# Multiscale studies of macromolecular systems: concepts and applications

## An Introduction

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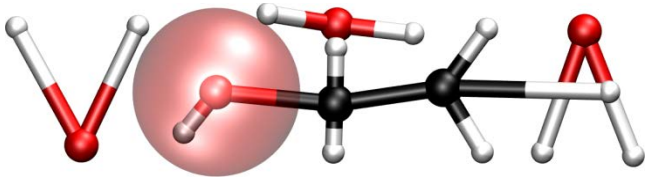
Max Planck Institute for Polymer Research, Mainz

**Seoul, June 22 – 26, 2015**

# Software

Versatile Object-oriented Toolkit for Coarse-graining Applications



**votca.org**

Apache license (free)

C++, scripting, test suite, hg, wiki pages, bug tracker

**votca-csg** modules (coarse-graining)
release 1.2
actively developed for 2 years
Google code: votca project

**votca-ctp** modules (charge transport)
Release planned for August this year
(you can try theta-version)
Google code: votca-ct project

**charge transport:** V. Ruehle, A. Lukyanov, F. May, M. Schrader, T. Vehoff, J. Kirkpatrick, B. Baumeier, D. Andrienko, submitted, 2011
**coarse-graining:** V. Ruehle, C. Junghans, A. Lukyanov, K. Kremer, D. Andrienko, J. Chem. Theor. Comp., 5, 3211-3223, 2009

# Software


J. D. Halverson, T. Brandes, O. Lenz, A. Arnold, S. Bevc, V. Starchenko, K. Kremer, T. Stuehn, D. Reith, *"ESPResSo++: A Modern Multiscale Simulation Package for Soft Matter Systems"*, Computer Physics Communications, 184 (2013), pp. 1129-1149
DOI: 10.1016/j.cpc.2012.12.004
Online access: http://dx.doi.org/10.1016/j.cpc.2012.12.004

# Outline

- **Soft and Nanostructured Matter**
- Coarse Graining
  - General Aspects
  - Specific Methods - Examples
- Dynamic Properties
- Adaptive Resolution Simulation: AdResS
- Conclusion/Outlook

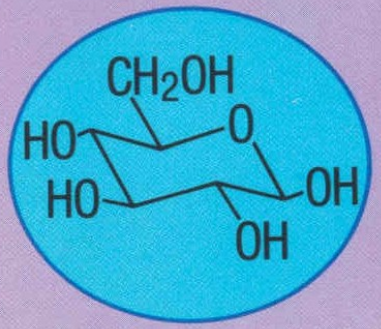
# Soft Matter - What Systems?

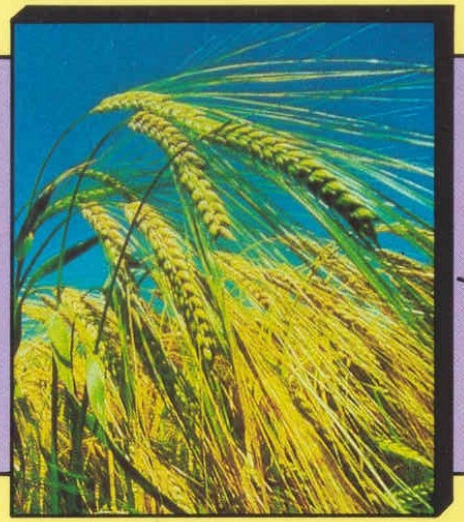
- **Organic Materials:**

- **Polymers**
- **Colloids**
- **Membranes**
- **Hard-Soft Composites (organic-anorganic)**

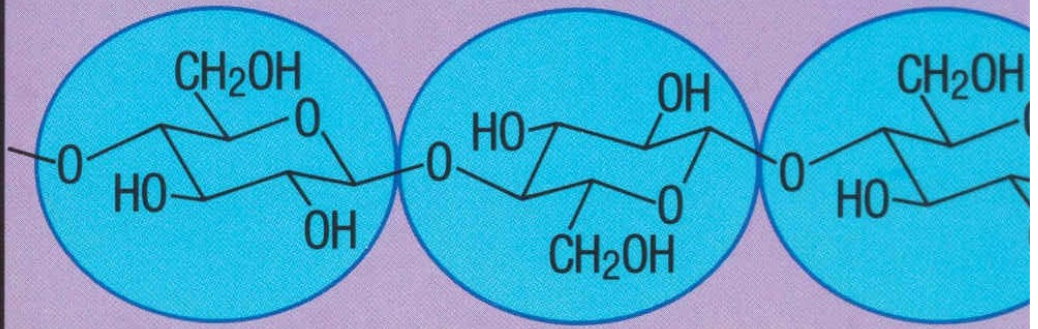
    - **Synthetic**
    - **Biological**

natürlich

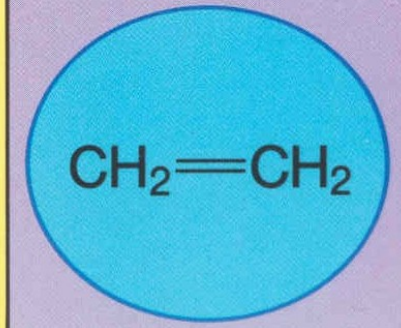


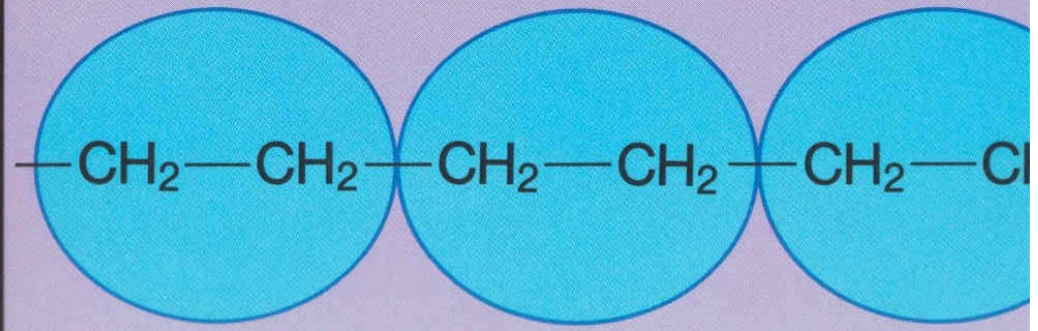
Cellulose




synthetisch

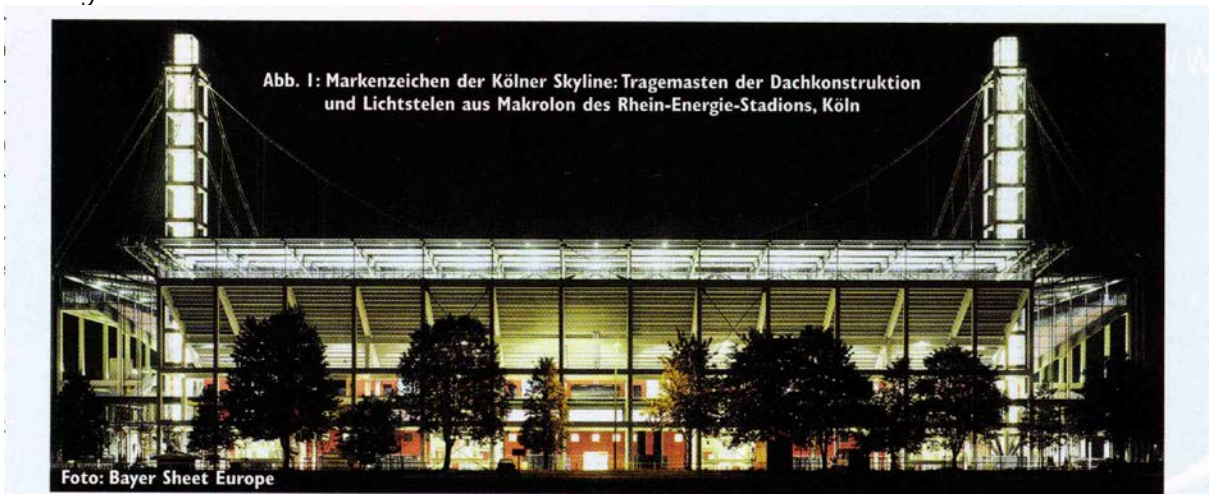



Polyethylen



# High Tech Commodity: Polycarbonate (PC)

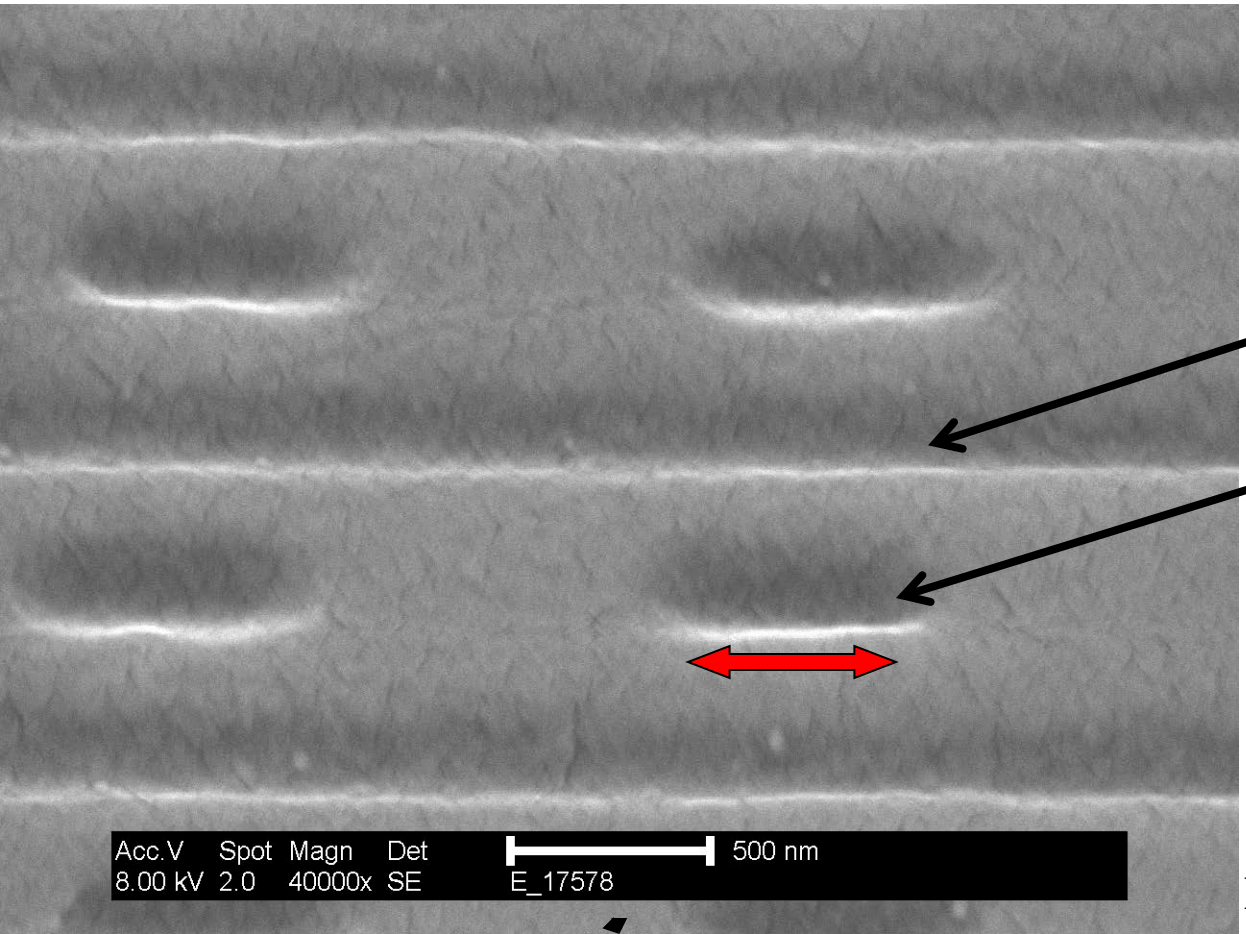
Bayer Materials




Yearly production more than 500000t/p.a.

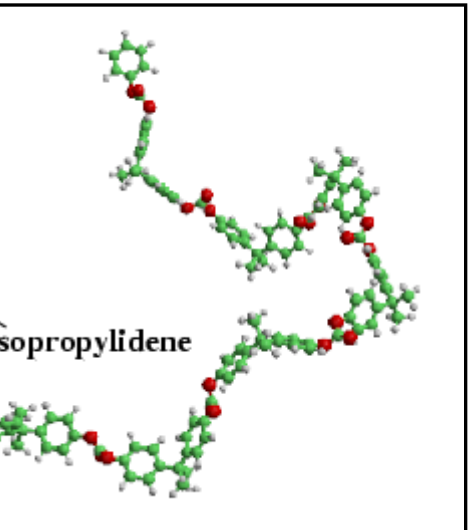
# Polycarbonate (PC) for CDs/DVDs…
# PC/Ni interface during dye cast process

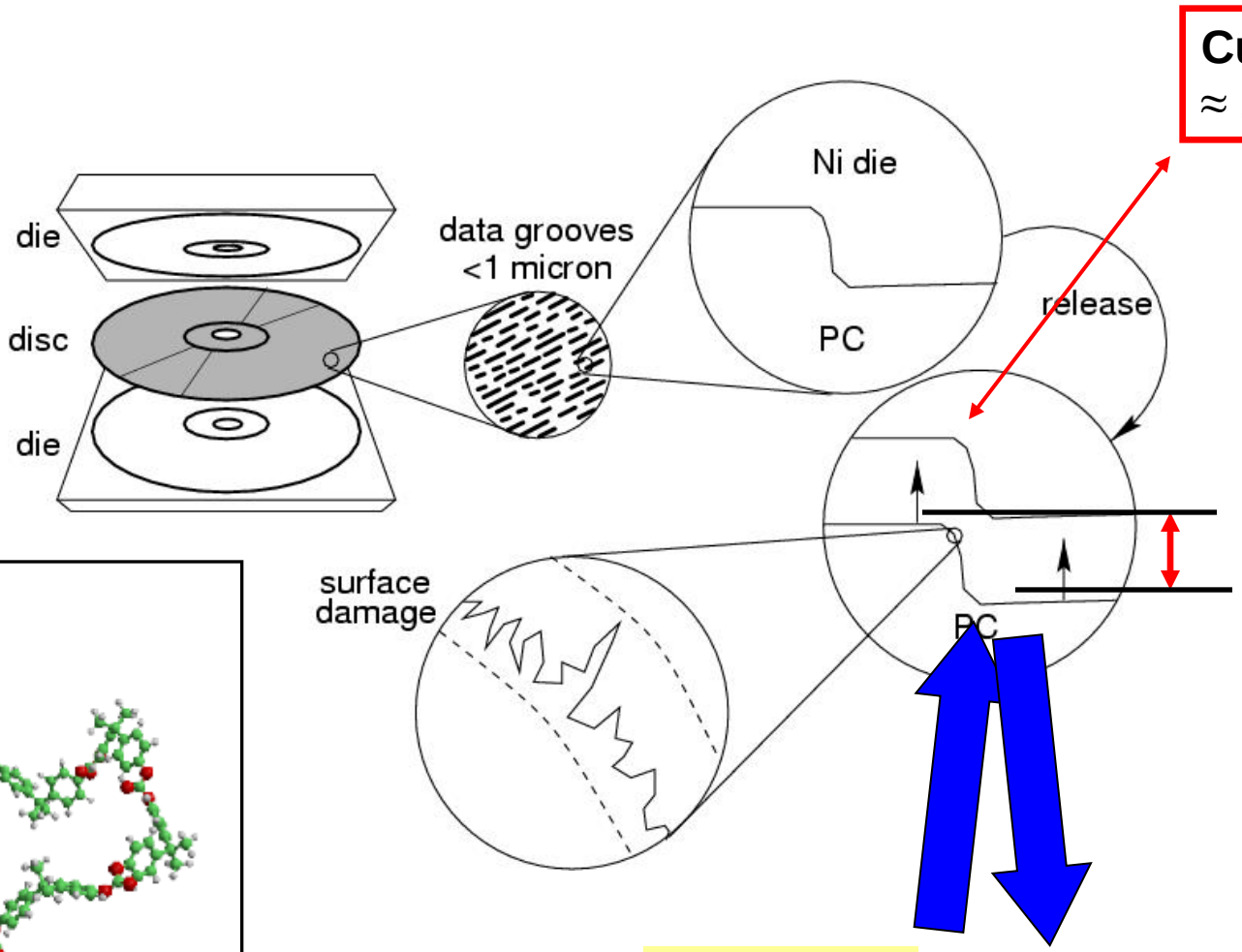
Data pits and guiding grove of a PC “blue laser optical disc”




Bayer Materials

# Why study Polycarbonate and the PC/Ni interface?



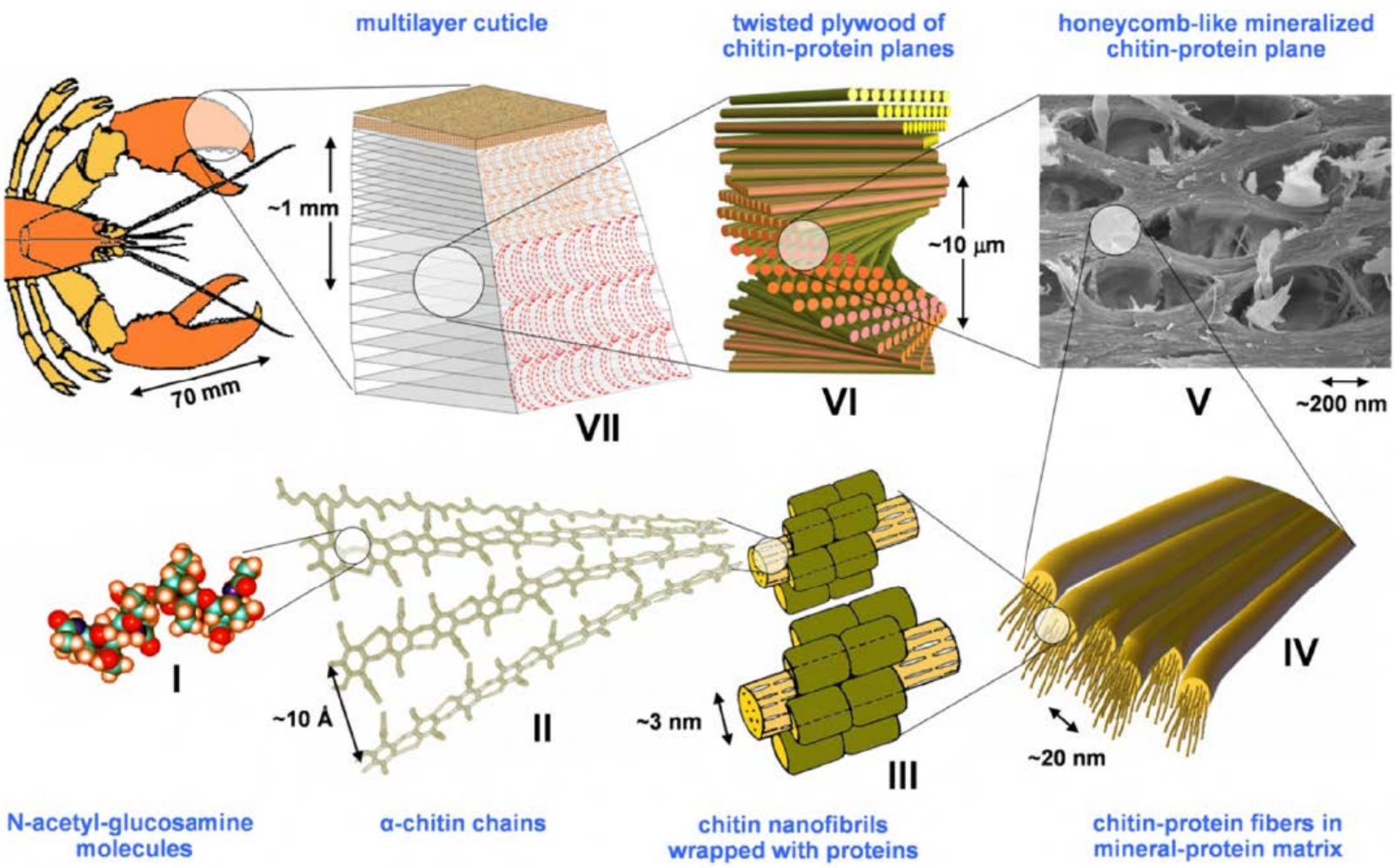




**Curvature radius**
**≈ 10-20 nm**

$d=\lambda/4$
$(\approx 100nm)$

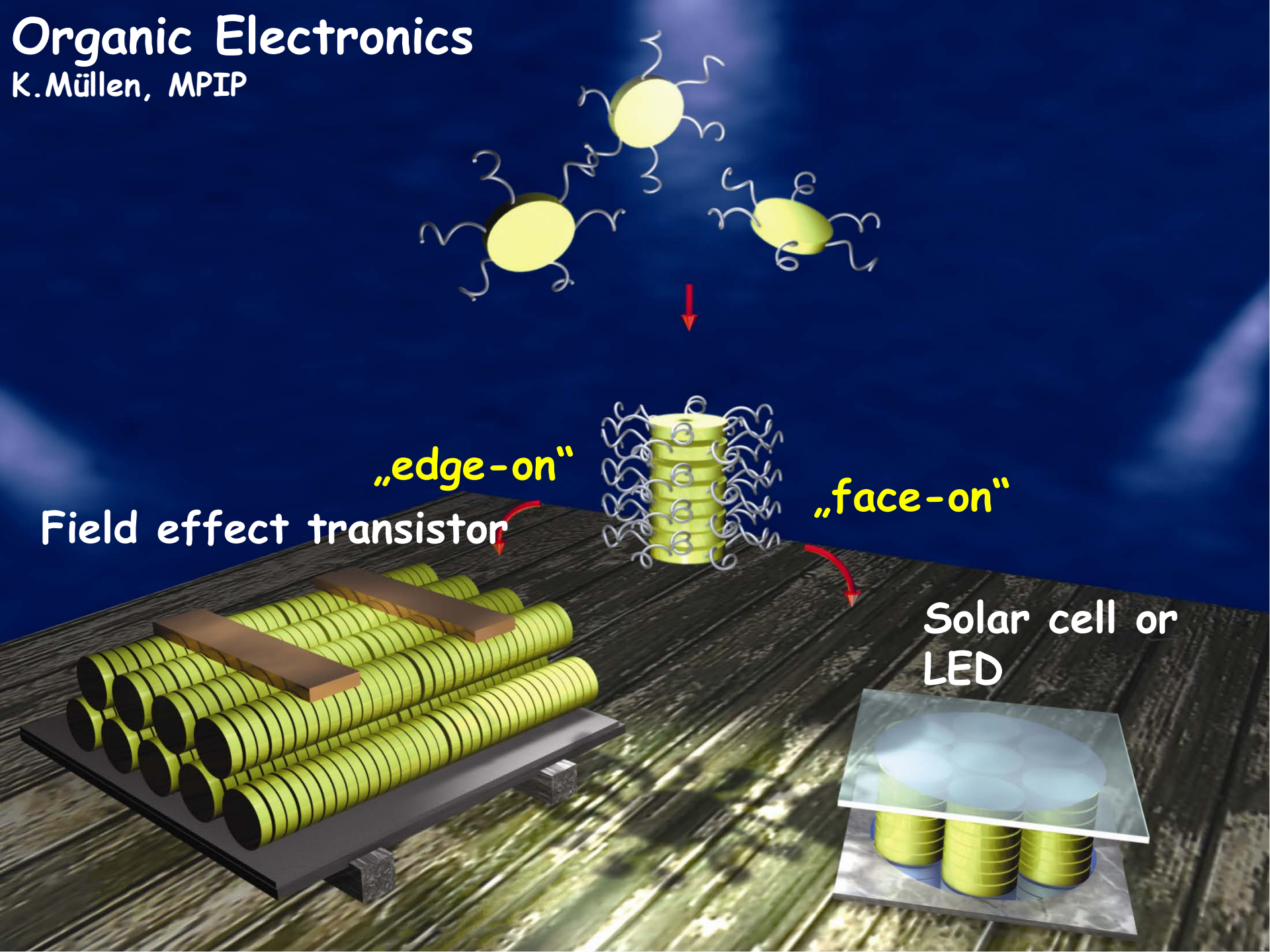
# Hard-soft, organic-inorganic composite

## Introduction - Hierarchical organization



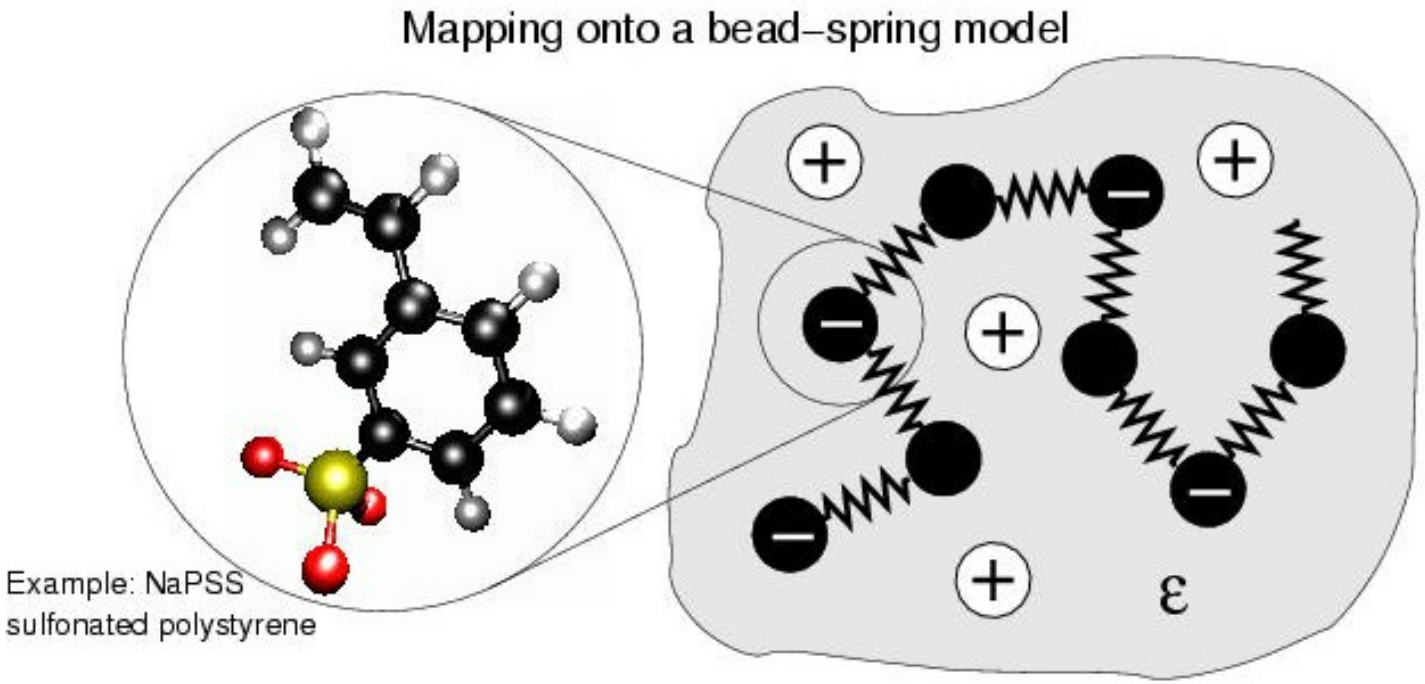
# Organic Electronics

K.Müllen, MPIP



# Organic Electronics:  Morphology and Processing

# Schematische Darstellung: Polyelektrolyte




monomers, ions → (charged) beads
bond potential → nonlinear spring
solvent → dielectric background ε
solvent quality τ → effective interaction

