Multiscale simulation of soft matter: Possibilities and challenges

Florian Müller-Plathe (www.theo.chemie.tu-darmstadt.de)

What is soft matter?

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- Energetic degeneracy: Many states of virtually the same energy
- Behaviour dominated by entropy differences

$$\Delta A = \underbrace{\Delta E}_{\text{hard}} - \underbrace{T\Delta S}_{\text{soft}}$$

- Examples
  - Polymers: melt, solution, glass, gels, networks, block copolymers, composites; structural proteins, polysaccharides, DNA, dendrimers
  - Liquid crystals, colloids, foams, ionic liquids
  - Non-polymer gels: organogels, clay solutions
  - Amphiphiles: micelles, membranes, emulsions, suspensions, Langmuir-Blodgett films, self-assembled monolayers, phospholipid membranes
  - Granular matter: sand piles; plasmas

Soft matter is often inherently multiscale

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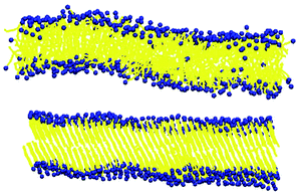
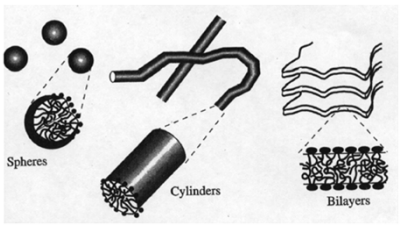
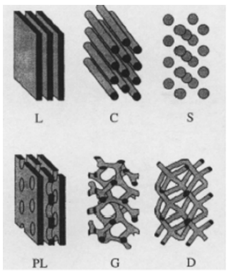
- Polymers
- Amphiphiles
  - atomistic scale: bilayer phases
  - molecular scale: aggregation into micelles
  - 1-10 nm: ordering of micelles or membranes into superstructures



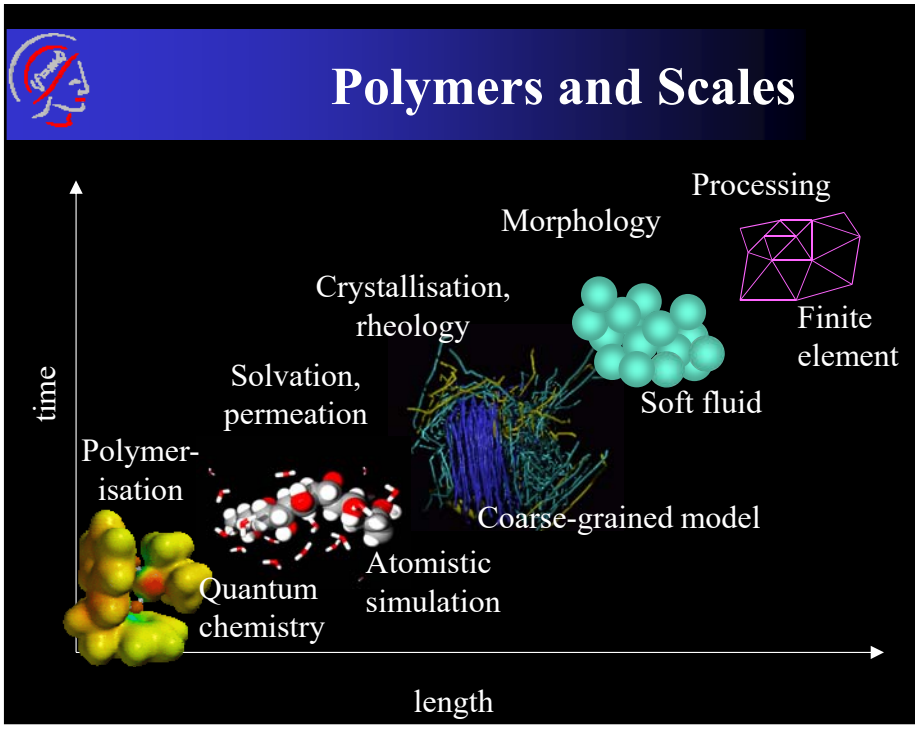
B. West, F. Schmid, Soft Matter **6**, 2010, 1275 - 1280





R.A.L. Jones, *Soft Condensed Matter*, Oxford University Press, Oxford (2002).

Polymers and Scales



Coarse-graining of ionic liquids

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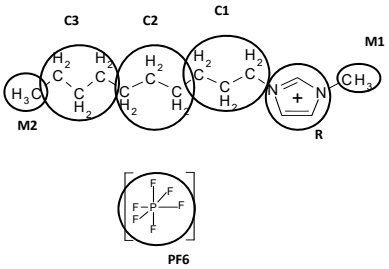
Coarse-grained model of ionic liquids by *Iterative Boltzmann Inversion*

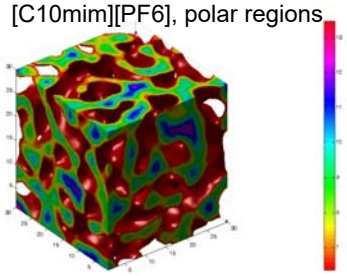
[C4mim][PF6], [C7mim][PF6], [C10mim][PF6]

3000-7000 ion pairs

Can study structure formation ("micellisation") for larger cations.



[C10mim][PF6], polar regions



H.A.Karimi-Varzaneh, F. Müller-Plathe, S. Balasubramanian, P. Carbone, Phys. Chem. Chem. Phys. **12**, 4714 (2010).

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Outline

- Intro – Soft matter
- Introductory example
  - room-temperature ionic liquid
- Status: Coarse graining procedure for polymers
  - iterative Boltzmann inversion
  - polymer melt
  - application: formulation of a suspension
- Challenges
  - temperature transferability
  - composition transferability
  - dynamics

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Viscosity of an ionic liquid: [bmim] [PF_6]

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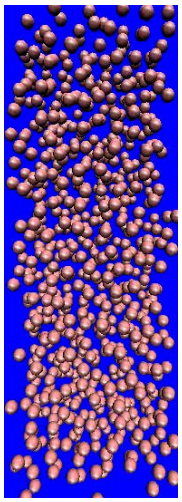
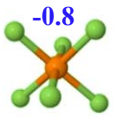
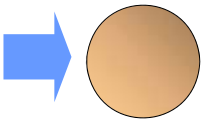


BMIM



PF_6



- 256 Ion pairs
- Atomistic simulation
- Reverse non-equilibrium molecular dynamics
  (RNEMD: F. Müller-Plathe, Phys. Rev. E **59**, 4894 (1999).)

W. Zhao, H. Eslami, W. Cavalcanti, and F. Müller-Plathe, Z. Phys. Chem. **221**, 1647-1662 (2007)

Shear viscosity of [bmim] [PF_6]

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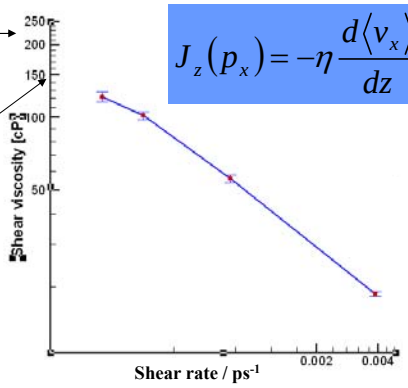
Experiment:
η_0=204 cP at 303K
[Seddon et al., Pure Appl. Chem. **72**, 2275(2000)]
others: 173-450 cP

Simulation:
$\eta_0 \rightarrow$133 cP at 300K

$$J_z(p_x) = -\eta \frac{d\langle v_x \rangle}{dz}$$



Analogous: diffusion coefficients

Exper. 0.7×10^{-7} cm^2/s
Sim. 1.3×10^{-7} cm^2/s

W. Zhao, F. Leroy, S. Balasubramanian, and F. Müller-Plathe, J. Phys. Chem. B **112**, 8129 (2008).

Transport in [bmim] [PF_6]

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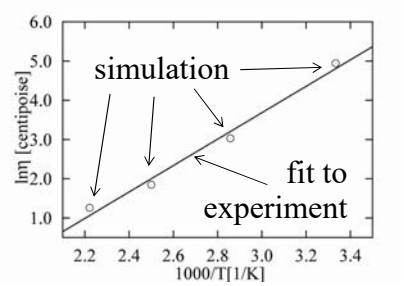
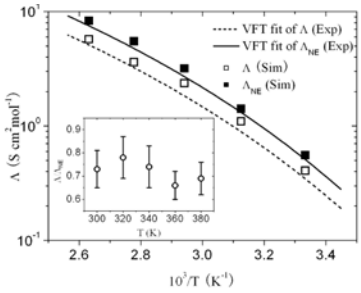
Temperature dependence of shear viscosity η



Specific ionic conductivity λ



W. Zhao, F. Leroy, B. Heggen, S. Zahn, B. Kirchner, S. Balasubramanian, and F.Müller-Plathe, J. Am. Chem. Soc. **131**, 15825 (2009).

Dynamics of "micelles", coarse-grained

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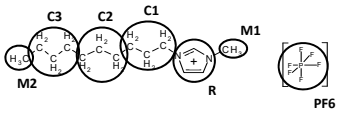
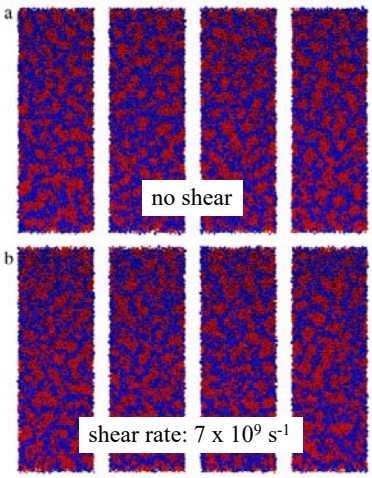
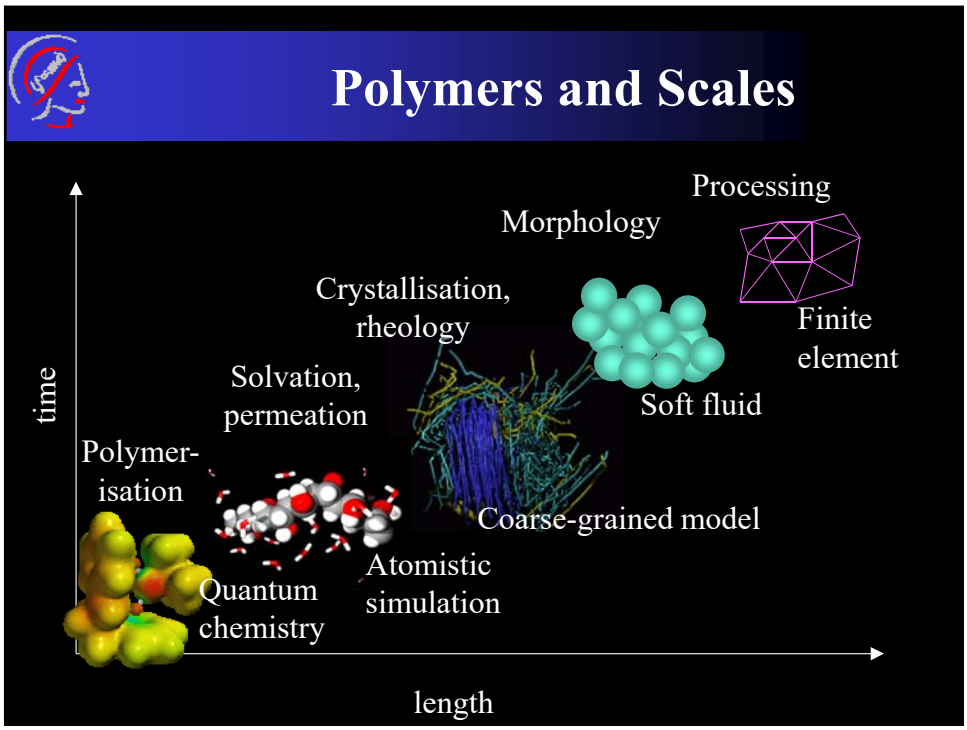
- [C10mim][PF6], coarse-grained



- Different shear rates applied using RNEMD.
- Polar and apolar regions form disordered, bicontinuous morphology.
- No change with shear rate.
- Quick disrution and reformation of morphology



S.N. Butler and F. Müller-Plathe, J. Mol. Liq. **192**, 114 (2014).



