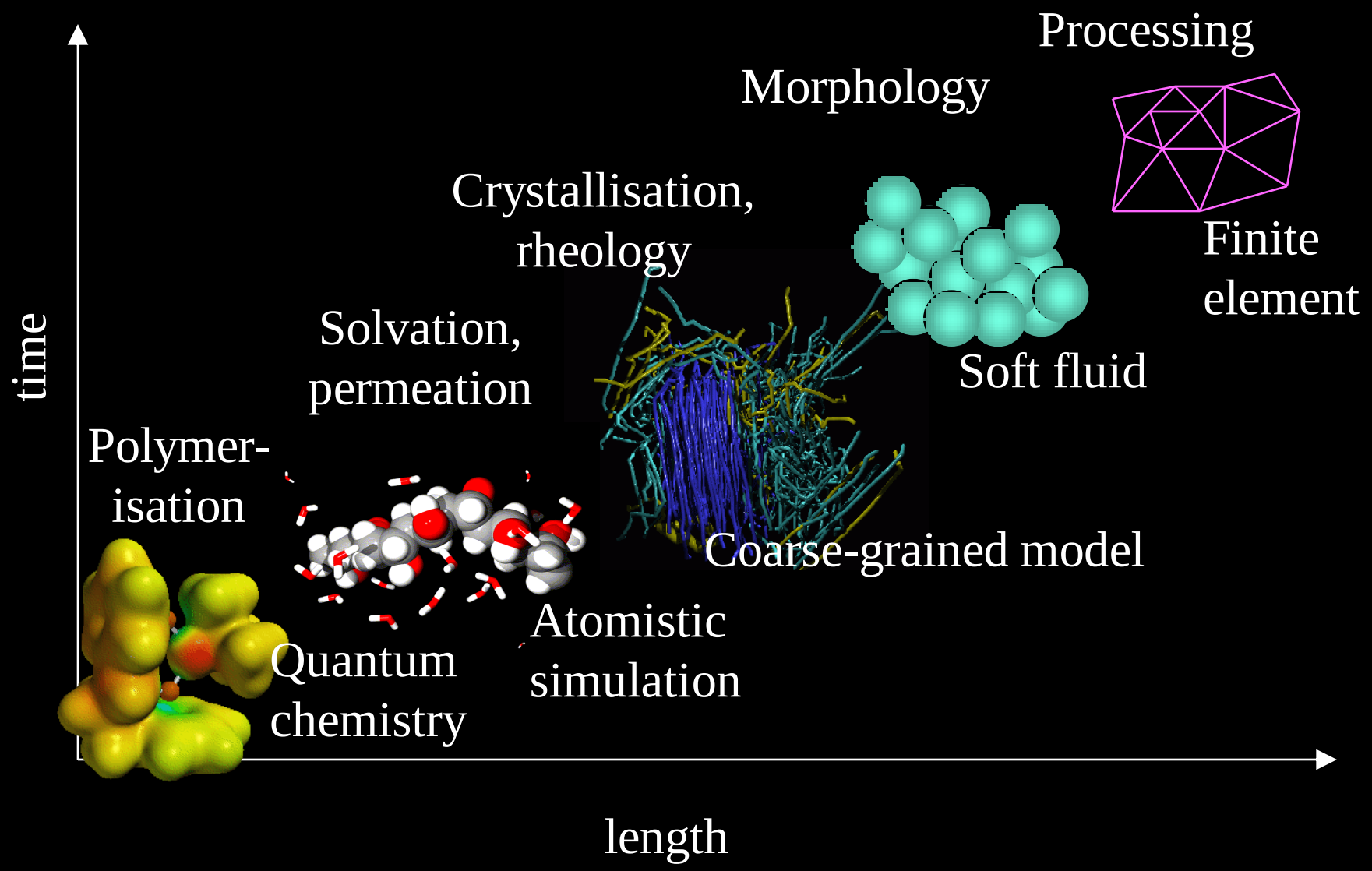
Trends in Materials Simulation: A Molecular Dynamics Miscellany

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

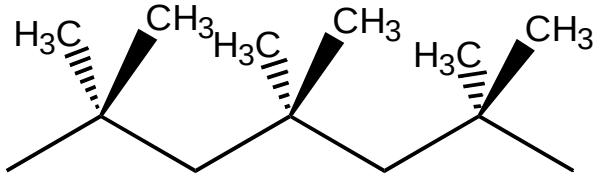
Polymers: Scales & Methods

Review: FMP, Soft Materials **1**, 1 (2003)

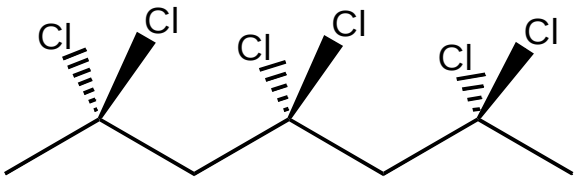


Polymers: Structure and Properties

- Chemistry

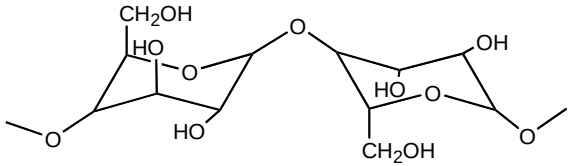


rubber

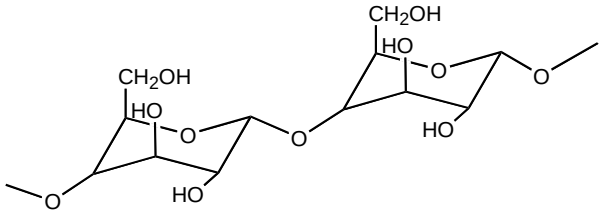


brittle

- Tacticity



insoluble



water-soluble

- Sequence

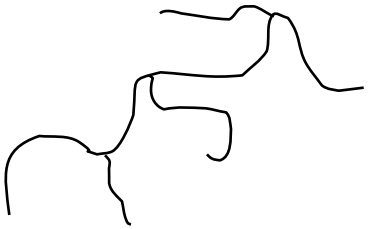
S-S-S-S-B-B-B-B

engineering plastic

S-B-S-S-B-S-B-B

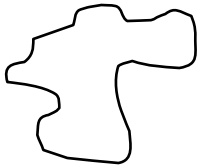
synthetic rubber

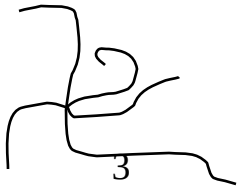
- Topology



shopping bag

bullet-proof vest





Multiscaling and Dynamics

Transport properties

Reverse nonequilibrium molecular dynamics

Successes and failures

Multiscale Methods

Structure-based coarse graining

Successes and failures

Attempt of a synthesis:
Dynamics of coarse-grained models

Transport Coefficients

- **Transport coefficient**

$$J = -\kappa E$$

driving force, field, thermodynamic force

flux, flow, current, ...

- **Non-equilibrium situation:** steady-state, periodic, ...
- **Linear response:** small perturbation
- **Isotropic medium:** liquid, melt, ...

Linear response

- **Mass** *Berthollet* 1803

$$J_1 = -D(\partial c / \partial z)$$ *Fick* 1854

- **Charge** *Ohm* 1826

$$I = -(1/R)(\partial \Phi / \partial z)$$

- **Energy** *Fourier* 1822

$$J_Q = -\lambda (\partial T / \partial z)$$

- **Momentum**

$$J(p_\perp) = -\eta (\partial v_\perp / \partial z)$$

$$[\sigma_{xy} = -\eta \dot{\gamma}]$$

- **Coupled energy and mass**

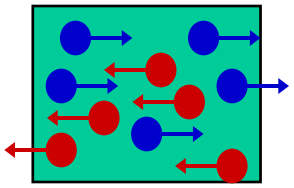
$$J_1 = -D_{12}\rho[(\partial w_1 / \partial z) + S_T w_1 (1 - w_1)(\partial T / \partial z)]$$

- $\mathbf{J} = -\mathbf{L}\mathbf{X}$ *Onsager* 1931

$$J_1 = -L_{11} \frac{\nabla_T \mu}{T} - L_{1Q} \frac{\nabla T}{T^2}$$

Calculation of Transport Coefficients by MD

- Equilibrium
  - Green-Kubo
  - Einstein
- Non-equilibrium
  - Periodic $\mathbf{J}(\omega,\mathbf{k})$
  - Steady-state $\mathbf{J}(\omega\rightarrow 0,\mathbf{k}\rightarrow 0)$
  - Boundary-driven
  - Synthetic



1st Ingredient: Reverse cause and effect

Traditional NEMD

$$\langle \mathbf{J} \rangle = -\kappa \mathbf{E}$$

calculate **impose**

Reverse NEMD

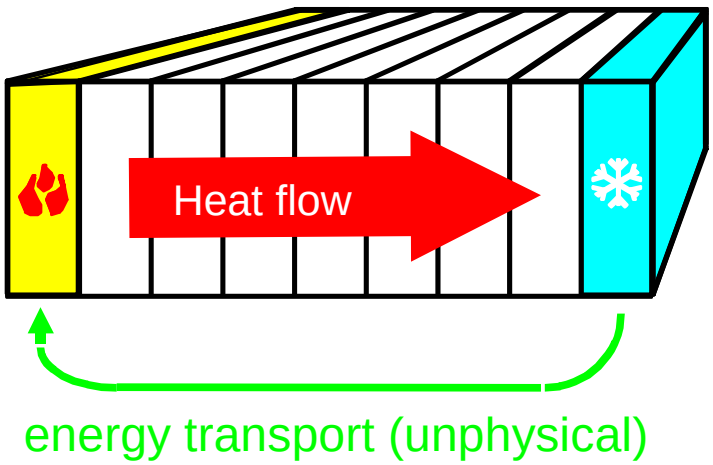
$$\mathbf{J} = -\kappa \langle \mathbf{E} \rangle$$

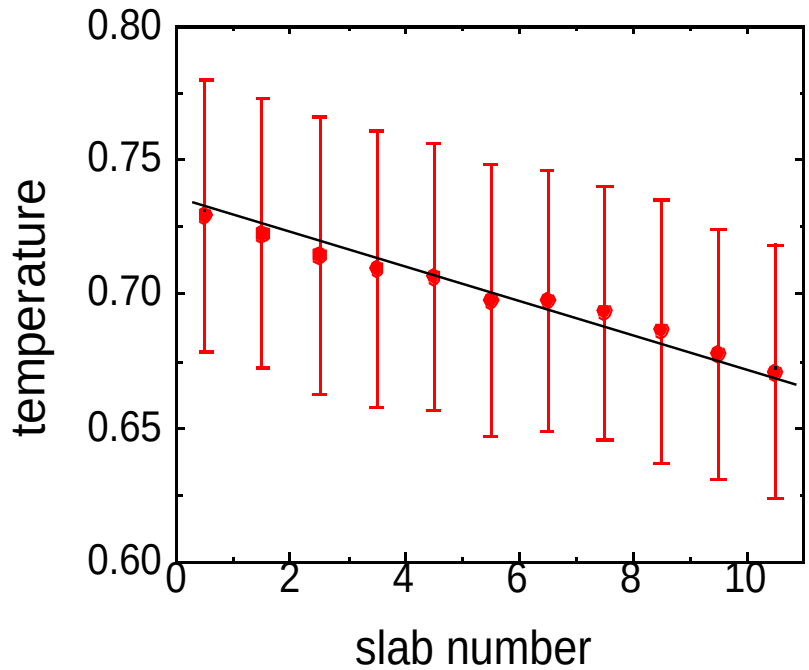
impose **calculate**

Examples:

- shear viscosity η
- thermal conductivity λ
- Soret coefficient S_T

Thermal Conductivity





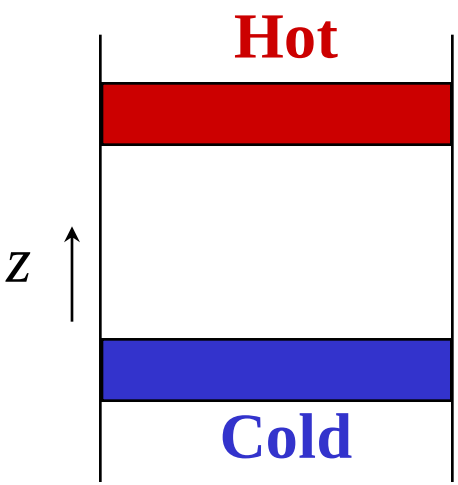
Repeat periodically, wait for steady state

Fourier's law: $J_Q = -\lambda \, dT / dz$

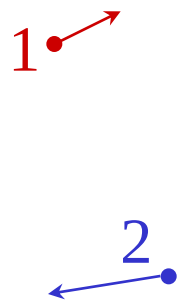
F. Müller-Plathe, J. Chem. Phys. **106**, 6082 (1997)

2nd Ingredient: Unphysical velocity exchange

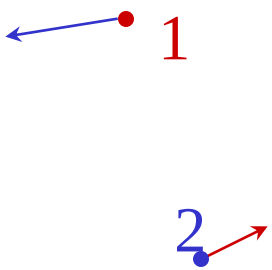
What we want



Find hottest particle in the cold region and coldest particle in the hot region



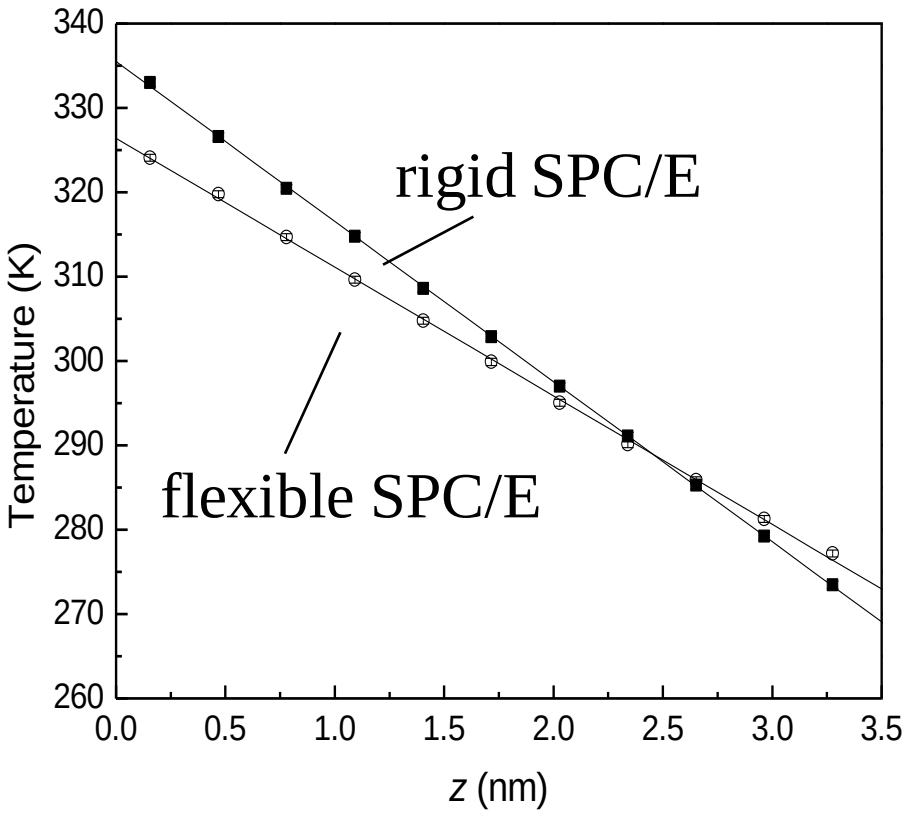
Swap their velocities **v**



If $m_1=m_2$:

no change in total linear momentum
no change in total kinetic energy
no change in total energy