# Hydrogels
# ≈O(1) (!!) Giant Molecule, swollen from water

Polymers, usually not water soluble

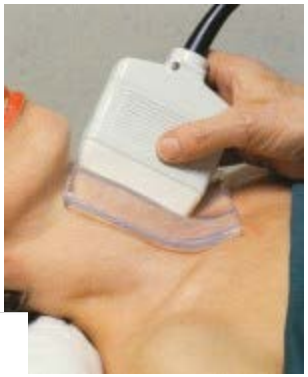
Exceptions e.g. electrically charged polymers:

**Polyelectrolytes** (holds for most biopolymers, e.g. DNA)

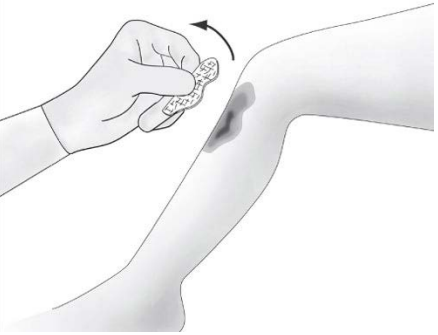
Tanaka, MIT

# Hydrogels, Superabsorber

DRACO Wundheilmittel
BASF



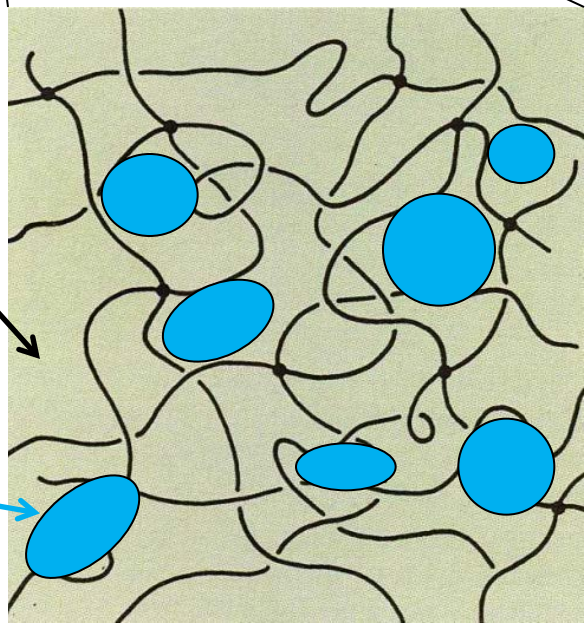




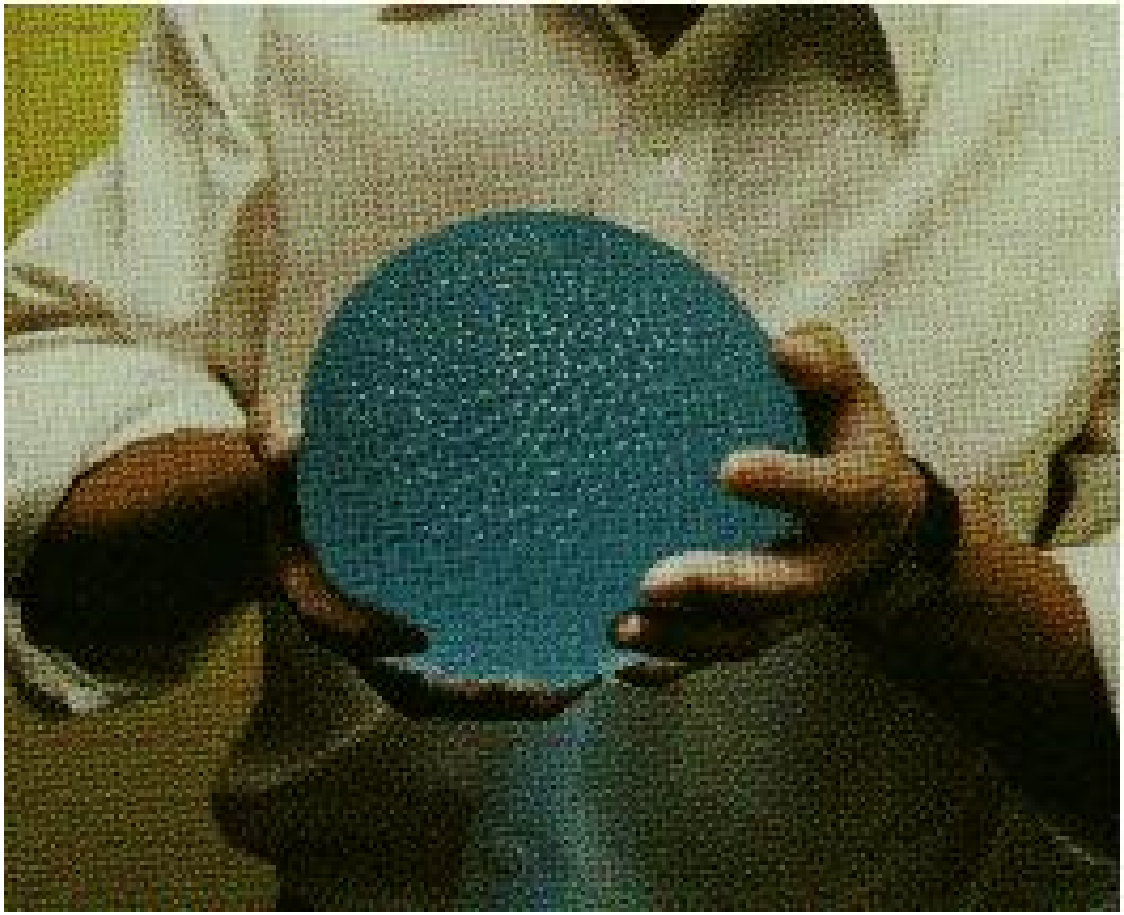



Fat

Water

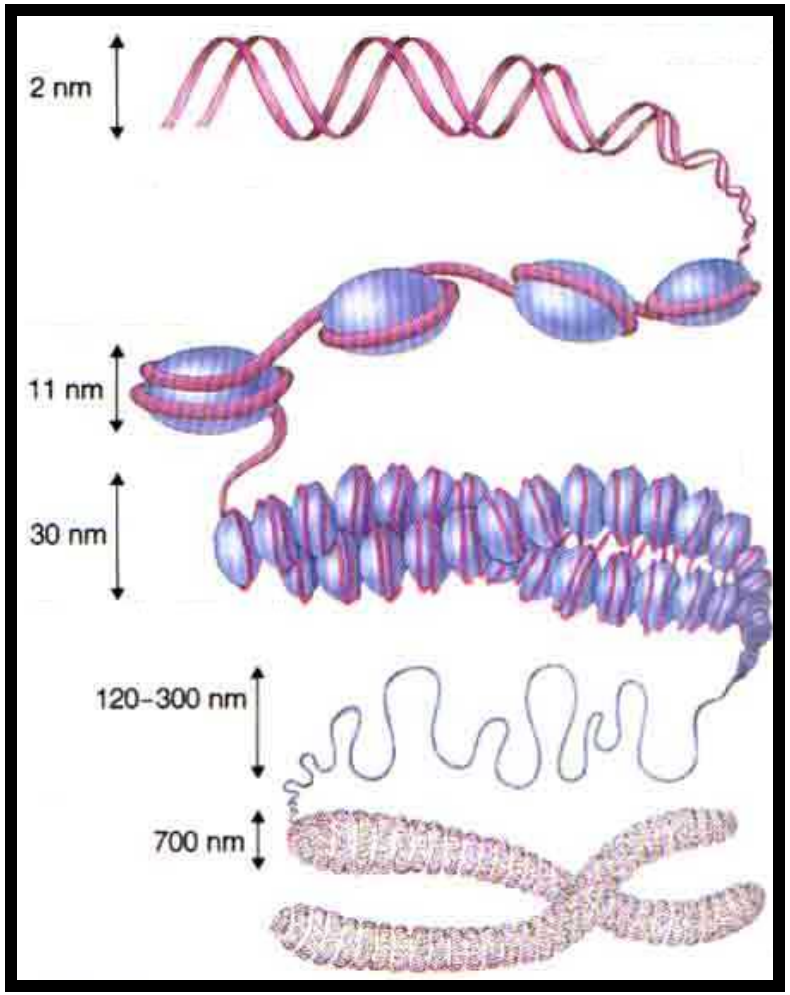


# Hydrogel
# O(1) (!!) Giant Molecules
## swollen from water

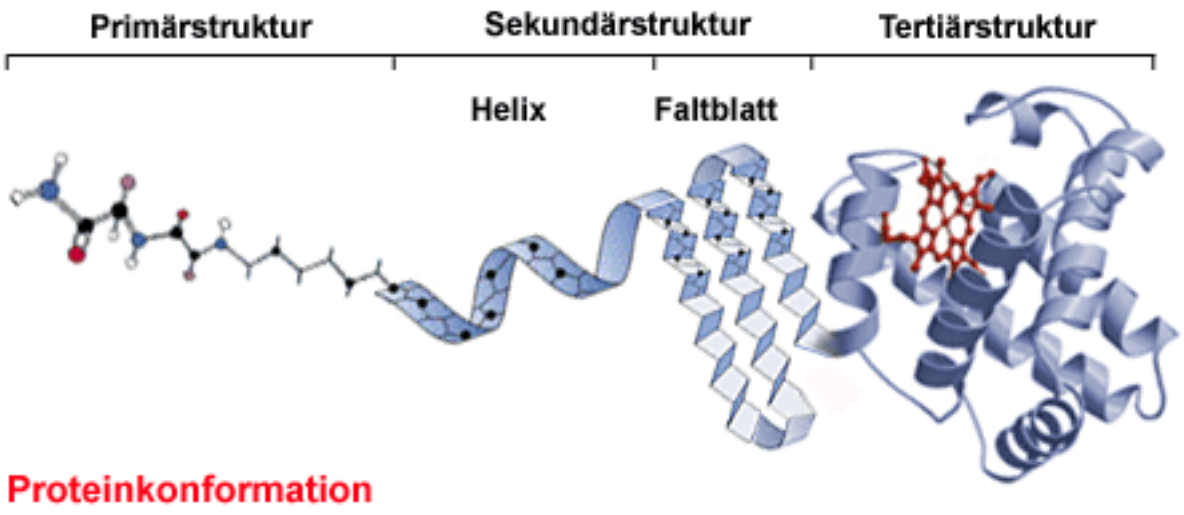


Tanaka, MIT

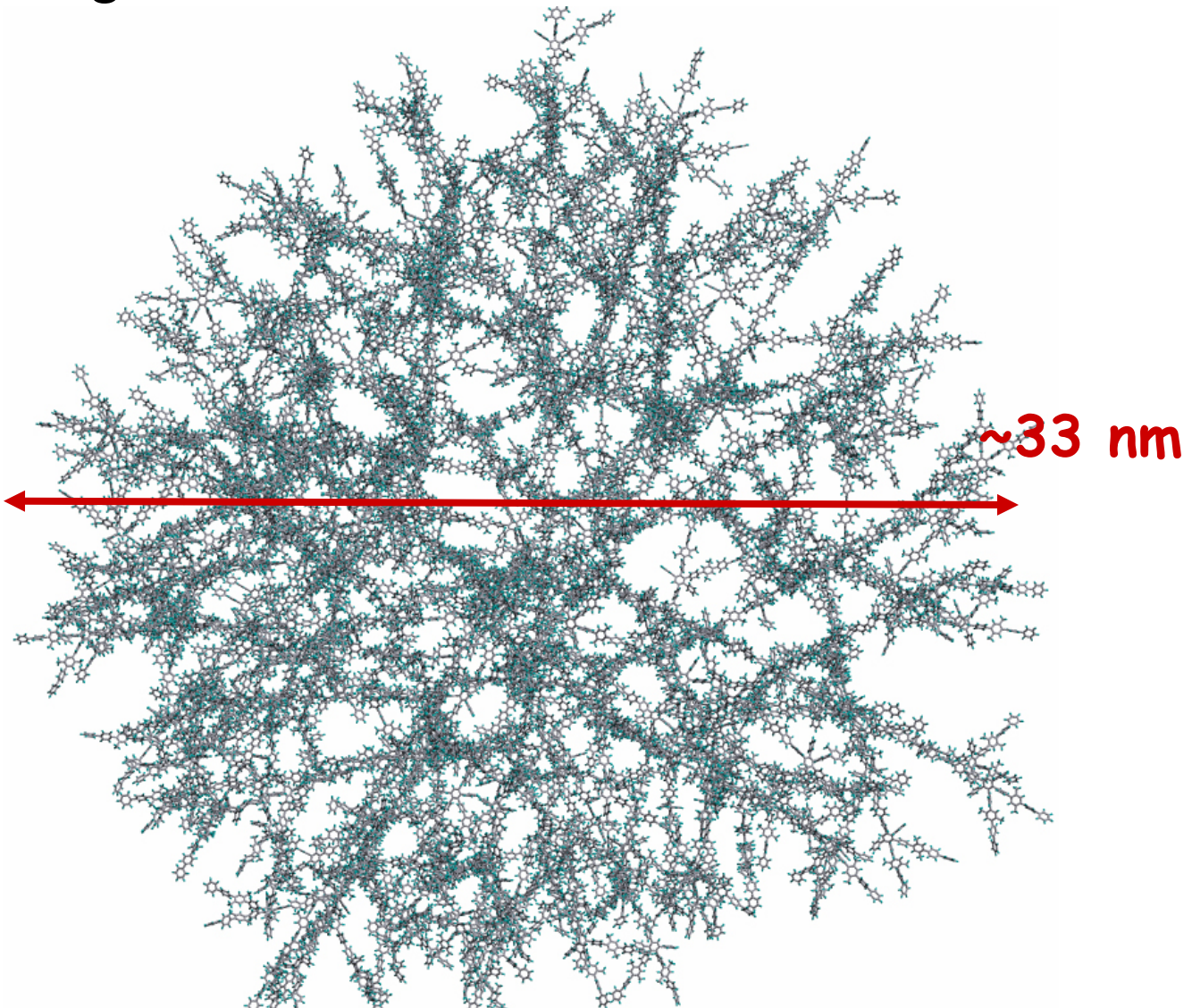
# DNA



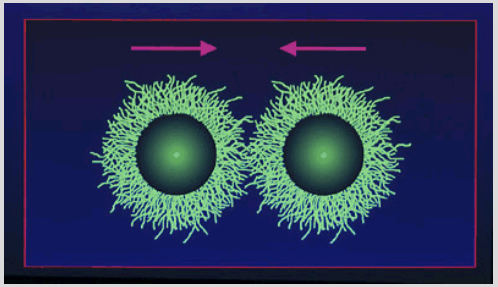
# Proteins


Primärstruktur
Sekundärstruktur
Tertiärstruktur
Helix
Faltblatt
Proteinkonformation

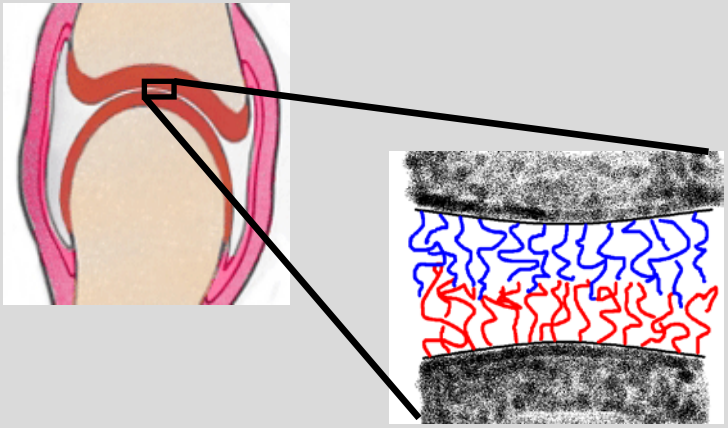
**Monodisperse, soluble, semi-rigid (3D) Polymer**
**MW = 546404 g/mol**
**5592 Benzene rings (K. Müllen)**

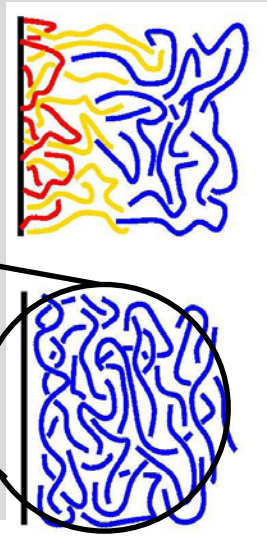


# Soft Matter - Polymers



- Adsorption of polymers, wetting of polymers
- Adsorption of a single chain – relation to surface magnetism





# Soft Matter

**“Soft” means:**

- **low energy density**
- **nanoscopic length scales ( 10Å …1000Å)**
- **large fluctuations**
- **<u>thermal energy $k_B T$</u>**
  **<u>relevant energy scale</u>**

100 to 100000 times “softer” than “normal” crystals

# Energy Scale $k_B T$ for T=300K

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

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

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

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

$$kT \approx 4.1 pNnm$$

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

$$kT \Rightarrow 0.6 kcal/mol$$

$$kT \Rightarrow 2.5 kJ/mol$$

**Electronic structure, CPMD**

**Quantum Chemistry**

**Biophysics Membranes, AFM**

**Spectroscopy**

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

$$E \approx 4kT - 10kT$$

**Chemical Bond**

**Hydrogen Bond**

# Energy Scale $k_B T$ for T=300K

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

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

$$kT \approx 4.1 pNnm$$

$$kT \Rightarrow 2$$

$$k$$ 3kcal / mol

$$k \Rightarrow 2.5 kJ / mol$$

**Green light photon ≈ 2-2.5 eV ≈ 100 kT**

**Electronic st MD**

**Qu istry**

**ophysics Membranes, AFM**

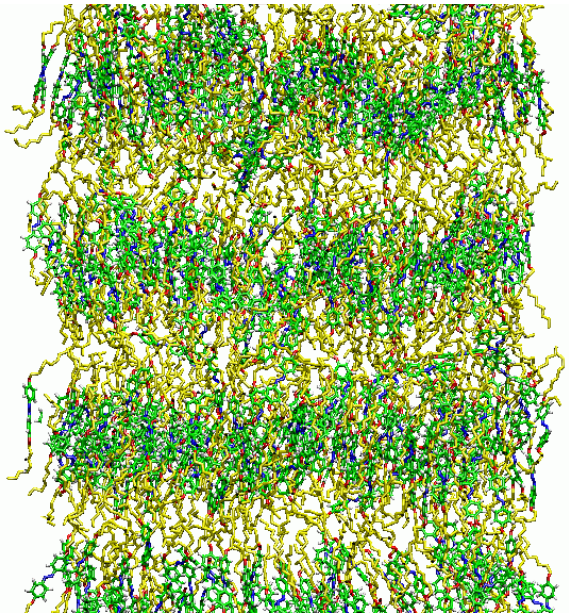
**Spectroscopy**

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

$$E \approx 4kT - 10kT$$

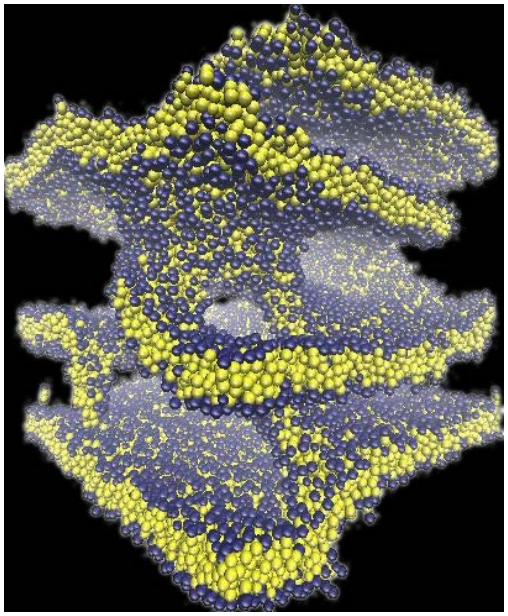
**Chemical Bond**
**Hydrogen Bond**

# Soft Matter – Nanostructured Matter



**Volume**
$V = L^3$

***A*: Surface and/or Interface Area**



**Nanoscopically Structured Material:**

**V/A << 1µm**

**=> Distinction Bulk vs Surface/Interface not useful**

**Definition of *A* depends on the question studied!!**

# Soft Matter

**“Soft” means:**

**Large fluctuations,**

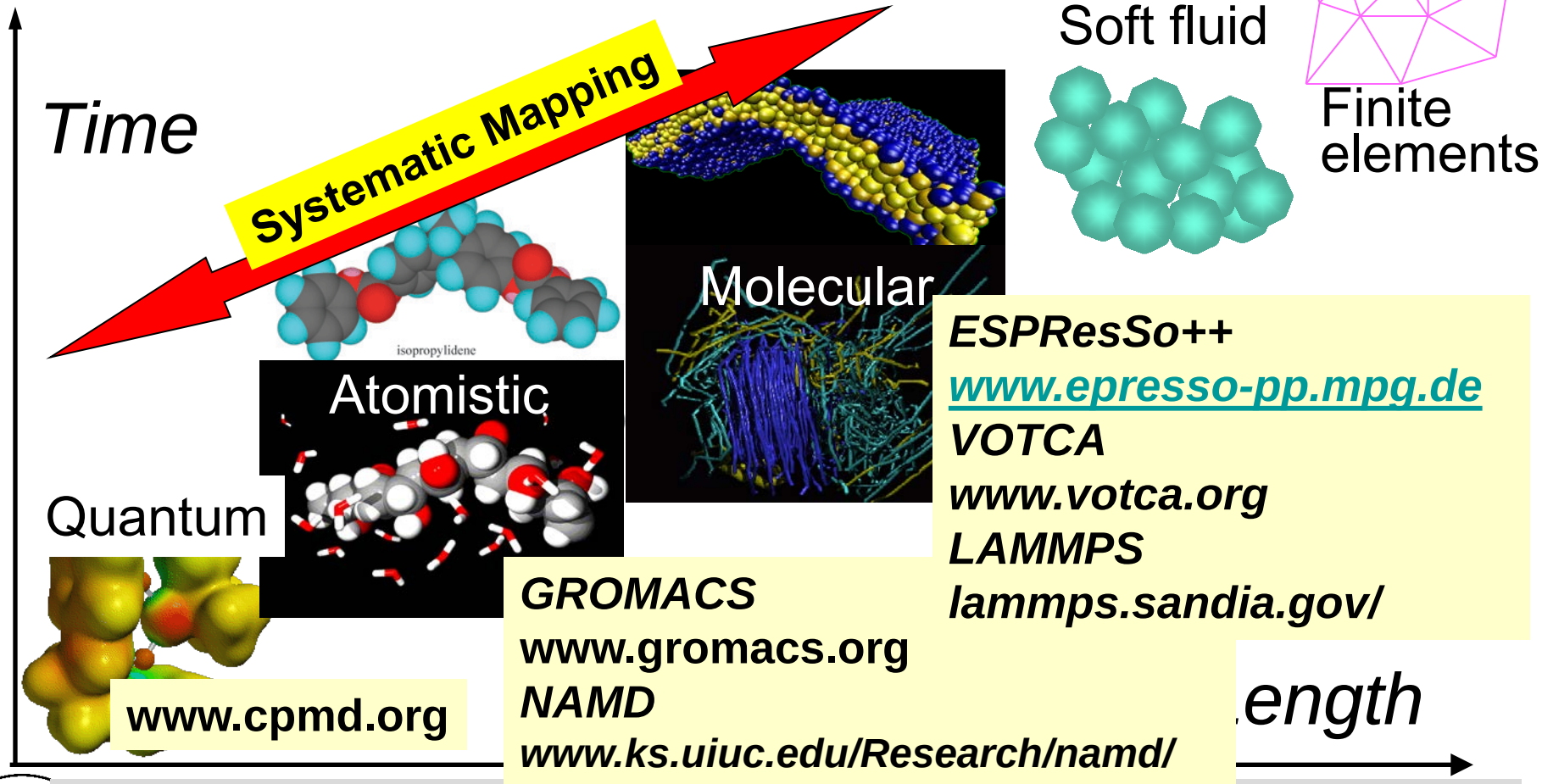
**conformational entropy**

**Or look for energies >> kBT**
**to dominate fluctuations**

***Often dominated by finite size effects!***

***Combination of generic and chemistry specific input needed!***

# Characteristic Time and Length Scales



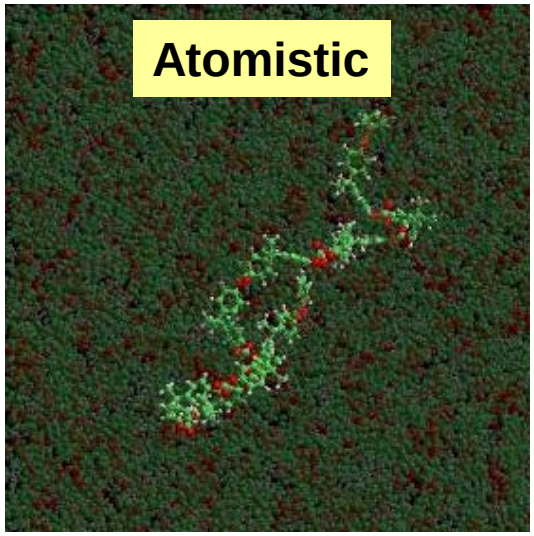

Local Chemical Properties --- Scaling Behavior of Nanostructures

Energy Dominance --- Entropy Dominance of Properties

# How can theory, simulations contribute?

# Polymers

## relevant interactions well defined

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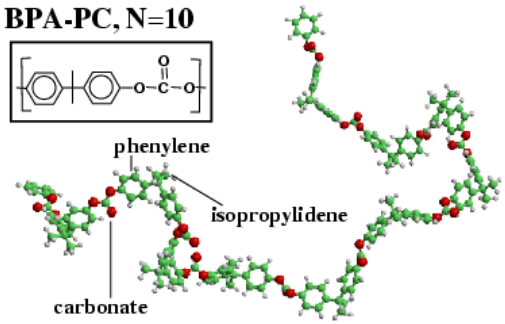
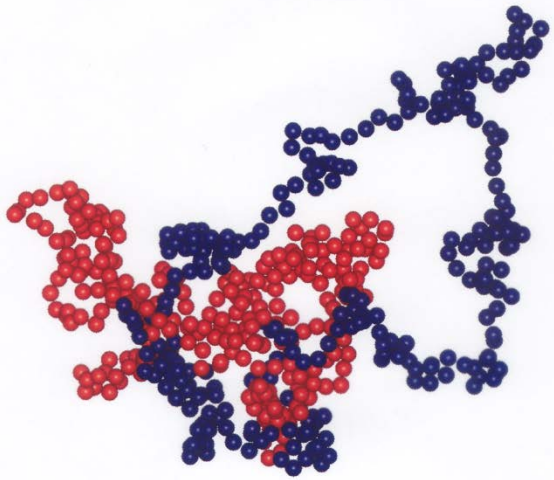



versus

**Scaling Laws**



Generic

...