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  - composition transferibility
  - dynamics

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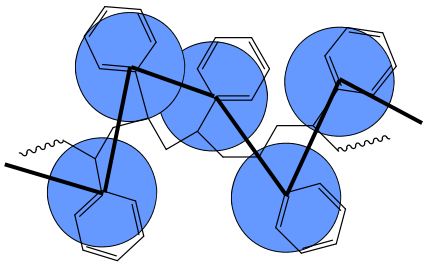
Coarse-grained Force Field



≈ 5 – 20 atoms → 1 "superatom"
1000-100000 times cheaper

Effective interactions:
"bonds", "angles", non-bonded

Systematic coarse-graining:

- interactions as realistic as possible
- model is material-specific
- no generic "bead-and-spring" model

Reviews: FMP, ChemPhysChem **3**, 754 (2002); Soft Materials **1**, 1 (2003).
H.A. Karimi & FMP, Top. Curr. Chem. **307**, 295 (2012).

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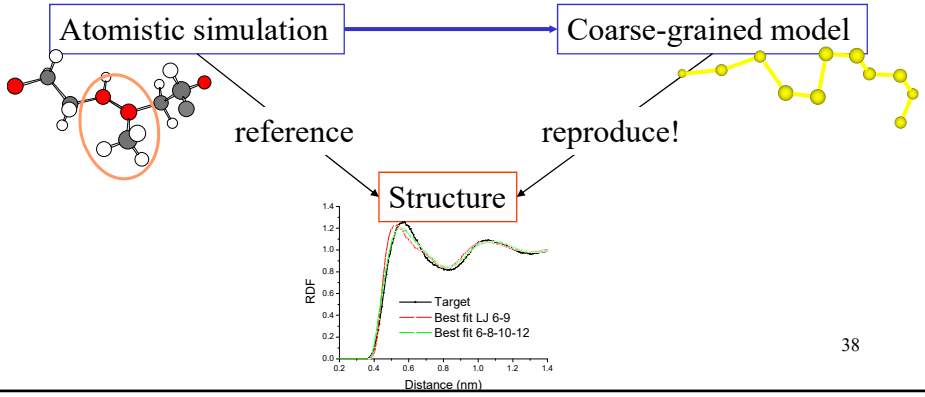
Coarse Graining: A Simple Principle

Coarse-grained model:

- Simpler than atomistic model:
  ≈10 real atoms → 1 superatom
- Reproduce structure of atomistic model



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Coarse-grained force field terms

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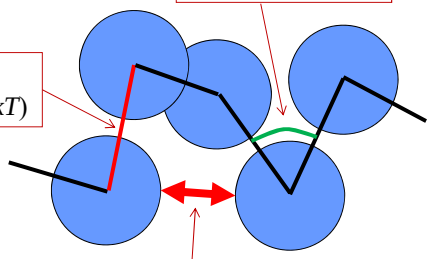
Terms between superatoms

Angles
- stiff (> kT)
- multiple minima

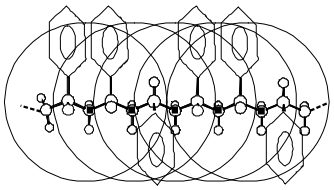
Bonds
- very stiff (>> kT)

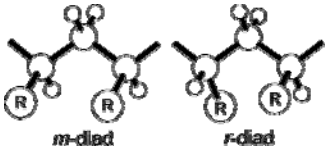


(Torsions
- very soft (< kT)
- multiple minima
- seldom necessary)

Nonbondeds
- soft (~ kT)
- multiple minima
- short-ranged

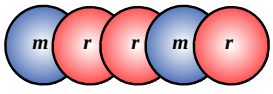
Example: Atactic Polystyrene Melt





RR or SS sequence *m* diad
RS or SR sequence *r* diad

distributions of three different bonds (*mm*, *mr*, *rr*)
six angles (*mmm*, *rrr*, *mmr*, etc.)
plus intermolecular and intramolecular RDFs



Treat as a "copolymer" of *m* and *r* superatoms

G. Milano and F. Müller-Plathe, J. Phys. Chem. B **109**, 18609 (2005).

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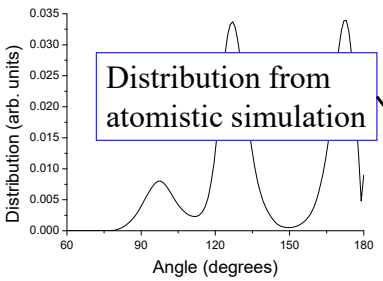
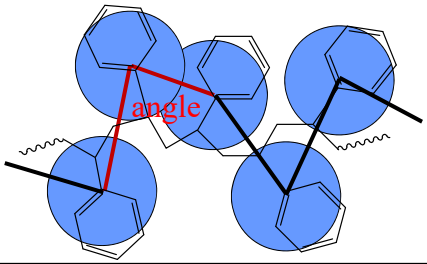
Bonded interactions: Angles



Distribution from atomistic simulation

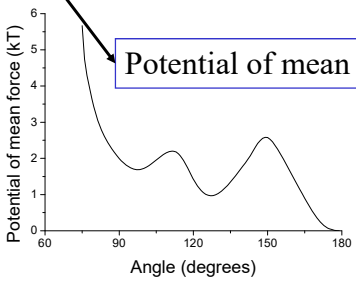


The easy part:

- Stiff degrees of freedom
- Direct Boltzmann inversion

$$-k_B T \ln P(\phi) = A(\phi) \approx V(\phi)$$

Potential of mean force



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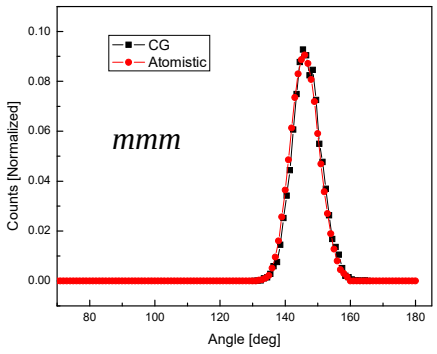
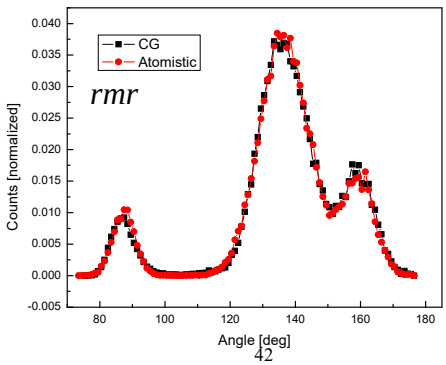
Bonded interactions: Angles

distributions of three different bonds (*mm*, *mr*, *rr*)

→ six angles (*mmm*, *rrr*, *mmr*, etc.)

plus intermolecular and intramolecular RDFs





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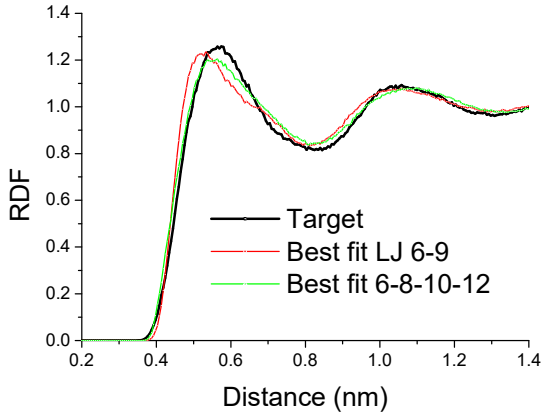
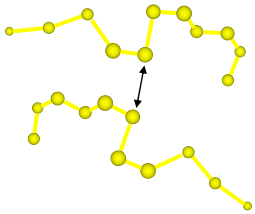
Nonbonded interactions





Less easy:

- soft degrees of freedom
- interacts with other modes
- potential of mean force ≠ potential energy
- cannot Boltzmann-invert directly

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Iterative Boltzmann Inversion

- Tabulated numerical potential $V(r)$
- Starting guess $V_0(r) \rightarrow \mathrm{RDF}_0(r) \neq \mathrm{RDF}_{\mathrm{target}}(r)$
- Potential correction

$$V_1(r) = V_0(r) + kT \ln \frac{\mathrm{RDF}_0(r)}{\mathrm{RDF}_{\mathrm{target}}(r)}$$

- Iterate

$$V_{n+1}(r) = V_n(r) + kT \ln \frac{\mathrm{RDF}_n(r)}{\mathrm{RDF}_{\mathrm{target}}(r)}$$

until $V_n(r) \rightarrow \mathrm{RDF}_n(r) = \mathrm{RDF}_{\mathrm{target}}(r)$

- Converges in few iterations
- Density/pressure correction can be added

D. Reith, M. Pütz, FMP, J. Comp.Chem. **24**, 1624 (2003).
D. Reith, H. Meyer, FMP, Comput. Phys. Commun. **148**, 299 (2002).

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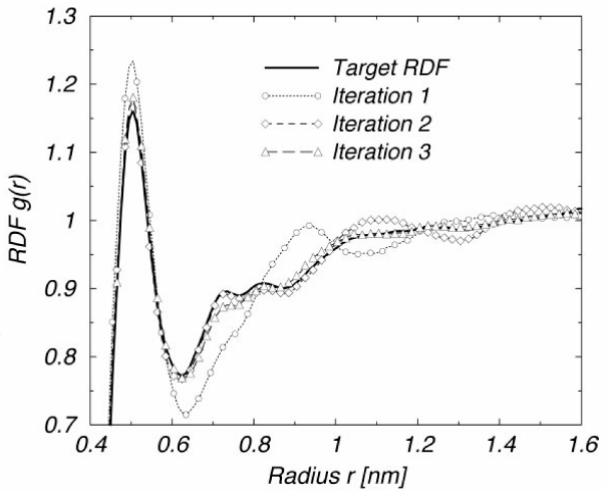
Iterative Boltzmann Inversion (2)

Polyisoprene, 9-mer melt



[D. Reith, M. Pütz, F. Müller-Plathe, J. Comp.Chem. **24**, 1624 (2003)]

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Nonbonded interactions

distributions of three different bonds (*mm*, *mr*, *rr*)
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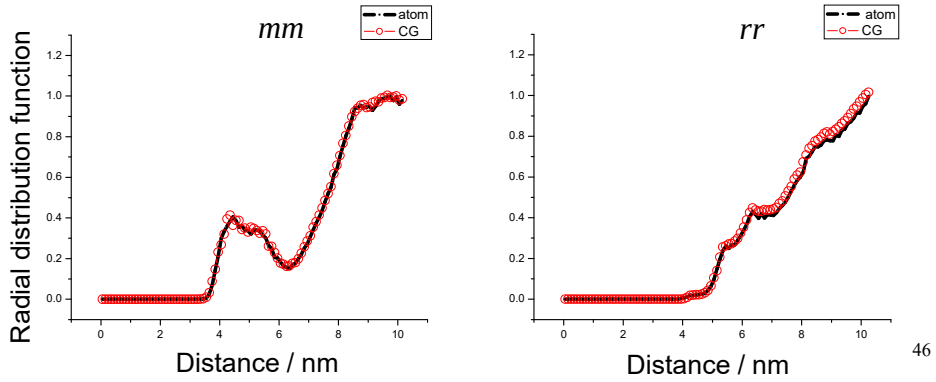
→ plus intermolecular and intramolecular RDFs