Analyse



- Calculate temperature profile $T(z)$
- Obtain gradient dT/dz
- Fourier's law

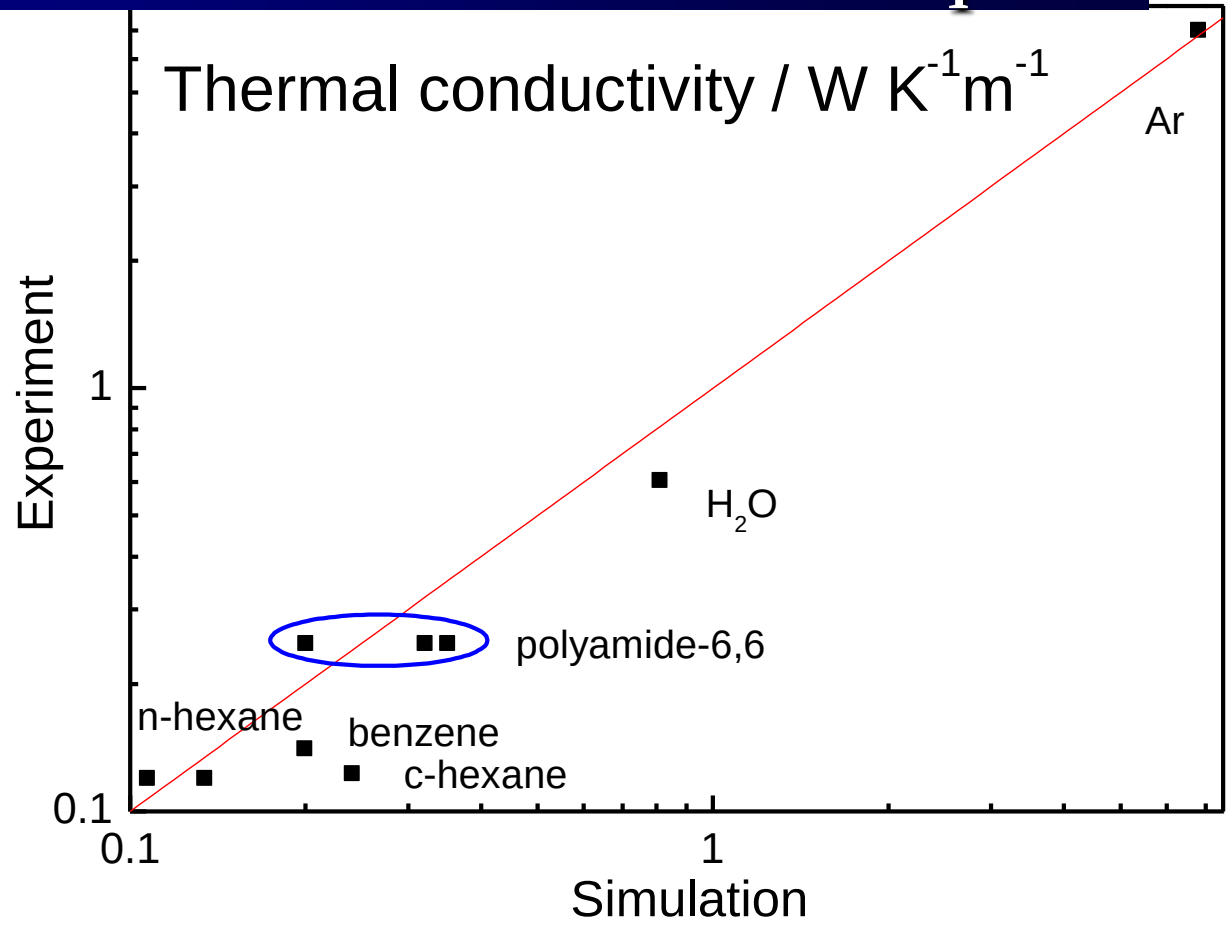
$$\lambda = -\frac{J_q}{\langle dT/dz \rangle}$$

Thermal conductivity

	λ ($Wm^{-1}K^{-1}$)
rigid	0.81±0.01
flexible	0.95 ±0.01
experiment	0.607

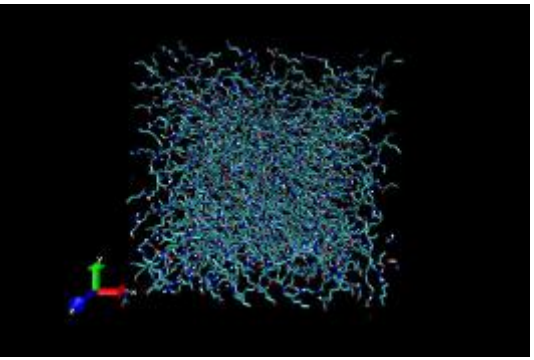
M. Zhang, E. Lussetti, L.E.S. de Souza, F. Müller-Plathe, J. Phys.Chem. B **109**, 15060 (2005).

Thermal conductivity of molecular liquids



M. Zhang, E. Lussetti, L.E.S. de Souza, F. Müller-Plathe, J. Phys.Chem. B **109**, 15060 (2005).

Thermal Conductivity of Polyamide-6,6



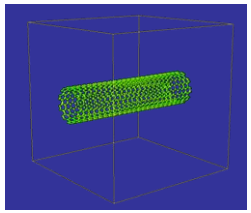
	Simulation	Experiment
	W/K m	W/K m
amorphous (1.07 g/cm^3)		
(flexible model)	0.33-0.35	~0.25
(semirigid model)	0.20	
stretched amorphous (0.95 g/cm^3)		
parallel to stretching	0.43	
perpendicular	0.20	

Enrico Lussetti, Takamichi Terao, FMP, J. Phys. Chem. B **111**, 11516-11523 (2007); Phys. Rev. E **75**, 057701 (2007).

Carbon nanotubes

M. Alaghemandi, E. Algaer, M. C. Böhm, FMP,

Nanotechnology **20**, 115704 (2009).

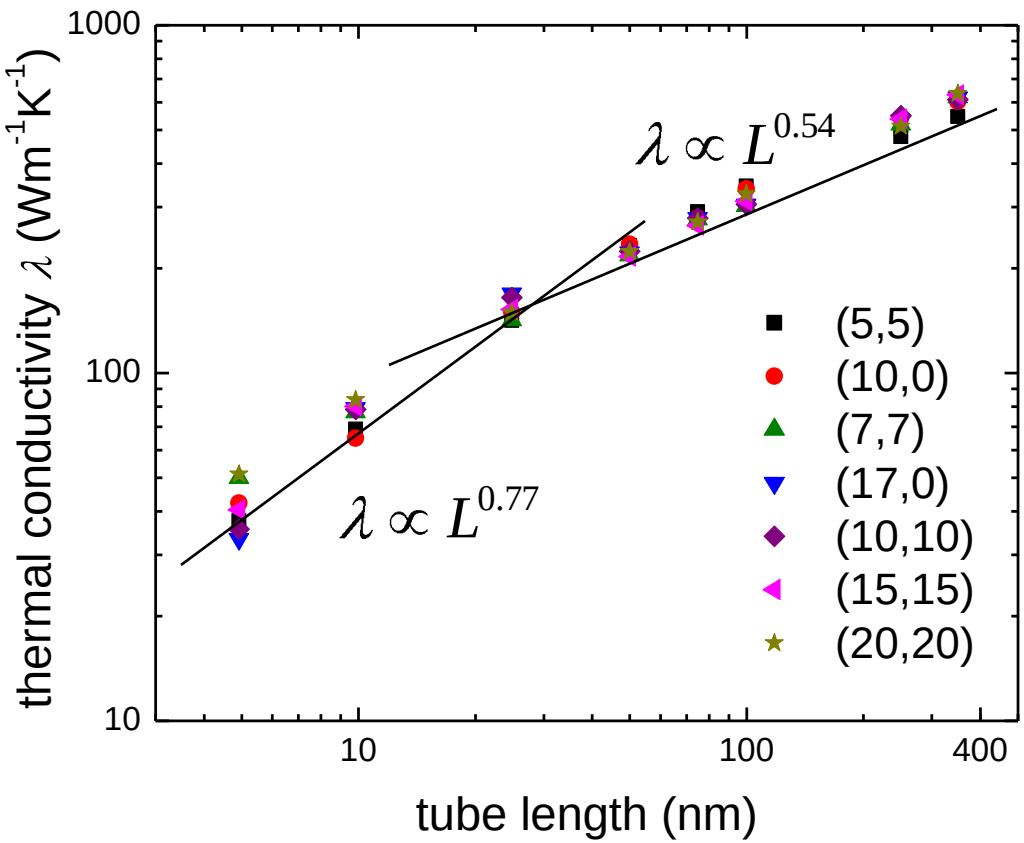


TECHNISCHE UNIVERSITÄT DARMSTADT

- λ depends on tube length

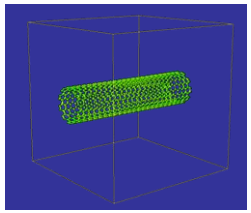
- power law
  $\lambda \propto L^{0.5-0.8}$
- Breakdown of Fourier's law

- Possibly different exponents for short and long tubes.
  Theory:
  $\alpha = 0.83 \rightarrow 0.35$
  J. Wang, J.-S. Wang, *Appl. Phys. Lett.* **88**, 111909 (2006)



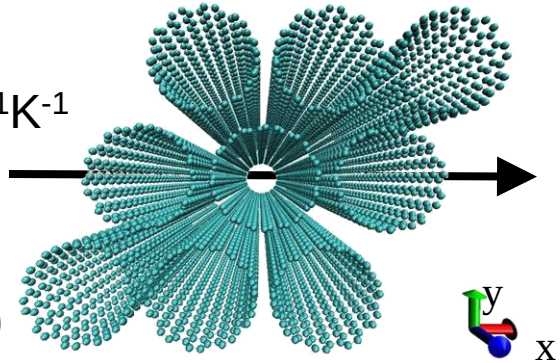
- Chirality of tube unimportant

Anisotropy of thermal conductivity

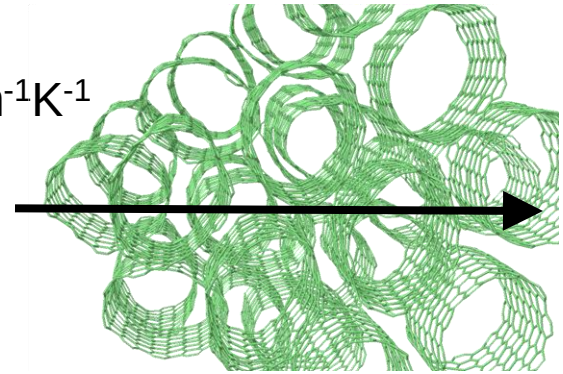


TECHNISCHE UNIVERSITÄT DARMSTADT

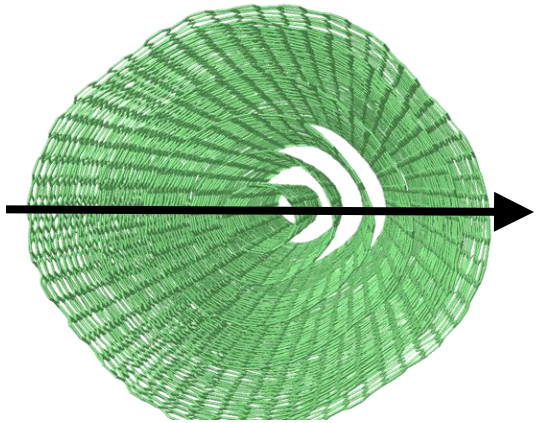
- CNT crystal
  - $\lambda_{||}$: 100 – 1000 W $m^{-1}K^{-1}$ (better than metal)
  - $\lambda_{\perp}$: 0.14 W $m^{-1}K^{-1}$ (worse than polymer)



- CNT bundle
  - $\lambda_{||}$: 100 – 1000 W $m^{-1}K^{-1}$
  - $\lambda_{\perp}$: 0.09 W $m^{-1}K^{-1}$



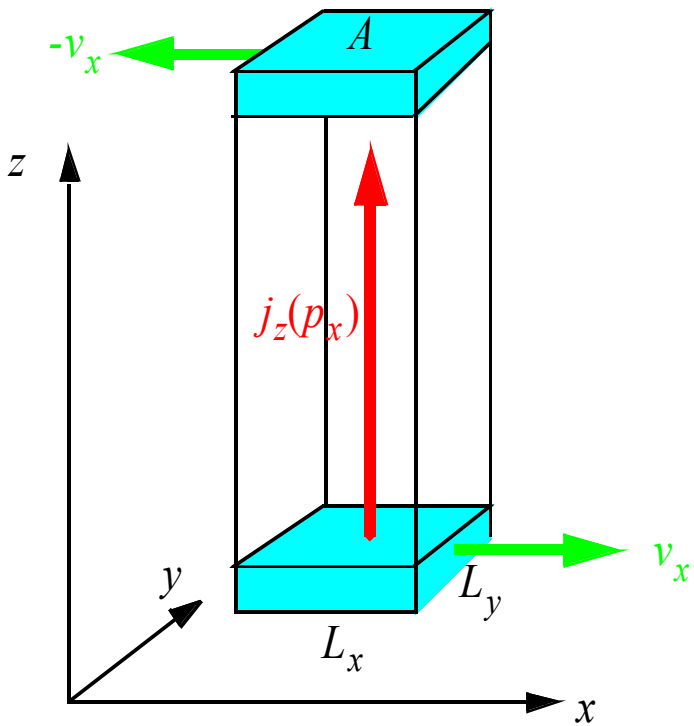
- Multiwall nanotube 10 nm
  - $\lambda_{||}$: 21 W $m^{-1}K^{-1}$
  - $\lambda_{\perp}$: 0.24 W $m^{-1}K^{-1}$