Structure Property Relations

# Simulation Models for Bilayers

## Relevant Variables – More Complex

much detail

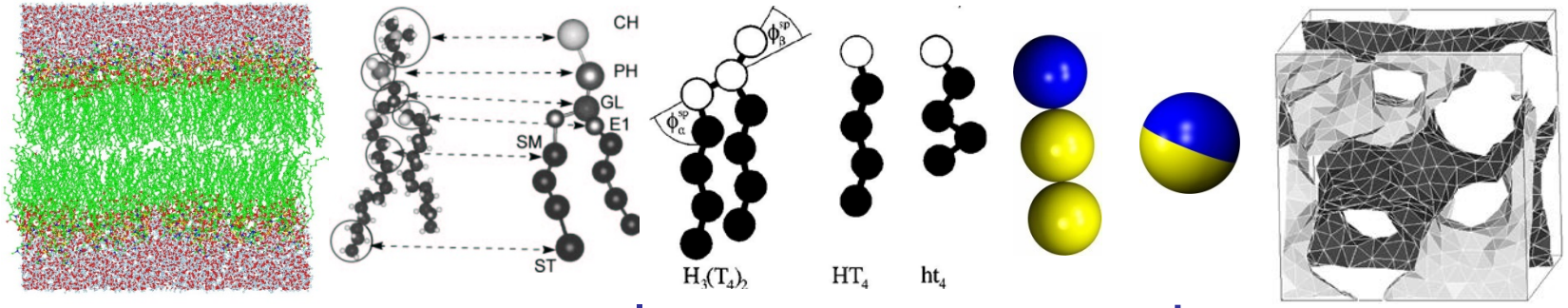
little detail

increasingly coarse grained

atomistic models

bead-spring models

triangulated surfaces




"standard" Lennard-Jones

DPD

solvent free

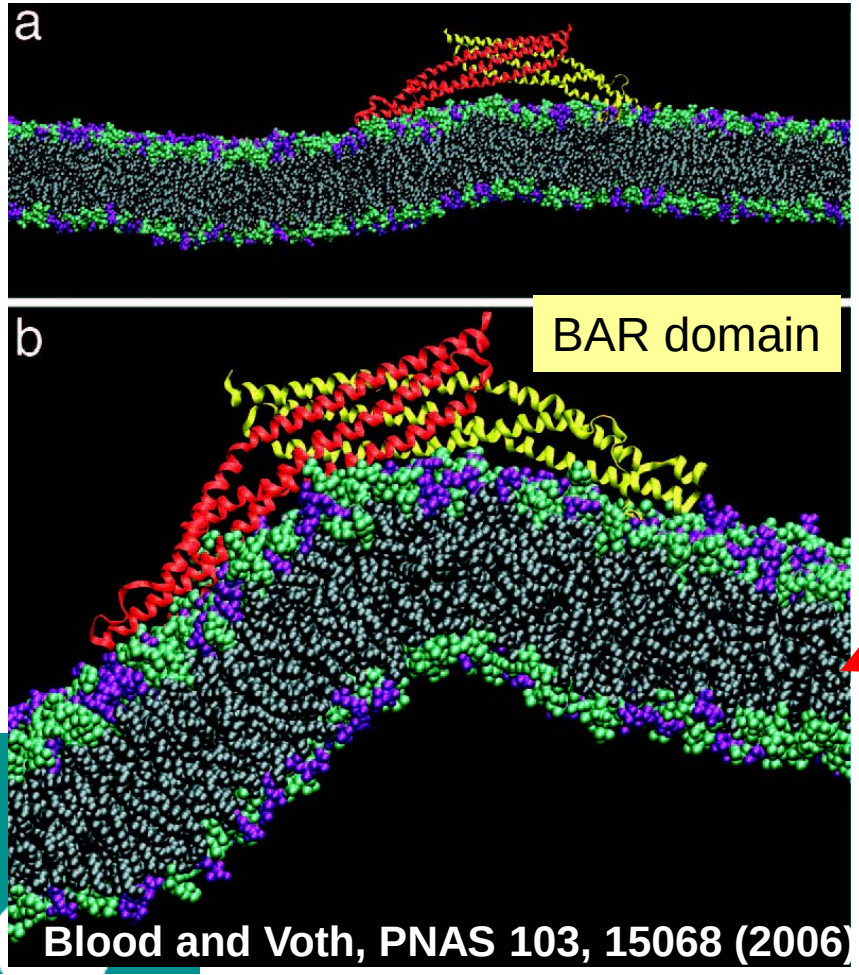
increasing numerical efficiency

But, what do we loose...

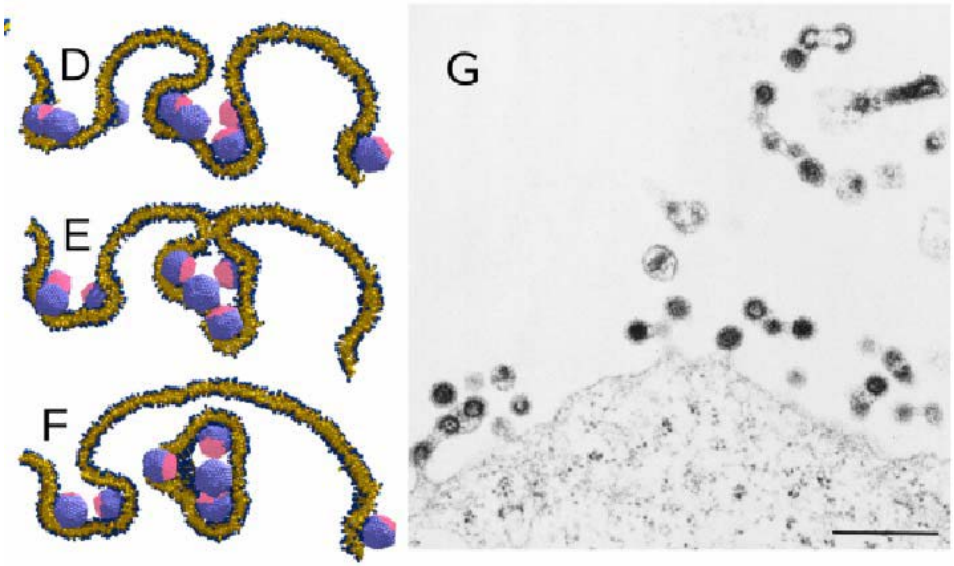
# Simulation Models for Bilayers

## Relevant Variables – More Complex

increasingly coarse grained

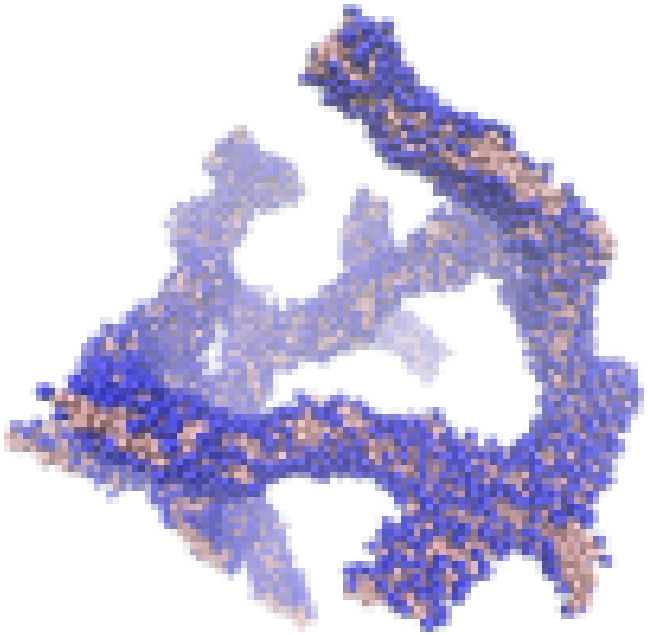


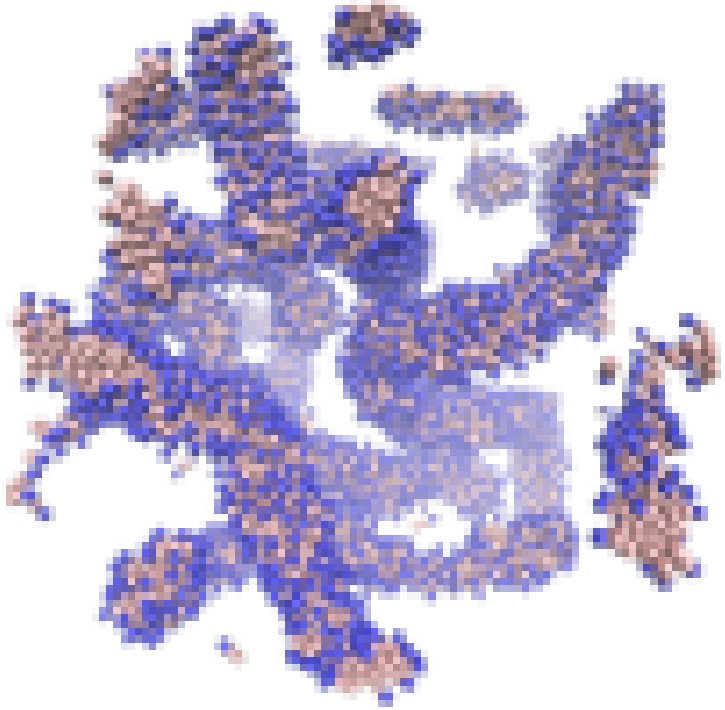

Blood and Voth, PNAS 103, 15068 (2006)

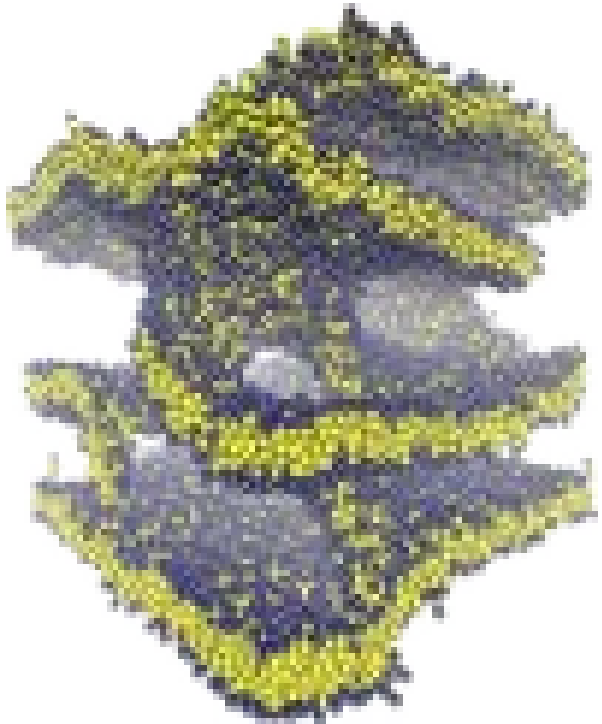


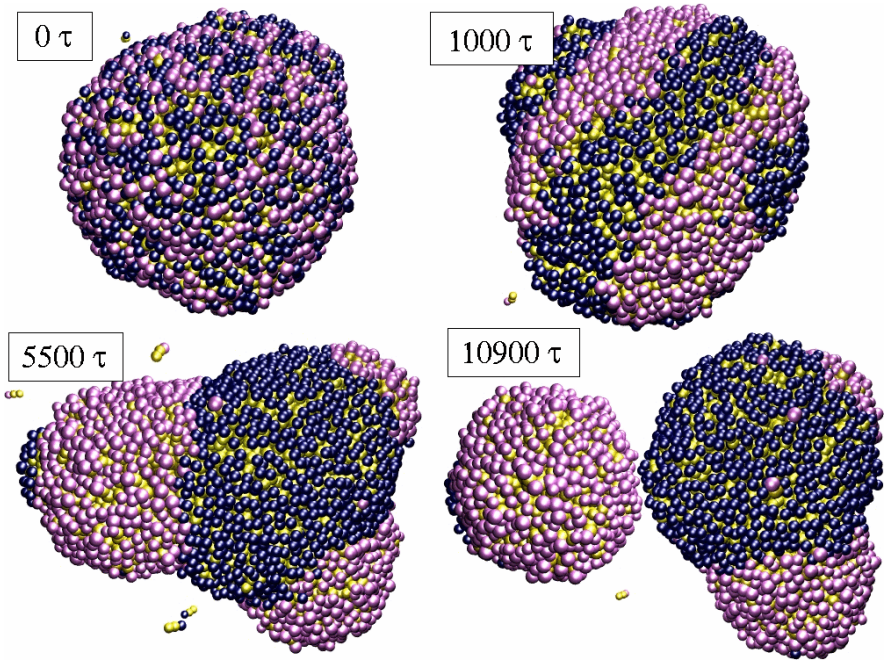

Deserno et al, **Nature, 2007**

DEISA
DISTRIBUTED EUROPEAN INFRASTRUCT



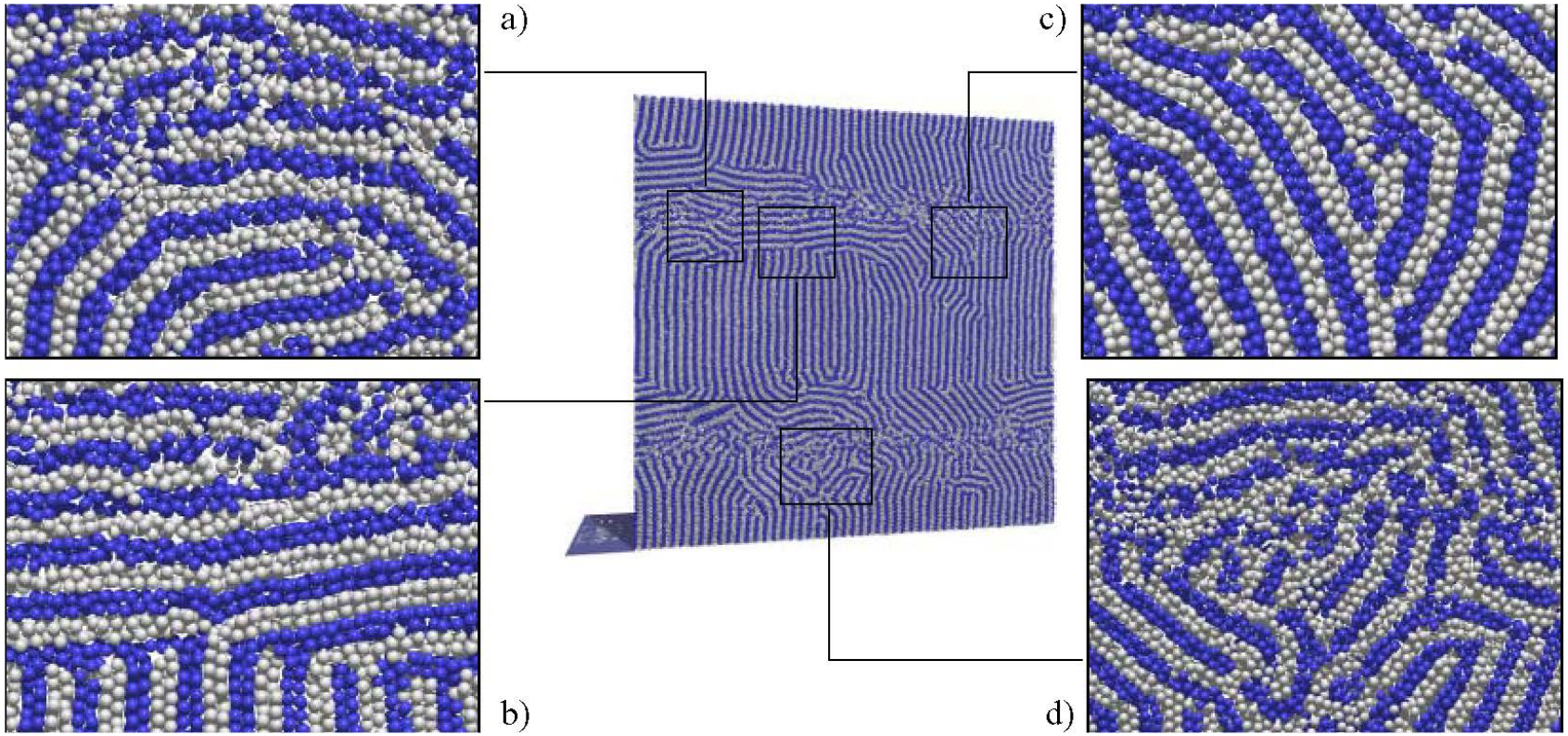





0 τ
1000 τ
5500 τ
10900 τ

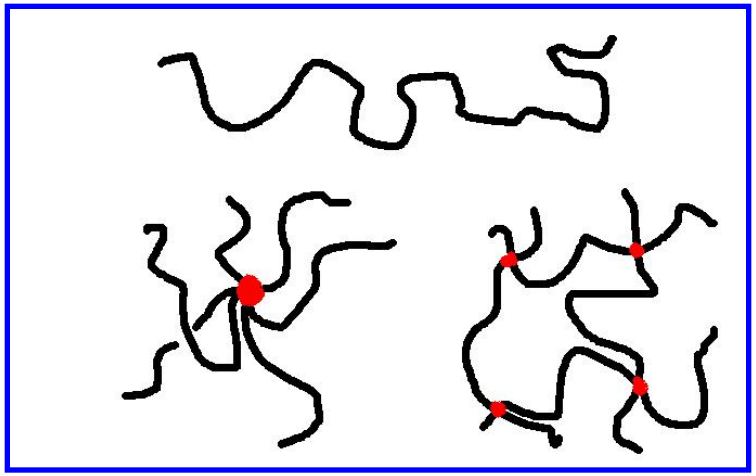
# Shearing Lamellar Systems: Dimers

**T. Soddemann, H. X. Guo, B. Dünweg, K. K., PRE 2003**



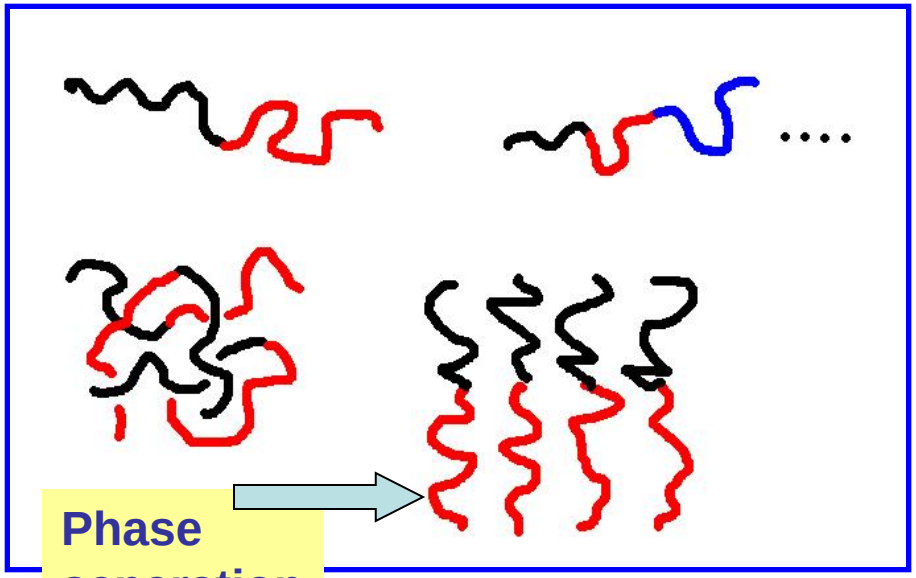
# Architectures

**Linear Polymers**



**Branched Polymers**

**Block Copolymers**




**Intramolecular entropy :**
**S = kT O(N)**

# Soft Matter - Polymers

**Polymer mixtures**
**(A. Sariban, H.P. Deutsch, M. Müller, D. P. Landau, K. Binder,…**
**later M. Müller, K. Daoulas**
**(SCFT-particle hybrid methods)**
**plus a huge body of literature from other groups**

**1/N power law**

# Soft Matter - Polymers

## Polymer mixtures

**1/N power law for critical interaction $\chi_c$**

$$\begin{aligned} \langle R^2(N) \rangle &\propto N \\ P(\vec{r}) &\propto \exp(-3r^2 / 2\langle R^2(N) \rangle) \\ \rho_{self} &\propto N / \langle R^2(N) \rangle^{3/2} \propto N^{-1/2} \end{aligned}$$

# Soft Matter - Polymers

## Polymer mixtures

**1/N power law for critical interaction $\chi_c$**

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

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

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

$$\chi_{eff} = \chi_{AB} - \chi$$

**Phase separation, critical interaction**

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

**"chemistry"** **"generic"**

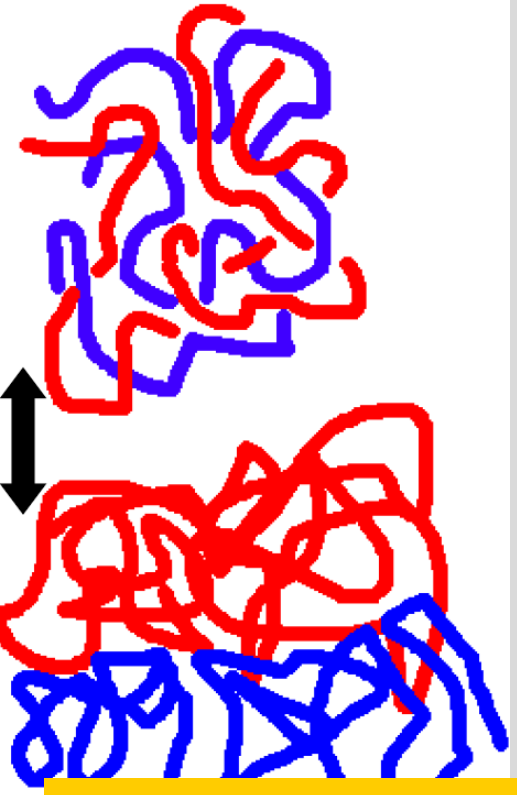
**Intra-chain entropy invariant => small energy differences => phase separation**

# Soft Matter - Polymers

## Polymer mixtures

**1/N power law for critical interaction $\chi_c$**

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



**Free Energy of Mixing:**

A-B interaction energy

$$\frac{\Delta F}{kT} = \frac{\phi_A \ln \phi_A}{N_A} + \frac{(1-\phi_A)\ln(1-\phi_A)}{N_B} + \phi_A(1-\phi_A)\chi_{eff}$$

Translational entropy per chain

$$\phi_A + \phi_B = 1$$

**Phase segregation:**

$$\frac{\partial^2 \Delta F}{\partial \phi_A^2} = \frac{\partial^3 \Delta F}{\partial \phi_A^3} = 0 \quad \Rightarrow \quad (\chi_{eff} N_A)_{crit} = 2$$

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

# Soft Matter - Polymers

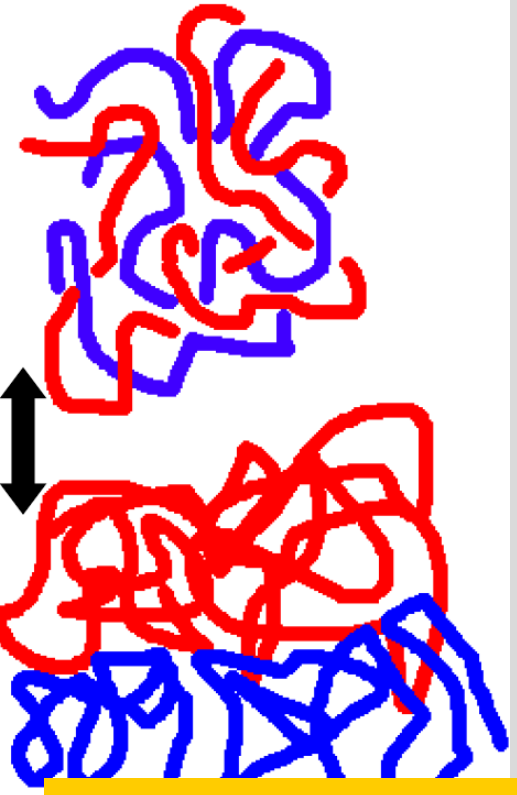
## Polymer mixtures

**1/N power law for critical interaction $\chi_c$**

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

**Free Energy of Mixing:**

A-B interaction energy



**Highly disputed proposal by K. S. Schweizer**

$$\chi_c \propto N^{1/2}$$

y per chain

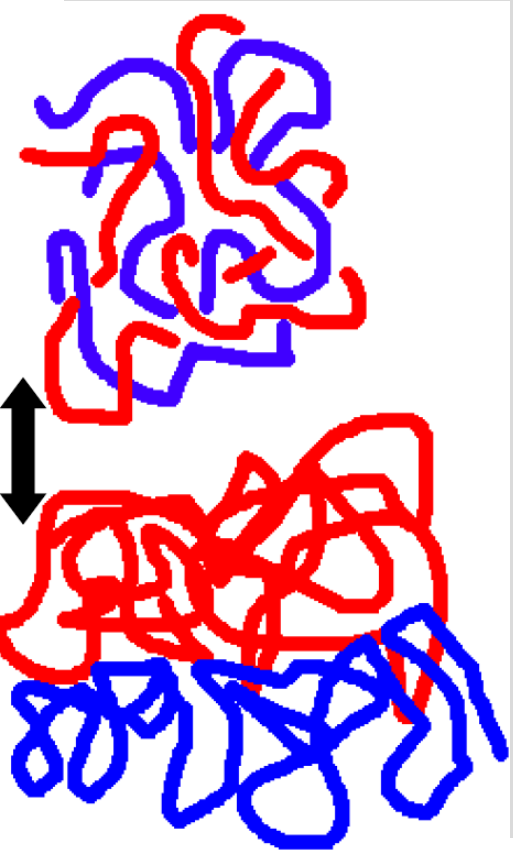
egation:

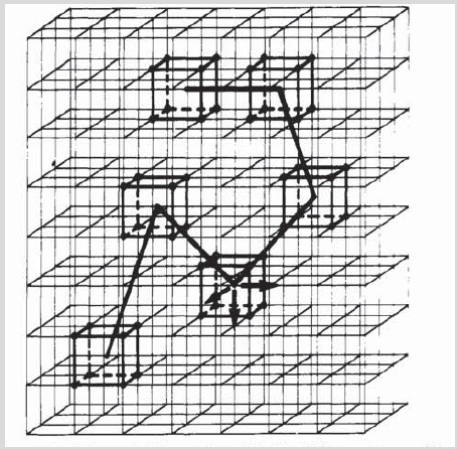
**Intra-chain entropy invariant => small energy differences => phase separation**

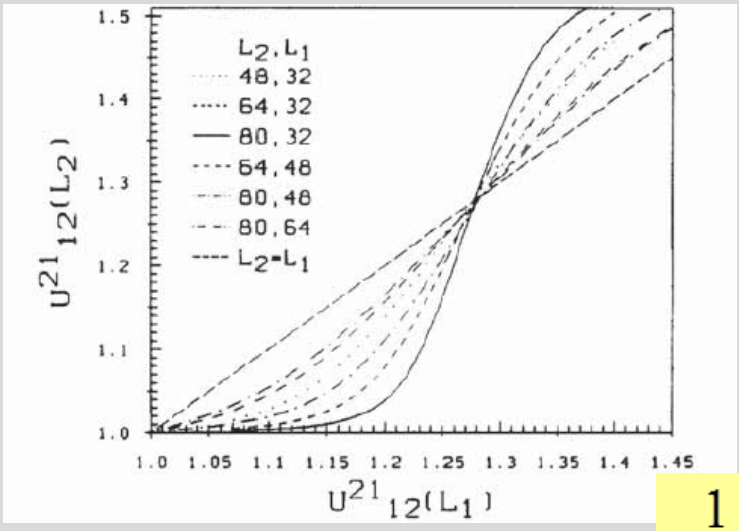
# Soft Matter - Polymers

**Check by Simulation: H.P. Deutsch, K. Binder 1992**

Monte Carlo Simulation
Extensive finite size
scaling analysis employing
Cumulants of
A-B density differences