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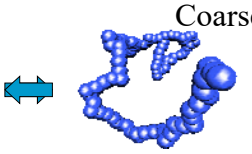
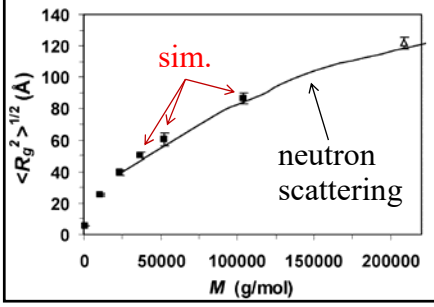
Atactic PS: Structure



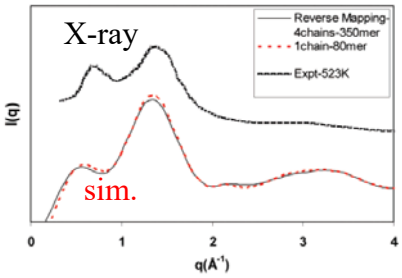
Coarse-grained: up to 16000 monomers

T. Spyriouni, C. Tzoumanekas, D. Theodorou, F. Müller-Plathe, and G. Milano, Macromolecules **40**, 3876 (2007).

Radius of Gyration



Scattering intensity (after backmapping)



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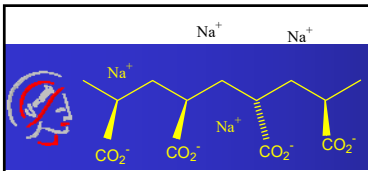
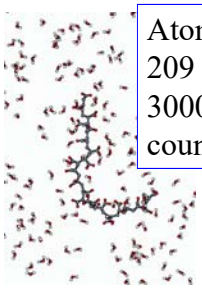
Poly(acrylic acid)





Atomistic:
209 atoms
3000 H_2O
counterions

Coarse-grained:
23 particles
no H_2O

Mapping: coarse-grained superatom ↔ centre of mass of atomistic monomer

Water: effective interaction, viscous medium

Parameters: iterative Boltzmann inversion

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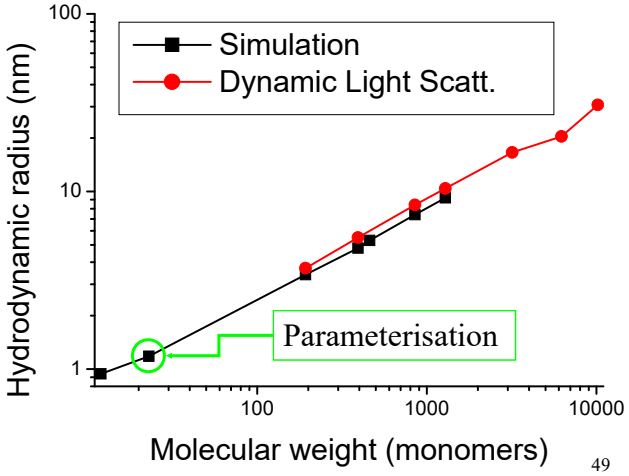
[D. Reith, B. Müller, FMP, S. Wiegand, J.Chem. Phys. **116**, 9100 (2002).]

Comparison with Experiment

$$\frac{1}{R_H} = \left\langle \frac{1}{N^2} \sum_{i,j} \frac{1}{R_{ij}} \right\rangle$$



[D. Reith, B. Müller, F. Müller-Plathe, S. Wiegand, J. Chem. Phys. **116**, 9100 (2002).]

Implementation issues for coarse-grained simulations

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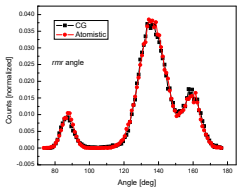
- Nonbonded interactions: tabulated potentials (IBI)
- Bonds, angles: tabulated (IBI) or expansion into Gaussians (direct Boltzmann inv.)
- Connectivity simpler than atomistic, no constraints
- Nonbonded interactions short-ranged
- Easily parallelised (distributed memory)



Our implementation IBIsCO

- tabulated potentials + Gaussians
- Equations of motion: MD, dissipative particle dynamics, Lowe-Anderson
- *NVT*, *NpT*
- reverse non-equilibrium MD (→ shear viscosity)
- special versions: reactive MD, slip-spring DPD
- surfaces, interfaces
- parallelised

H.A. Karimi-Varzaneh, H.J. Qian, X. Chen, P. Carbone, and F. Müller-Plathe, J. Comp. Chem. **32**, 1475 (2011).

Real Application: Stabilisation of a suspension

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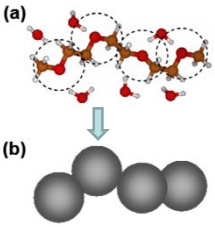
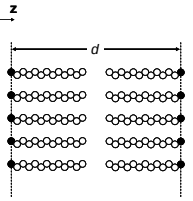
- Suspension: particles aggregate → reduced shelf life
- Stabilise by grafting water-soluble poly(ethylene oxide): "hairy particles" repel each other



- Simulation task:
  How much PEO of which chain length is needed?
- Simulation strategy:
  1) Atomistic simulation of PEO oligomer in water
  2) Coarse grain by iterative Boltzmann inversion (no more water)
  3) Graft CG chains onto opposing surfaces
  4) Calculate repulsive force



R. Cordeiro, F. Zschunke, FMP, Macromolecules **43**, 1583 (2010).

Real Application: Stabilisation of a suspension

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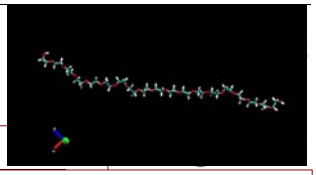
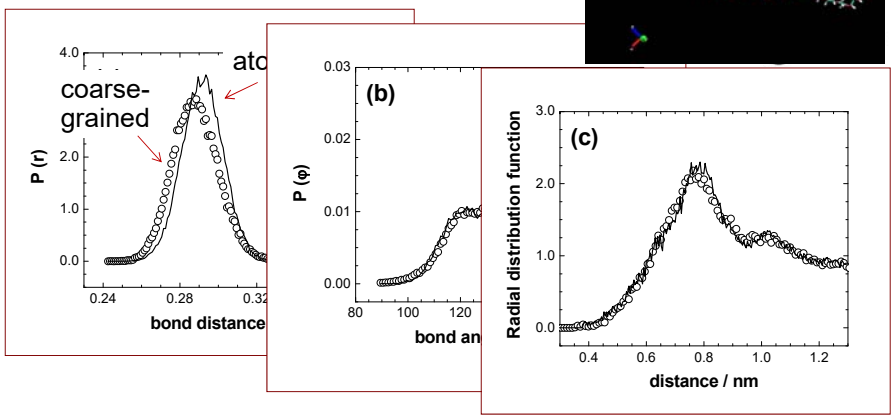
- 1), 2) Making the coarse-grained model
- Single poly(ethylene oxide) chain in water





R. Cordeiro, F. Zschunke, FMP, Macromolecules **43**, 1583 (2010).

Real Application: Stabilisation of a suspension

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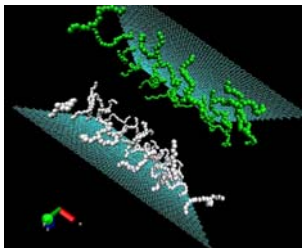
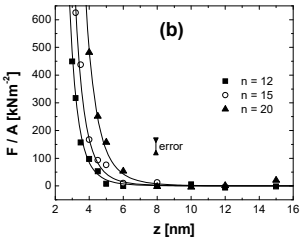
- 3) Graft coarse-grained PEO chains on surface



- 4) Calculate repulsive force as a function of distance



R. Cordeiro, F. Zschunke, FMP, Macromolecules **43**, 1583 (2010).

Systems coarse-grained

Polymer melts:

- Poly(vinyl alcohol)
  D. Reith, H. Meyer, FMP, Macromolecules **34**, 2235 (2001).
- Polyisoprene
  trans: R. Faller, FMP, Polymer **43**, 621 (2002); *cis*: T. Spyriouni, C. Tzoumanekas, D. Theodorou, FMP, G. Milano, Macromolecules **40**, 3876 (2007).
- Amorphous cellulose
  S. Queyroy, S. Neyertz, D. Brown, FMP, Macromolecules **37**, 7338 (2004).
- Atactic polystyrene
  G. Milano, FMP, J. Phys. Chem. B **109**, 18609 (2005).
- Amorphous polyamide-6,6
  P. Carbone, H. A. Karimi Varzaneh, X.Y. Chen, FMP, J. Chem. Phys. **128**, 064904 (2008)

Polymer Solutions

- Poly(acrylic acid) / water
  D. Reith, B. Müller, F. Müller-Plathe, S. Wiegand, J. Chem. Phys. **116**, 9100 (2002).
- Poly(ethylene oxide) / water
  R. Cordeiro, F. Zschunke, FMP, Macromolecules **43**, 1583 (2010).

54

Systems coarse-grained

Non-polymers

- Liquid: Diphenyl carbonate
  H. Meyer, O. Biermann, R. Faller, D. Reith, FMP, J. Chem. Phys. **113**, 6265 (2000).
- Liquid: Ethylbenzene
  H.-J. Qian, P. Carbone, X. Chen, H. A. Karimi-Varzaneh, C. C. Liew, FMP, Macromolecules **41**, 9919 (2008).
- Liquid: *n*-Hexane
  K. Farah, A. Fogarty, M. C. Böhm, FMP, Phys. Chem. Chem. Phys. 13, 2894 (2011).
- PAMAM dendrimers
  P. Carbone, F. Negri, FMP, Macromolecules **40**, 7044 (2007).
- Ionic liquid: [bmim][PF_6]
  H.A. Karimi Varzaneh, FMP, S. Balasubramanian, P. Carbone, Phys. Chem. Chem. Phys.**12**, 4714 (2010) .

55

Outline

- Intro – Soft matter
- Introductory example
  - room-temperature ionic liquid
- Status: Coarse graining procedure for polymers
  - iterative Boltzmann inversion
  - polymer melt
  - application: formulation of a suspension
- Challenges
  - temperature transferability
  - composition transferability
  - dynamics

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Advertisement: Quantum chemistry on your telephone

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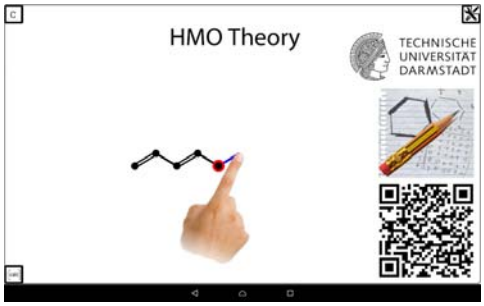
Hueckel Molecular Orbital HMO
by **Patrick Giel**, with help from Michael Böhm and substantially less help from FMP

Android app from Google Play Store (no iphone, sorry)

- Draw molecules on your telephone.
- Calculate orbital energies, orbital shapes, bond orders, …
- Common heteroatoms.
- Great tool for e-teaching theoretical, physical and organic chemistry
- Can even be abused to explain concepts in tight-binding.