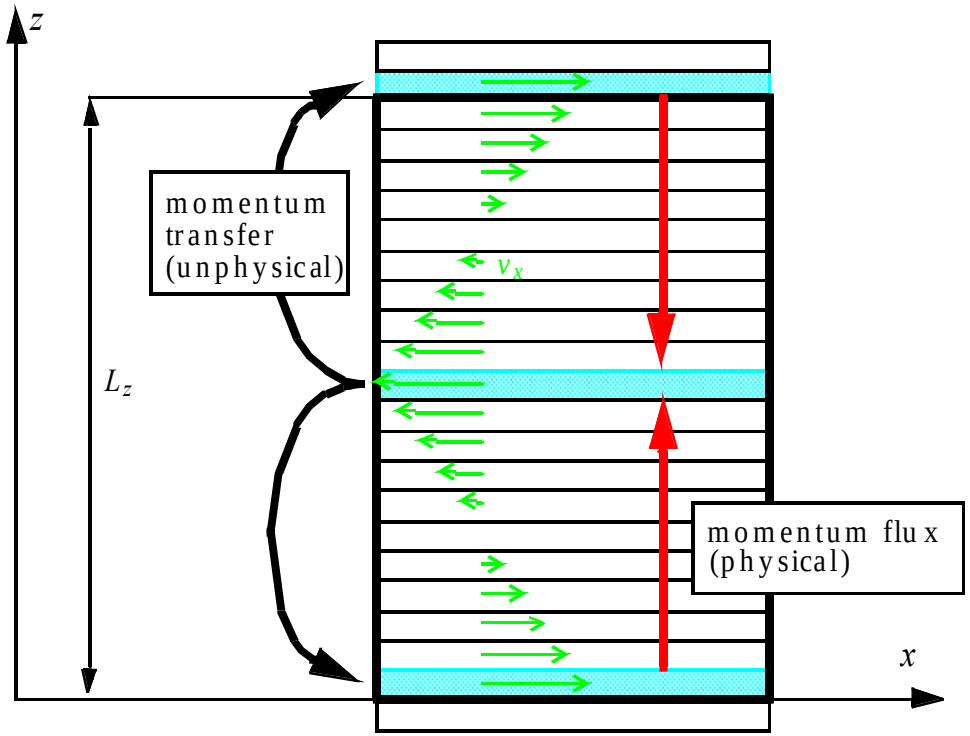


- Extreme anisotropies!

- Fast parallel mechanism (phonons) ↔ slow lateral mechanism (collisions between neighbouring tubes).

Shear viscosity

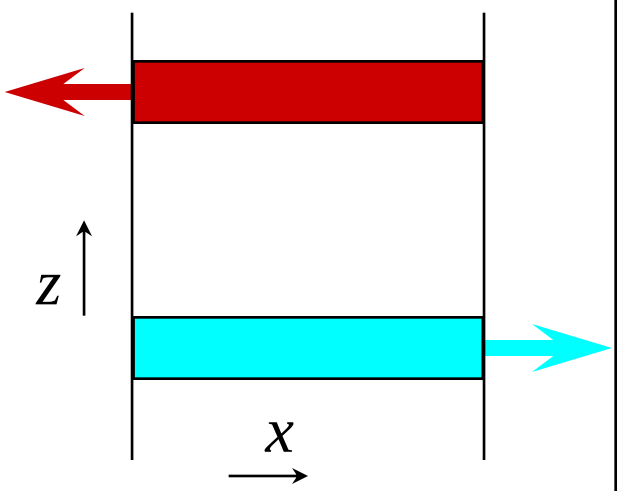




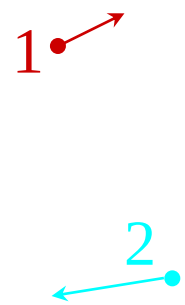
F. Müller-Plathe, Phys. Rev. E **59**, 4894-4899 (1999).

Exchange of velocity component

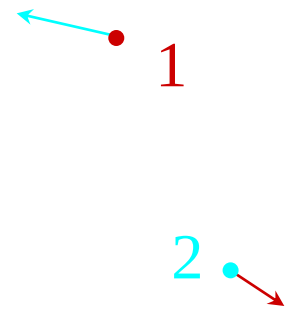
What we want



Find 2 particles that move **against** the current



Swap their v_x



If $m_1=m_2$: no change in total linear momentum
no change in total kinetic energy
no change in total energy
→ no thermostat!

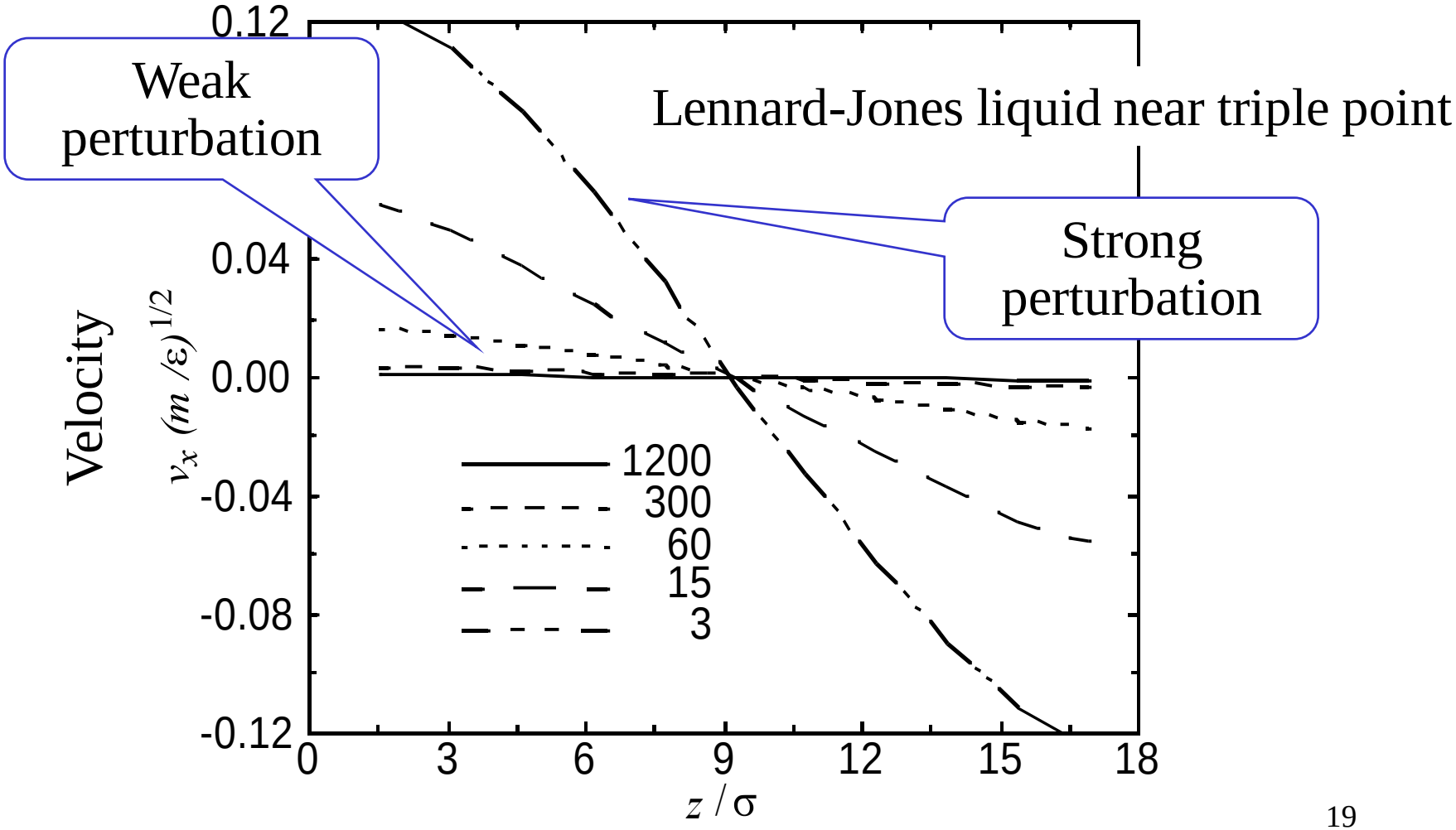
Shear viscosity

- What have we done?
  - Impose a flux of transverse linear momentum $J(p_\perp)$ = apply a shear force
  - higher perturbation = swap velocities more often

- What still needs to be done?
  - Measure shear rate:
    Measure profile of flow velocity, determine $dv_\perp/dz$
  - Viscosity η is proportionality constant

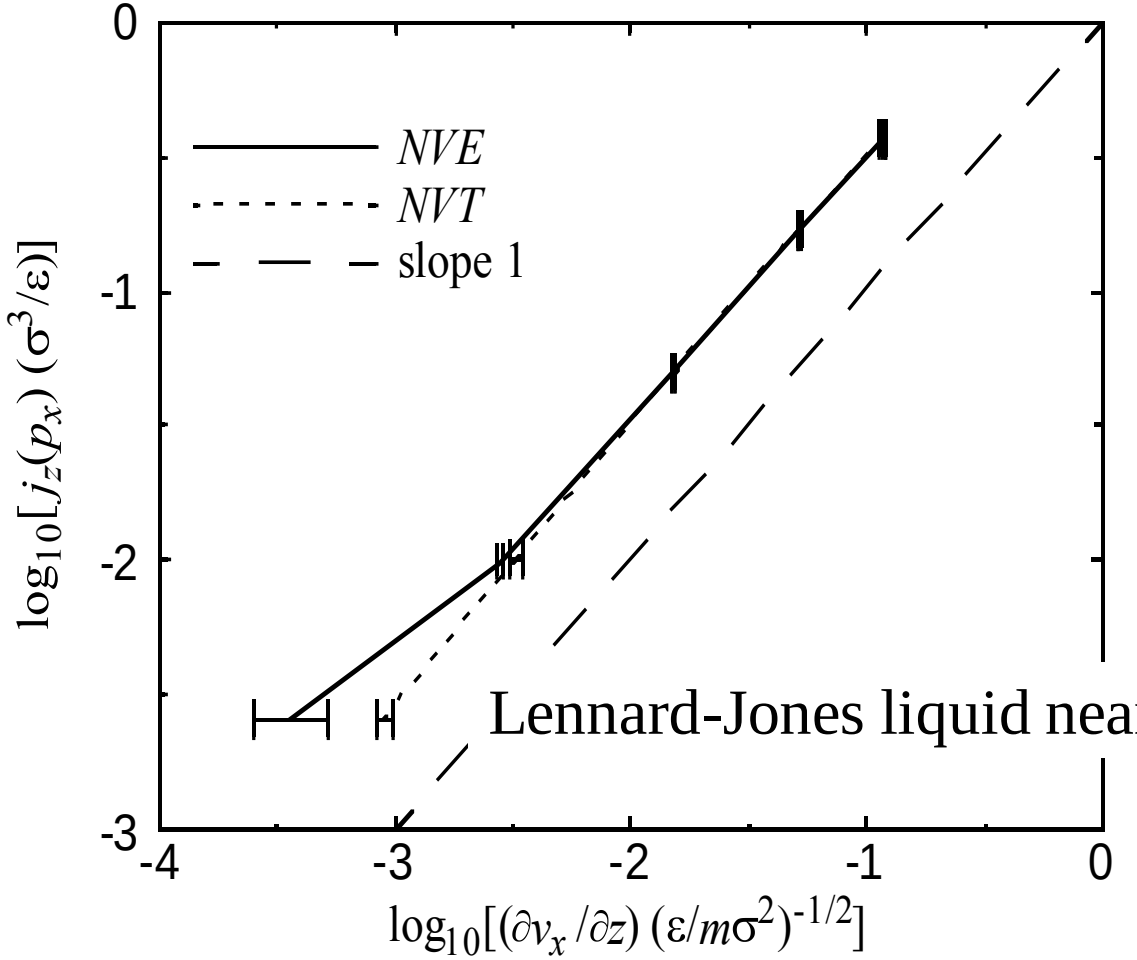
$$\boxed{J(p_\perp) = -\eta \frac{dv_\perp}{dz}}$$

Velocity profiles



Linear response holds

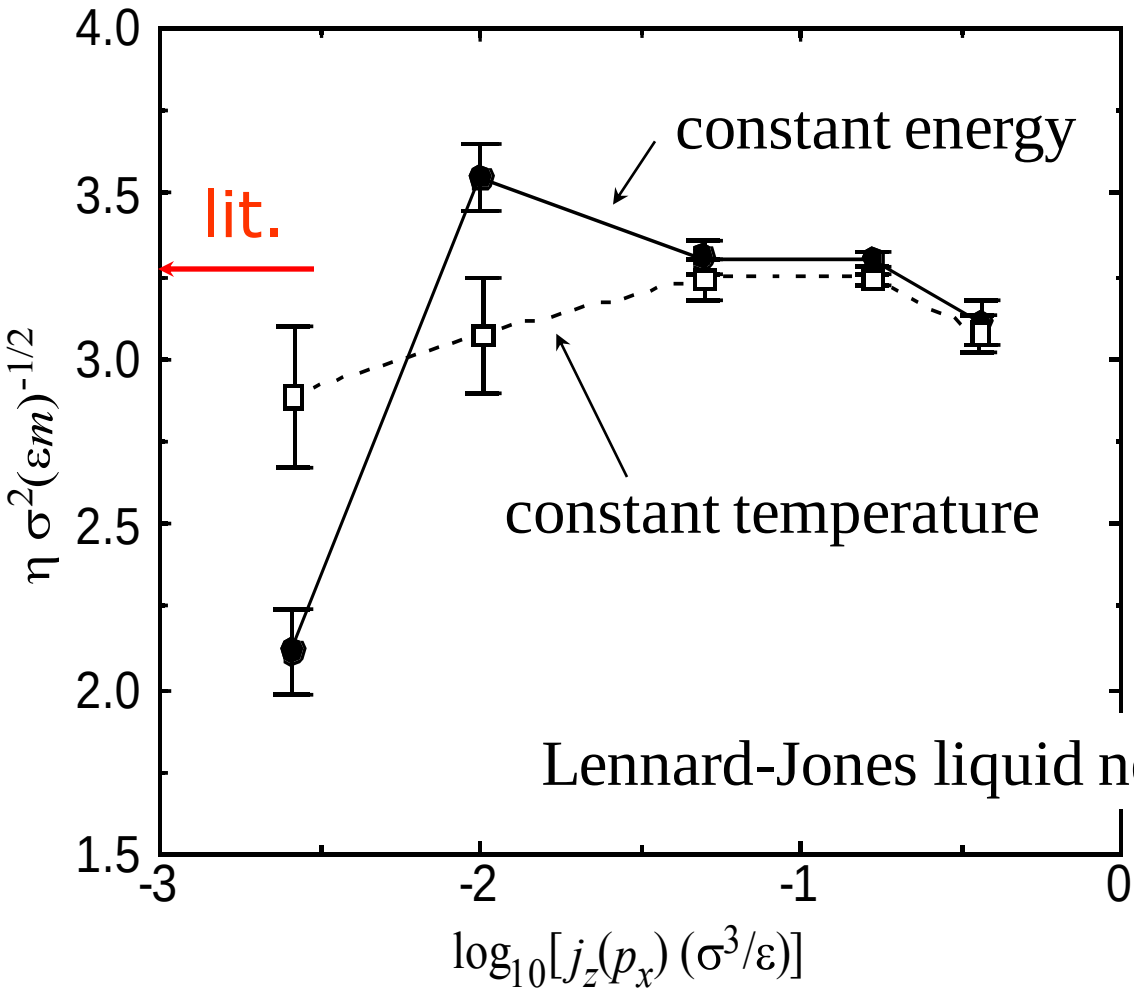
Transverse momentum flux
= shear force



Lennard-Jones liquid near triple point

Velocity gradient = shear rate

Shear viscosity η of the Lennard-Jones fluid



Lennard-Jones liquid near triple point

Viscous flow without viscous heating?