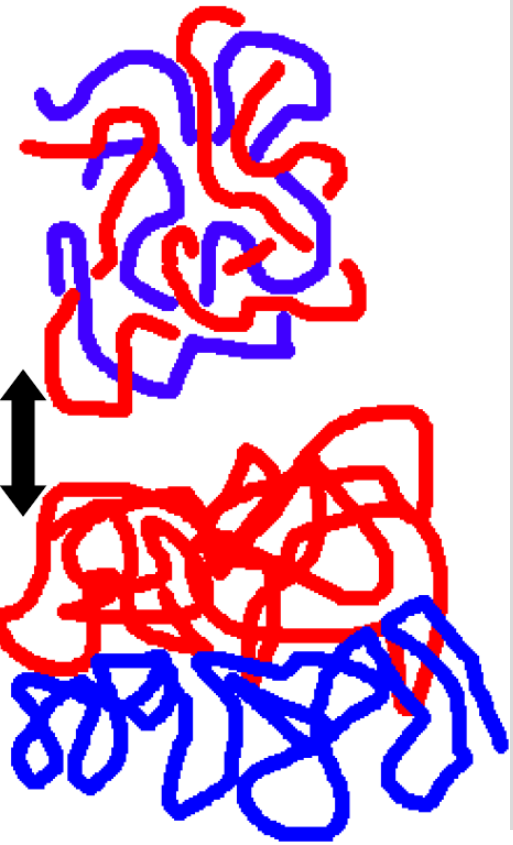

$$\frac{1}{\chi_{eff}^{crit}} = \frac{kT}{\varepsilon} = 2.15N + 1.35$$

# Soft Matter - Polymers

**Check by Experiment (shortly after simulations):**
**F. S. Bates et al. 1992**

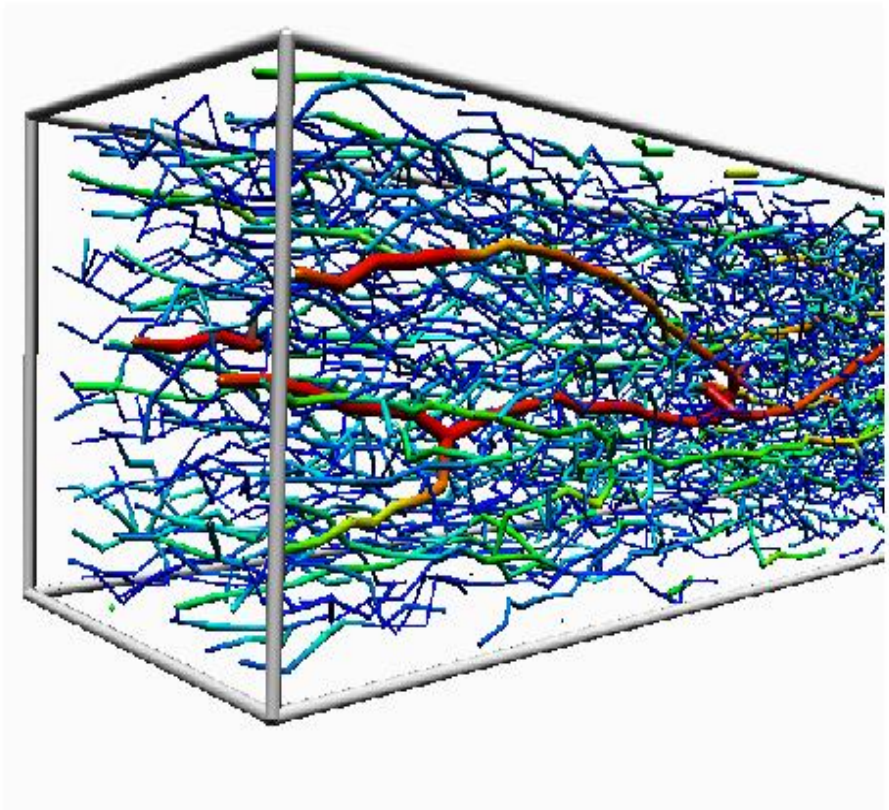
N-scattering experiments on partially deuterated Poly(ethylene-propylene) copolymers

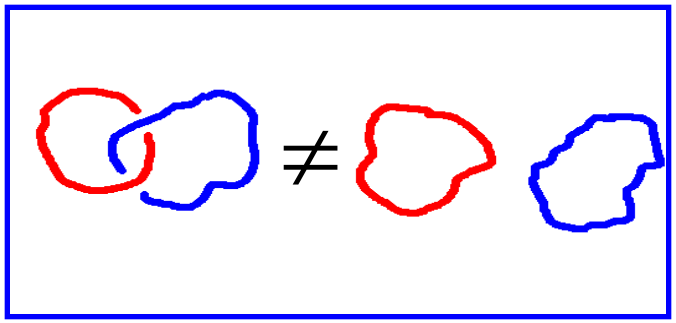
**$(C_5D_xH_{(10-x)})_N$ mixed with $(C_5H_{10})_N$**



$$\chi_{eff}^{crit} \propto N^{-\delta} \qquad \delta = 1.01 \pm 0.05$$

# Universal Confinement: Links &Stress





Local stress distribution

- SMALL STRESS
- **LARGE STRESS**

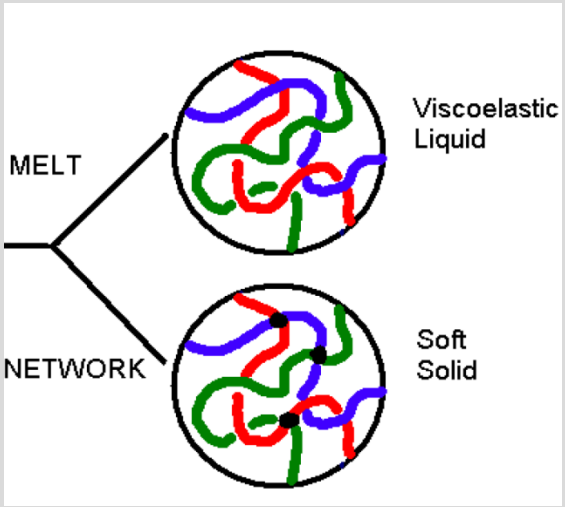
**R Everaers&K. K (1996), RE (1999)**

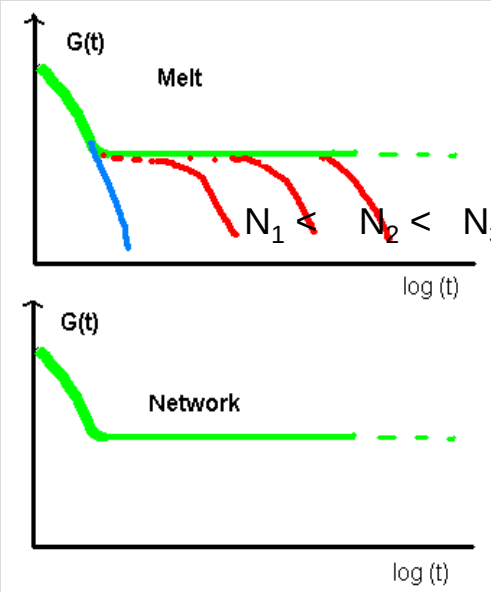
# Soft Matter - Polymers

**Edwards, de Gennes**

**Tube model, reptation concept**

## Classical Problem: MELT ←→ NETWORK

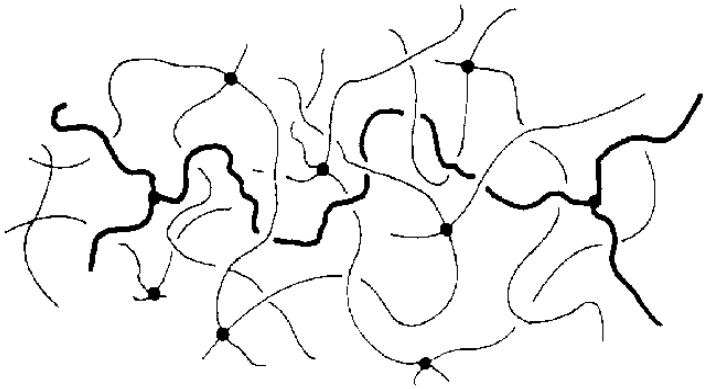


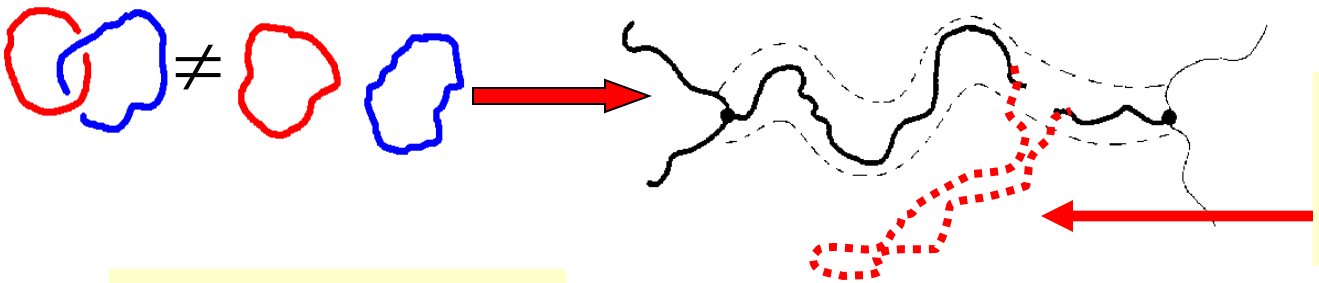

**G(t): Time dependent (shear) modulus:**

**Long chains between crosslinks, G(t) independent of N**

# Tube Model

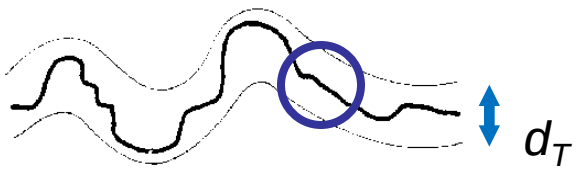


Edwards 1967



"Tube leakage":
Entropy penalty (O(L/2))
for defects too large

De Gennes 1971




$$d_T \propto N_e^{1/2}$$

$$G^0 \propto N_e^{-1}$$

$$\tau_e \propto N_e^2$$

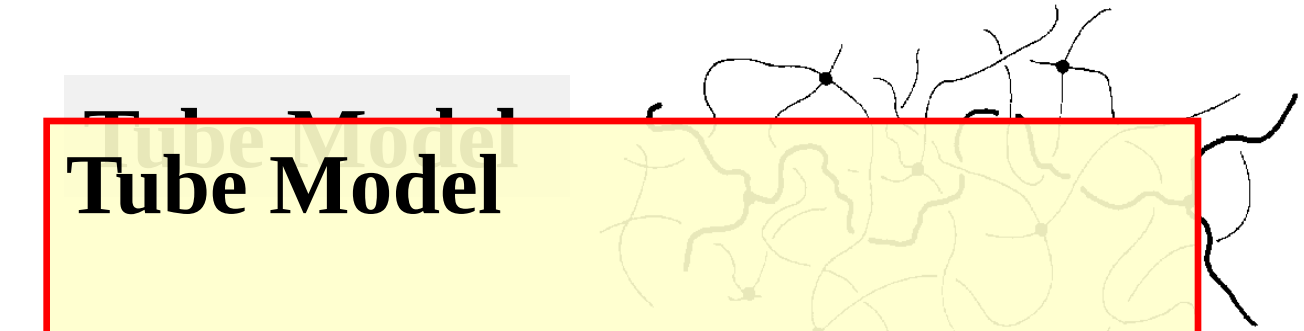
*Unique length* $d_T$

# Tube Model

**Concept, based entirely on conformational statistics of networks (soft solid) and melts (liquid).**

**→**

**$N_e$ should be determined from conformational statistics of the polymers.**



Edwards 1967

"Tube leakage": Entropy penalty (O(L/2)) for defects too large

De Gennes 1971

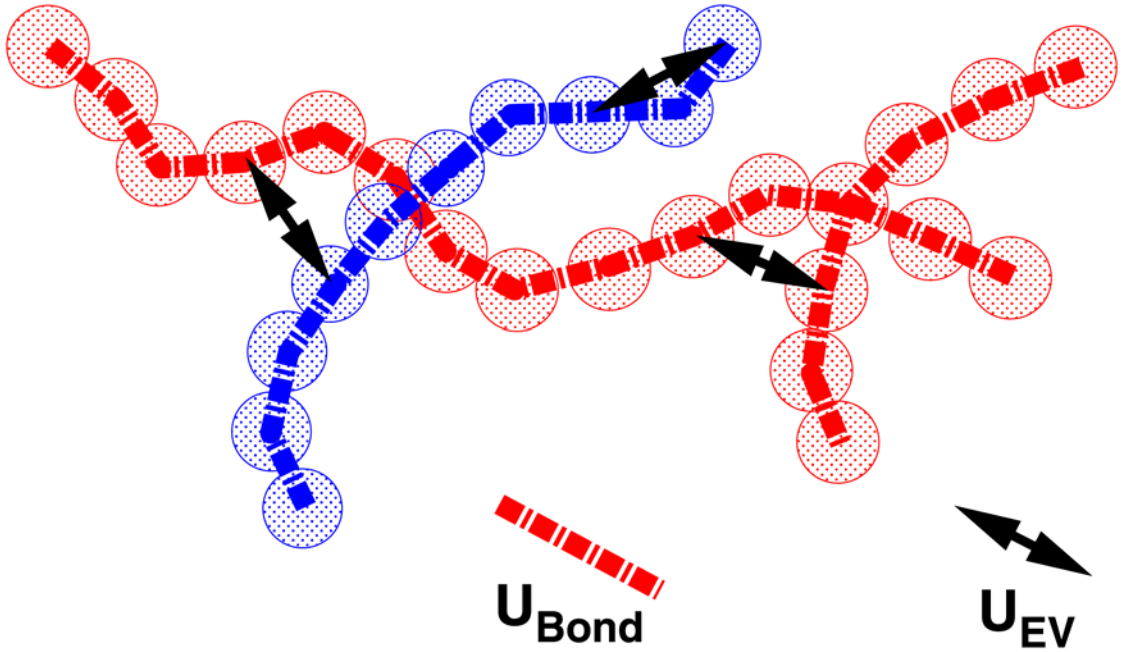
$d_T$

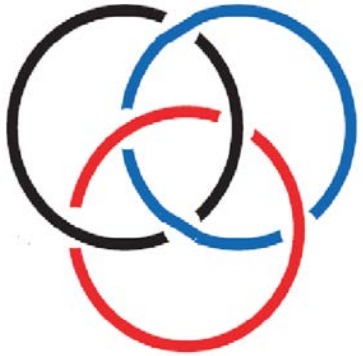
$$d_T \propto N_e^{1/2}$$

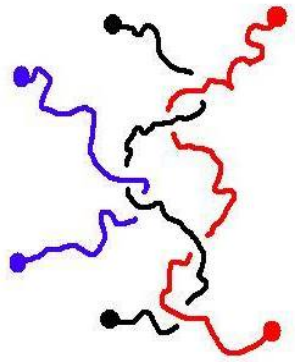
$$\tau_e \propto N_e$$

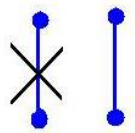
*Unique length* $d_T$

# (Semi) generic methods: MC, MD





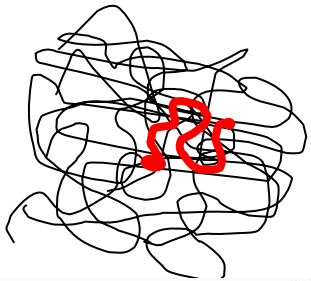


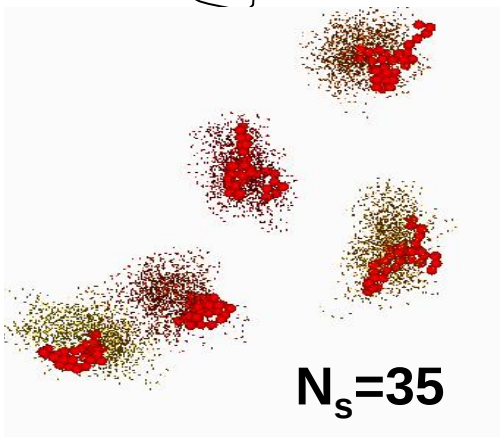
$$U_{EV}(r) = \varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \frac{1}{4}\right)$$

$$U_{Bond} = -30\ k_B T \ln\{1 - (\frac{r}{R_c})^2\}$$

# •Endlinked melts

Edgardo R. Duering, KK, Gary S. Grest
JCP, 1994

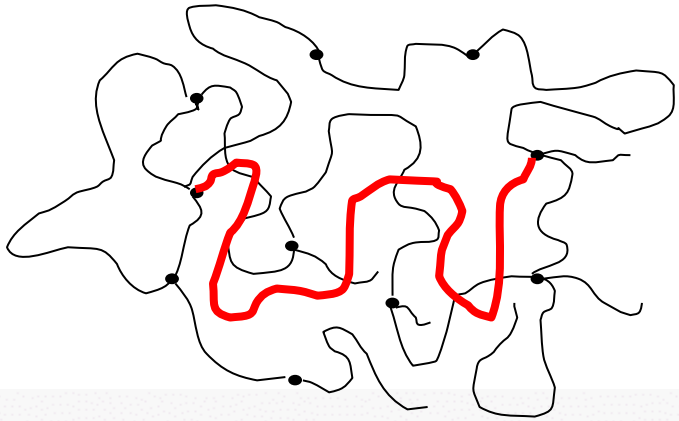


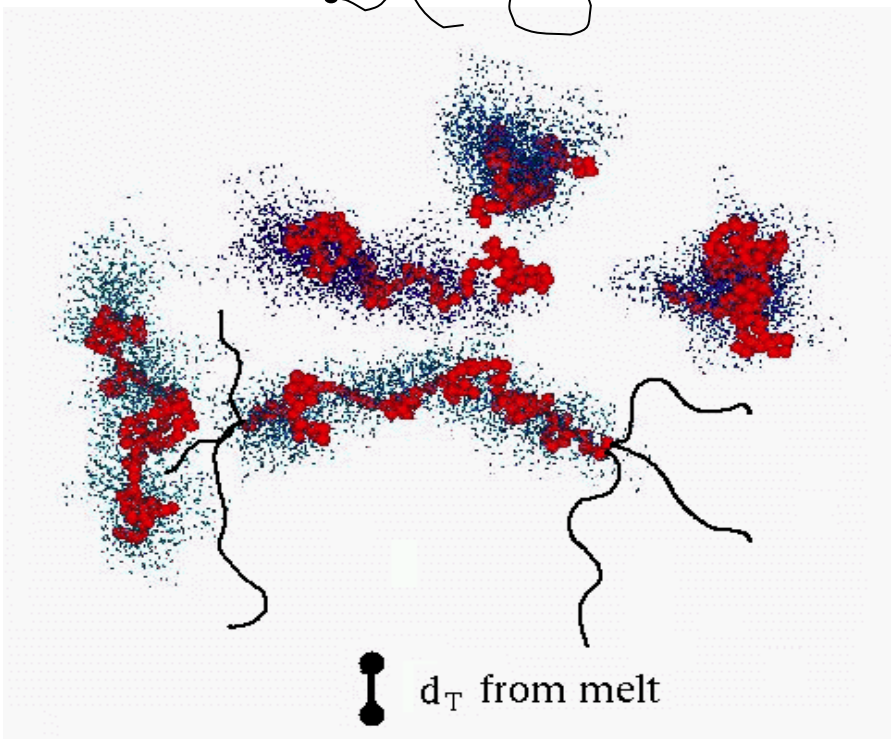


$N_s$=35

$R^2 \propto d_T^2$

$N_e \propto 70$



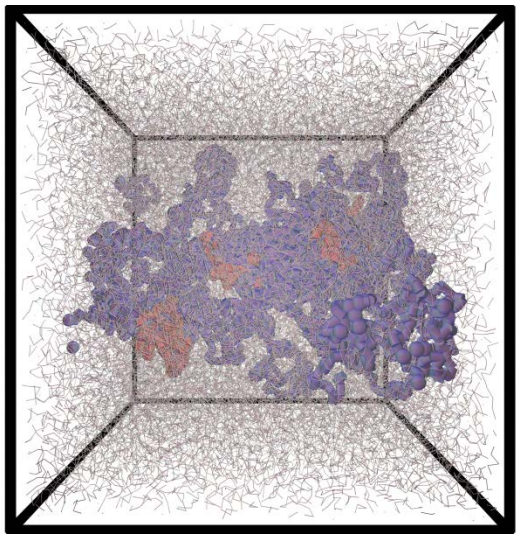


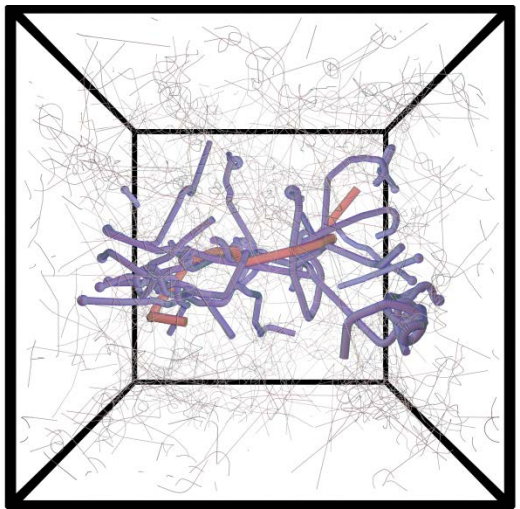

$N = 100$

Initial conformation

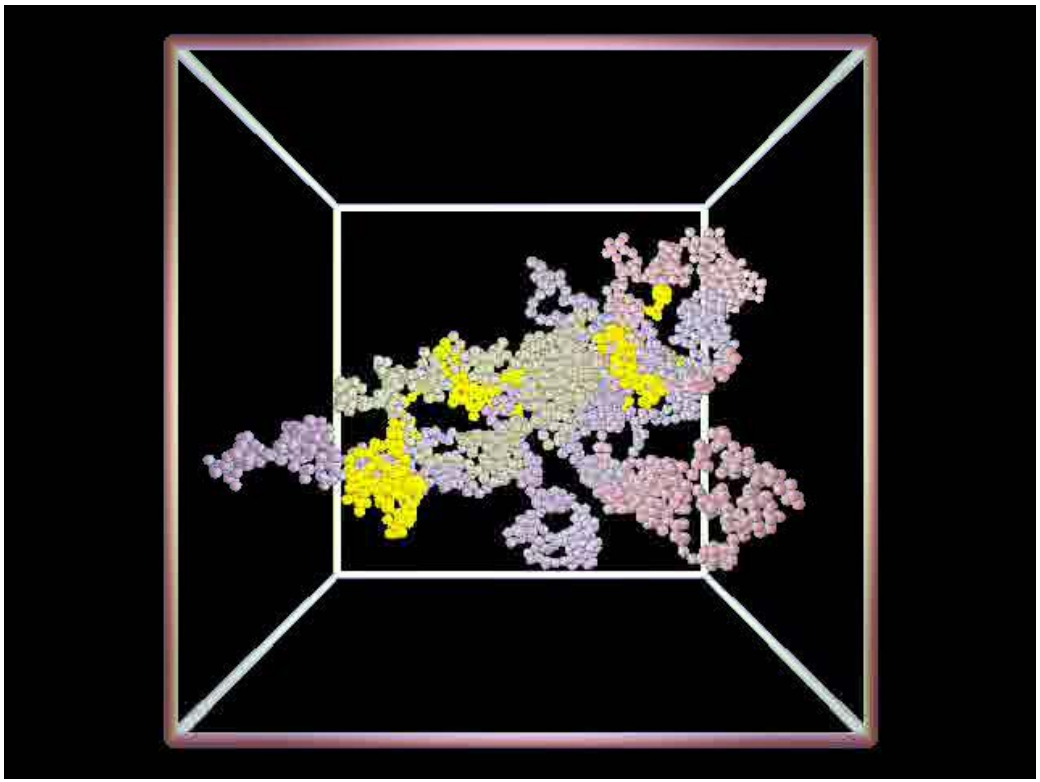
All conformations

# Entanglements: Primitive Path Analysis





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



Related work: Theodorou, Kroeger, Larson, Briels…

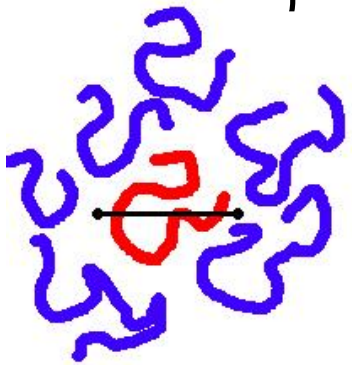
# Characteristic Lengths: $l_K$ and $p$

$$p = \frac{N}{\rho} \frac{1}{\langle R^2(N) \rangle}$$

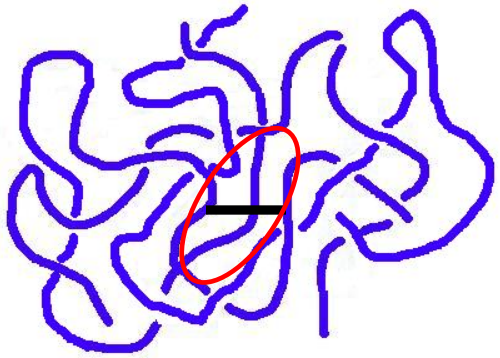
ρ/N = chain density

**Packing Length *p***

Solution at ρ*: ***p*** ≈ ***R***



Melt: ***p*** ≈ strand-strand distance

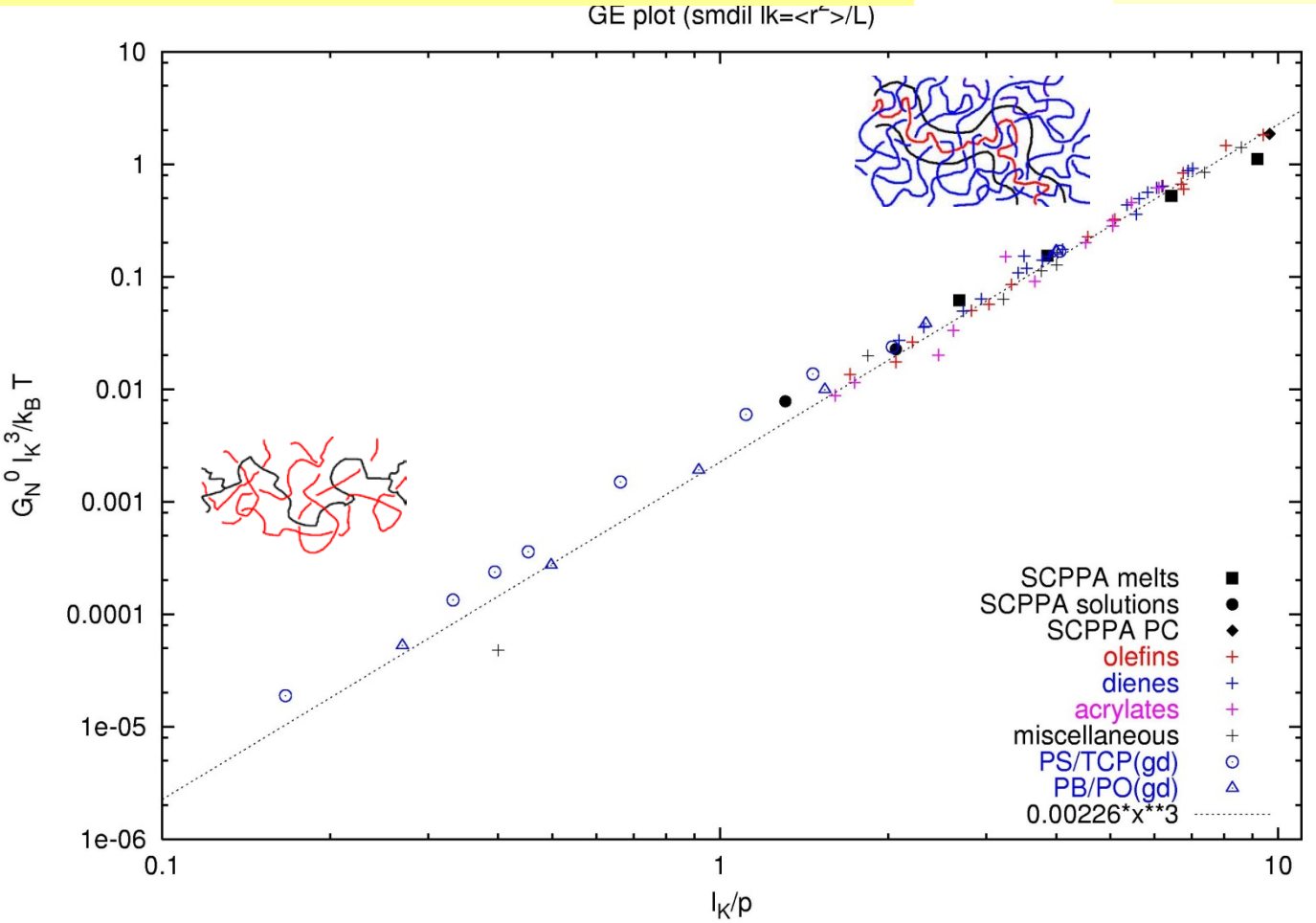


# Plateau Modulus $G_N^0$ Different Polymers

## Melts and Solutions: Tological analysis and experiment

$$G_N^0 l_k^3 / kT \quad vs \quad l_k / p$$

**NO adjustable Parameters**




**BPA-PC**

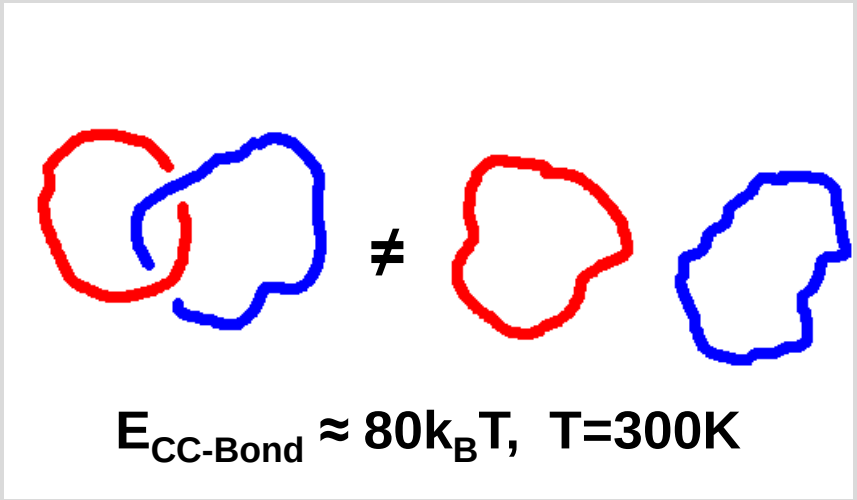
**Everaers et al Science 2004, Leon et al Macrom. 2005**