- Demonstration video on Youtube
- Chemie in unserer Zeit **50**, 2 (2016).

- Free, ad-free and non-intrusive



Coarse-graining in the Arts

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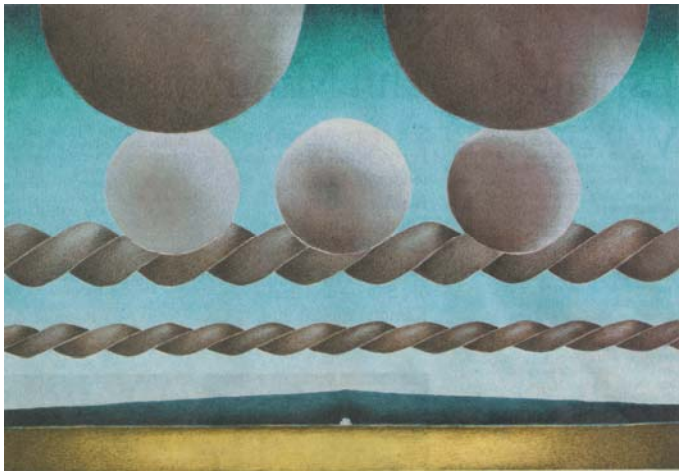
John Constable, Landscape with Grey Clouds, ca. 1821

Coarse-graining in the Arts



Mark W. Leonard, Constable Study II, 2011

Coarse-graining in the Arts

Florian Müller-Plathe, Kraneled/Møn, 2013

Coarse-graining for macromolecules

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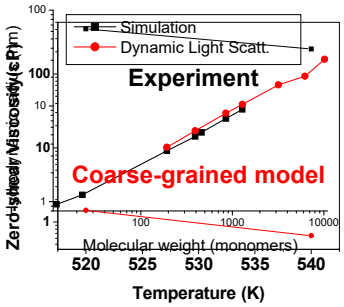
- State of the art for polymer **structure**
- Alternatives available
  - Iterative Boltzmann inversion
  - Inverse Monte Carlo
  - Force matching
- Substantial challenges for
  - Connection between particle models and continuum models
  - **Dynamical** properties: mobility, viscosity, rheology
  - Application to **real systems**

Polystyrene melt (1 kDa)

X. Chen, P. Carbone, F. Müller-Plathe, S. Wiegand, J. Chem. Phys. **116**, 5190 (2002).
Macromolecules **40**, 8087 (2007).



The challenge of dynamics

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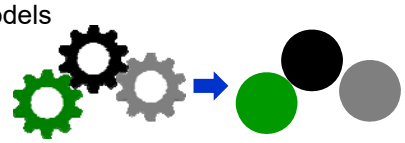
Known feature of coarse-grained potentials

- repulsion (excluded volume interaction) softer and less structured than in atomistic models
- less friction
- faster dynamics: higher D, lower η



Why is this a problem?

- Atomistic is no option, and coarse-grained is not predictive.

How to fix the problem?

- Construct coarse-grained model with correct mobility: Dynamics as one target property in model optimisation
- Change the equations of motion to restore the missing friction
- Determine the spurious acceleration in the coarse-graining process; rescale dynamics

Coarse-graining and dynamics

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Bottom-up – Excess entropy scaling
- Start with accurate model: **atomistic**
- Make a simplified model, which retains some of the accuracy, but is faster: **coarse-grained**

Top-down – Slip-spring DPD
- Start with a simple and fast model, which has the wrong dynamics: **very coarse-grained**
- Modify it to restore some of the correct dynamics: **still coarse-grained, but less so**

Real-world application with classical coarse-graining
- Curing reaction of an epoxy glue
- Glass transition in the interphase

Dynamics top-down

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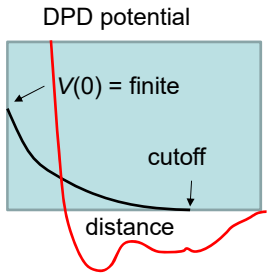
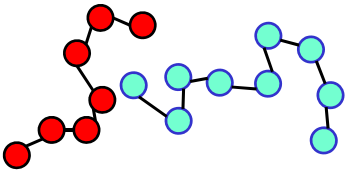
Very coarse-grained model
- Polymer: DPD beads + harmonic springs
- Advantage: very fast
- Disadvantages:
  - chains can cross
  - polymer does not entangle, no reptation
  - polymer behaves like a low-molecular-weight liquid
  - unphysical rheology

- Can the DPD model be taught to entangle?





F. Müller-Plathe | If you teach quantum mechanics or computational chemistry, try our free Android app HUECKEL MOLECULAR ORBITAL.

Introduce slip-springs

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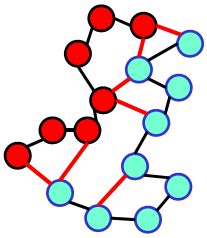
- Temporary slip-springs mimic entanglements; modelled as additional harmonic springs
- Slip-springs are mobile
  - MC moves slip-springs along chains
  - Slip-spring relocation moves alternate with DPD particle moves
  - Slip-springs can appear/disappear at chain ends
  - Total number of slip-springs constant
  - "Entanglement length" is input parameter



M. Langeloth, Y. Masubuchi, M. C. Böhm, FMP, J. Chem. Phys. **138**, 104907 (2013).

- Similar approach by:
  V. C. Chappa, D. C. Morse, A. Zippelius, M. Müller, Phys. Rev. Lett. **109**, 148302 (2012).

Does it work? Polymer melt

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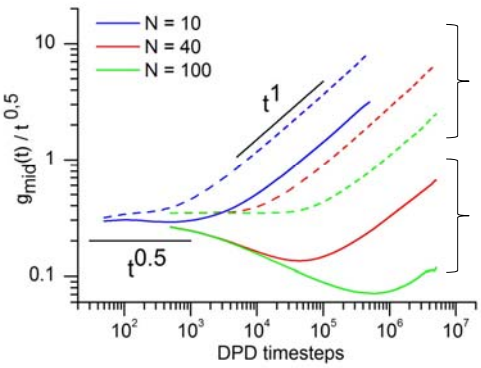
Mean-square displacement of central monomer



No slip-springs: Rouse

With slip-springs: reptation (N_e = 5)

M. Langeloth, Y. Masubuchi, M. C. Böhm, FMP, J. Chem. Phys. **138**, 104907 (2013).

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Slip-spring DPD vs. hard-core MD

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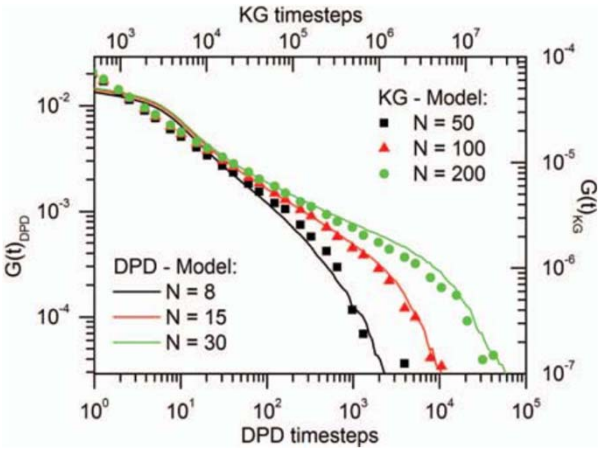
- **Relaxation modulus**



Symbols:
Kremer-Grest model
(WCA + FENE)

Lines:
DPD + slip-springs
(same entanglement
density as Kremer-Grest)

M. Langeloth, Y. Masubuchi,
M. C. Böhm, FMP,
J. Chem. Phys. **138**, 104907 (2013).

Bi-disperse melt: Tube dilation

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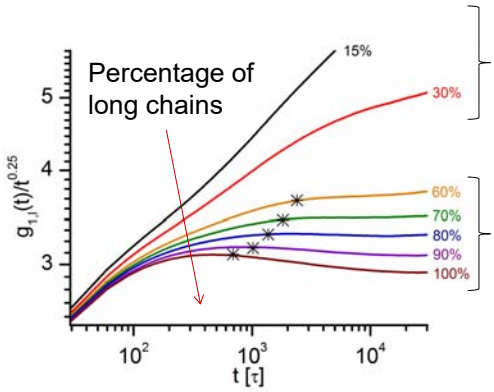
- **Mixtures of long (*N* = 300) and short chains (*N* = 10)**

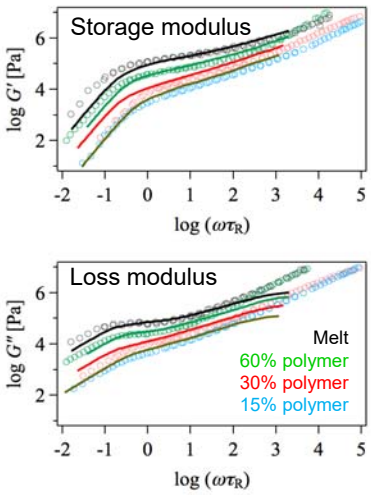


No reptation. Short chains
act like solvent.

Reptation

M. Langeloth, Y. Masubuchi, M. C. Böhm,
F. Müller-Plathe, J. Chem. Phys. **141**, 194904 (2014).

Polymer solutions



Rheological properties of polystyrene solutions in tricresyl phosphate

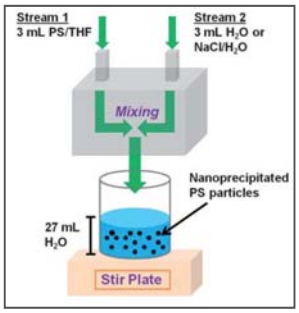
- Frequency dependent moduli
- Agreement between simulation (lines) and experiments (symbols)
- when using dimensionless frequencies: frequencies normalised by Rouse times

Y. Masubuchi, M. Langeloth, M. C. Böhm, T. Inoue, F. Müller-Plathe, Macromolecules **49**, 9186 (2016).

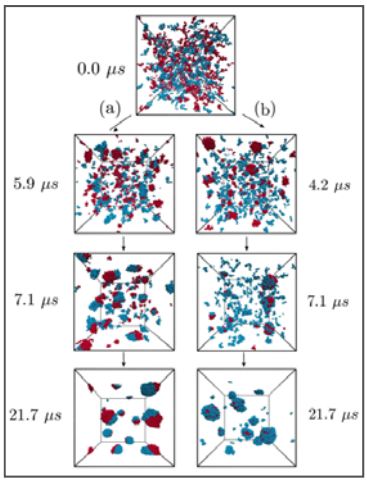
Slip-spring DPD: Summary & Outlook

- Incorporates entanglement effects into DPD
- Works for polymer melts and solutions
- Entanglement density is an input parameter (~ # of slip-springs)
- Very fast: 10^2 – 10^3 times faster than MD with hard-core potential (Kremer-Grest)
- Good for problems, which are well described by very coarse-grained soft particles
  - Morphology development
  - Phase-separation dynamics
  - Polymer-nanoparticle systems, colloids and composites

Flash Nano-Precipitation

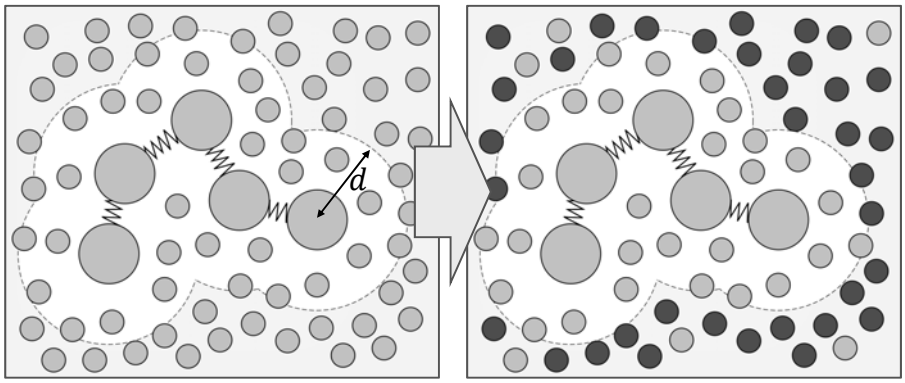


Prud'homme, Priestley et al.
(Princeton)
Zhang *et al.*, Soft Matter **8** (2012)