Recall:

- Total energy is conserved: microcanonical (*NVE*)

But:

- Viscous flow → friction → heating !!!

Question:

- How is the heat removed?

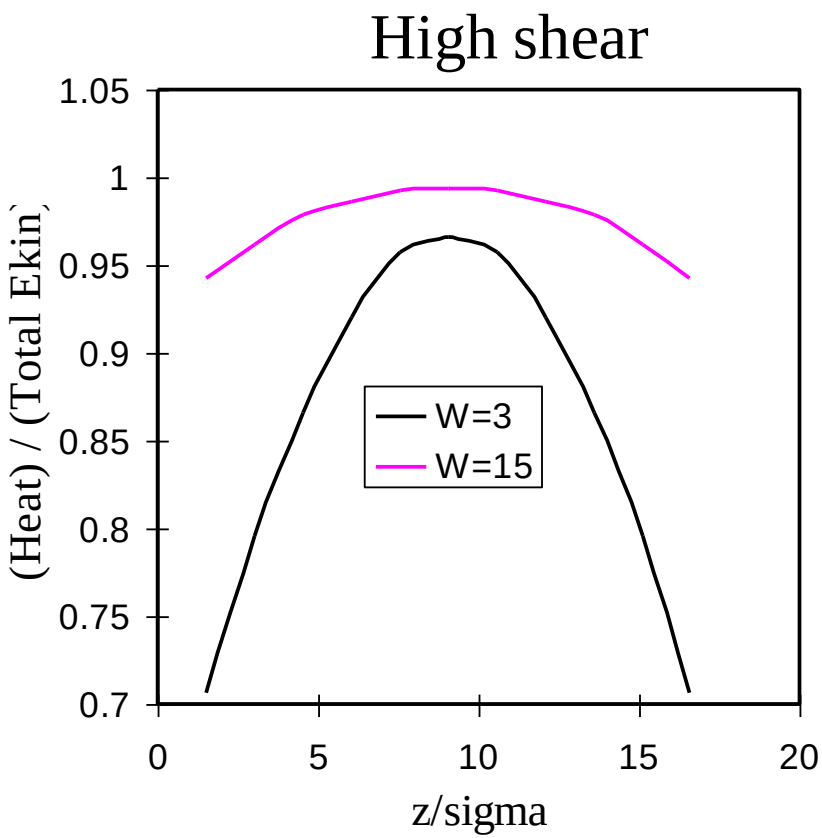
Answer: Maxwell demon

- Undirected motion (heat) → Directed motion (flow)
- Cooling in exchange regions

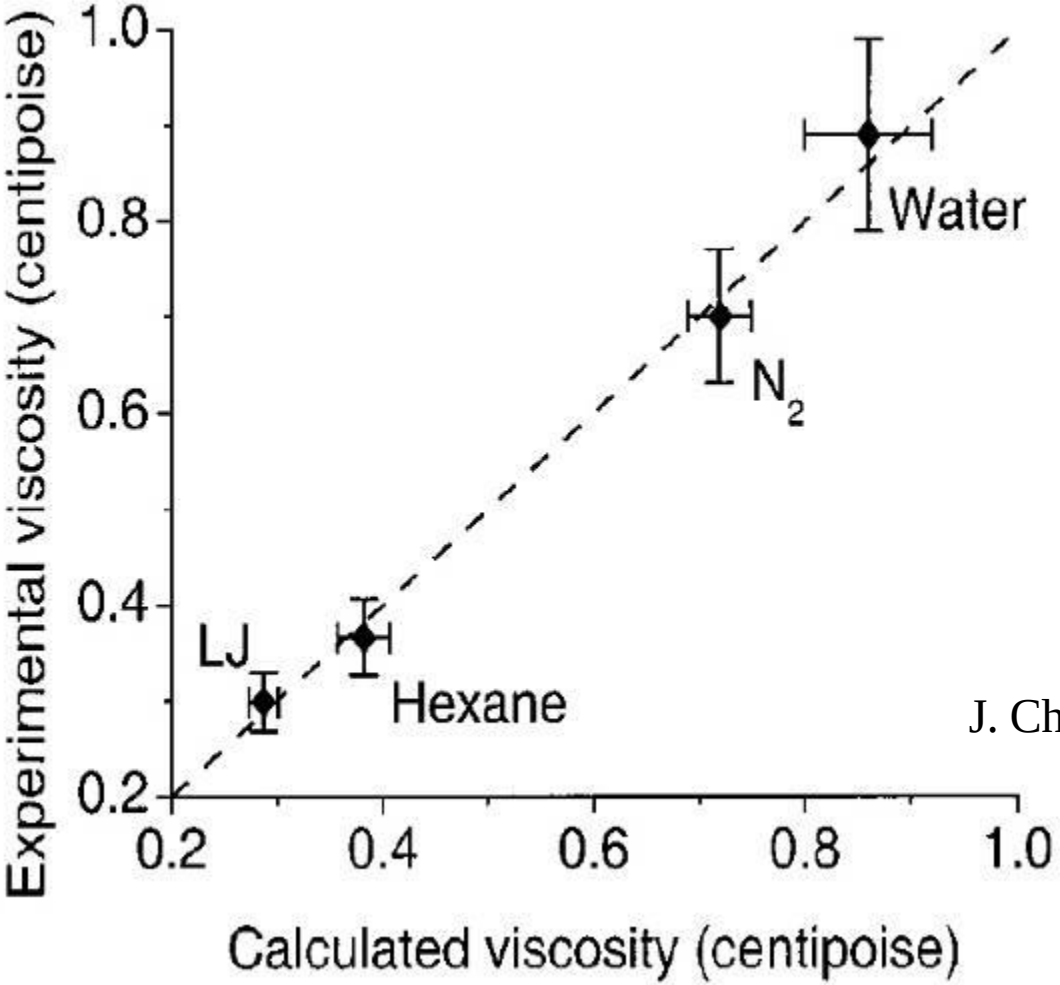
Proof: temperature profile

- E_{kin}(total) = E_{kin}(temperature) + E_{kin}(flow)
- Peculiar velocity $\mathbf{u}_i = \mathbf{v}_i - \langle \mathbf{v} \rangle$ defines temperature

Temperature profile from peculiar velocities

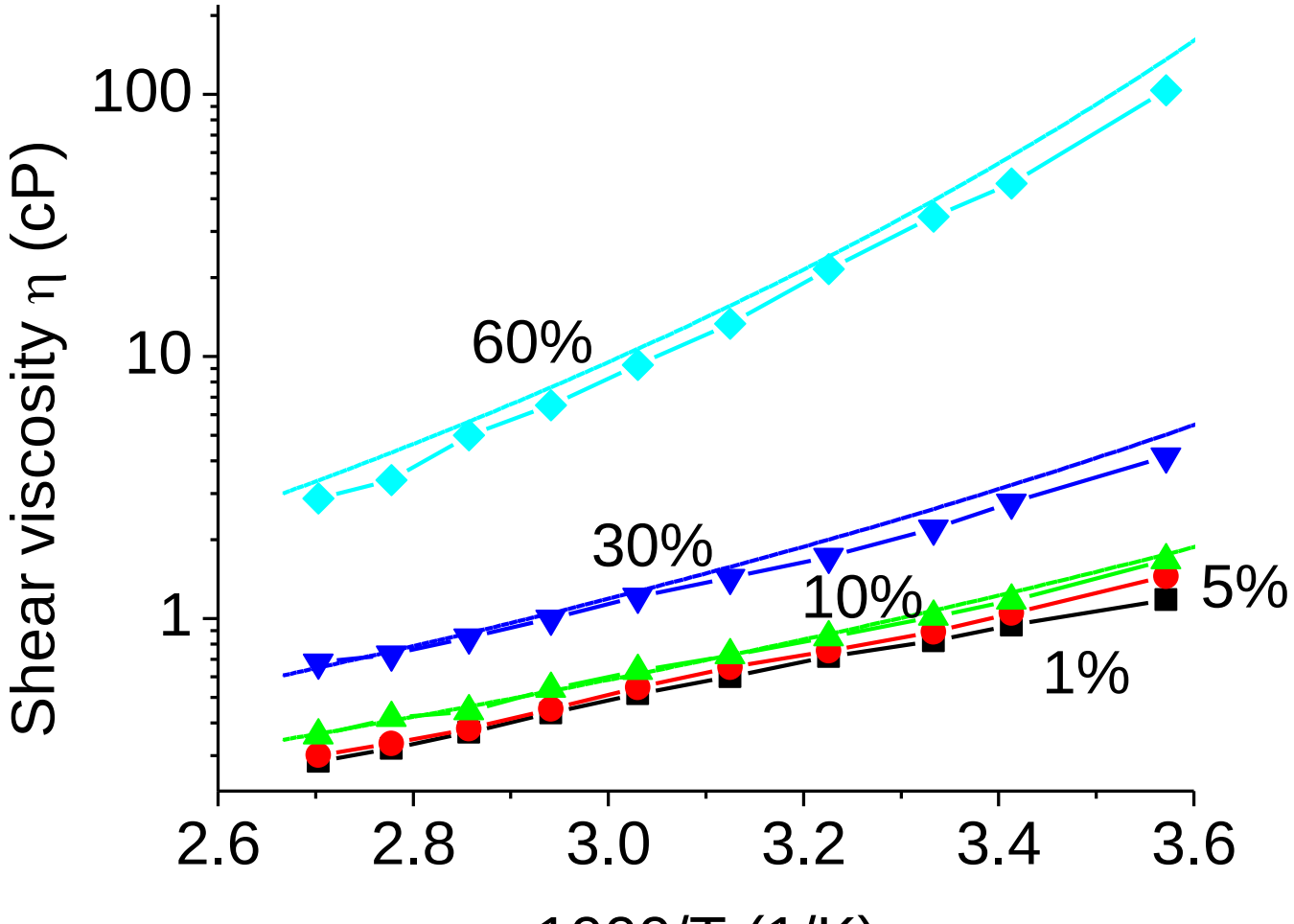


Molecular Liquids



P. Bordat, F. Müller-Plathe,
J. Chem. Phys. **116**, 3362 (2002)

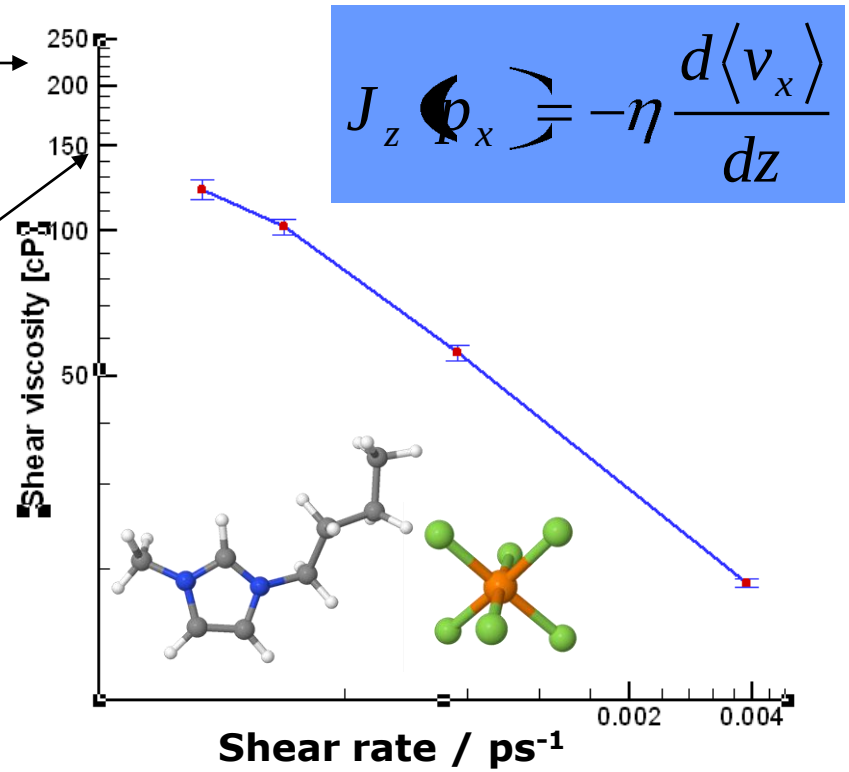
Aqueous solutions of saccharose



Ionic liquids: Shear viscosity of [bmim][PF_6]

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).