# Soft Matter

**“Soft” means:**

**Large fluctuations,**
**conformational entropy, O(L)**

**(L contour length of the molecule)**



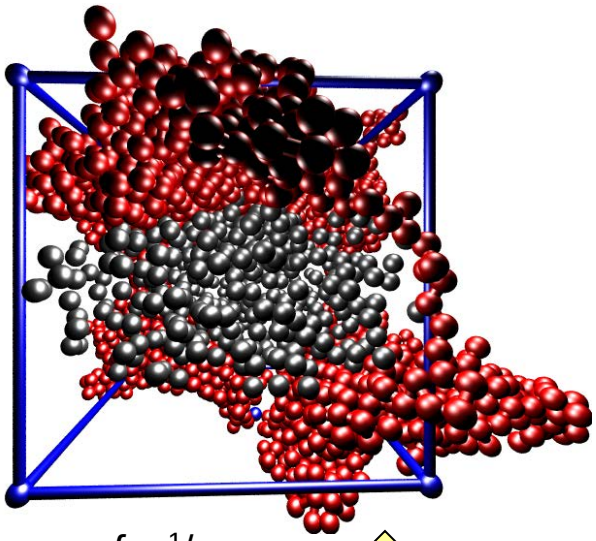

**and/or**

**if energies >> $k_B T$**
**fluctuations are constrained**

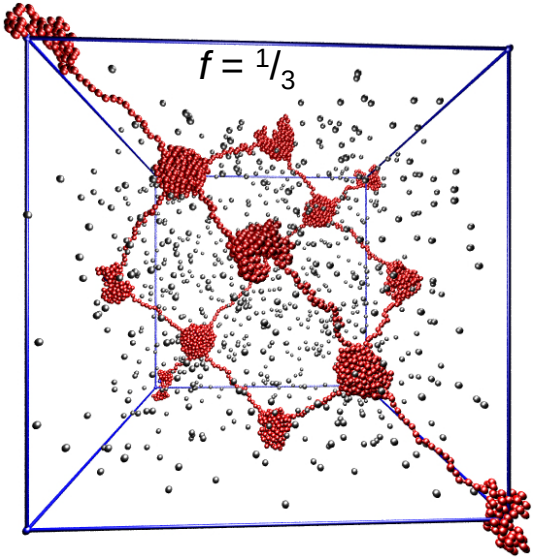
# Shrinking Gels: Poor Solvent Hydrogels

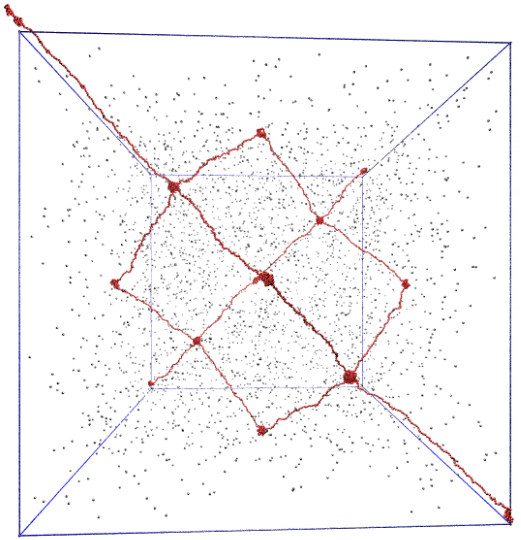
**high salt** … **low salt**

**Low charge fraction** … **high charge fraction**



$f = {}^1/_8$



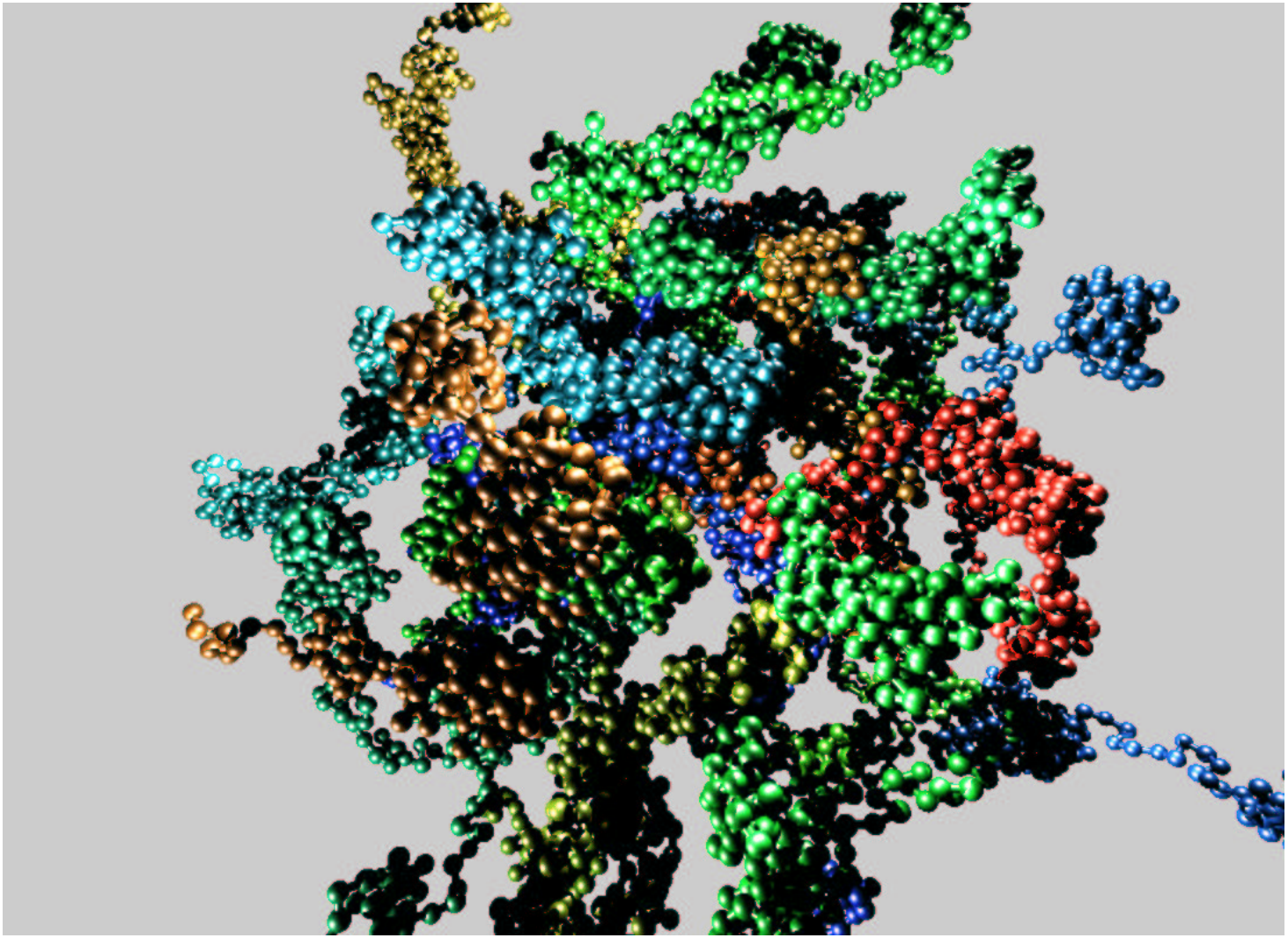



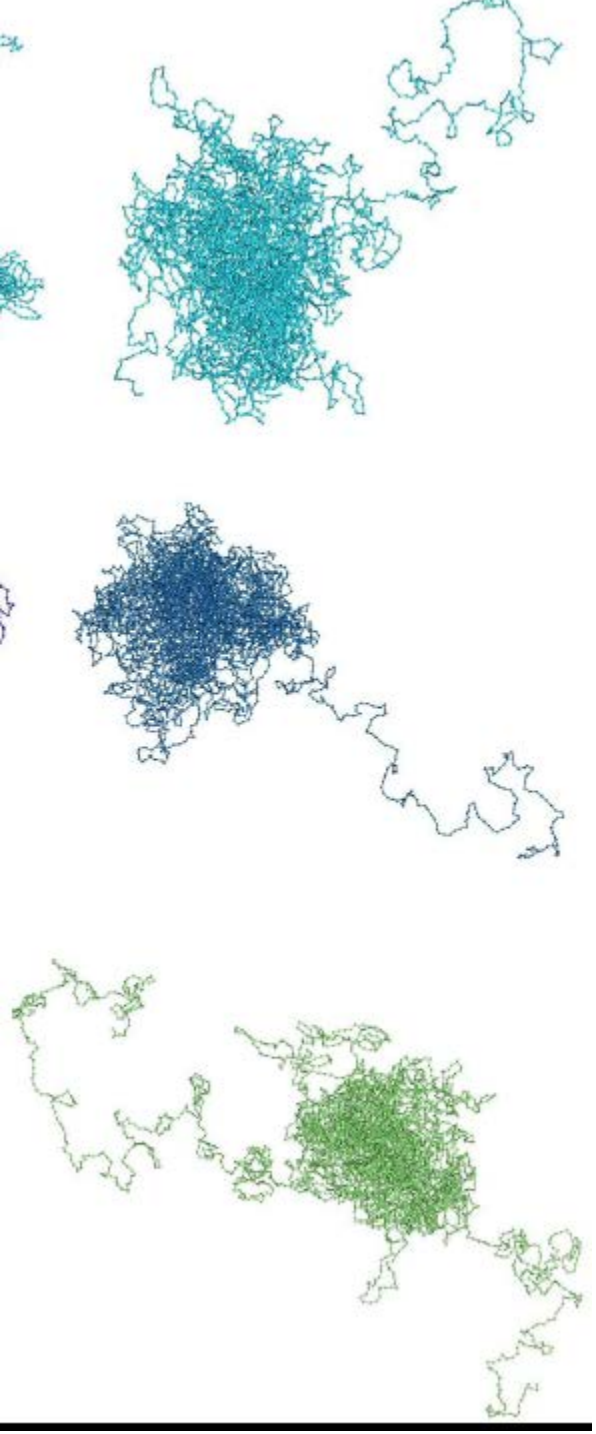
$f = {}^1/_1$

Segregated strands?

- **osmotic pressure of "counterions" enforces swelling (↔ good solvent picture)**
- **nodes act as condensation nuclei**
- **"pearls" form due to balance with surface tension (↔ Rayleigh instability)**

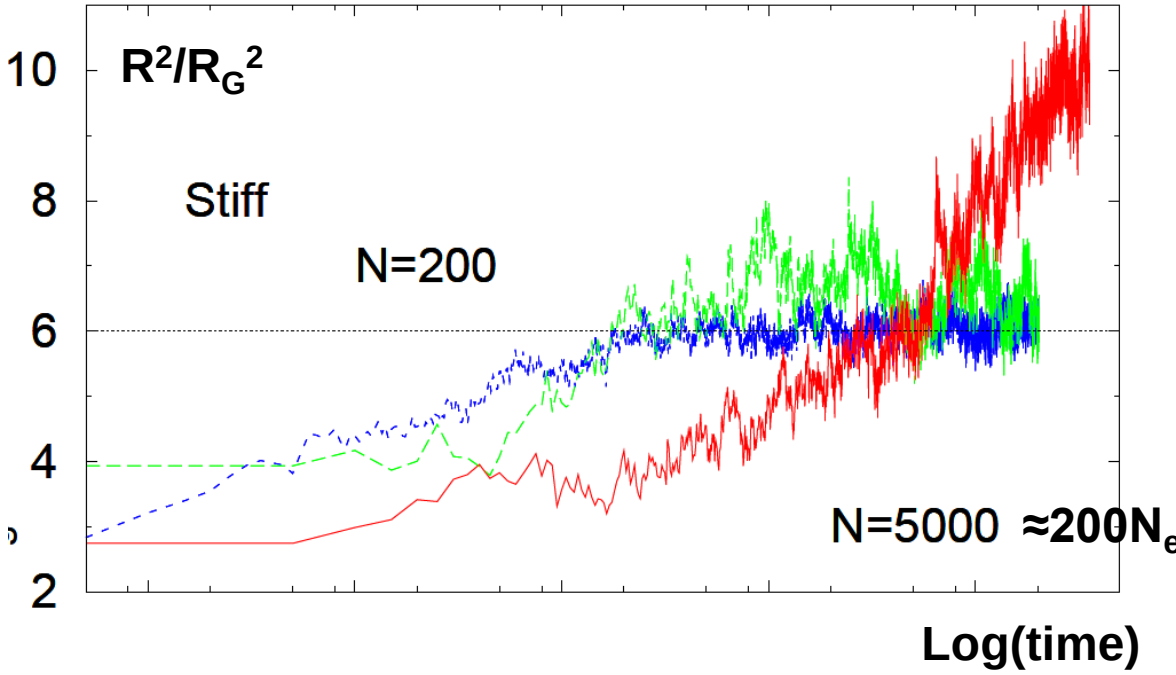
# Collapsing polyelectrolyte chains





# Melt of collapsed linear polymers: Make “use” topological constraints

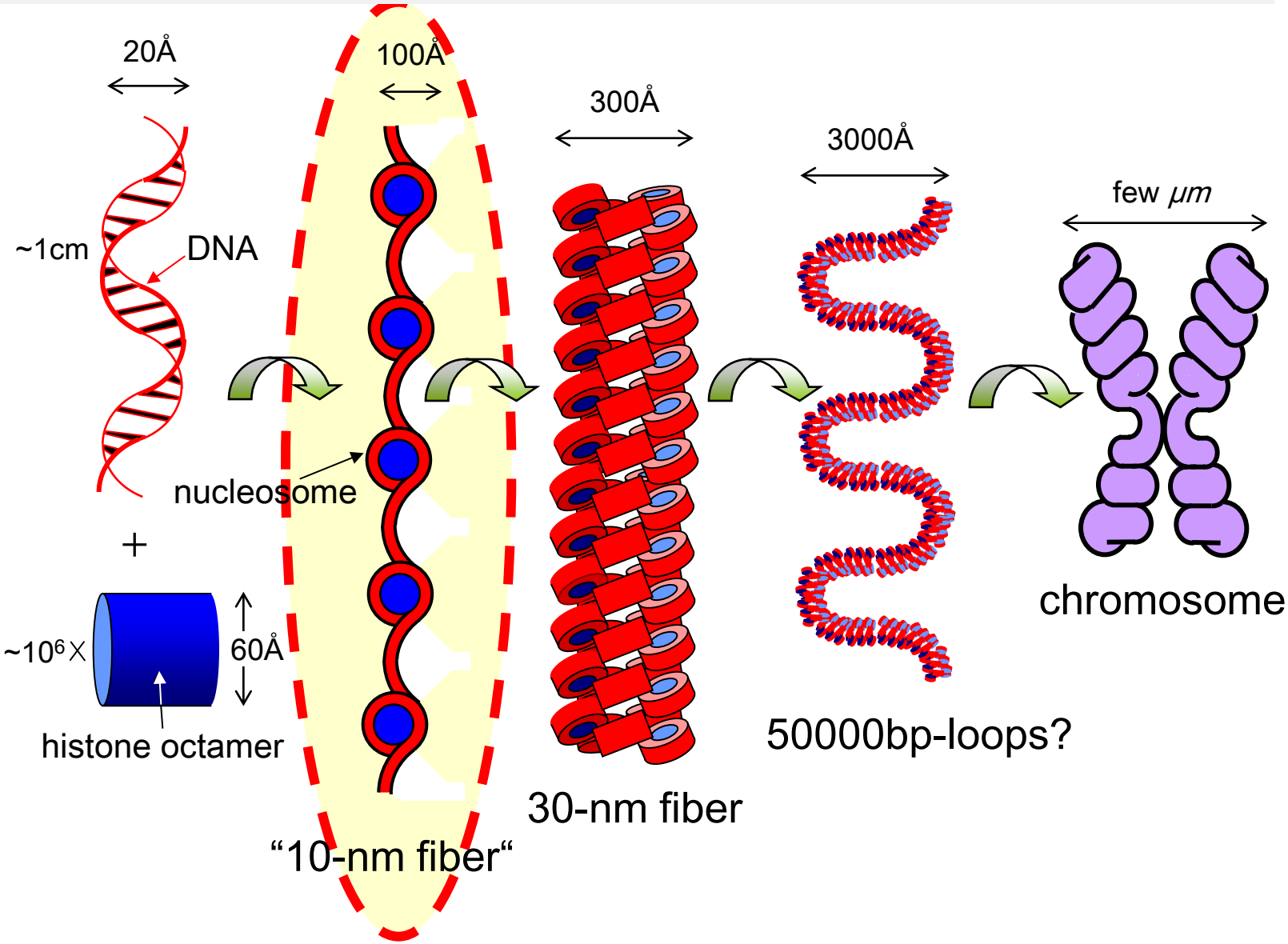
T. Vettorel, KK, MTS 2010




**See also work on crystals: Rastogi, Spiess, McLeish**

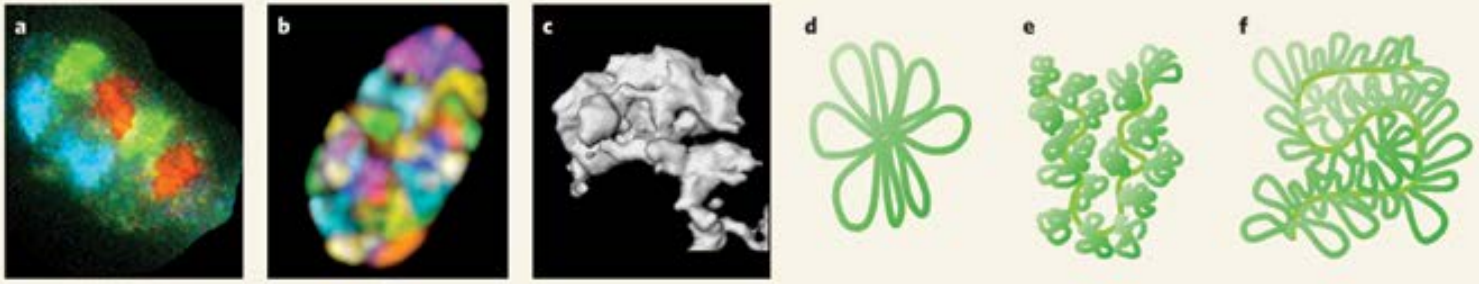
# Structure of Chromatin

from review H. Schiessel, „The physics of chromatin“, J. Phys.: Condens. Matter 15 (2003) R699

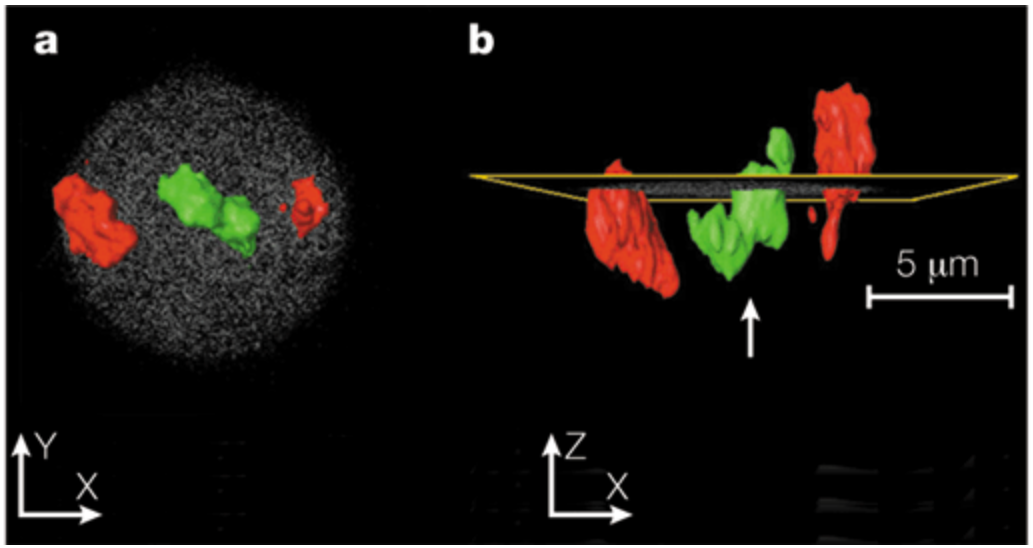


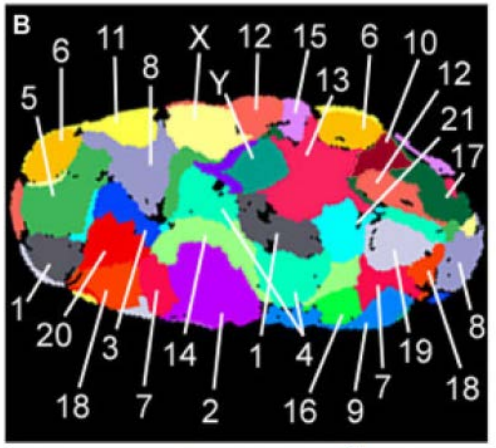
# Chromosome Territories

K.J. Meaburn, T. Mistelli, Nature 445, 379-381(2007)