Li *et al.*, Langmuir **33** (2017)

Solvent-to-Antisolvent Exchange



Single Chain Collapse (a) Influence of *d*

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- **Simulation Model**
  - Single Chain (25 beads) in 80975 solvent beads
  - Exchange distance $d = 0, 1, 2, 3, 4, 6, 8, 12$

- **Analytical Model**
  - Diffusion equation: Diffusion from a limited volume into a sphere

$$x^*_{AS}(t) = x^*_{AS}(\infty)\left[1 + \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1)\exp(-Dq_n^2 t/a^2)}{9 + 9\alpha + q_n^2\alpha^2} \frac{a}{r} \frac{\sin(q_n^2/a)}{\sin(q_n^2)}\right]$$

$$\tan(q_n) = \frac{3q_n}{3 + \alpha q_n^2};\ \alpha = \frac{3V}{4\pi a^3}$$

Crank, *The Mathematics of Diffusion*, 2nd ed.; Oxford University Press: Oxford, 1975

Single Chain Collapse (a) Influence of *d*

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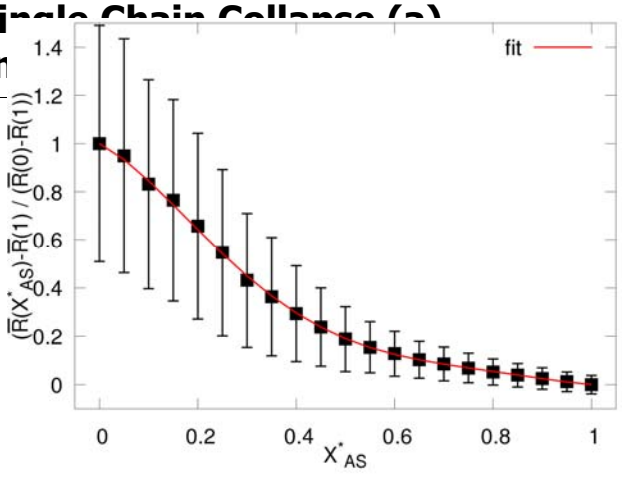

me into a sphere

$$\frac{a}{r} \frac{\sin(q_n^2/a)}{\sin(q_n^2)}\Big]$$

$$\tan(q_n) = \frac{}{}$$

$$\bar{R}(t) = 1 - 1.0x^*_{AS}(t) - 7.0\left(x^*_{AS}(t)\right)^2 + 19.0\left(x^*_{AS}(t)\right)^3 - 17.9\left(x^*_{AS}(t)\right)^4 + 5.9\left(x^*_{AS}(t)\right)^5$$

Single Chain Collapse
Influence of Diffusion Distance *d*

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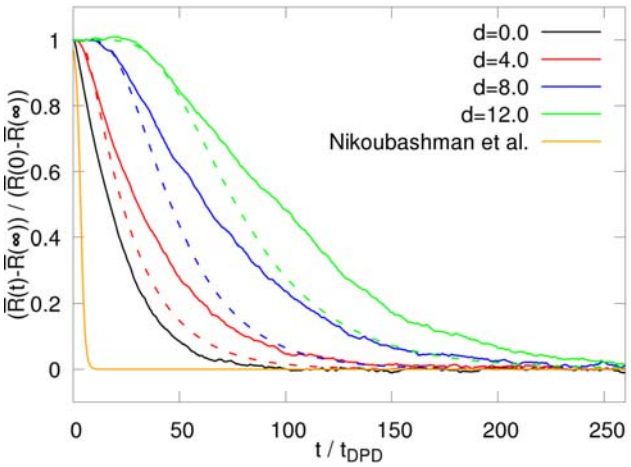

Continuous lines:
Simulations

Dashed lines:
Analytical Model

100

Single Chain Collapse (a)
Influence of diffusion distance *d*

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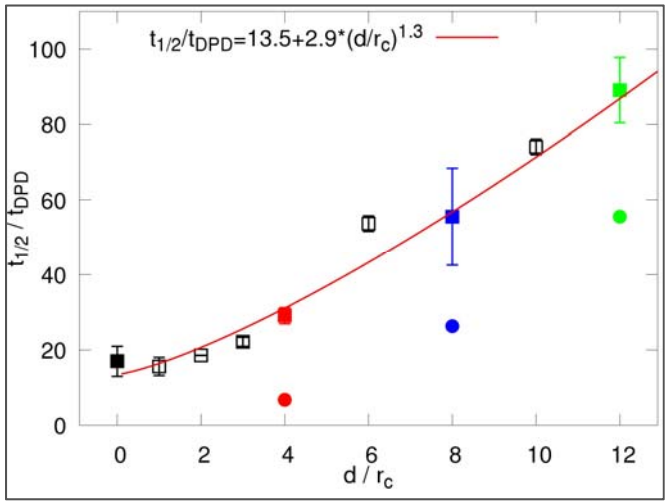

Squares:
Simulations

Circles:
Analytical Model

101

Single Chain Collapse (b) Influence of Slip-Links

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- **Simulation Model**
  - Single Chain (100 beads) in 139868 solvent beads
  - Slip-Links $N = 0,1,2,3,4,5,10$
  - Collapse with d=12

Single Chain Collapse (b) Influence of Slip-Links

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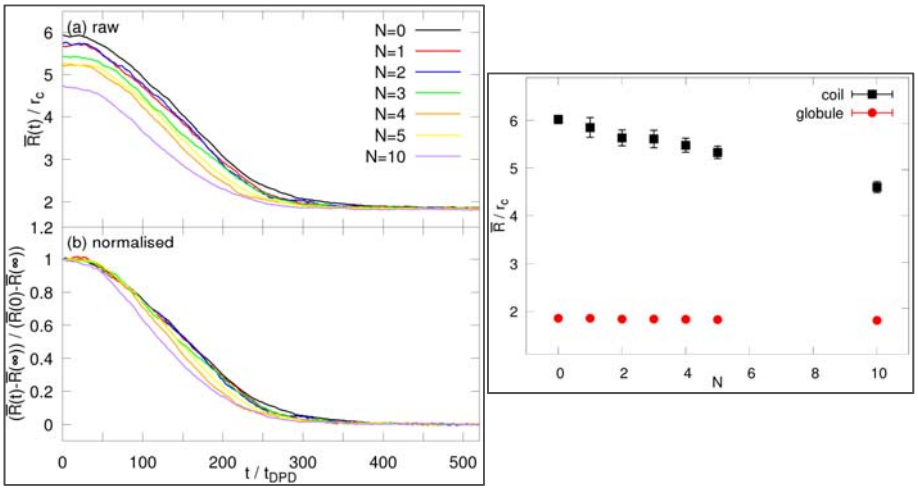
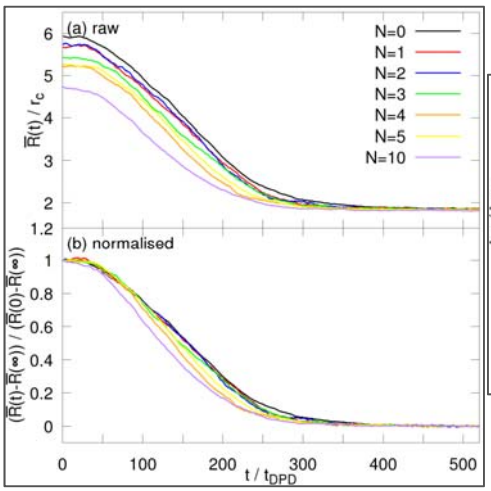
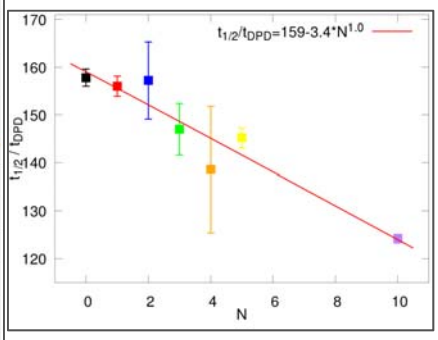


Single Chain Collapse (b) Influence of Slip-Links

TECHNISCHE UNIVERSITÄT DARMSTADT





Multi-Chain Precipitation

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- **Equilibration**
  - $324, 675, 1350, 2700$ chains à 25 beads in 273375 total beads $(45\ r_c)^3$
  - $X_{I,P} = 0.03, 0.06, 0.12, 0.24$
  - No slip-springs
- **EQ-Simulations**
  - Exchange random solvent beads until $X^*_{AS} = 0.5, 0.6, 0.8, 1.0$
- **Precipitation Simulations**
  - Extract $(15\ r_c)^3$ box and place it into eq.-solvent
  - Exchange solvent with $X^*_{AS} = 0.5$
  - $d = 0, 4, 8, 12$
  - $12, 25, 50, 100$ chains per system

Multi-Chain Precipitation

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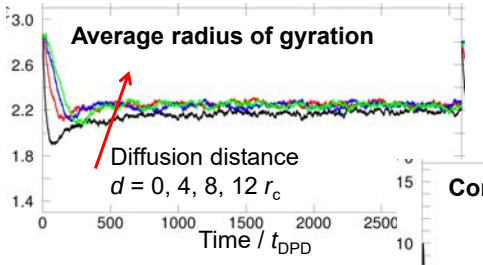
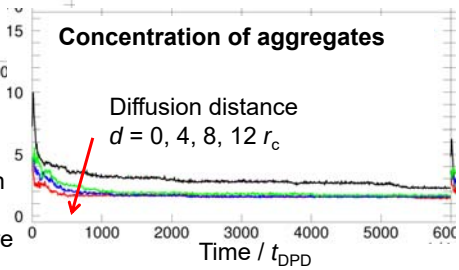


- Quick single-chain collapse
- Followed by slow expansion



- Most pronounced for d = 0
- For longer anti-solvent diffusion distances, chain collapse and chain aggregation become more similar in time-scale.