Multiscaling and Dynamics

Transport properties

Reverse nonequilibrium molecular dynamics

Successes and failures

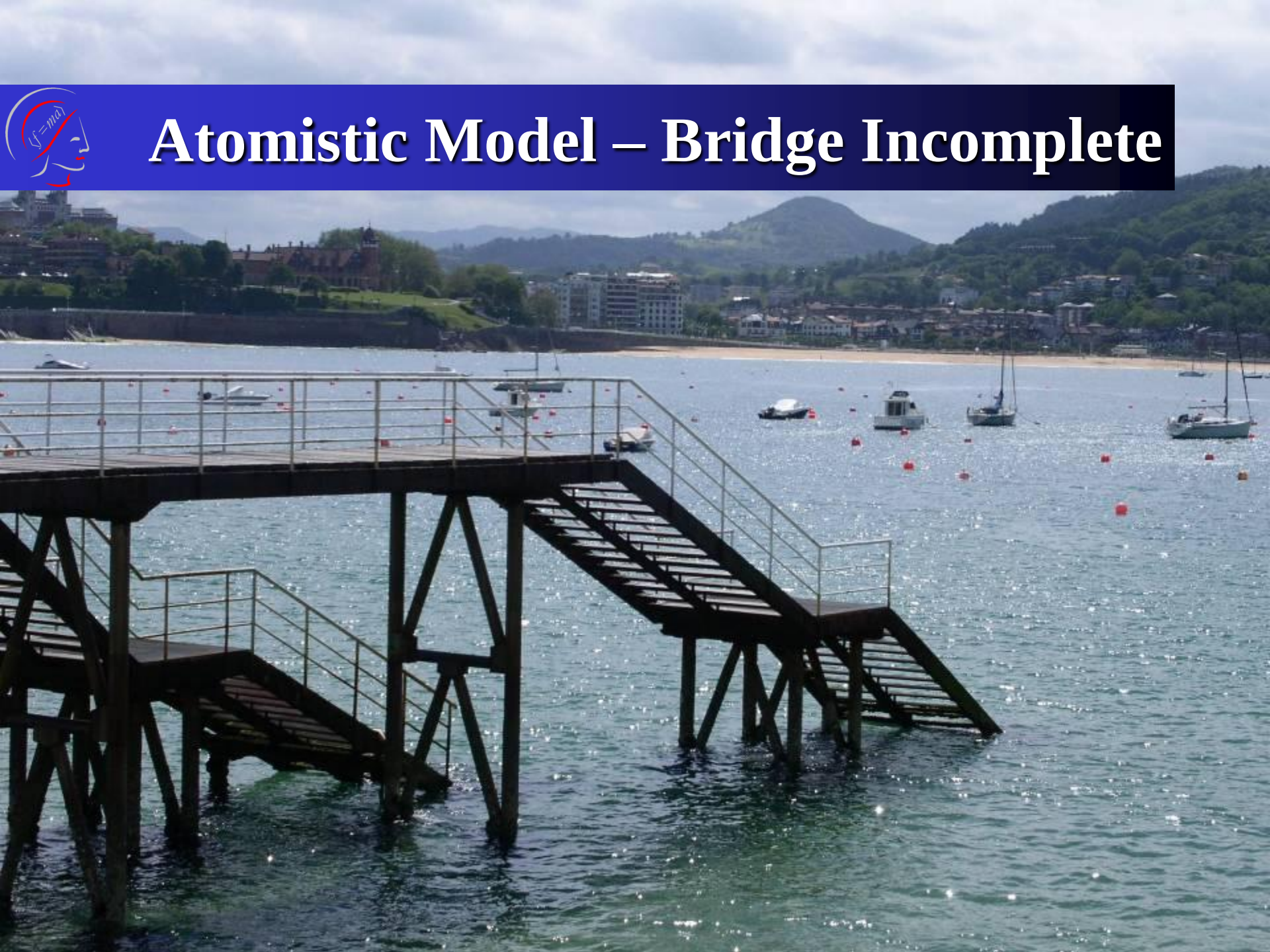
Multiscale Methods

Structure-based coarse graining

Successes and failures

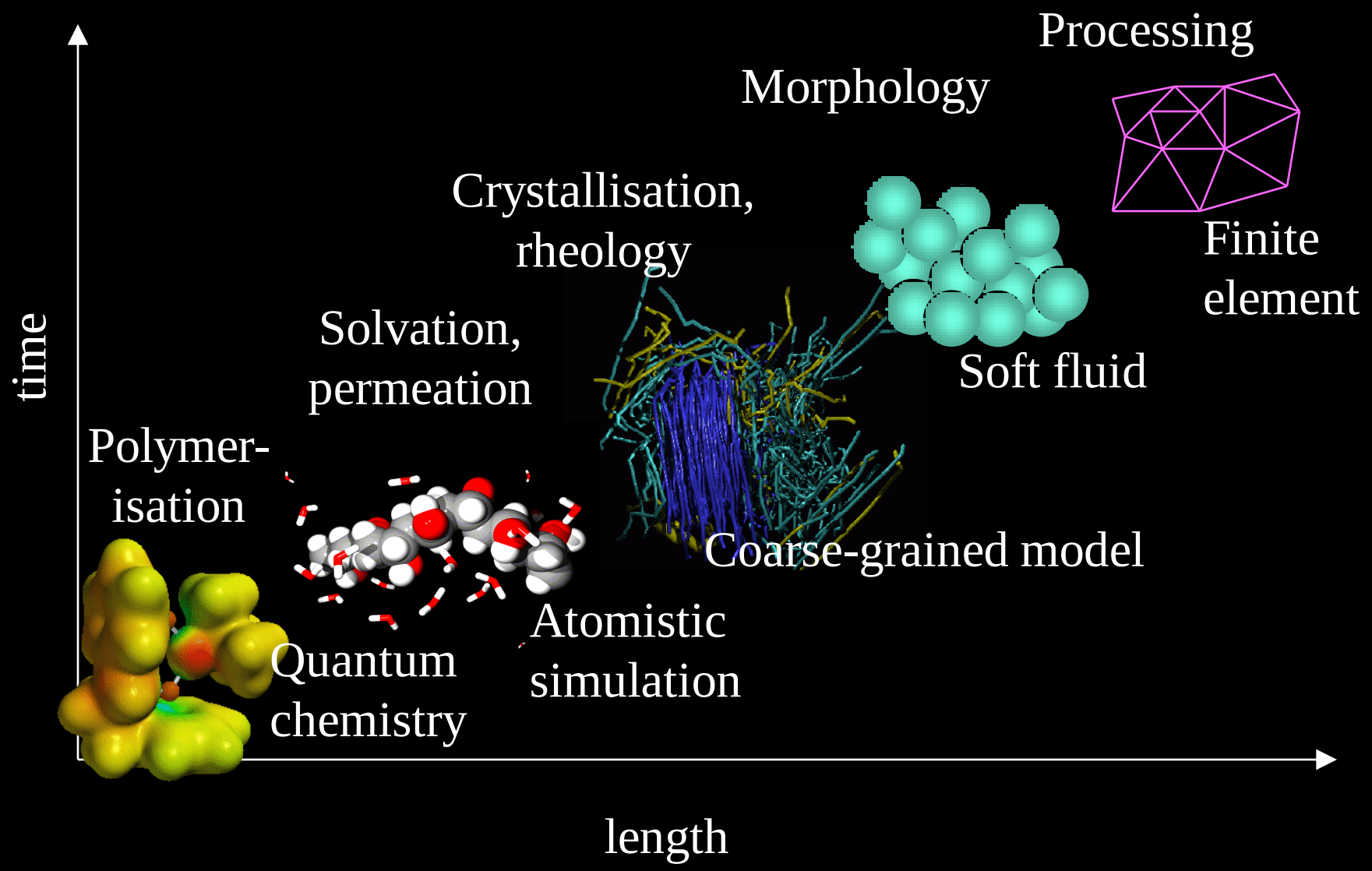
Attempt of a synthesis:
Dynamics of coarse-grained models

Atomistic Model – Bridge Incomplete

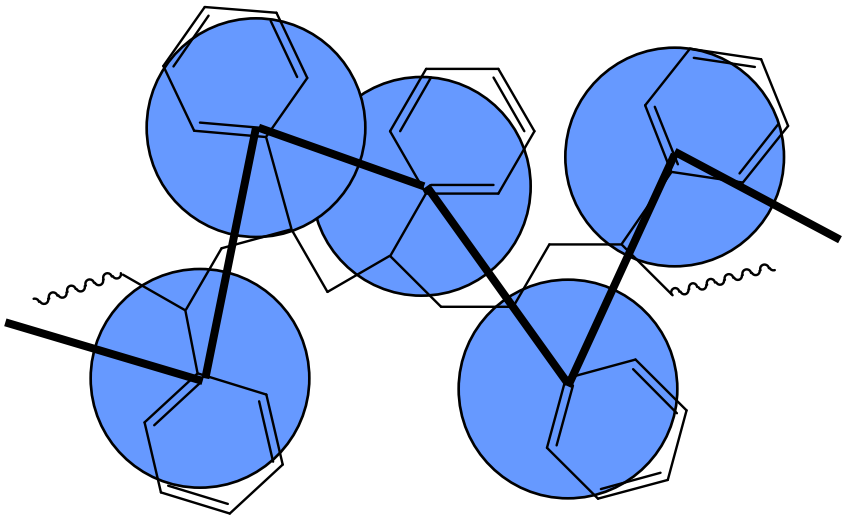


Polymers: Scales & Methods

Review: FMP, Soft Materials **1**, 1 (2003)



Coarse-grained Force Field



~10 atoms → 1 superatom

1000-100000 times cheaper

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

Systematic coarse-graining:

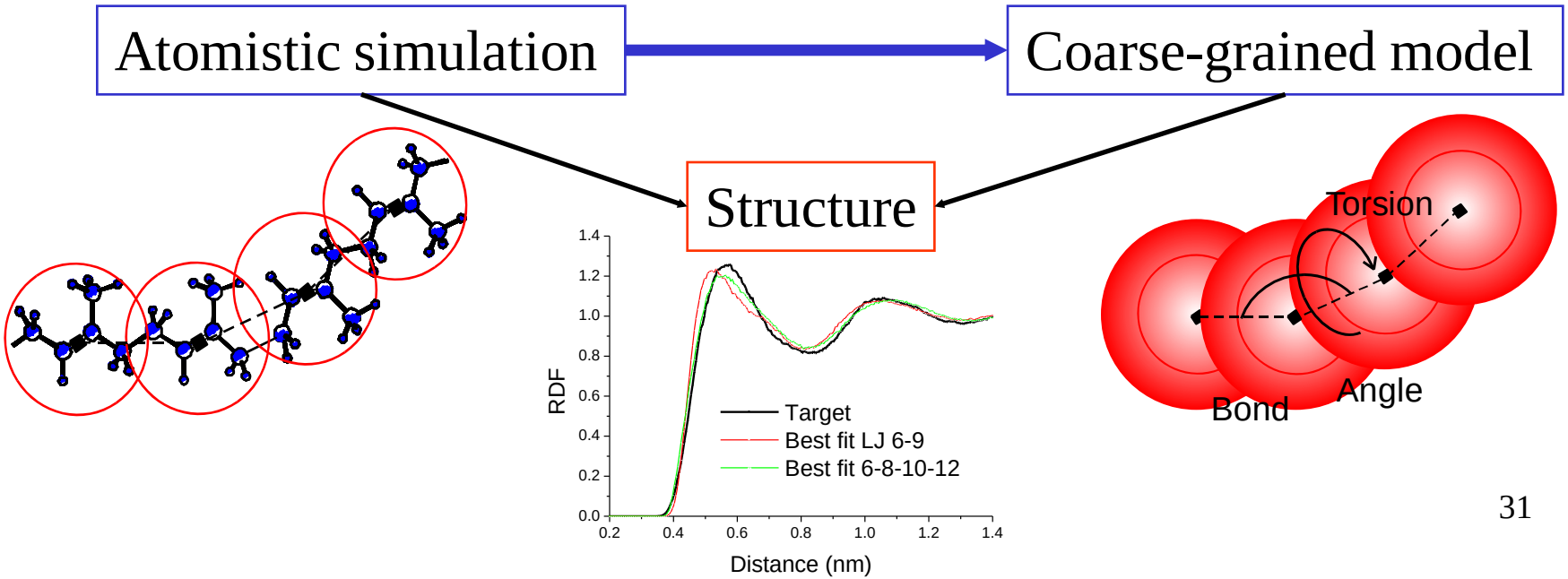
- interactions as realistic as possible
- model is material-specific
- no generic "bead-and-spring" model

Reviews: F. Müller-Plathe, ChemPhysChem **3**, 754 (2002); Soft Materials **1**, 1 (2003).