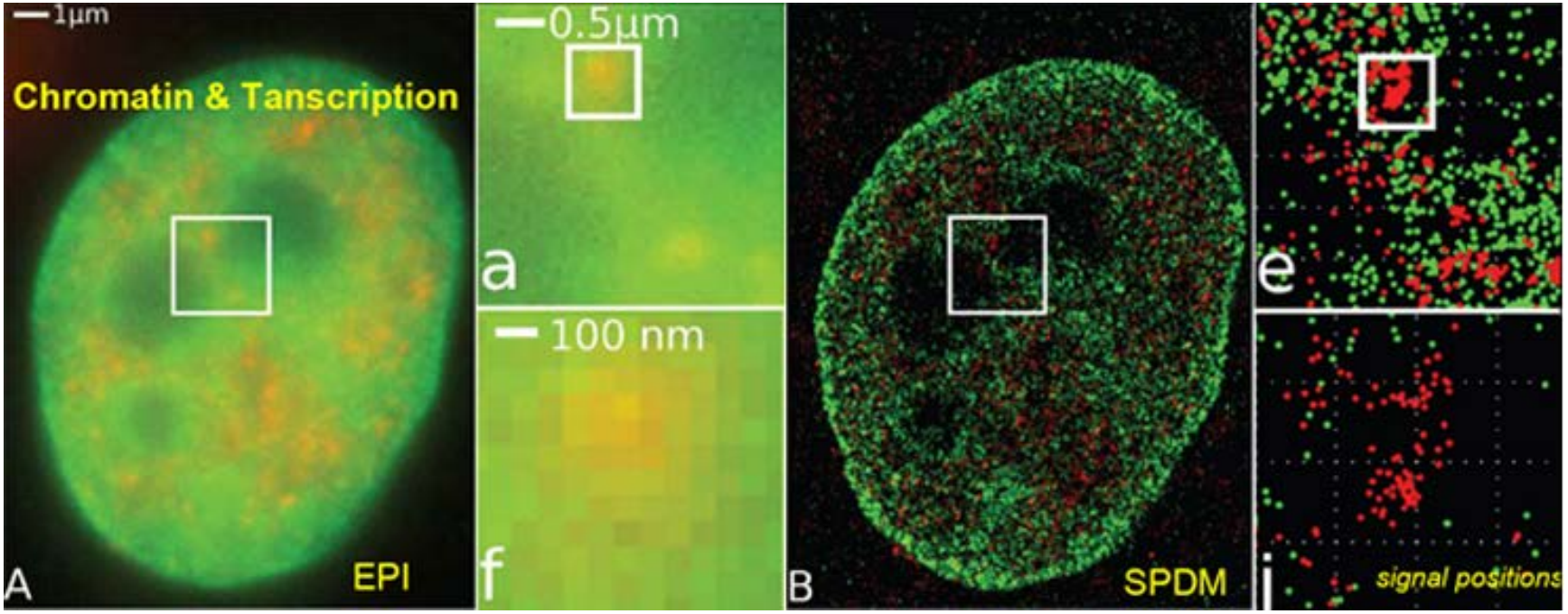



T. Cremer, C. Cremer, Nature Reviews Genetics vol. 2, pp. 292-301 (2001)

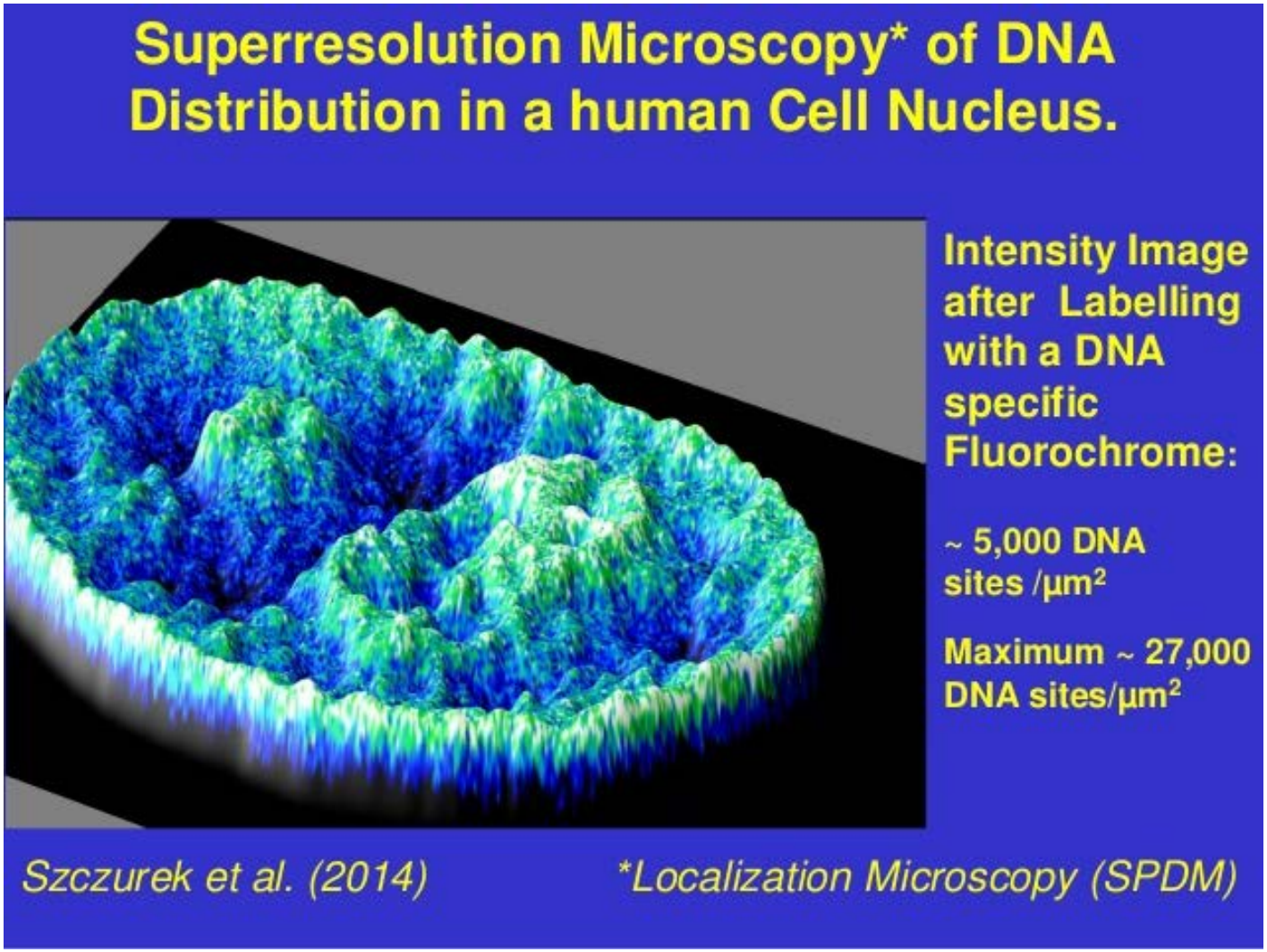


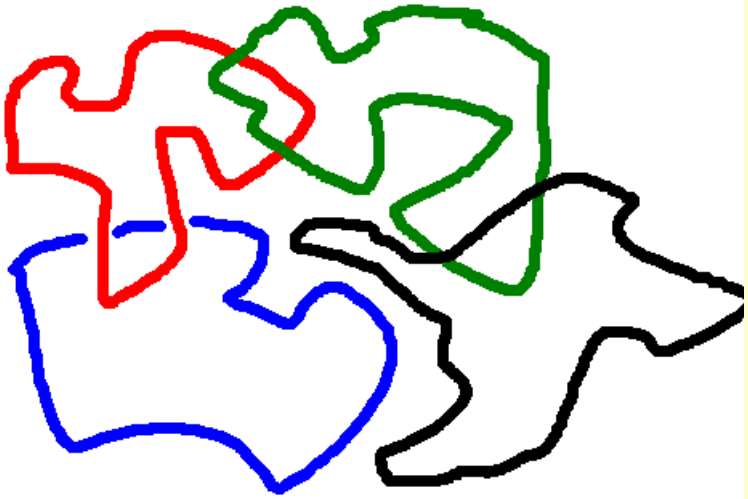
# Cremer Lab, IMB Mainz

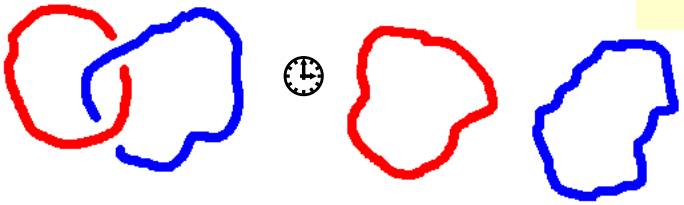


# Cremer Lab, IMB Mainz



# Melt of non concatenated ring polymers





## Conformation of the rings?

**Random walk**: $R^2(N) \propto N^{2\nu}$, $\nu=1/2$

**=> Rings interpenetrate each other**

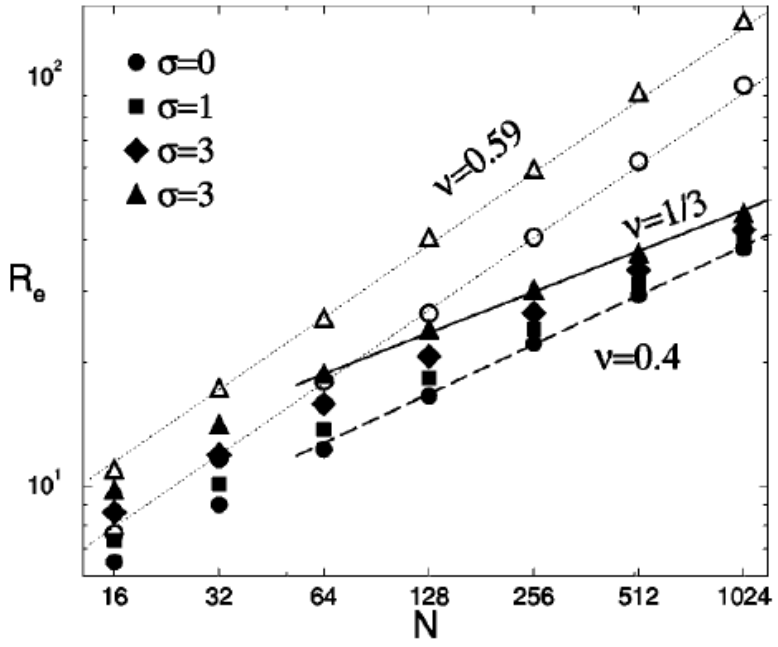
**Collapsed ring**: $R^2(N) \propto N^{2\nu}$, $\nu=1/3$

$\Rightarrow$ **Rings segregate,**
**finite number of neighbors**

PHYSICAL REVIEW E VOLUME 61, NUMBER 4

## Topological effects in ring polymers. II. Influence of persistence length

M. Müller,[1,2] J. P. Wittmer,[2,3,*] and M. E. Cates[2]




**Speculation of higher order contributions**

$$F \propto kT(R^d / N)^\alpha$$

**Osmotic pressure**

$$+ kTN / R^2$$

**Surface term of EV interaction**

$$\Rightarrow$$

$$\nu = (\alpha + 1)/(3\alpha + 2)$$

$$\alpha = 1 \rightarrow \nu = 0.4$$

$$\alpha = \infty \rightarrow \nu = 1/3$$

**New Flory theory, based on lattice**
**animal concept**
**ν=1/3, d=3**
**A. Y. Grosberg,**
**Soft Matter Nov. 2013**

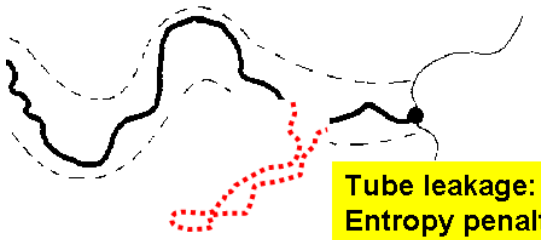
# Too(?) simple Physical picture

## Grosberg, Vettorel, KK

- **If rings collapse, (naively) expect core plus corona**

**(first simple picture)**

$d_T^2 \approx N_e$



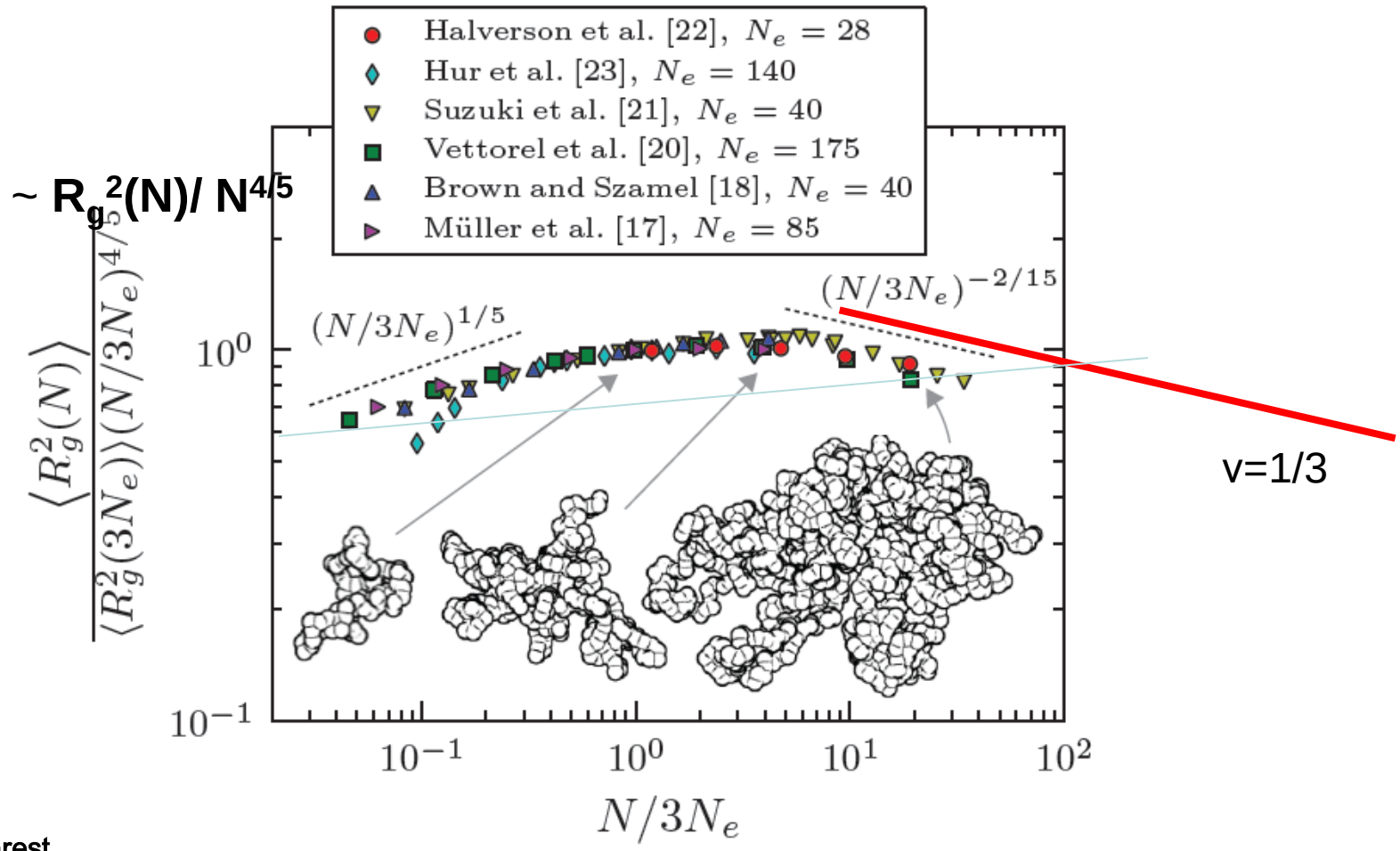
Tube leakage: Entropy penalty for defects too large

$N \le N_e$ **No effect, random walk**

$N_e \le N \le O(\approx 10 N_e)$ **Begin "shrinking",**

$N \ge O(\approx 10 N_e)$ **Segregation regime**

# Ring extensions: Collection of data

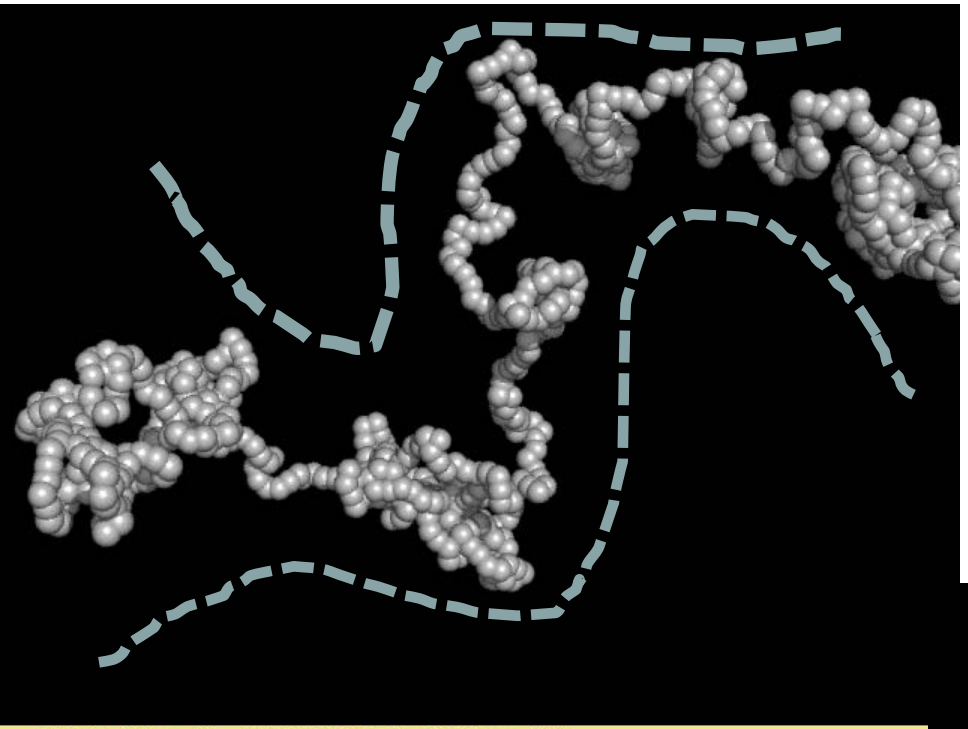



~ $R_g^2(N)/ N^{4/5}$

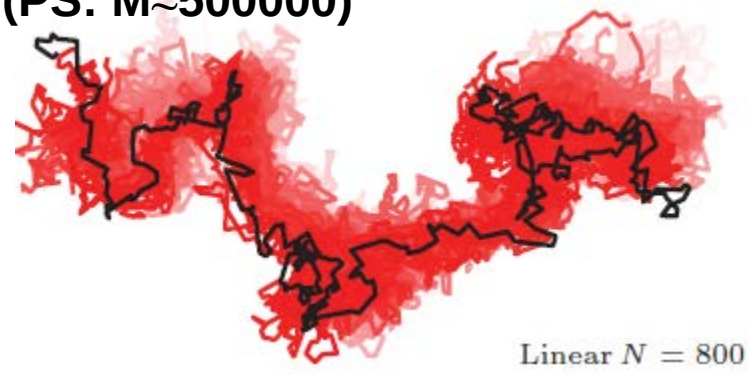
v=1/3

J. Halverson, G.S. Grest, A. Grosberg, KK, PRL 2012

cf A. Y. Grosberg, Soft Matter 20

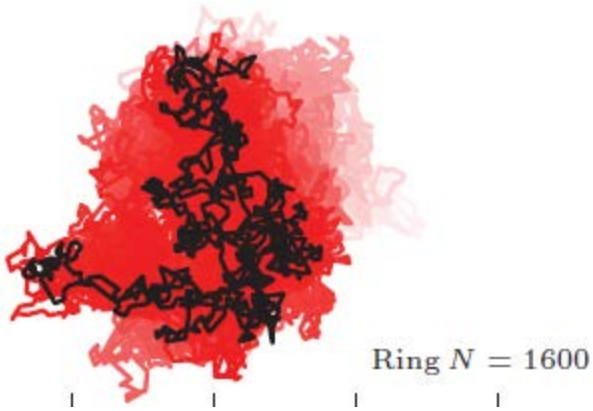


Linear, N=800 ≈ 29 $N_e$
(PS: M≈500000)

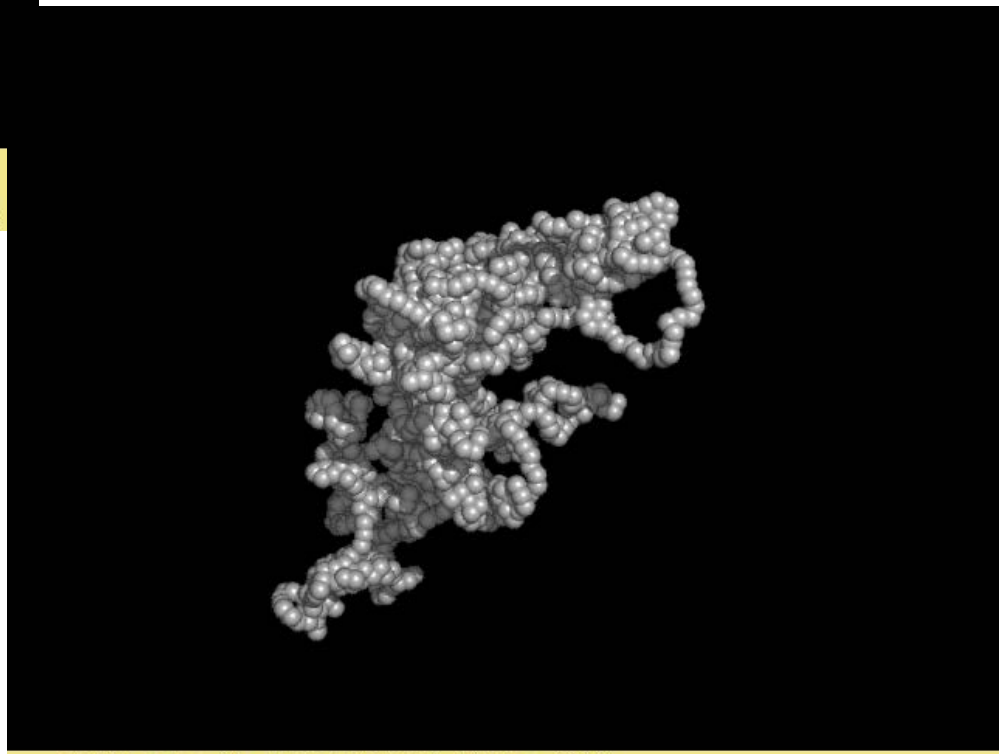



chain id = 78, monomers per chain = 800

time = 5.664e+06 tau  Rg(t)/<Rg> = 1.22  sqrt[g3(t)]/<Rg> = 0.00



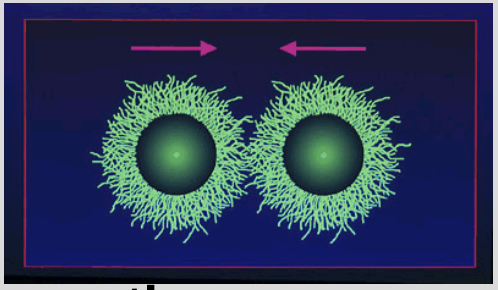

Ring, N=1600
(PS: M≈1000000)



chain id = 29, monomers per ring = 1600

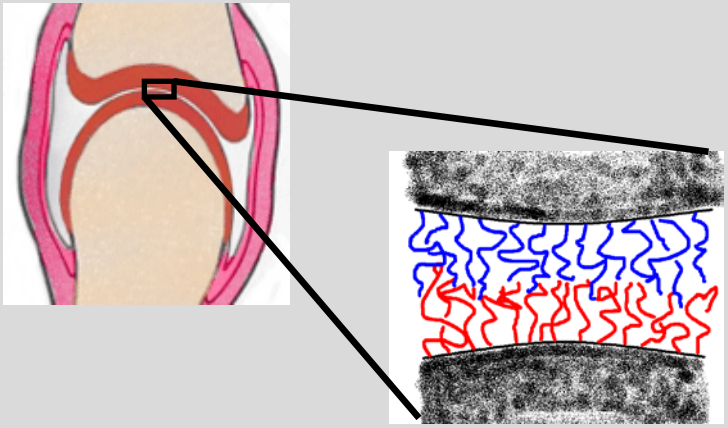
time = 1.00e+04 tau  Rg(t)/<Rg> = 1.13  sqrt[g3(t)]/<Rg> = 0.00

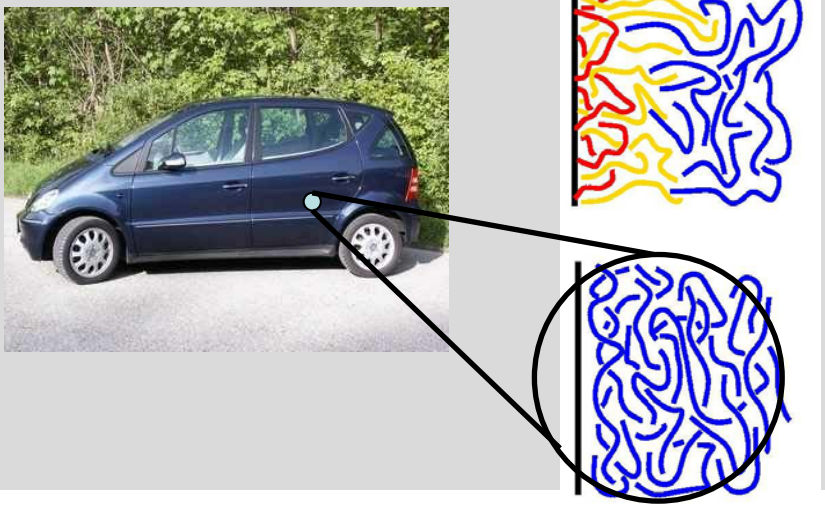
# Surfaces



**Back to Spin analogy:**

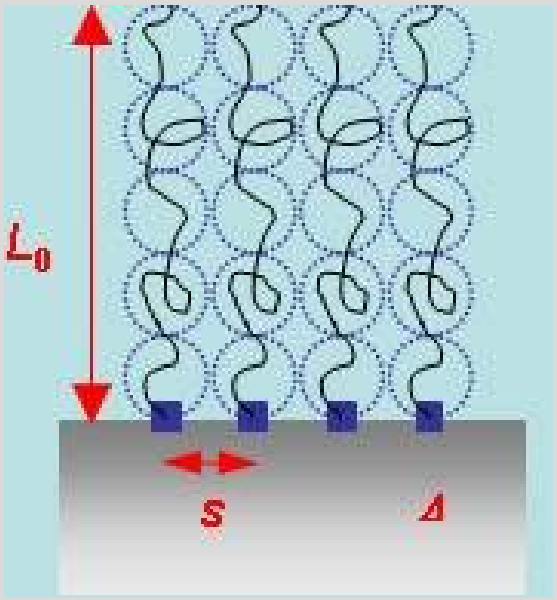
**- Adsorption of polymers, wetting of polymers**
**- Adsorption of a single chain – relation to surface magnetism**

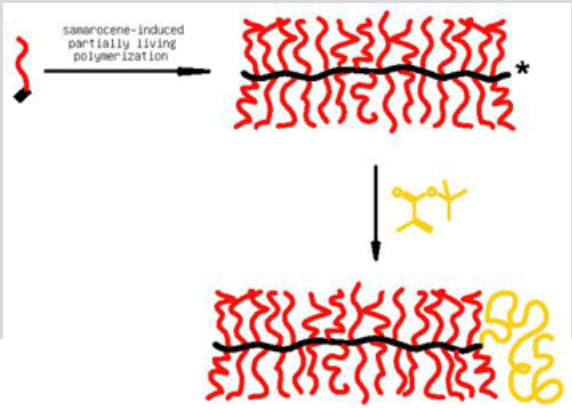




# Soft Matter - Polymers

## Many chains close to surfaces: Brushes



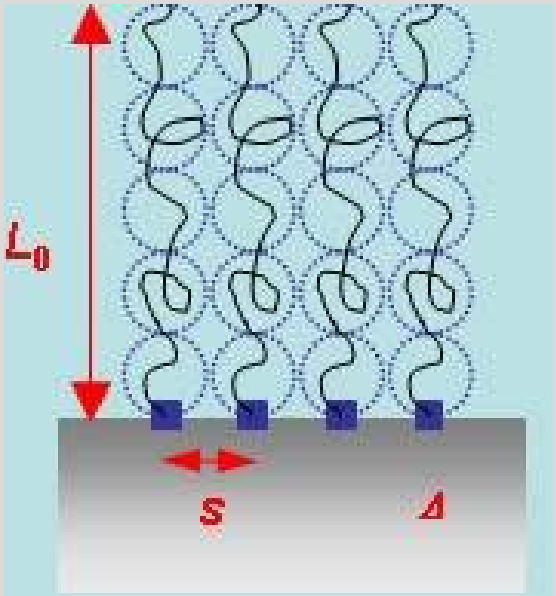




## Bottle – Brushes

**M. Schmidt et al, K. Binder, H.P. Hsu, W. Paul et al, SFB625**

# Soft Matter - Polymers

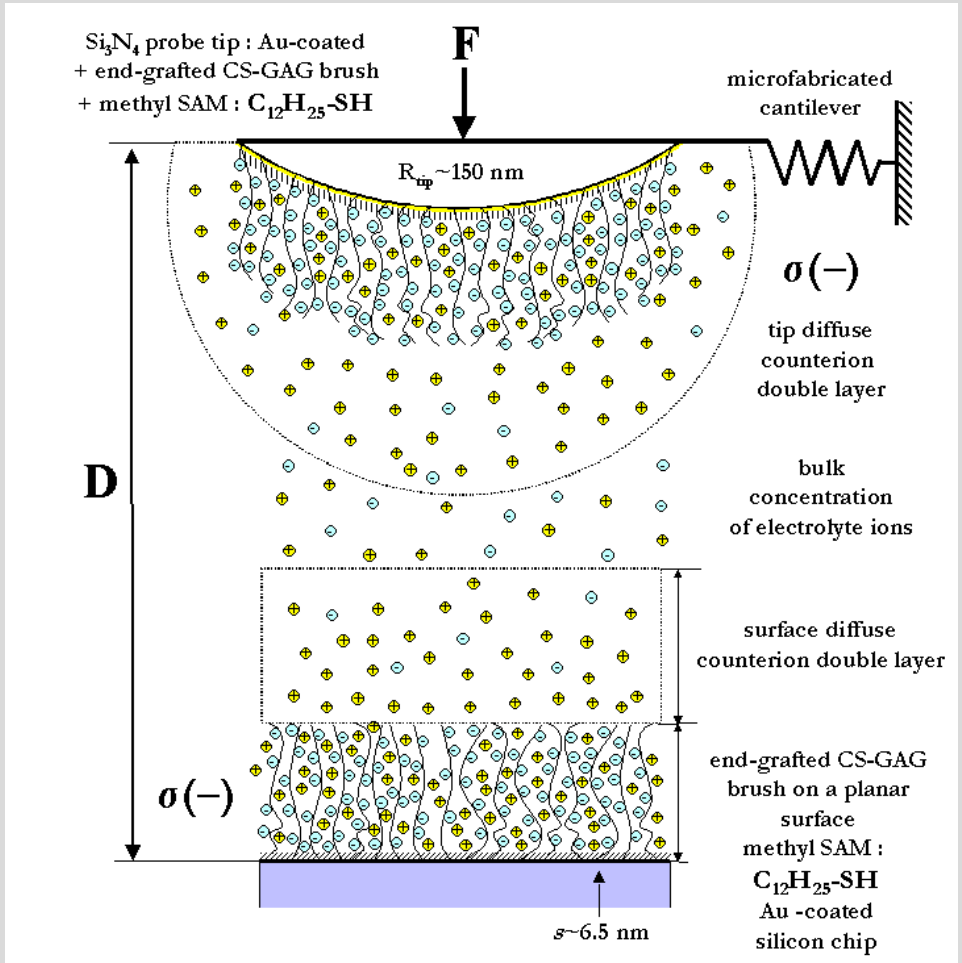
## Many chains close to surfaces: Brushes