Multi-Chain Precipitation

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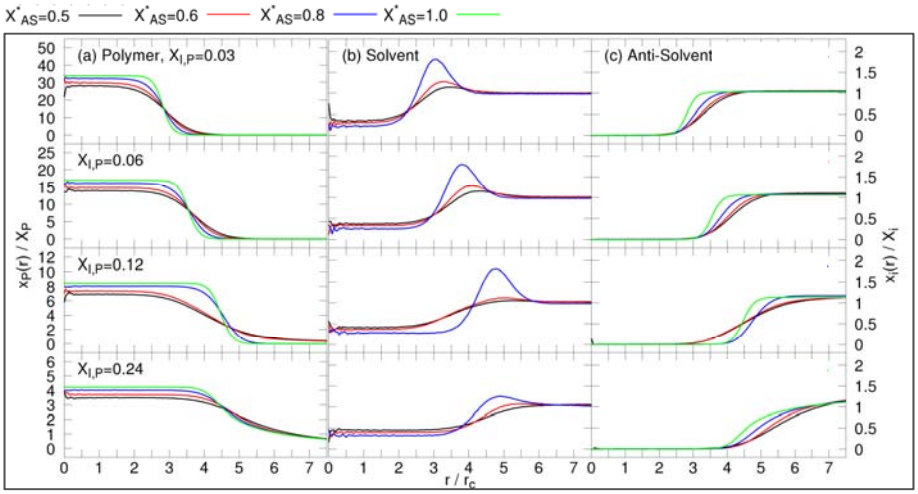

Flash Nano-Precipitation

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- **Slip-spring DPD: working tool**
  - In-detail studies of precipitation process
  - Explicit solvent and anti-solvent
  - Hydrodynamics
  - Polymer entanglements
- **Slip-spring DPD + Reverse Nonequilibrium MD**
  - Polymer precipitation under shear flux
- **Flash Nano-Precipitation**

Slip-spring DPD: Summary & Outlook

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- Incorporates entanglement effects into DPD
- Works for polymer melts and solutions
- Entanglement density is an input parameter (~ # of slip-springs)
- Very fast: 10^2 – 10^3 times faster than MD with hard-core potential (Kremer-Grest)
- Good for problems, which are well described by very coarse-grained soft particles
  - Morphology development
  - Phase-separation dynamics
  - Polymer-nanoparticle systems, colloids and composites

F. Müller-Plathe | If you teach quantum mechanics or computational chemistry, try our free Android app HUECKEL MOLECULAR ORBITAL.

Coarse-graining and dynamics

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Bottom-up – Excess entropy scaling
- Start with accurate model: **atomistic**
- Make a simplified model, which retains some of the accuracy, but is faster: **coarse-grained**

Top-down – Slip-spring DPD
- Start with a simple and fast model, which has the wrong dynamics: **very coarse-grained**
- Modify it to restore some of the correct dynamics: **still coarse-grained, but less so**

Real-world application with classical coarse-graining
- Curing reaction of an epoxy glue
- Glass transition in the interphase

Coarse-graining in the Arts

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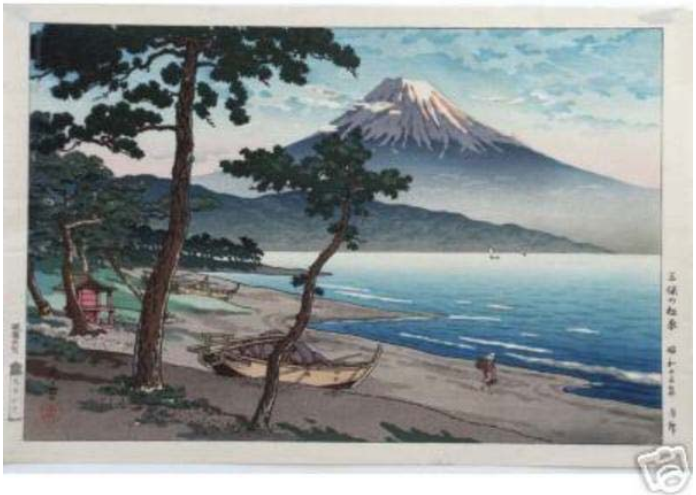

Tsuchiya Koitsu, Miho in Matsubara, 1938

Coarse-graining in the Arts

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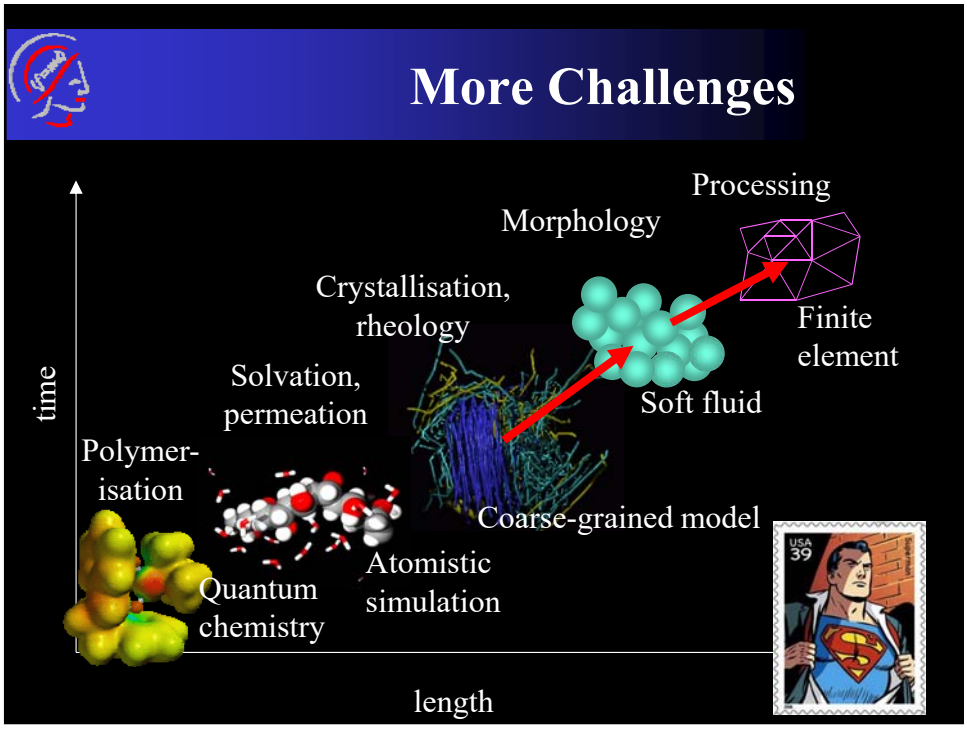
Yuki/Gan Rei, Blue Flags, ca. 1970



Embedding into continuum

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Goal

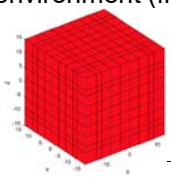
- Large deformations of macroscopic sample
- Include molecular-level processes
  - Yielding
  - Crazing
  - Failure

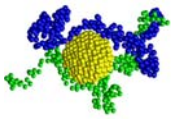
Path

- Combine MD core with continuum environment (finite elements)

Current position

- Small deformation
- Elastic response





Combining particles and continuum: MD-FEM for structural mechanics

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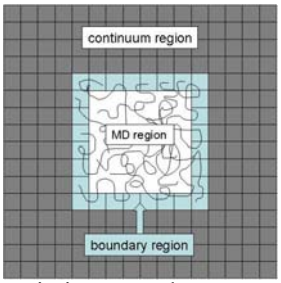
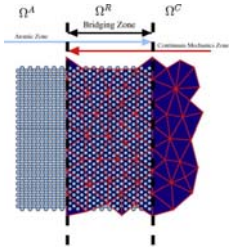
- Embed MD region (interesting) in FEM (surroundings)
- Purpose: interfaces in composites, failure



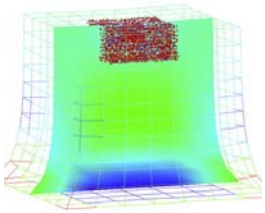
Challenges

- Marrying two completely different partners needs pragmatic solutions
- Boundary region:
  Communicate forces between MD and FEM
- MD: nonperiodic boundary conditions
- Keep MD region from changing shape and evaporating, mimic external pressure
- Tethered anchor points for force transmission
- Avoid scattering of sound waves at the boundary: stochastic dynamics
- EU project Nanomodel: Amin Rahimi with group of Paul Steinmann, U. Erlangen
- DFG: Shengyuan Liu

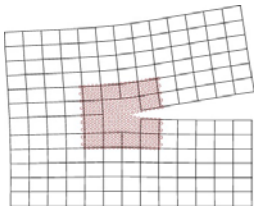
Hybrid Schemes

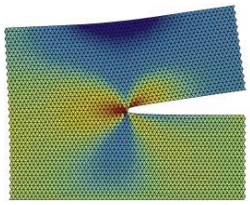


Comput. Methods Appl. Mech. Engrg. 253 (2013) 28–38



Comput. Methods Appl. Mech. Engrg. 198 (2009) 799–818

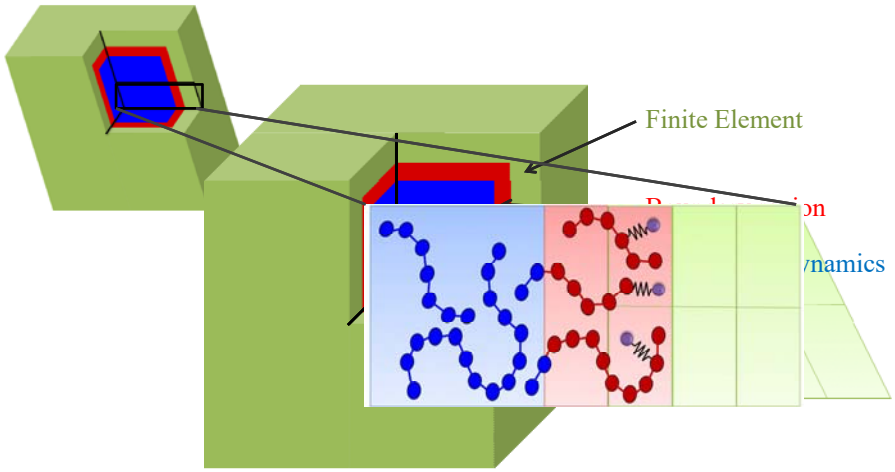




Comput. Methods Appl. Mech. Engrg. 198 (2009) 1887–1901

All hybrid schemes have been limited to crystalline materials with atoms on a lattice.

Hybrid Scheme for Polymers



Outline

TECHNISCHE UNIVERSITÄT DARMSTADT

- Motivation
- **Technical obstacles**
- How to overcome the obstacles
- Simulation of pure polystyrene
- Simulation of nanocomposite
- Summary

Obstacle: 1

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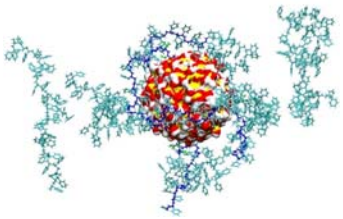
The physically interesting regions are large compared to those accessible by atomistic simulations.

System:

One silica nanoparticle and polystyrene

Box ~ 10 nm
Atoms ~ 100000
1 ns ~ 1 week

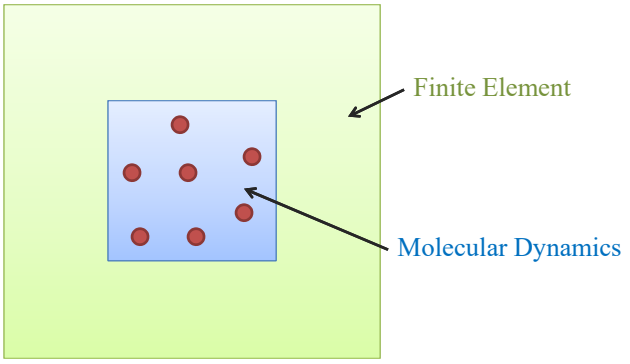
Box ~ 20 nm
Atoms ~ 800000
1 ns ~ ?



Ndoro et al., *Macromolecules*,2011,44,2316

Obstacle: 2

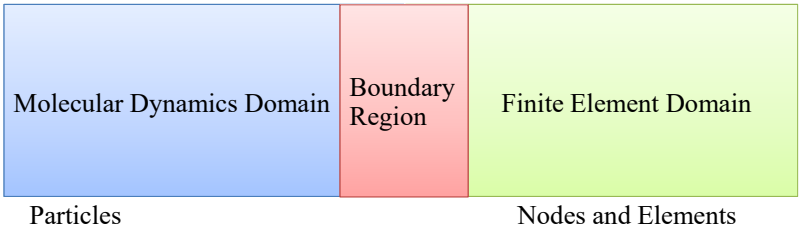
Nonperiodic boundary conditions must be used.



