atom snapshot

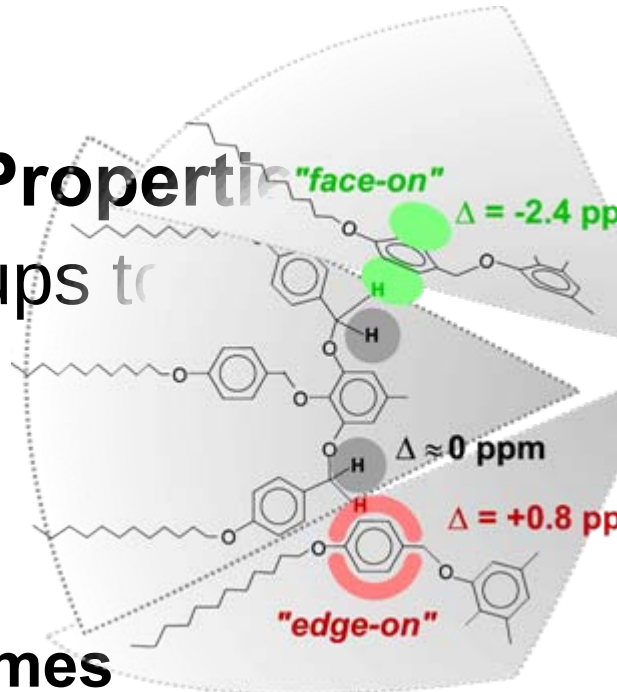
C. Peter

Coarse grained model,
Alkyl chains as for
Hexabenzene-Coronenes



Conclusion: A few Challenges

- **Dual-Triple… Scale Simulations/Theory**
  - **Adaptive** quantum⇔force field⇔coarse grained …
- **Nonbonded Interactions: NEMD, Morphology…**
  - Accuracy k_BT***O(1/N)*** needed!
- **Conformations ⇔ Electronic Properti**
  - E.g. coupling of aromatic groups t backbone conformation, or to other chains
- **Online Experiments:**
  - **Nanoscale Experiments, long Times**



THEORY GROUP

Max-Planck-Institut für Polymerforschung

Max Planck Institute for Polymer Research

10 Years Theory at the MPIP, Oct. 2005