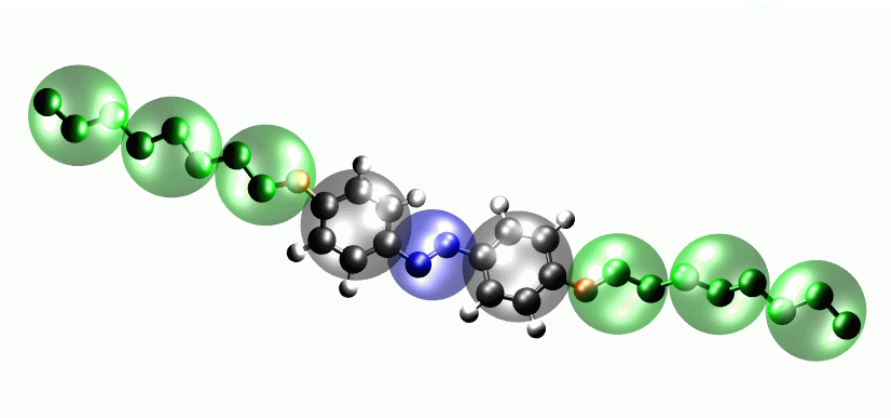

e.g. J. Klein et al

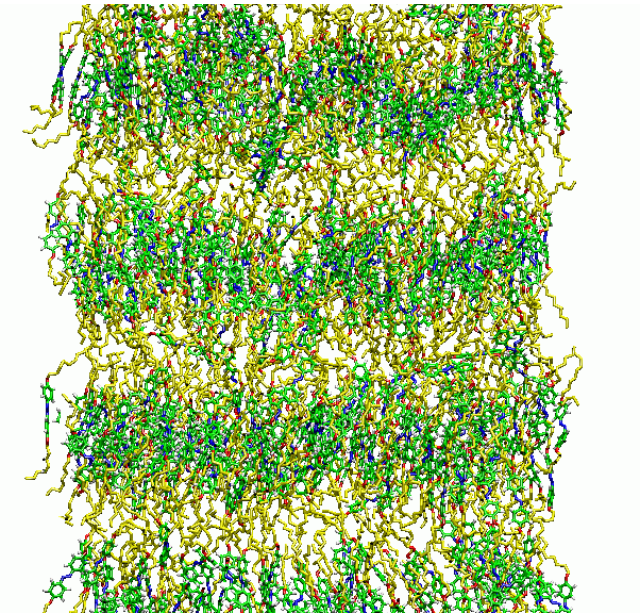
**Forces between surfaces etc.**

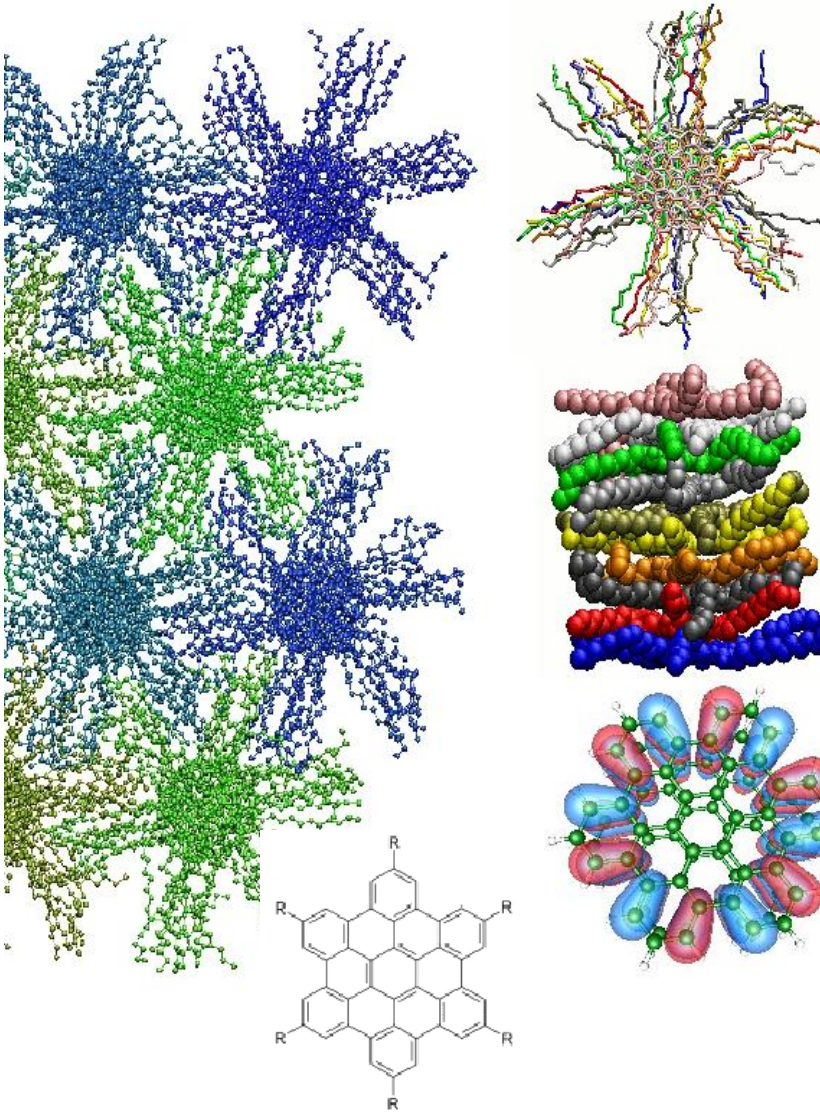
**Wetting phenomena …**
**SCF Theory, simulations…**



# Goal: Application to complex systems





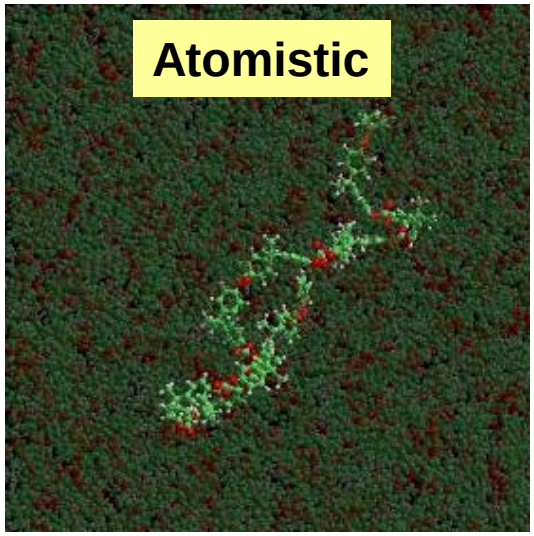



C. Peter et al, Soft Mat. 2008

Andrienko et al, PRL 2007,Nature Mat. 2009

# Polymers

## relevant interactions well defined

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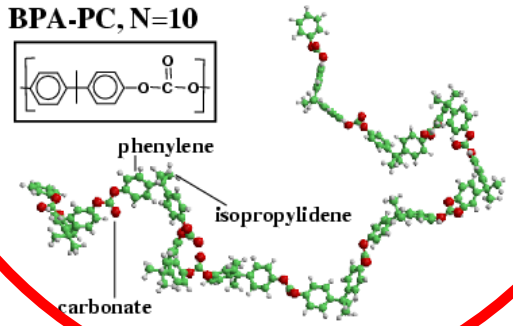
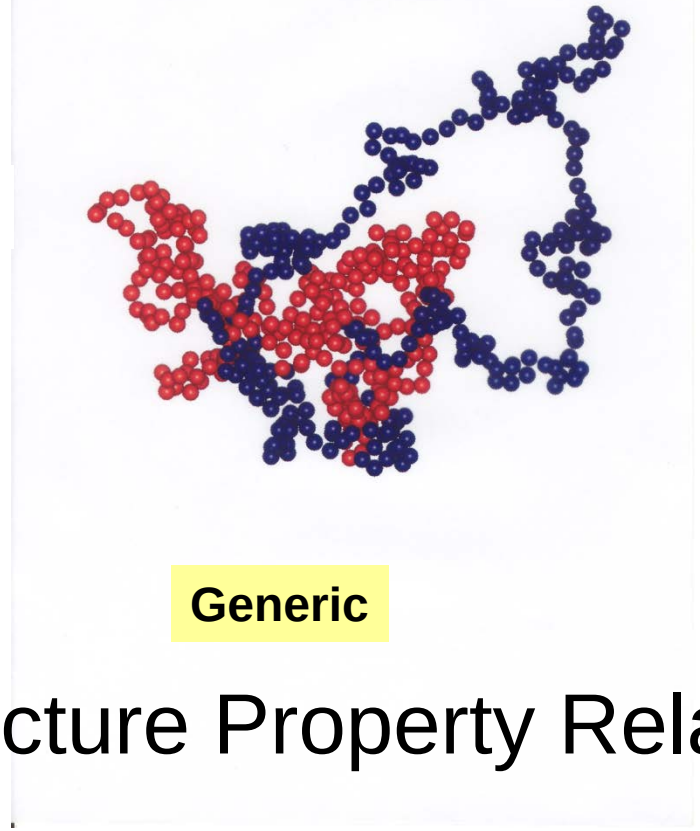



versus

## *Scaling Laws*

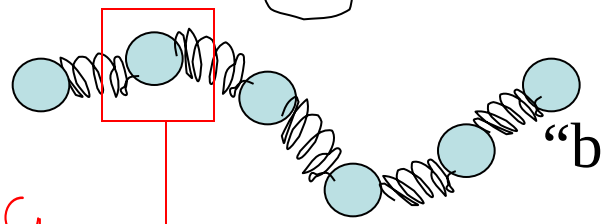



...

Structure Property Relations

# Polymers
## "oil soluble"


"path" in space



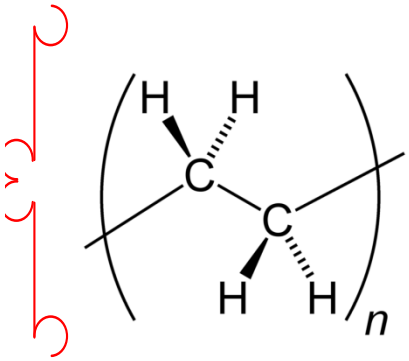
"bead spring" chain

**PE**

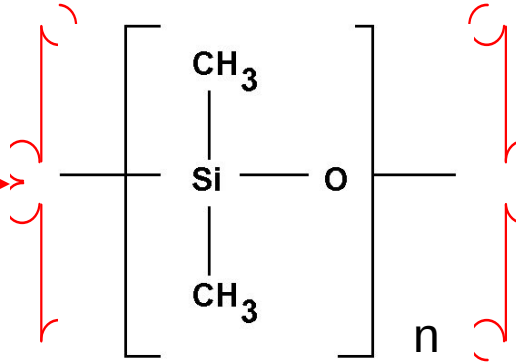
$N_e \approx 50$

$M_e \approx 1400$

$T_G \approx 150K$




**PDMS**




$M_e \approx 9000$

$N_e \approx 120$

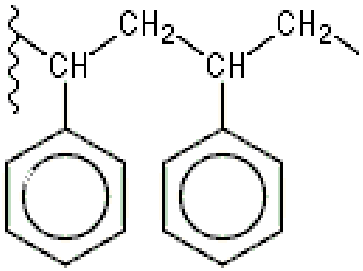
$T_G \approx 160K$

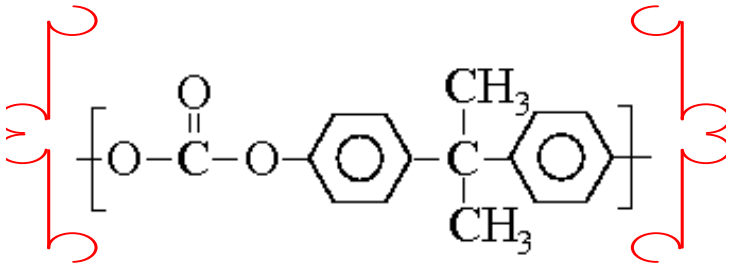
**PS**

$M_e \approx 18000$

$N_e \approx 170$

$T_G \approx 370K$




**BPAPC**

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

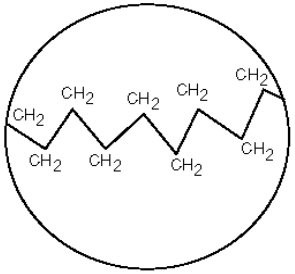
$T_G \approx 420K$

# Glass transition temperature $T_G$ of polymers

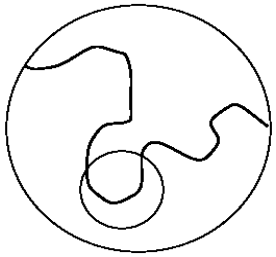
| Polymer | $T_G$ (K) |
|---|---|
| **Polyethylene (LDPE)** | **150K** |
| Polypropylene (PP, atactic) | 250K |
| Poly(vinyl acetate) (PVAc) | 300K |
| Polyethylene terephthalate (PET) | 350K |
| Poly(vinyl alcohol) (PVA) | 360K |
| Poly(vinyl chloride) (PVC) | 355K |
| Polystyrene (PS) | 370K |
| Polypropylene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

**Most polymers are glassy at room temperature**

# Example Viscosity $\eta = AN^x$ of a polymer melt (extrusion processes ....)




↕



**Microscopic** — **materials/ chemistry specific Prefactor**

**L ≅ 1Å – 3Å** (e.g. function of $T_G$, glass transition)

**T ≅ $10^{-13}$ sec** $\eta = A\,N^x$

**"Energy dominated"**

**Mesoscopic** — **generic/universal Properties**

**L ≅ 10Å – 50Å** $\eta = A\,N^x$ **X = 3.4**

**T ≅ $10^{-8}$ – $10^{-4}$ sec** **M molecular weight**

**"Entropy dominated"**

$\eta = A\,N^x$

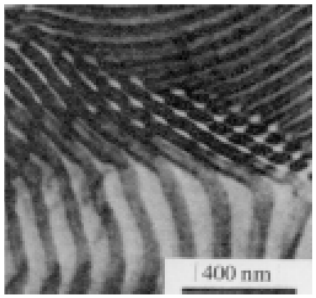
**varies many decades**

**e.g.: increase η =>10η**

**specific: T=500K => 470K (BPA-PC)**

**generic: N => 2N**

# Time and length scales

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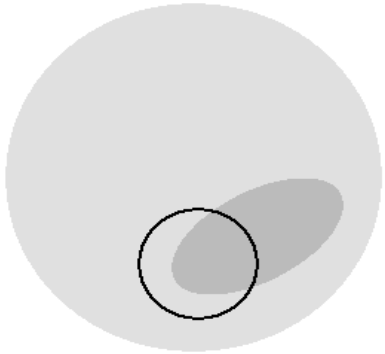
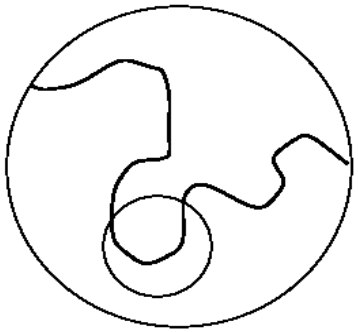


⇔

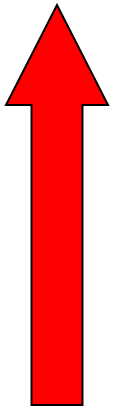


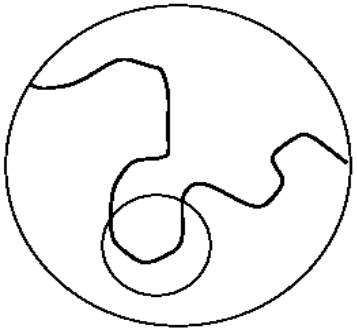
**Macroscopic domains etc.**

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

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

**Material Properties**





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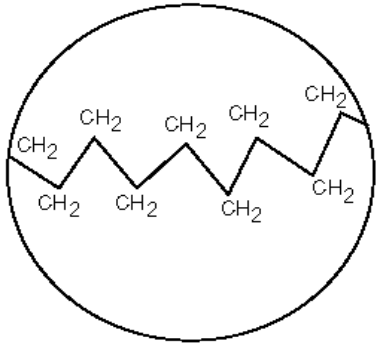
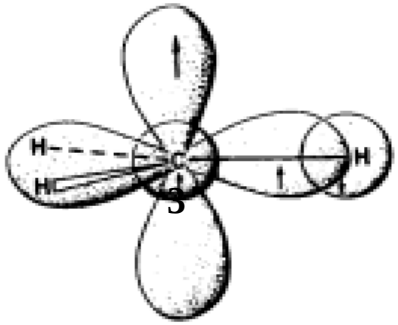



⇔



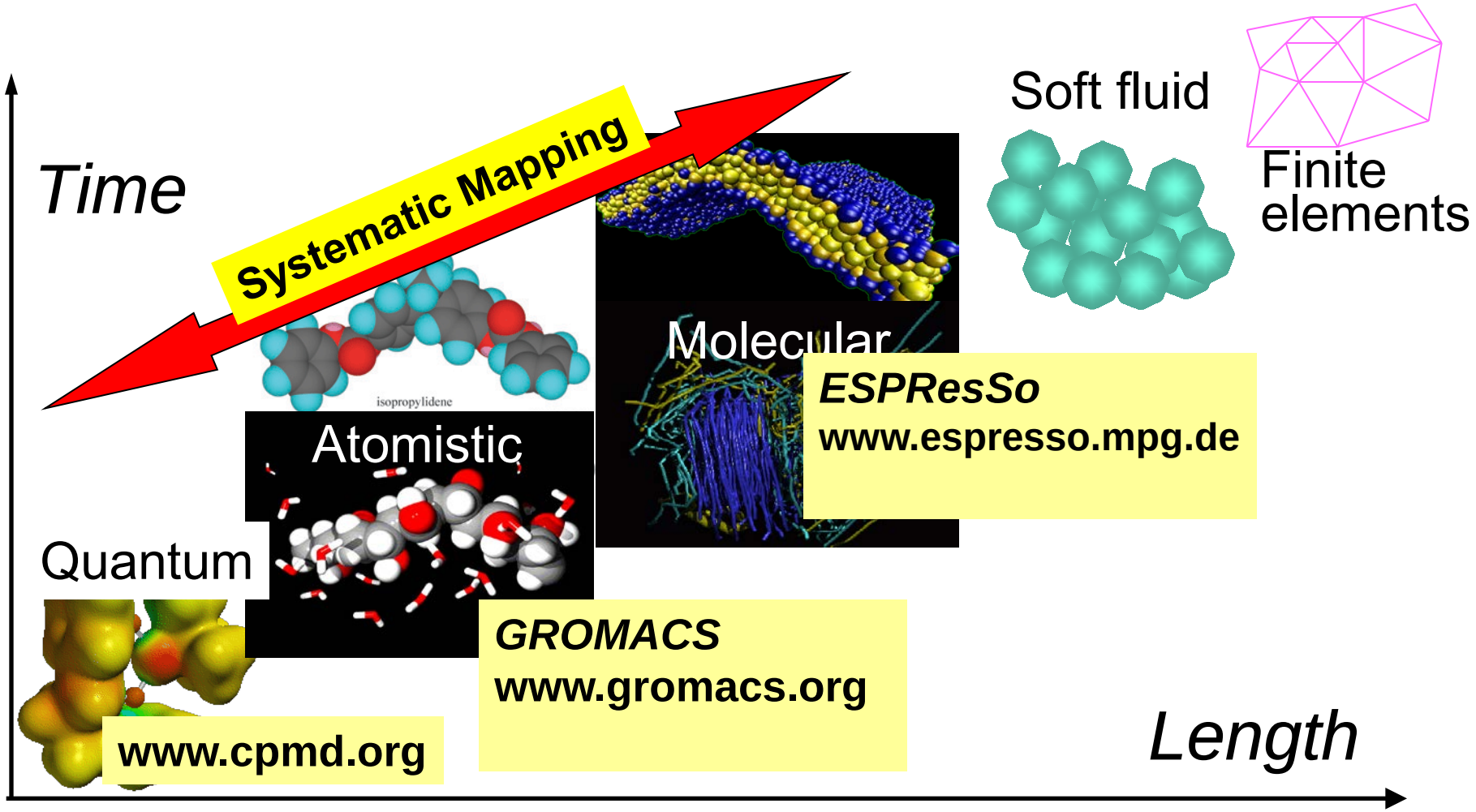

**Mesoscopic**
**L ≈ 10Å - 50Å**
**T ≈ $10^{-8}$ - $10^{-4}$ sec**
**Entropy dominates**

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

**(Sub)atomic**
**electronic structure**
**chemical reactions**
**excited states**

**generic/universal AND chemistry specific**

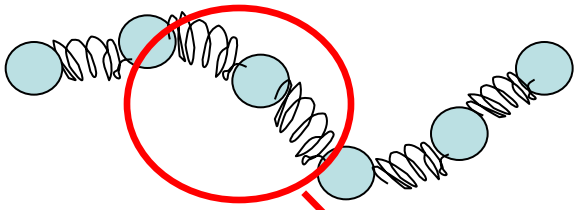
# Characteristic Time and Length Scales



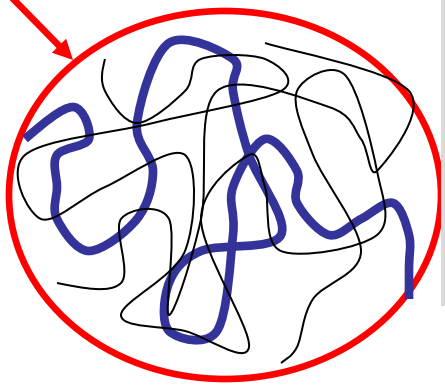

Local Chemical Properties --- Scaling Behavior of Nanostructures
Energy Dominance --- Entropy Dominance of Properties

# Detour: Rouse Reptation – Most Basic Aspects

## "Rouse Model" 1953



"bead spring" chain



**entropic spring**

**viscous background**

**Brownian dynamics of chain (random walk) of harmonic springs:**

$$\zeta \dot{r}_i = \frac{3kT}{l^2}(2r_i - r_{i-1} - r_{i+1}) + f_i$$

$$\left\langle f_i(t)\, f_j(t') \right\rangle = 2dkT\delta_{ij}\delta(t-t')$$

# Rouse model

**Rouse Modes**

$$X_p(t) = \frac{1}{N-1}\sum_{i=1}^{N-1} r_i(t)\cos\left(\frac{p\pi(i+1/2)}{N-1}\right)$$

$$p = 0,1,2,3,\ldots$$

**Equation of motion**

$$\varsigma_p \dot{X}_p = k_p X_p + f_p$$

**Relaxation time**

$$\tau_p = \frac{\varsigma\left\langle R^2(N)\right\rangle^2}{3\pi^2 l l_K k_B T p^2} \propto \frac{N^2}{p^2}$$

$$\tau_{Rouse} = \tau_{p=1}$$

# Rouse model

**Modulus**

$$G(t) = \frac{\rho k_B T}{N} \sum_p \exp(-2tp^2 / \tau_R)$$

**Viscosity**

$$\eta = \int_0^\infty G(t)dt = \rho\varsigma \frac{\langle R^2 \rangle}{36} \propto N$$

**Chain diffusion constant**

$$D = \frac{k_B T}{N\varsigma}$$

**Agrees to experiments of short chains**

# Rouse model

**Networks!!**
**(classical)**

**Modulus**

$$G(t) = \frac{\rho k_B T}{N} \sum_p \exp(-2tp^2 / \tau_R)$$

**viscosity**

$$\eta = \int_0^\infty G(t)dt = \rho\varsigma \frac{\langle R^2 \rangle}{36} \propto N$$

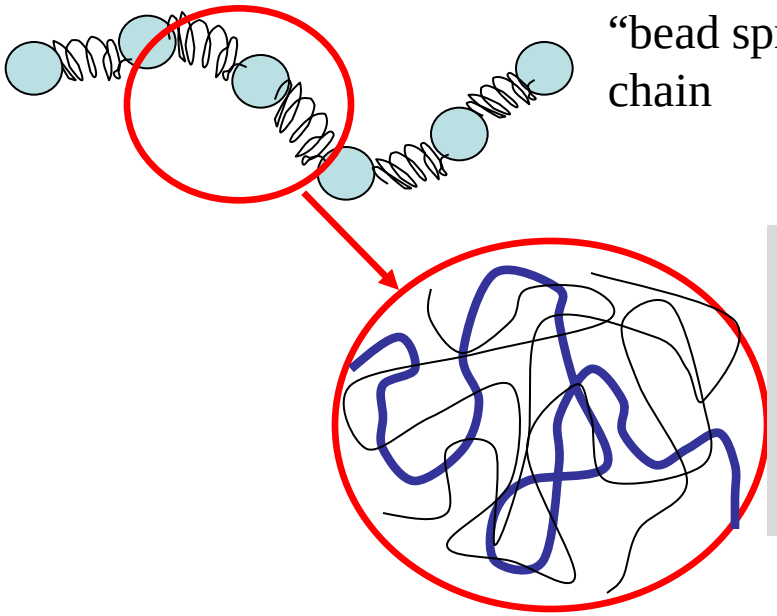
**Chain diffusion constant**

$$D = \frac{k_B T}{N\varsigma}$$

**Agrees to experiments of short chains**

# Mean square displacements

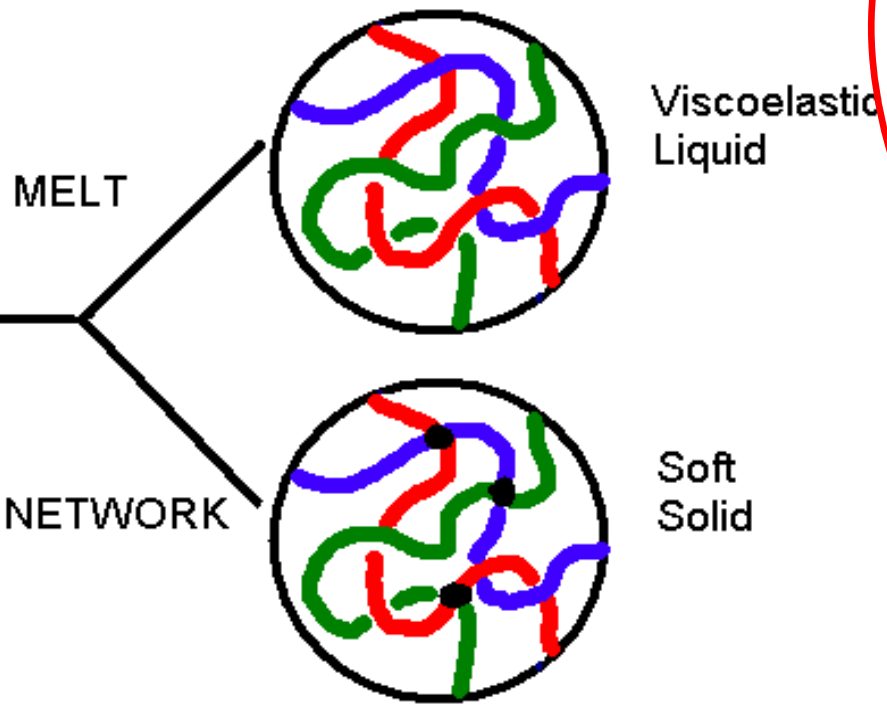
## “Rouse Model”1953

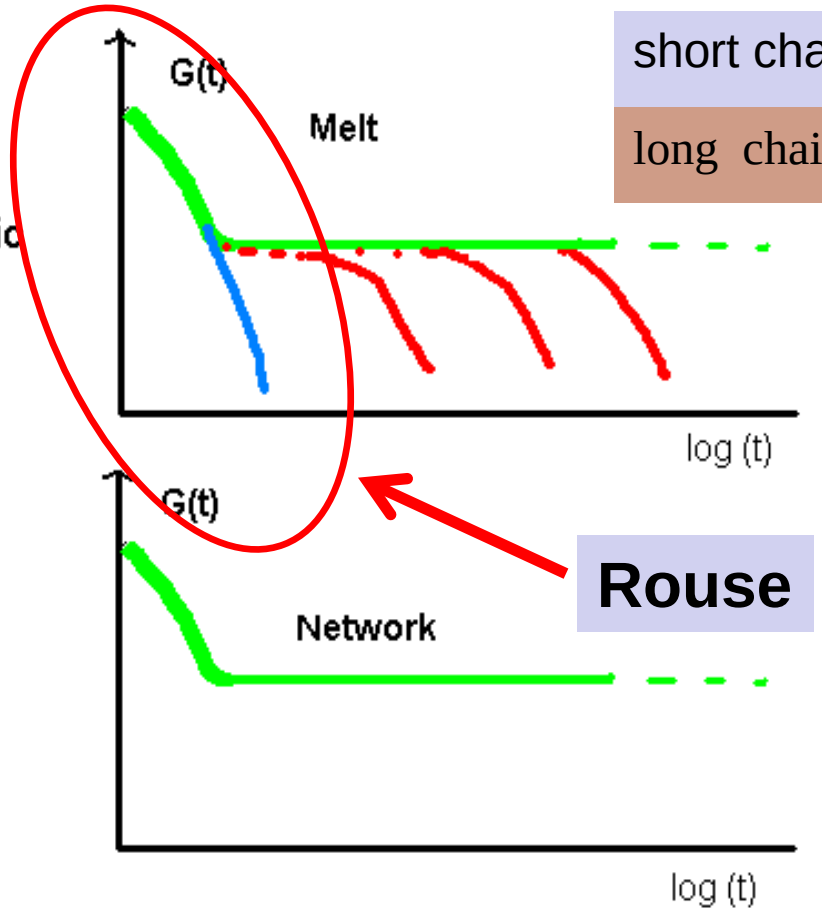



**Brownian dynamics of chain of harmonic springs:**

$$g_1(t) = \left\langle (r_i(t) - r_i(0))^2 \right\rangle \propto \begin{cases} t, & t < \tau_0 \\ t^{1/2}, & \tau_0 < t < \tau_R \\ t, & t > \tau_R \end{cases}$$