Obstacle: 3

Information must be transferred between the MD and the FE description.

- A boundary region must be defined between two domains.
- Boundary region conserves physical quantities at interface.



Particles	Nodes and Elements
Interaction potential	Energy density
Pressure, Time, Temperature	Stress and Strain

Obstacle: 4

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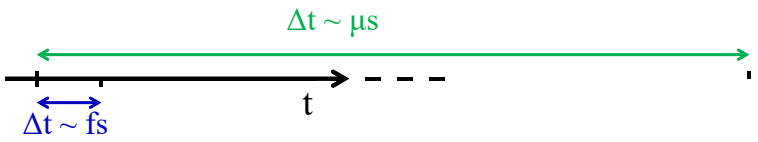
The time scales of the molecular dynamics and finite element domains are very different



1 FE step ~ 1,000,000,000 MD steps

Outline

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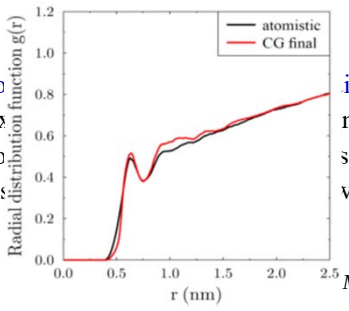
Obstacle: 1

Coarse-Grained

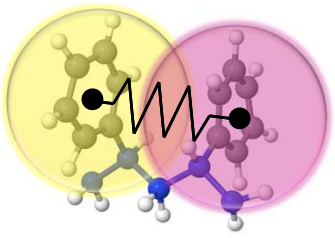
Principle of coarse-graining: Merging groups of atoms into superatoms

System: Atactic Polystyrene

Same structure



Ato ined
Box m
Ato s ~ 6000
1 ns v hours

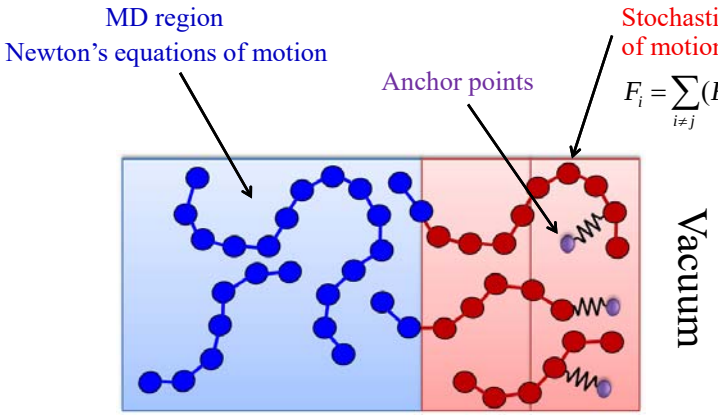


Coarse-Grained Atomistic

Macromolecules, ***2012***,*45*, *572-584*

Obstacle: 2

Nonperiodic Stochastic Boundary Conditions



Obstacles 2

Simulation under Stochastic Boundary Conditions

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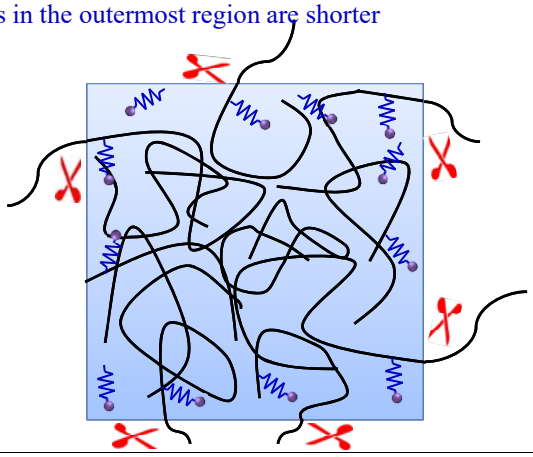
Dividing the simulation box into a smaller fragments

Polymer chains in the outermost region are shorter



Validation of MD Simulations with Nonperiodic Stochastic Boundary Conditions

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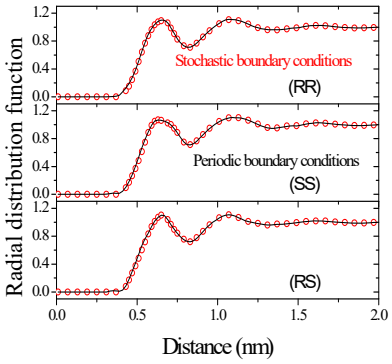
Simulation of polystyrene oligomers in CG representation (20 mers)

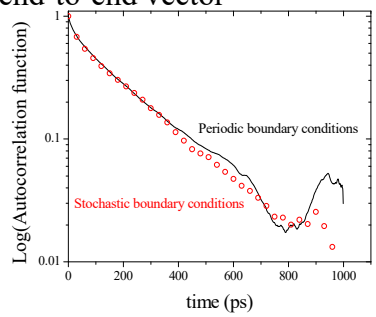
Number of beads = 82080
Number of beads in DPD region = 41400
Number of beads in MD region = 40680
Simulation time = 10 ns

	Number of anchor points	Density (kg/m^3)	Temperature (K)	Squared radius of gyration (A^2)	Squared end to end distance (A^2)	Relaxation time of end to end vector (ps)
PBC	-	1020.75	300	100.4	617	162.54
SBC	7262	1015.17±2.5	300.67±0.91	100.61±0.32	619.24±4.03	160.9
SBC	10954	1016.69±0.8	300.72±1.08	100.81±0.15	618.14±1.9	163.2
SBC	13780	1019.43±2.5	301.25±1.12	100.62±0.18	618.90±2.21	161.8

Validation of MD Simulations with Nonperiodic Stochastic Boundary Conditions



Autocorrelation function of the end-to-end vector



Journal of chemical physics **2011**, *134*, 154108

Obstacle 3

Arlequin Method

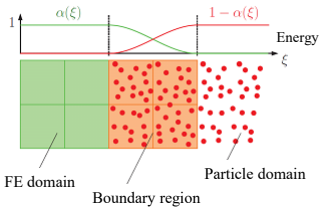
A static approach to couple a FE domain to a particle domain

$$E_{tot} = E_{FE}^{\text{int}} + E_{P}^{\text{int}} - E^{ext}$$

In Boundary region $\| u - r \| = 0$

FE domain displacement

Particle domain displacement



$$L(\lambda, u, r) = E_{tot} + \int \lambda.[u - r] dV$$

$$\frac{\partial L}{\partial r} = 0 \Rightarrow \frac{\partial E_{tot}}{\partial r} = \frac{\partial E_{P}^{\text{int}}}{\partial r} = \vec{f}_{p}$$

Forces

Obstacle 3

Coupling Scheme

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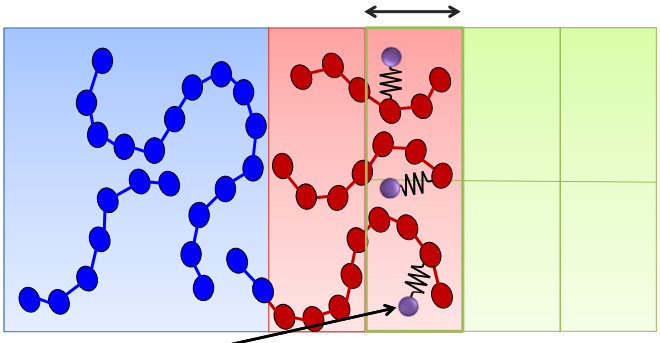
The two domains have an overlap in the boundary region



Anchor points play the role of static particles in the Arlequin method.

Time average forces

Obstacle 4

Staggered Algorithm

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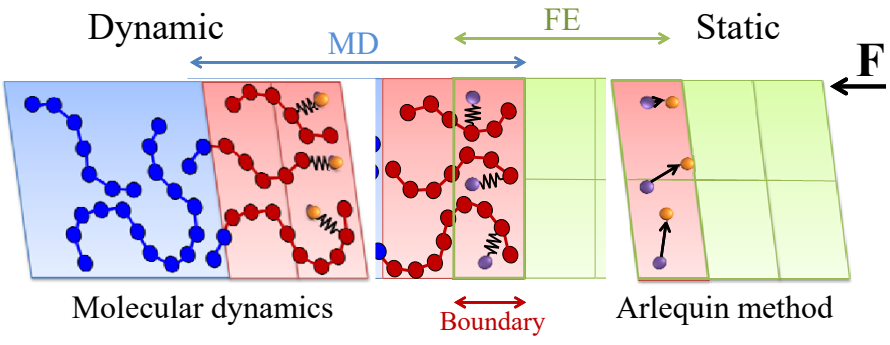

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TECHNISCHE UNIVERSITÄT DARMSTADT

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Equilibration

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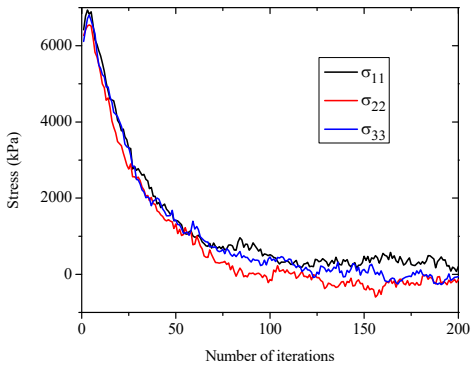
- Anchor point positions have been chosen randomly
- Density deviation in boundary region due to the shorter chain lengths

Couple MD domain to FE domain without applying external force



Identification Finite Element Parameters

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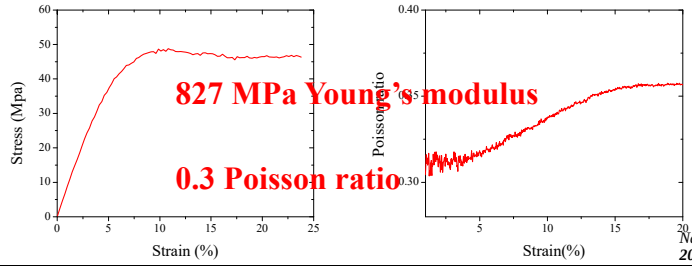
System: Atactic Polystyrene

300 Polymer chains	Experimental data
200 Monomers	0.32 Poission ratio
100 K Simulation temperature	3500 MPa Young's modulus
170 K Glass transition	370 K Glass transition

The material parameters to be used in the finite element domains are identified from a pure molecular dynamics simulation in a coarse-grained scale.