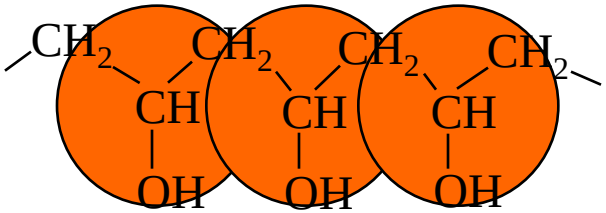
Coarse Graining

Objectives for coarse-grained model:

- Simpler than atomistic model: ~10 real atoms → 1 "superatom"
- Material-specific
- Reproduce structure of atomistic model



1st Example: Poly(vinyl alcohol)



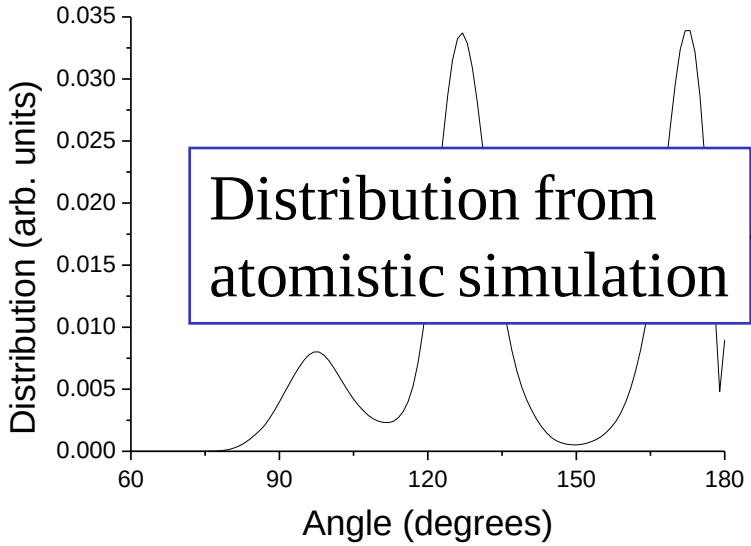
- Polymer in the melt
- 48 decamers

- Use:
  - Packaging: O_2 barrier
  - Fishing nets: same refractive index as water
  - Pervaporation membranes:
    remove water from organic solvents

Coarse-Graining PVA: Angles

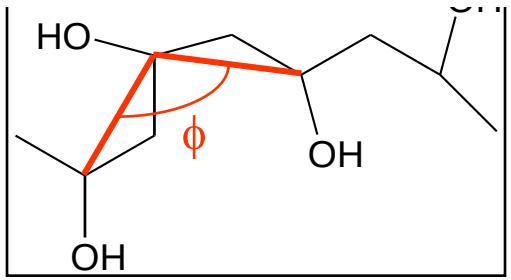
The easy part:

- Stiff degrees of freedom
- Direct Boltzmann inversion

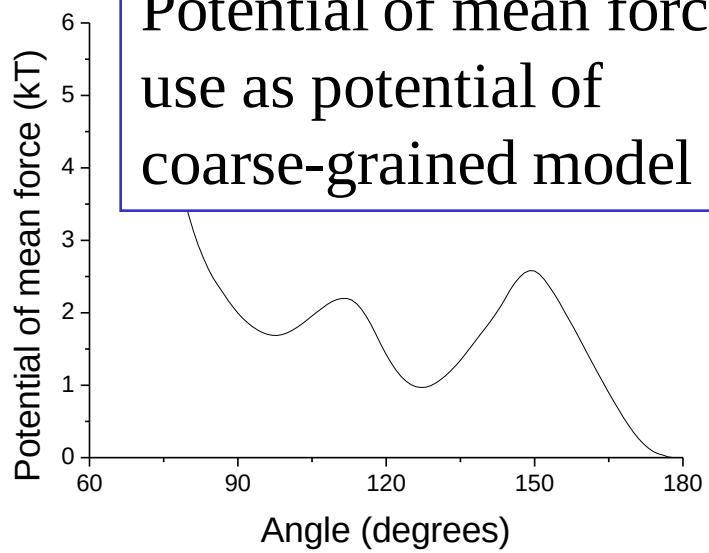


Distribution from atomistic simulation

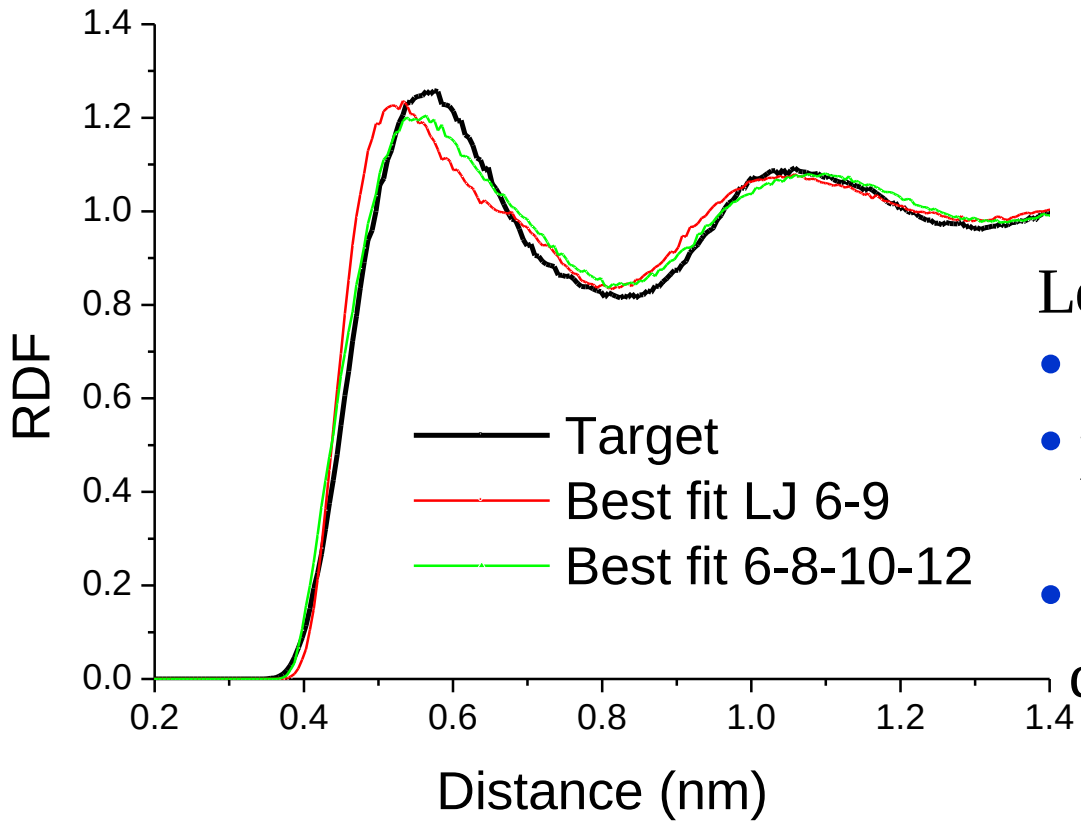
$$-\frac{V(\phi)}{kT} = \ln P(\phi)$$

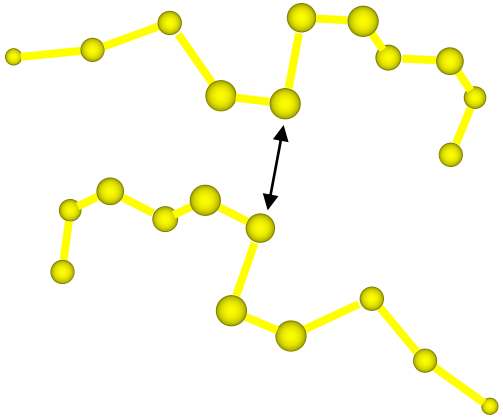


Potential of mean force, use as potential of coarse-grained model



Coarse-Graining PVA: Nonbonded





Less easy:

- soft degrees of freedom
- potential of mean force
  $\neq$ potential energy
- cannot Boltzmann-invert directly

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

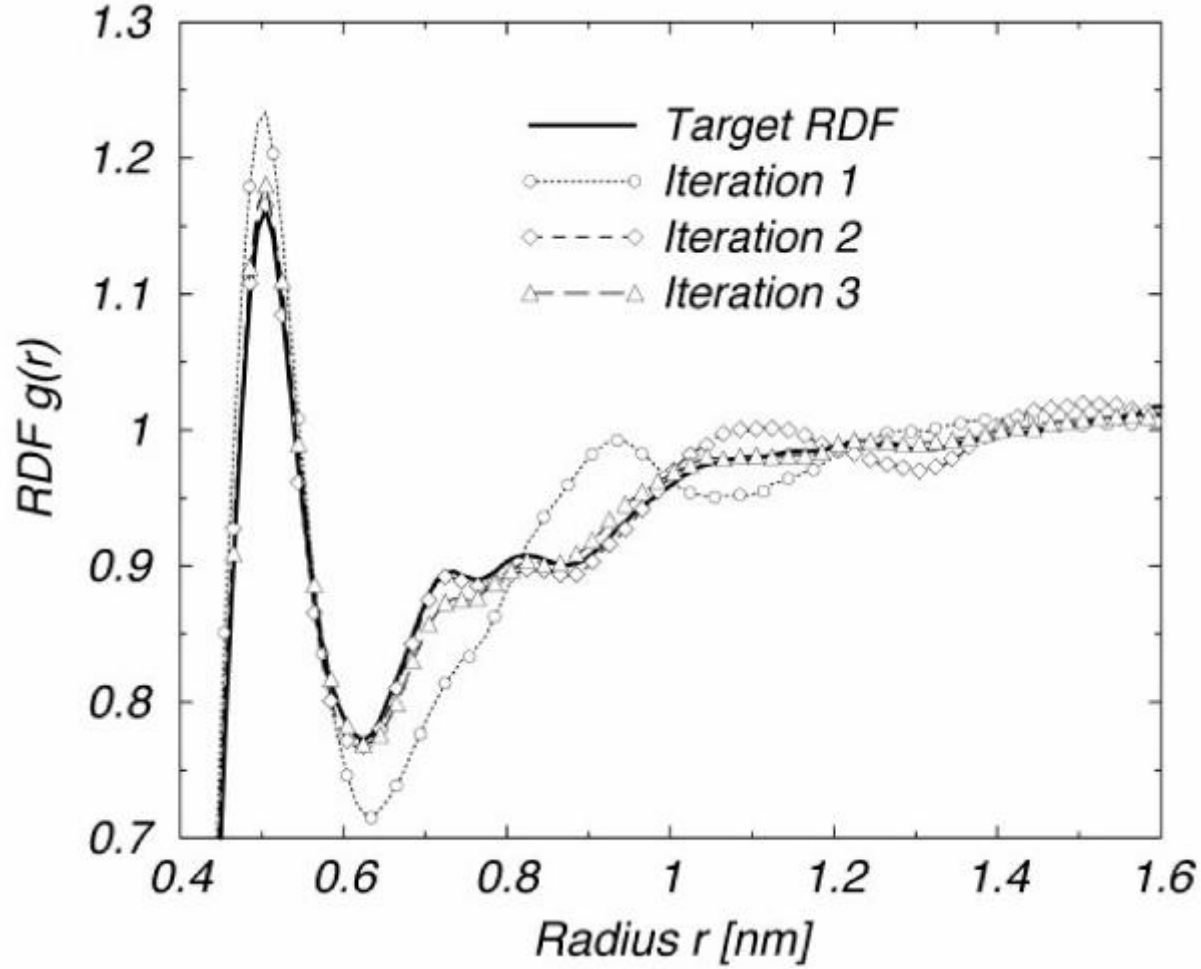
$$V_{n+1}(r) = V_n(r) + kT \ln \frac{\mathrm{RDF}_n(r)}{\mathrm{RDF}_{\mathrm{target}}(r)}$$

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

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

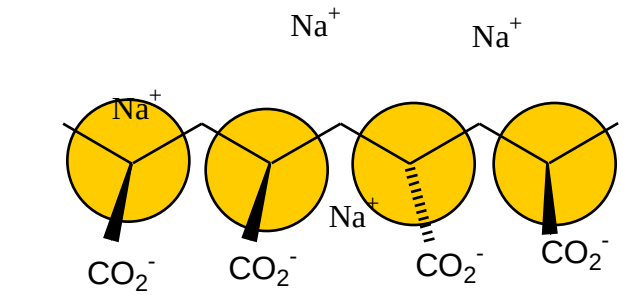
D. Reith, H. Meyer, FMP, Comput. Phys. Commun. **148**, 299 (2002).

Iterative Boltzmann Inversion (2)



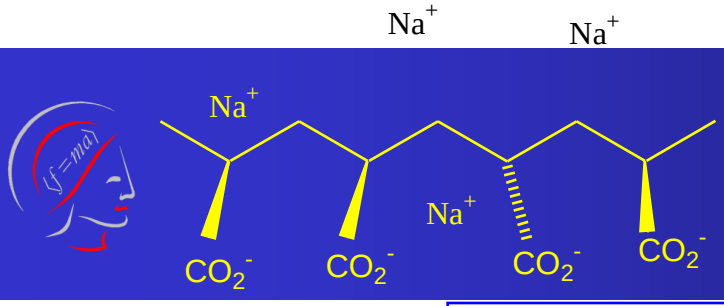
[D. Reith, M. Pütz, F. Müller-Plathe, J. Comp.Chem. **24**, 1624 (2003)]

2nd Example: Poly(acrylic acid)

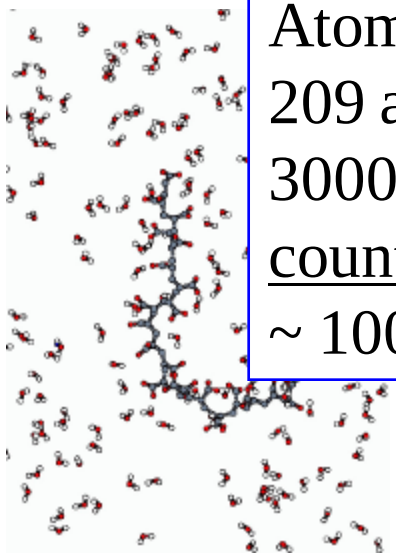


- Polymer in solution
- 23-mer, Na salt, 2 wt.% in water

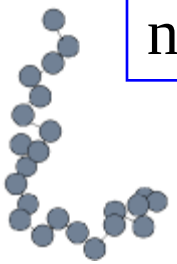
- Use:
  - Additive in washing powders, detergents, etc.
  - Flocculation agent in water treatment
  - Disposable nappies



Poly(acrylic acid)



Atomistic:
209 atoms
3000 H_2O
<u>counterions</u>
~ 10000 atoms



Coarse-grained:
23 particles
no H_2O

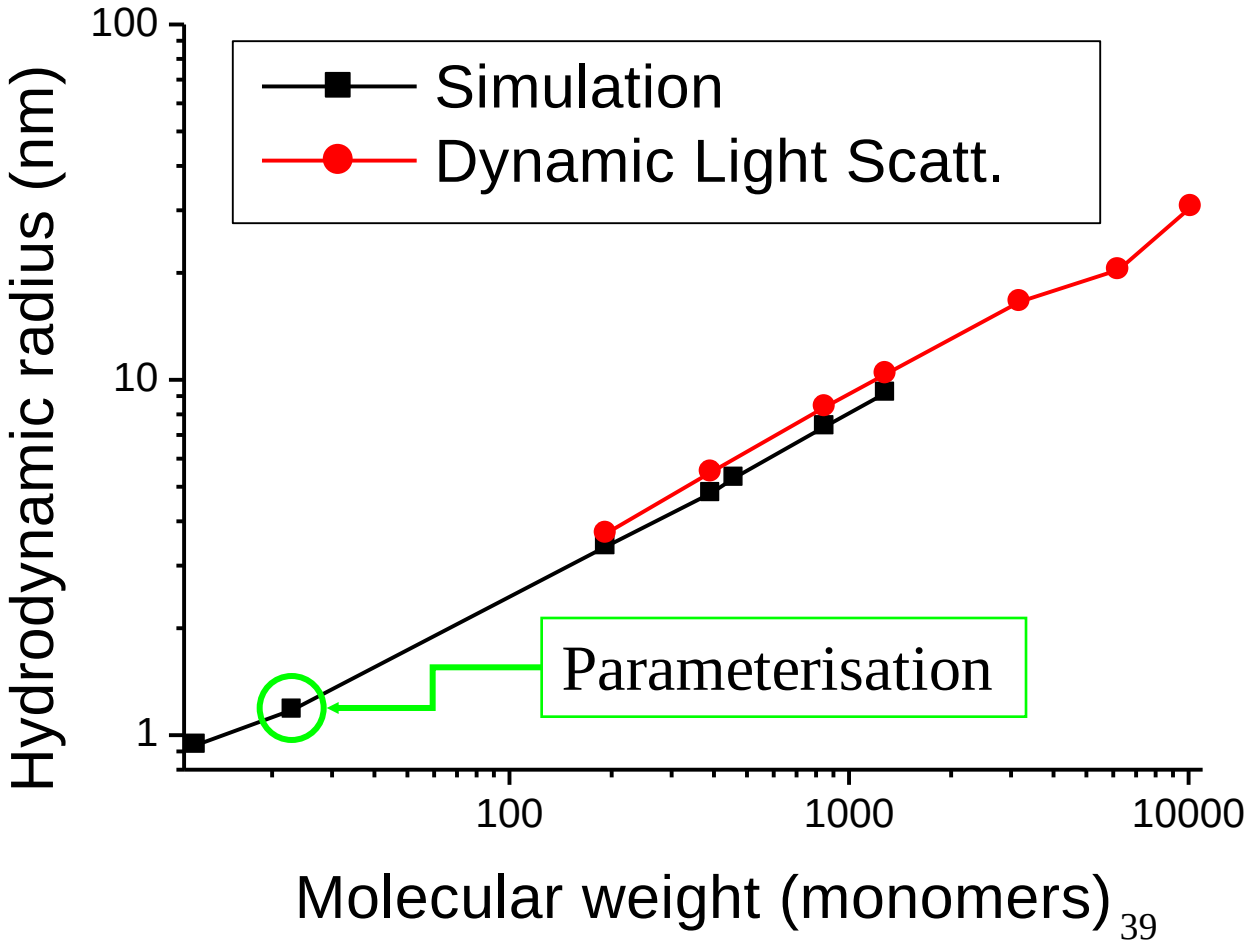
Mapping: coarse-grained superatom ↔ centre of mass of atomistic monomer

Water: effective interaction, viscous medium

[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).]

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)
  D. Reith, B. Müller, F. Müller-Plathe, S. Wiegand, J. Chem. Phys. **116**, 9100 (2002).
- Poly(ethylene oxide)
  R. Cordeiro, FMP, in preparation.

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).
- PAMAM dendrimers
  P. Carbone, F. Negri, FMP, Macromolecules **40**, 7044 (2007).
- Ionic liquid: [bmim][PF_6]
  W. Zhao H.A. Karimi Varzaneh, FMP, in preparation.
- Carbon nanotubes
  G. Illya, H.A. Karimi Varzaneh, FMP, in preparation.
- Phospholipid membranes
  G. Illya, T.J. Müller, H.A. Karimi Varzaneh, FMP, in preparation.

Robust Bridge?

Multiscaling and Dynamics

Transport properties

Reverse nonequilibrium molecular dynamics

Successes and failures

Multiscale Methods

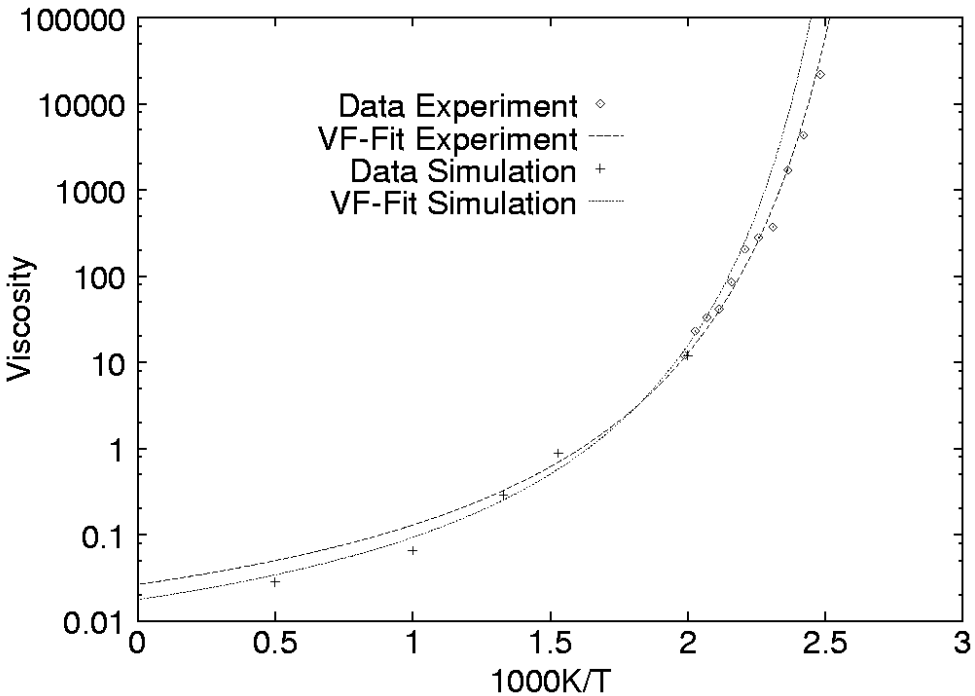
Structure-based coarse graining

Successes and failures

Attempt of a synthesis:
Dynamics of coarse-grained models

Challenge #1: Dynamics

- One known case: polycarbonate
- Temperature dependence (Vogel-Fulcher) reproduced after empirical curve shift

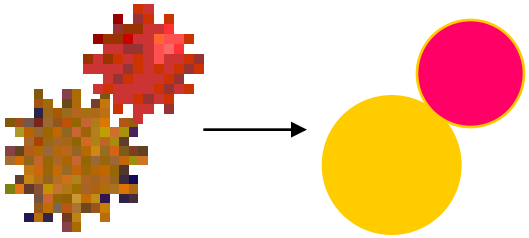


[W. Tschöp, K. Kremer, J. Batoulis, T. Bürger, O. Hahn, Acta Polym. **49**, 61 (1998); ibid. **49**, 75].

Dynamics

Known feature of coarse-grained potentials

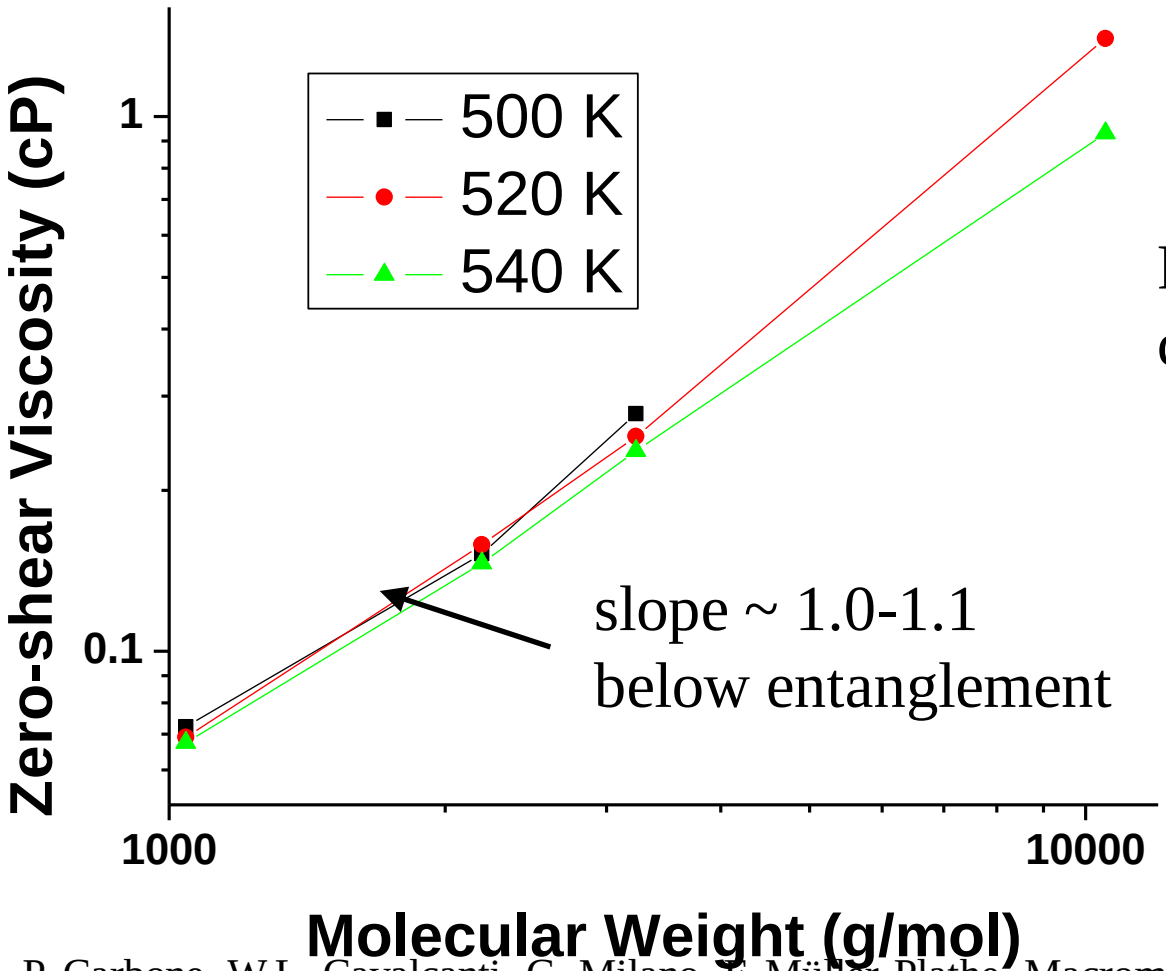
- repulsion (excluded volume) softer than atomistic
- less friction
- faster dynamics: higher D, lower η



Questions

- Can coarse-grained models be constructed with correct dynamics?
- Is there a constant scale factor?

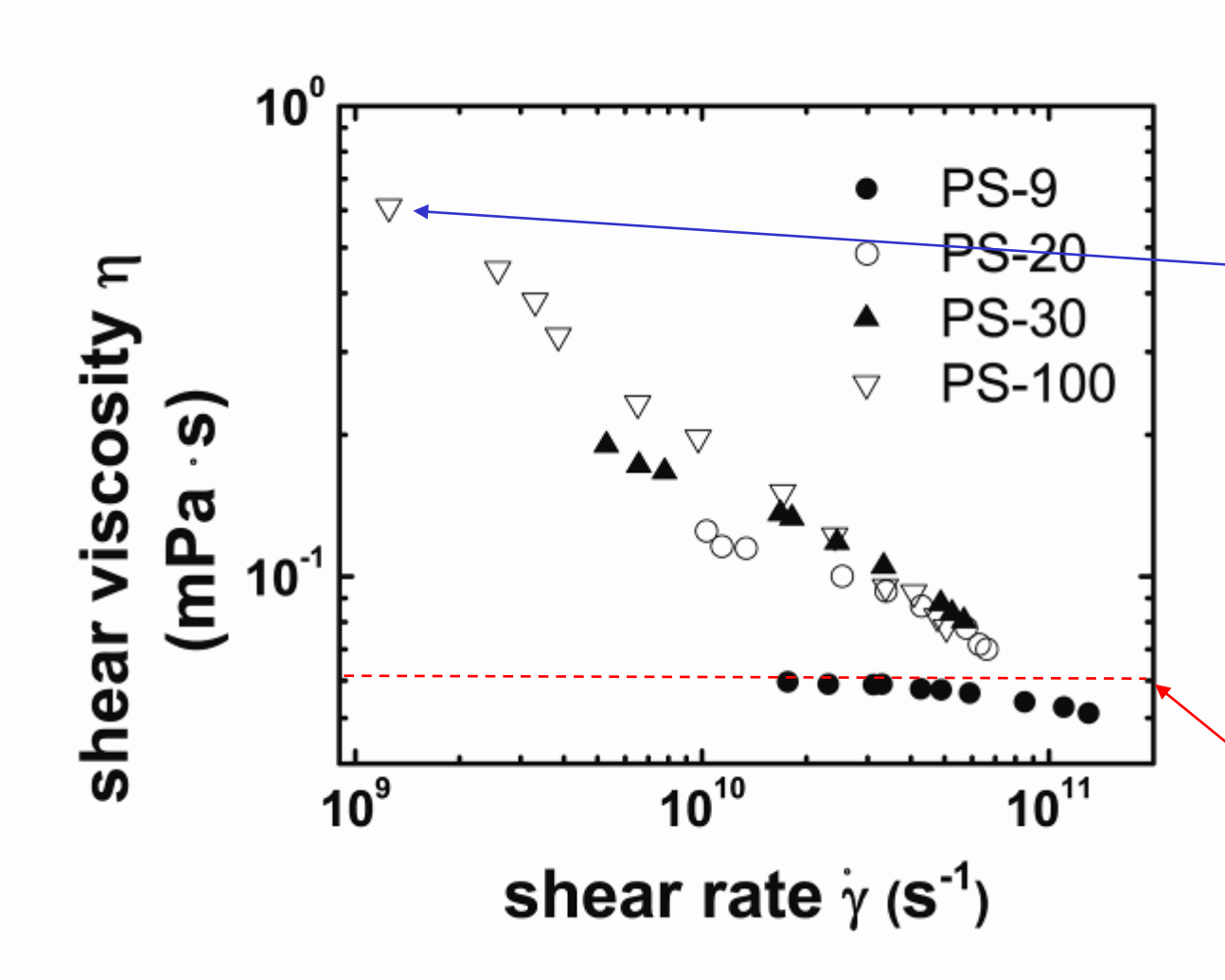
Viscosity: MW dependence



Polystyrene
coarse-grained model

X. Chen, P. Carbone, W.L. Cavalcanti, G. Milano, F. Müller-Plathe, Macromolecules **40**, 8087 (2007).

Viscosity: shear-rate dependence



100 Monomers:

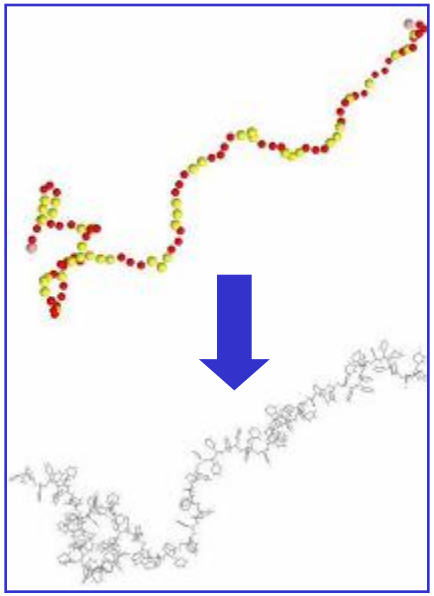
- zero-shear limit not yet reached
- melt is not Newtonian