Nanothechnology ***2012***, *23, 305702*

Uniaxial Tension Test

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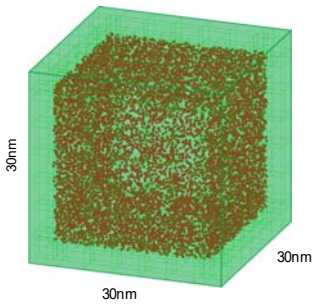
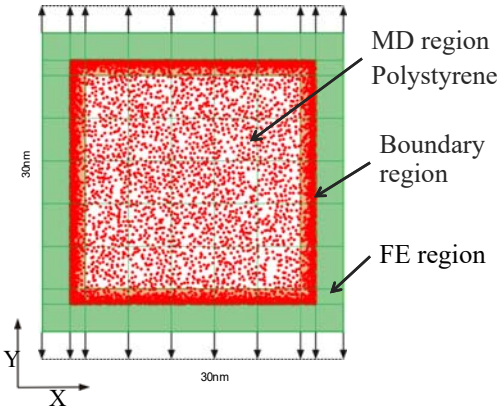




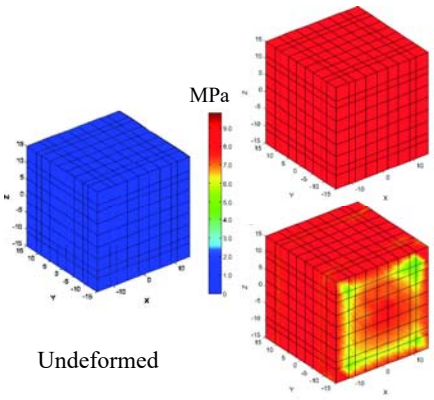
Polymer system

polystyrene, 60.000 MD particles, 9004 anchor points, overall edge length 30nm

Uniaxial tension test

prescribed displacements at the top and the bottom, 1% strain

Comparison of Pure FE and Hybrid Method



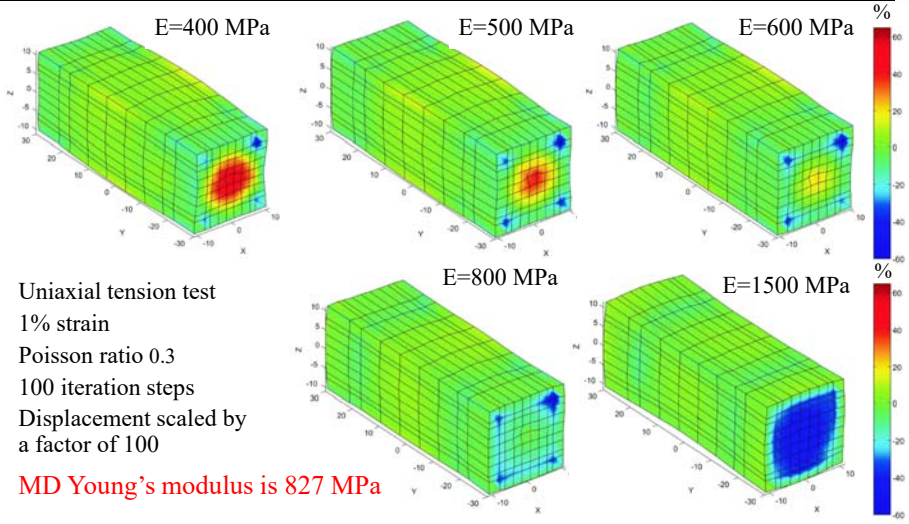
Pure FE simulation

Hybrid simulation

$$e^{\sigma} = \frac{|\sigma^{Hybrid} - \sigma^{FE}|}{|\sigma^{FE}|}$$

Stress deviation

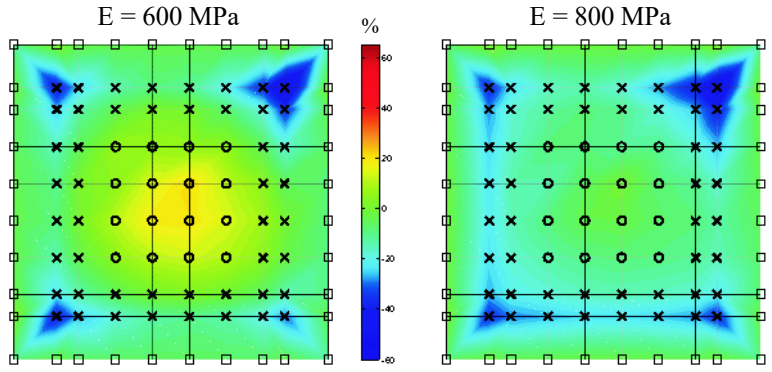
Stress Deviation with Different FE Young's Modulus



Uniaxial tension test
1% strain
Poisson ratio 0.3
100 iteration steps
Displacement scaled by a factor of 100

MD Young's modulus is 827 MPa

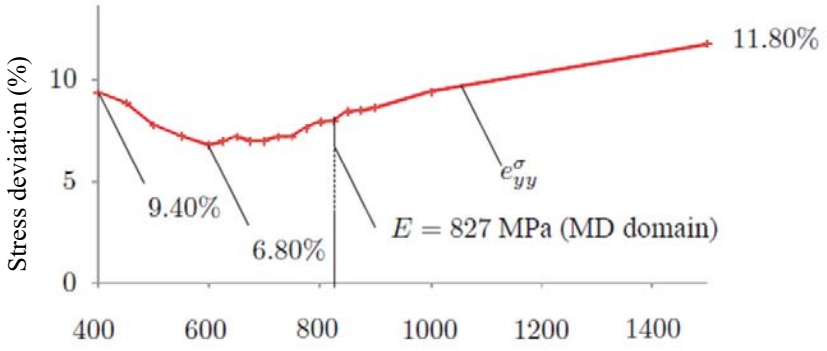
Stress Deviation with Different FE Young's Modulus



MD Young's modulus is 827 MPa

- Artificial behavior of polymer in the boundary region
- Shorter polymer chains in the boundary region (20 times shorter)

Stress Deviation with Different FE Young's Modulus



Young's modulus E (MPa) in FE domain

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Simulation of Nanocomposite

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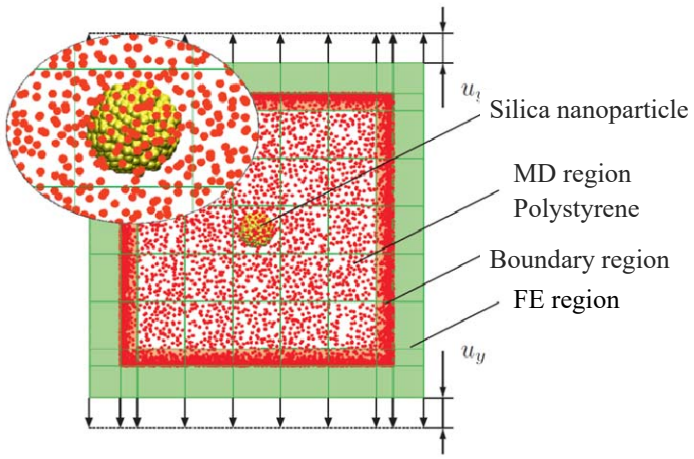
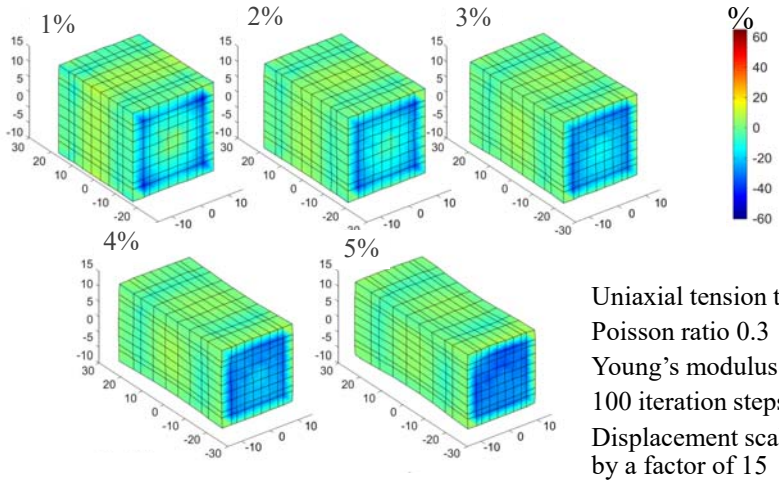
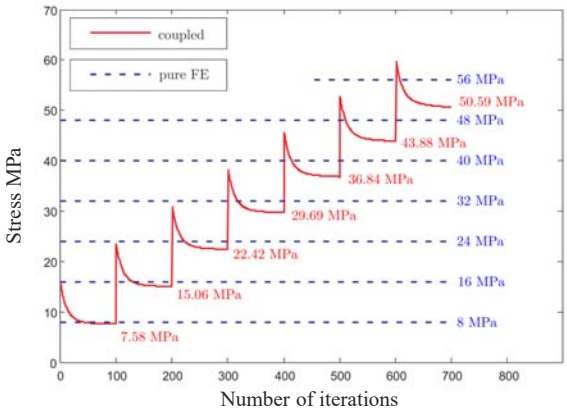


Applying Several Load Steps



Uniaxial tension test
Poisson ratio 0.3
Young's modulus 800
100 iteration steps
Displacement scaled by a factor of 15

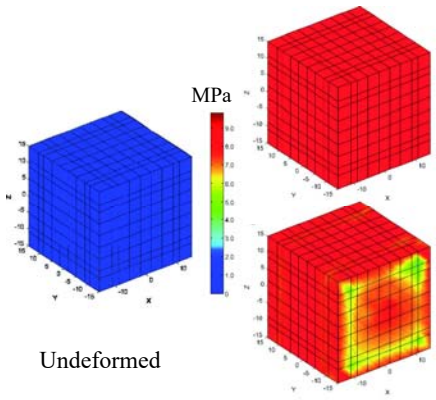
Applying Several Load Steps



Future Plan

Extend the hybrid method to simulation of large deformation (non-linear regime)

Back to stress deviation



$$e^{\sigma} = \frac{|\sigma^{Hybrid} - \sigma^{FE}|}{|\sigma^{FE}|}$$

Stress deviation

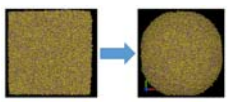
The reason is a non-uniform distribution of chain lengths.

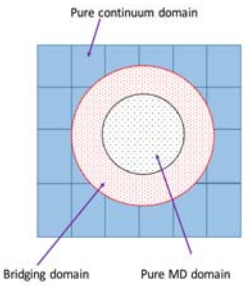
There are more short chains in the cube corners.

Material is softer.

Back to stress deviation

- Solution: spherical MD domain
- Surface is more uniform.
- Number of short chains near surface is more uniform.

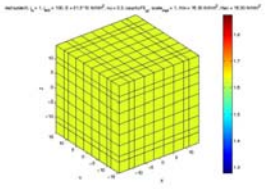




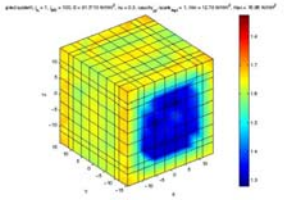
Back to stress deviation

Spherical MD domain: stress deviation smaller and more uniform

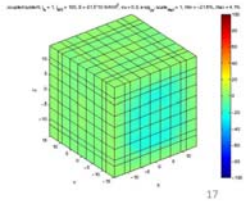
Pure FE

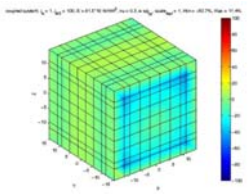


Hybrid FE-MD



Difference





For comparison:
cubic MD region

New work by Yunfeng Mao

Outline

- Motivation
- Technical obstacles
- How to overcome the obstacles
- Simulation of pure polystyrene
- Simulation of nanocomposite
- **Summary**

Summary

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- We have developed new nonperiodic boundary conditions to couple a molecular dynamics to a finite element domain.
- A staggered coupling procedure was employed to couple the MD to the FE domain.
- Finite element parameters have been obtained from pure MD simulations.
- We have validated the hybrid scheme by comparing the results of a hybrid simulation and a pure FE simulation.
- Hybrid method has been employed to study nanocomposite materials

Combining particles and continuum: MD-FE for structural mechanics

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- First attempt for polymeric materials
- Completely new coupling strategy
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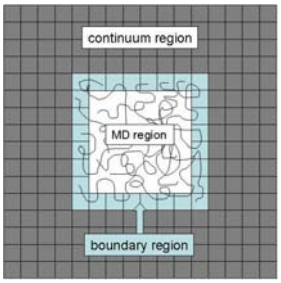

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Thank you for your attention!

Have patience. All things are difficult before they become easy.

Saadi, 1210 – 1292

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