9 Monomers: zero-shear limit

X. Chen, P. Carbone, W.L. Cavalcanti, G. Milano, F. Müller-Plathe, Macromolecules **40**, 8087 (2007).

Chain structure under shear

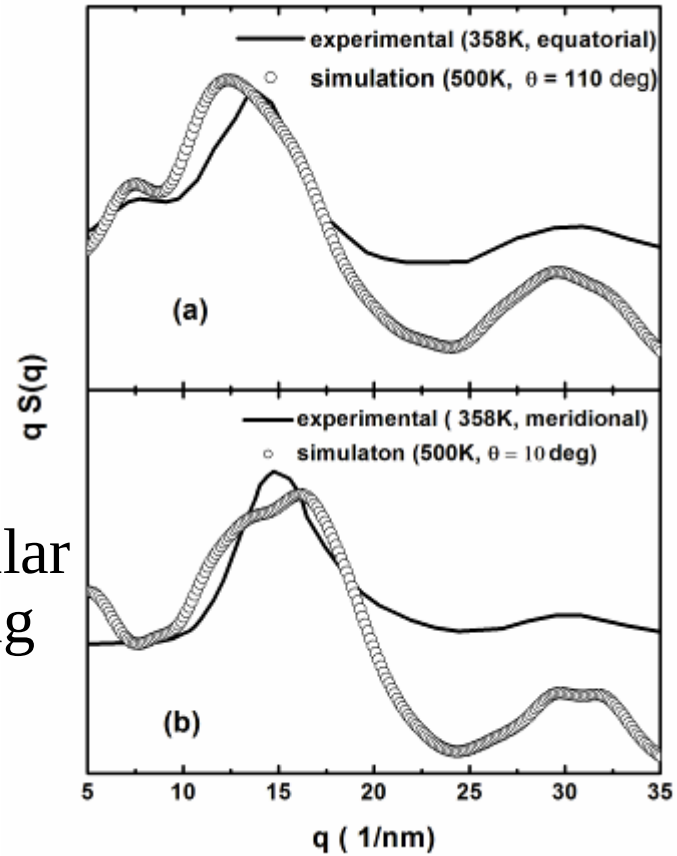
Atomistic structure after re-insertion of the atoms: "backmapping"



n scattering, PS-30

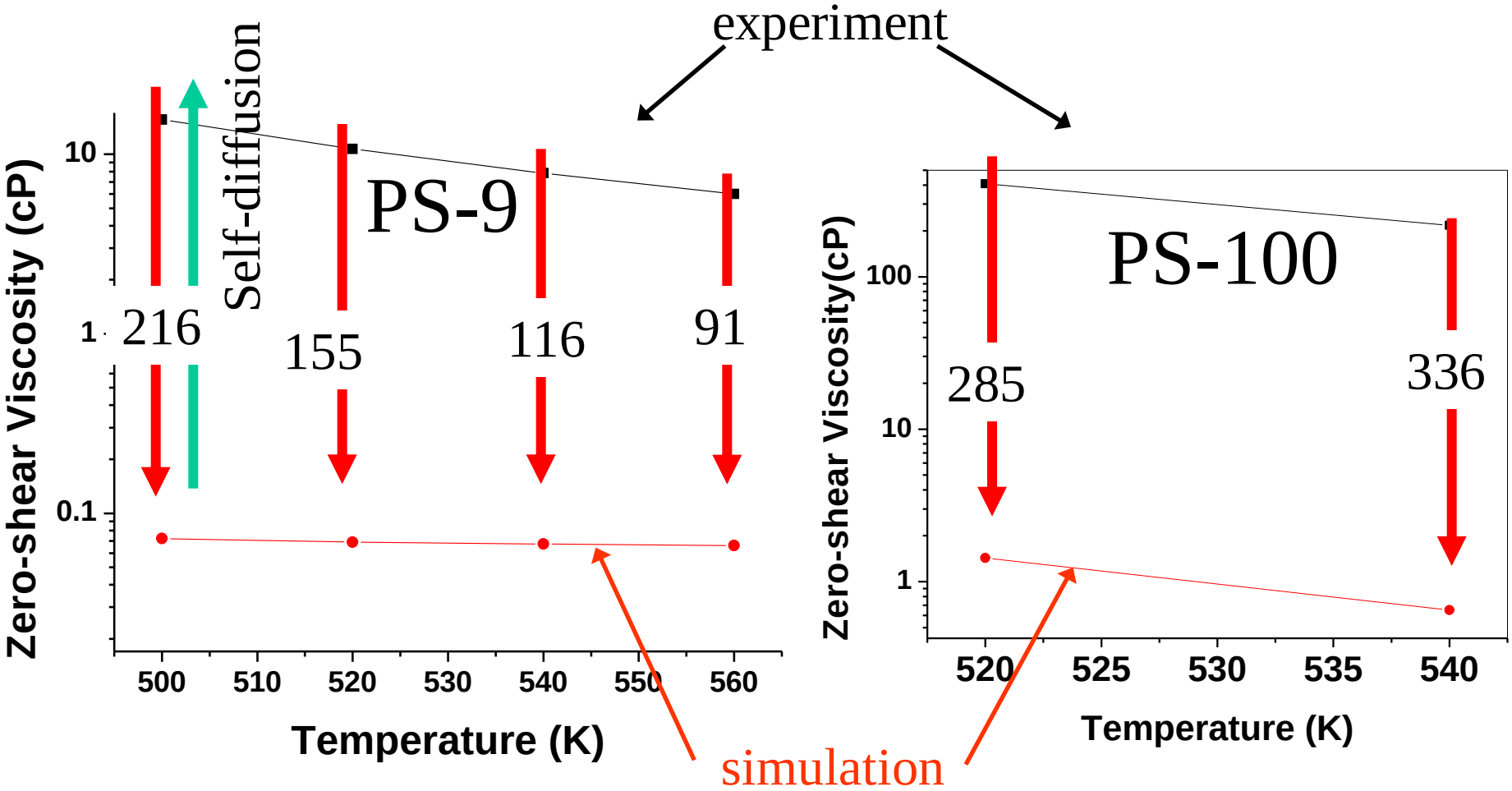
parallel to stretching

perpendicular to stretching



G. Santangelo, A. di Matteo, F. Müller-Plathe, G. Milano, J. Phys. Chem. B **111**, 2765 (2007).
X. Chen, P. Carbone, G. Santangelo, A. di Matteo, G. Milano, FMP, Phys. Chem. Chem. Phys. **11**, 1977 (2009)

Viscosity: Comparison with Experiment

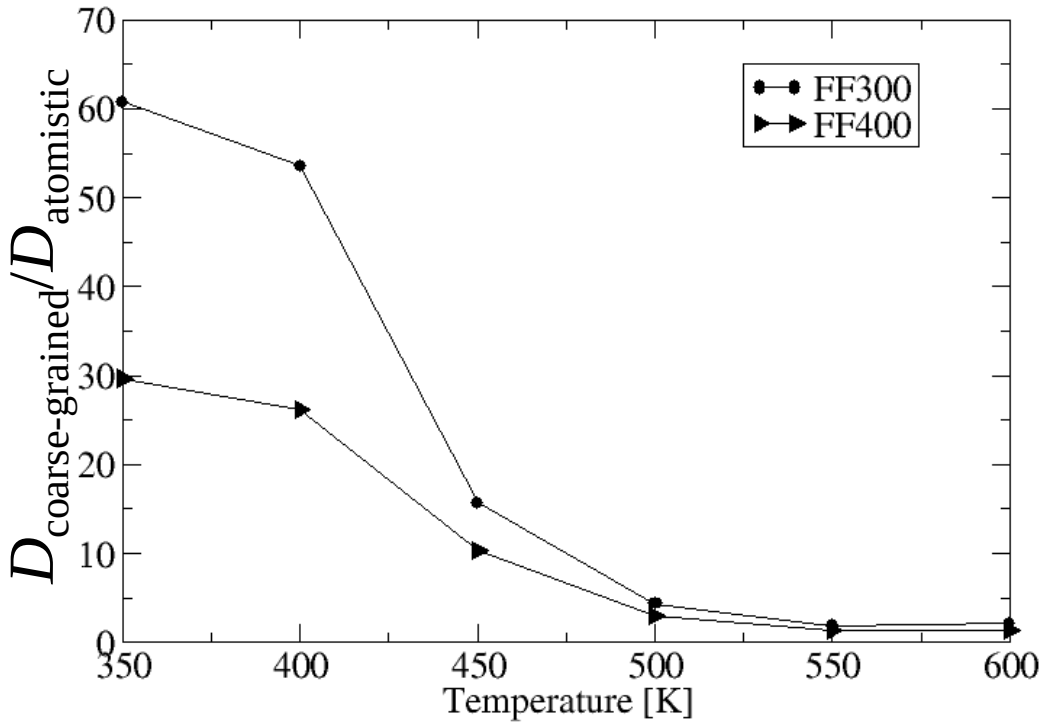


But…

Polyamide-6,6 above 500 K:
coarse-grained dynamics
→ atomistic dynamics

"finer coarse-graining"
6, 7, or 9 atoms/superatom
(polystyrene: 18)

Chain diffusion coefficient



Explanation???
Interaction details unimportant at high *T*?
Only excluded volume matters?

H.A. Karimi Varzaneh, X. Chen and F. Müller-Plathe, J. Chem. Phys. **128**, 064904 (2008)

Challenge #1: Dynamics

- RNEMD works technically also for coarse-grained models
- Reproduce qualitative features: MW dependence, microstructure, …
- Deviation from experiment: 1-2 orders

- Coarse-grained model reproduces simultaneously:
  - structure
  - density
  - ~~absolute dynamics~~
  - ~~temperature dependence~~

- Instead: try the equations of motion

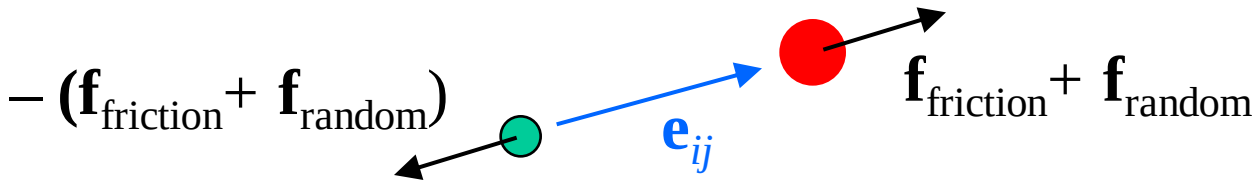
Dynamics: Cure the Symptoms (2)

[H.-J. Qian, C. C. Liew, FMP, Phys. Chem. Chem. Phys. **11**, 1962 (2009).]

Newtonian dynamics → Dissipative particle dynamics

$$\mathbf{f}_{ij} = \mathbf{f}_{ij}(\text{interaction}) \underbrace{-\zeta(\mathbf{v}_{ij}\cdot\mathbf{e}_{ij})\mathbf{e}_{ij}}_{\text{friction}} + \underbrace{\sigma\frac{\text{rand}()}{\Delta t^{1/2}}\mathbf{e}_{ij}}_{\text{random}}$$

friction forces and random forces act between *pairs* of atoms



no net momentum is added/lost

DPD is momentum-conserving → can be used with RNEMD

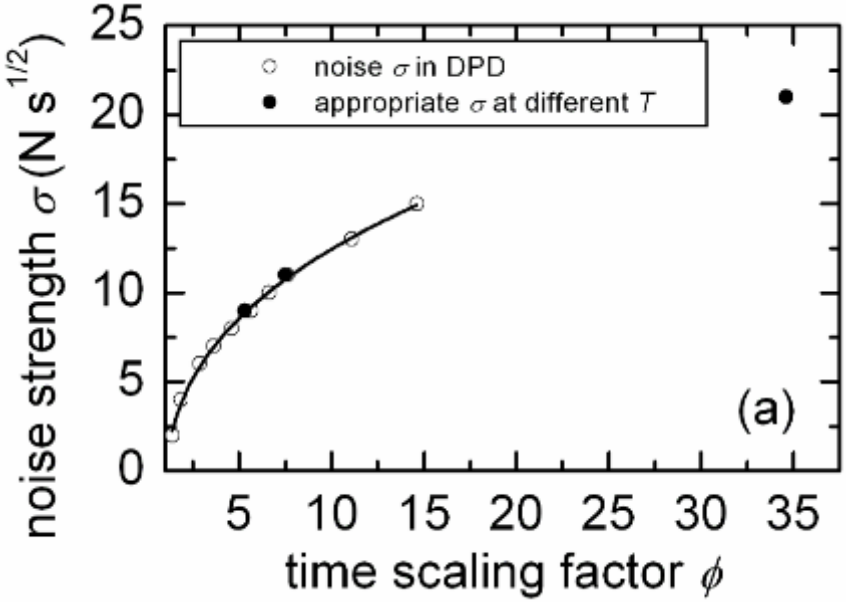
Dynamics: Cure the Symptoms (3)

[H.-J. Qian, C. C. Liew, FMP, Phys. Chem. Chem. Phys. **11**, 1962 (2009).]

1. Determine time scaling factor ϕ between coarse-grained dynamics and reference dynamics (atomistic or experiment), e.g. $\phi = D^{CG,MD} / D^{ref,MD}$

2. Empirical rule for optimum DPD noise strength

$$\sigma[\mathrm{N}\cdot\mathrm{s}^{1/2}] = 7.2(\phi - 0.9)^{0.35} + 3.4$$



Developed for ethyl benzene (298 K);
Holds for:

- ethyl benzene (238 K – 380 K)
- polystyrene melts
- ionic liquid [bmim] PF_6

Analogous rule for Lowe-Anderson dynamics

Not a Bridge yet!

Summary

Reverse non-equilibrium MD

- Works robustly for thermal conductivity and shear viscosity
- Is as accurate as the force field
- Cannot beat the inherent relaxation times
- Proliferation of RNEMD

Multiscale simulation

- Iterative Boltzmann Inversion works robustly
- Structure-based coarse graining for many systems
- proliferation of IBI

Coarse-grained dynamics

- Cannot fix the potential
- EOM with friction works phenomenologically
- Needed: friction contribution of removed degrees of freedom

Thanks!

< 2002

2002-2005

>2005

BASF, Rhodia, BMBF, EU (Marie-Curie), DFG, Max-Planck-Gesellschaft (IMPRS-PMS), Humboldt-Stiftung, Fonds der Chemischen Industrie