# MELT ←→ NETWORK

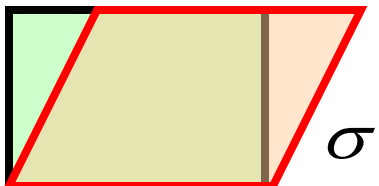



short chains

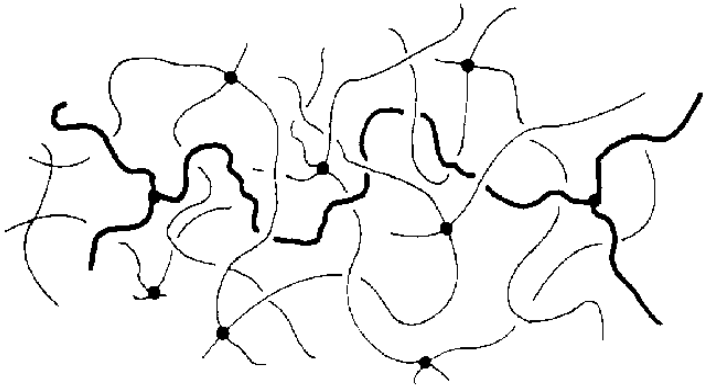
long chains

G(t): Time dependent (shear) modulus:

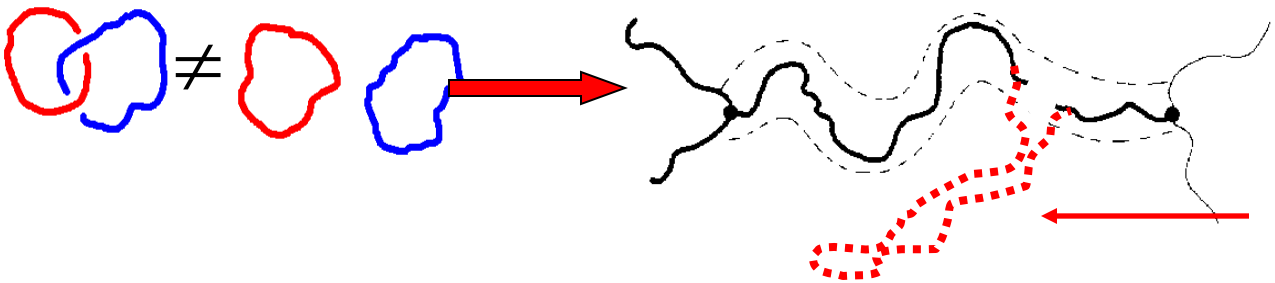


$$\sigma(t) = G(t)(\lambda - 1)$$

# Tube Model



Edwards `67



"Tube leakage": Entropy penalty for defects too large

De Gennes `71

$$d_T \propto N_e^{1/2}$$

$$G^0 \propto N_e^{-1}$$

*Unique length* $d_T$

**Rouse model subject to tube constraints**

## Polymer Melts

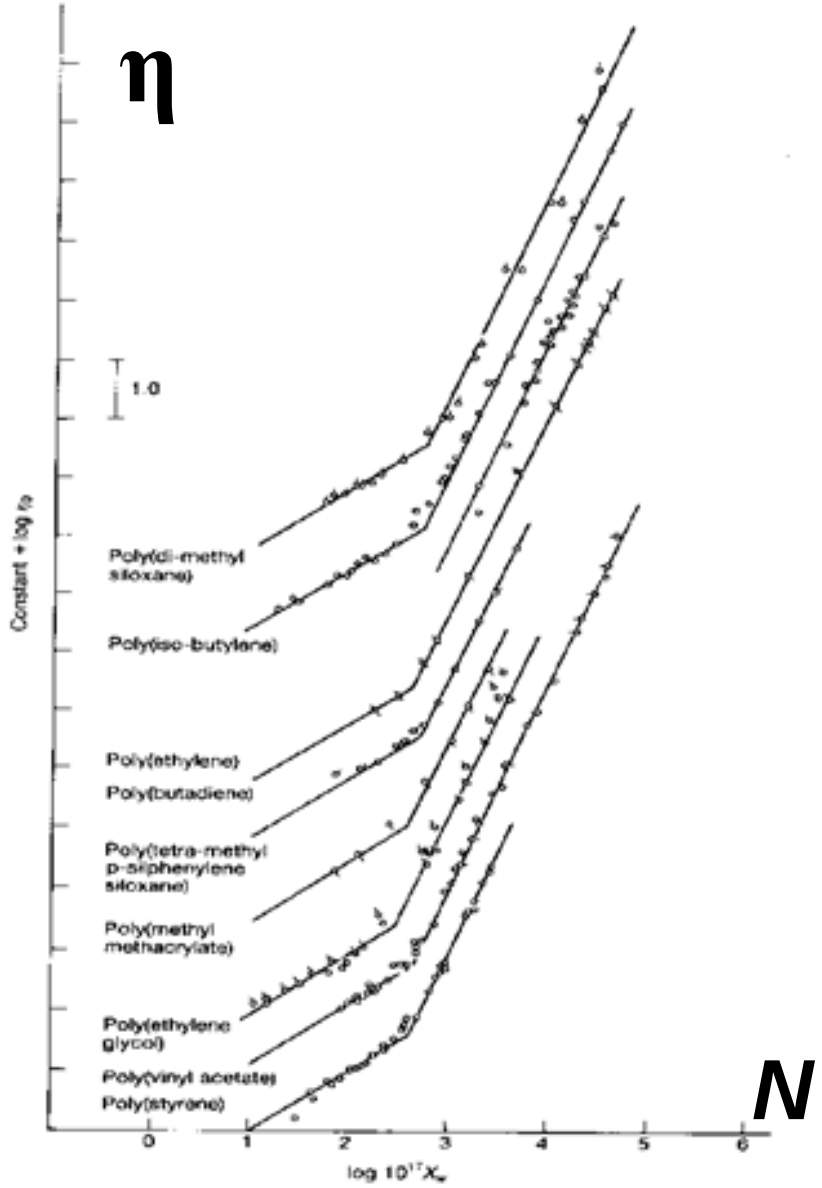
**Short Chains N < $N_e$** | **$N_e$ < N Long Chains**

| | | |
|---|---|---|
| $D \propto N^{-1}$ | Diffusion | $D \propto N^{-2}$ |
| $\tau_R \propto N^2$ | Relaxation Time | $\tau_d \propto N^{3....}$ |
| $\eta \propto N^1$ | Viscosity | $\eta \propto N^{3.4}$ |
| $G^0 = 0$ | Modulus | $G^0 \sim \frac{kT}{N_e} \propto N^0$ |
| | | $(t << \tau_d)$ |

- **Rouse** Model
  - Chain motion subject
  - background and heat bath
- **Reptation** Model
  - Chain motion subject to
  - **TUBE CONCEPT**

**UNIVERSAL PROPERTIES**

# Melt viscosity vs chain length

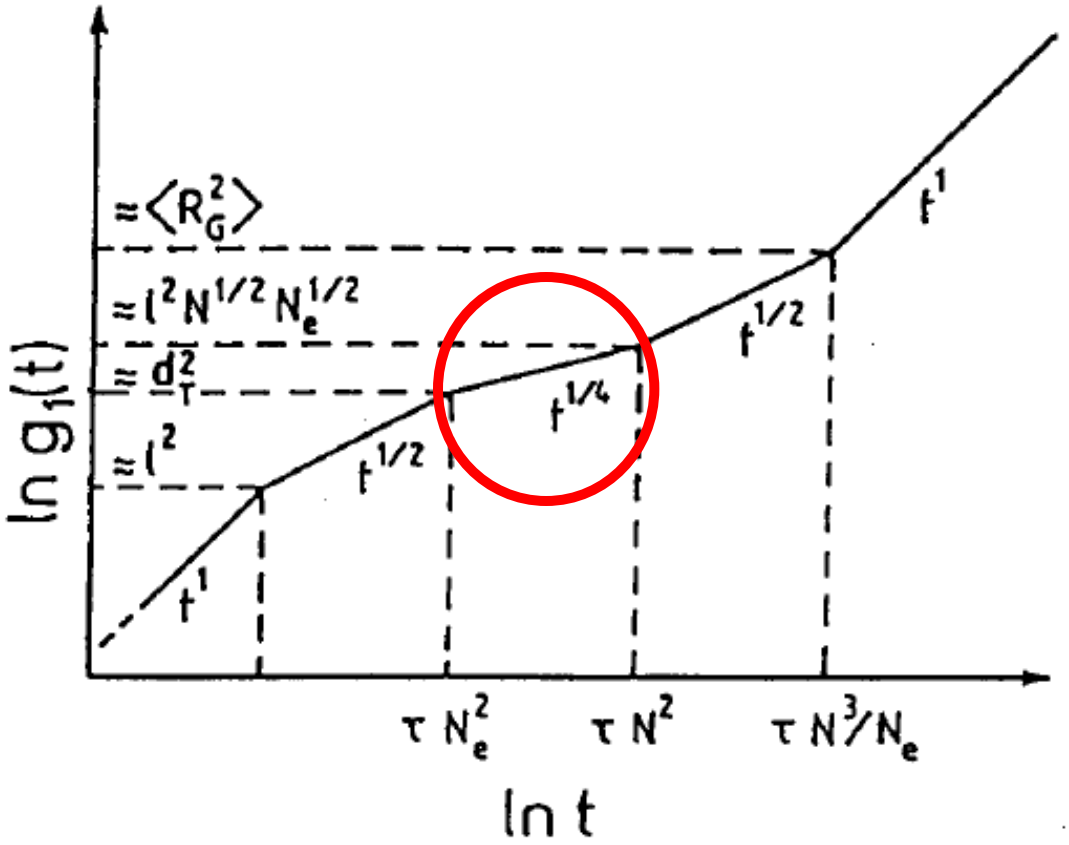



From Doi and Edwards

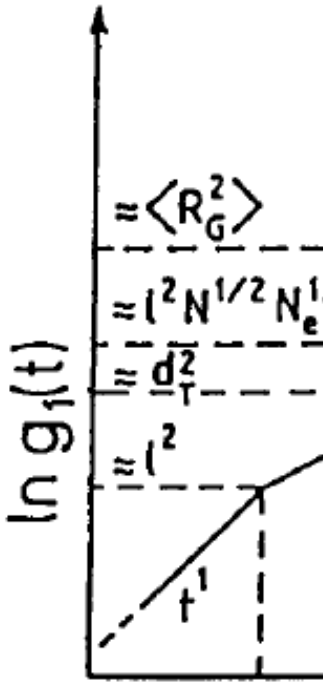
# Mean square displacements: reptation

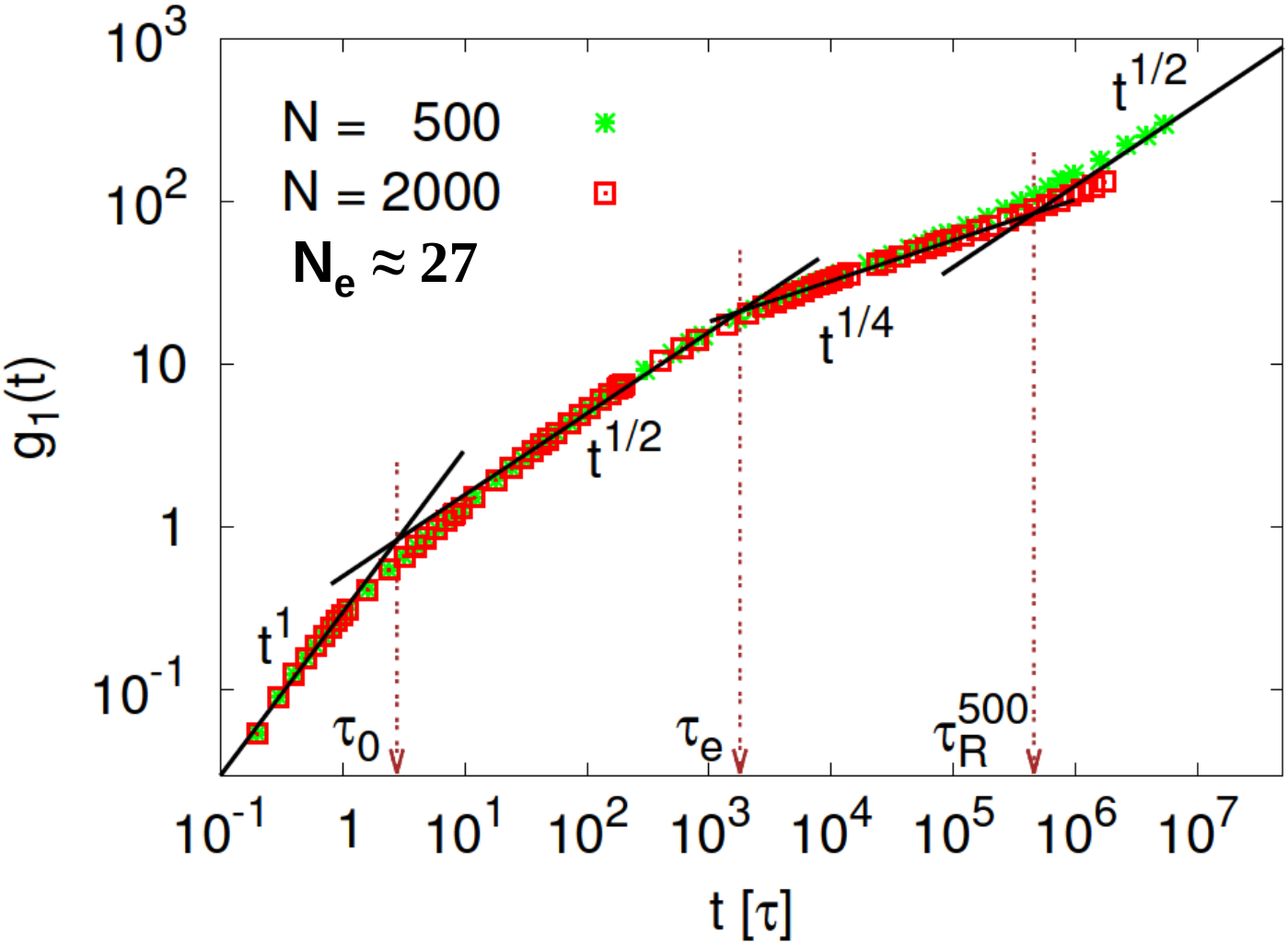
$$g_1(t) = \left\langle (r_i(0) - r_i(t))^2 \right\rangle \propto \begin{cases} t, & t < \tau_0 \\ t^{1/2}, & \tau_0 < t < \tau_e \approx N_e^2 \\ t^{1/4}, & \tau_e < t < \tau_R \approx N^2 \\ t^{1/2}, & \tau_R < t < \tau_d \approx N^3 / N_e \\ t, & t > \tau_d \end{cases}$$

$$g_3(t) = \left\langle (r_{cm}(t) - r_{cm}(0))^2 \right\rangle \propto \begin{cases} t, & t < \tau_e \\ t^{1/2}, & \tau_e < t < \tau_R \\ t, & t > \tau_R \end{cases}$$




**Famous $t^{1/4}$ power law for mean square displacement**

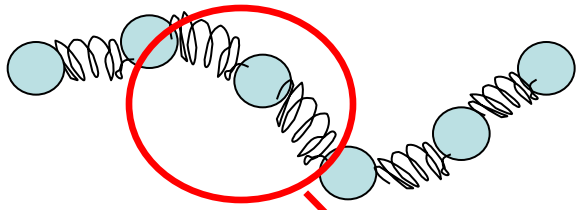

ln g1(t)
≈⟨R_G^2⟩
≈l^2 N^1/2 N_e^1
≈d_T^2
≈l^2
t^1


g1(t)
N = 500
N = 2000
N_e ≈ 27
t^1
t^1/2
t^1/4
t^1/2
τ0
τe
τR^500
t [τ]

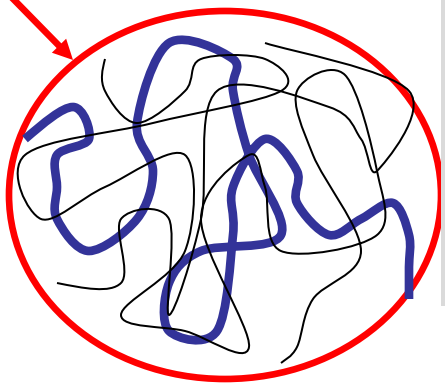
H. P. Hsu

# End Detour: Rouse Reptation – Most Basic Aspects

## "Rouse Model" 1953

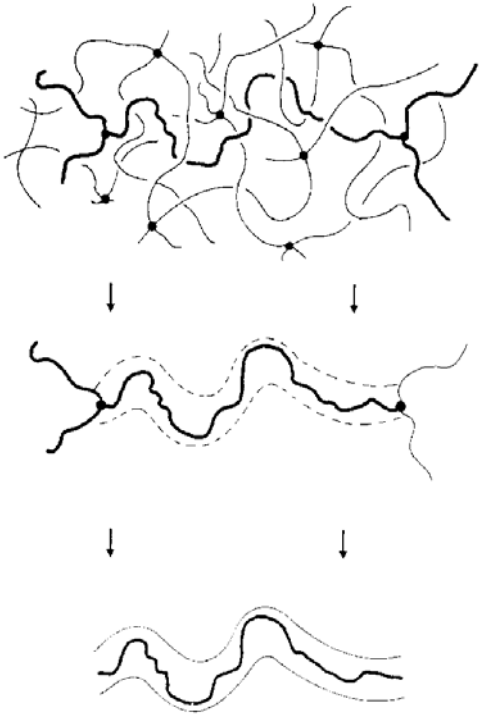


"bead spring" chain



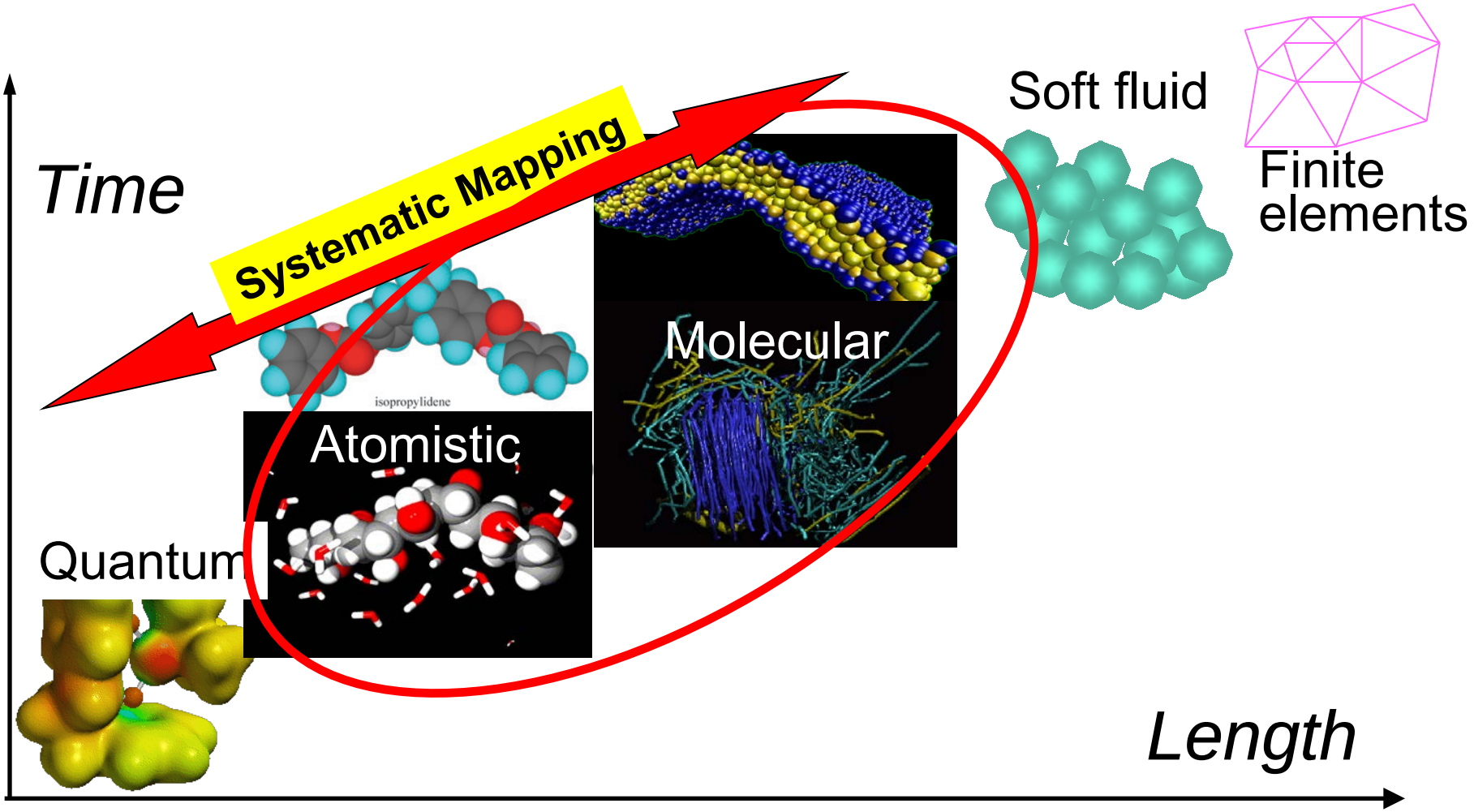
**entropic spring**

**viscous background**



## "Reptation/Tube Model" 1967,71

# Coarse Graining




Local Chemical Properties --- Scaling Behavior of Nanostructures

Energy Dominance --- Entropy Dominance of Properties

# Coarse Graining (CG)

**Micro-Meso Simulation**

**Interplay Energy ⇔ Entropy**

**Free Energy Scale: $k_B T$**

***atomistic model => parameterize cg model***

***Different general strategies:***

**Structure based**

**Force based**

**Potential based**

***Methods to calculate CG interactions:***

**(Iterative) Boltzmann Inversion**

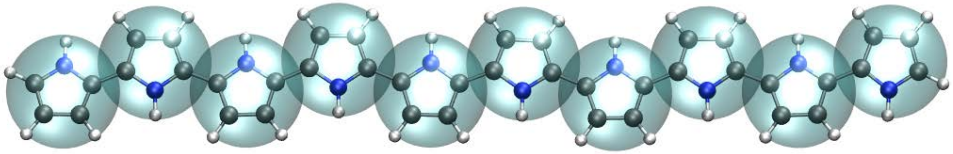
**Inverse MC,**

**Force Matching**

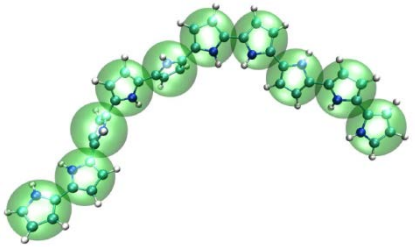
**Relative Entropy**

# Coarse-graining of atomistic systems

Atomistic system (polypyrrole chain)



Coarse-grained system (10 PPY repeat units)



$$\boldsymbol{r}^n = \{\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n\}$$

$$\boldsymbol{p}^n = \{\boldsymbol{p}_1, \ldots, \boldsymbol{p}_n\}$$

$$h(\boldsymbol{r}^n, \boldsymbol{p}^n) = \sum_{i=1}^{n} \frac{1}{2m_i} \boldsymbol{p}_i^2 + u(\boldsymbol{r}^n)$$

$$\boldsymbol{R}^N = \{\boldsymbol{R}_1, \ldots, \boldsymbol{R}_N\}$$

$$\boldsymbol{P}^N = \{\boldsymbol{P}_1, \ldots, \boldsymbol{P}_N\}$$

$$H(\boldsymbol{R}^N, \boldsymbol{P}^N) = \sum_{I=1}^{N} \frac{1}{2M_I} \boldsymbol{P}_I^2 + U(\boldsymbol{R}^N)$$

canonical ensemble (NVT)

$$p_{rp}(\boldsymbol{r}^n, \boldsymbol{p}^n) = p_r(\boldsymbol{r}^n) p_p(\boldsymbol{p}^n)$$

$$p(\boldsymbol{r}^n) \sim \exp[-\beta u(\boldsymbol{r}^n)]$$

$$p(\boldsymbol{p}^n) \sim \exp\left[-\beta \sum_{i=1}^{n} \frac{\boldsymbol{p}_i^2}{2m_i}\right]$$

$$P_{RP}(\boldsymbol{R}_N, \boldsymbol{P}_N) = P_R(\boldsymbol{R}_N) P_P(\boldsymbol{P}_N)$$

$$P(\boldsymbol{R}_N) \sim \exp[-\beta U(\boldsymbol{R}^N)]$$

$$P(\boldsymbol{P}_N) \sim \exp\left[-\beta \sum_{I=1}^{N} \frac{\boldsymbol{P}_I^2}{2M_I}\right]$$

W. Noid et al., J. Chem. Phys. 120, 244114 (2008)

# Basic standard methods

- **Boltzmann inversion (structure based cg)**

The idea of Boltzmann inversion stems from the fact that in a canonical ensemble *independent* degrees of freedom $q$ obey the Boltzmann distribution, i. e.

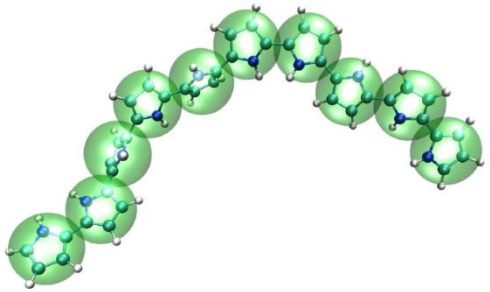
$$P(q) = Z^{-1} \exp\left[-\beta U(q)\right] \ , \tag{2.19}$$

where $Z = \int \exp\left[-\beta U(q)\right] \mathrm{d}q$ is a partition function, $\beta = 1/k_{\mathrm{B}}T$. Once $P(q)$ is known one can invert eq. 2.19 and obtain the coarse-grained potential, which in this case is a potential of mean force

$$U(q) = -k_{\mathrm{B}}T \ln P(q) \ . \tag{2.20}$$

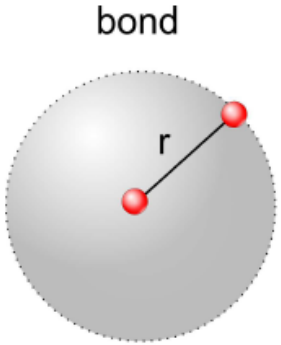
**Apply this concept to g(r), the radial distribution function**

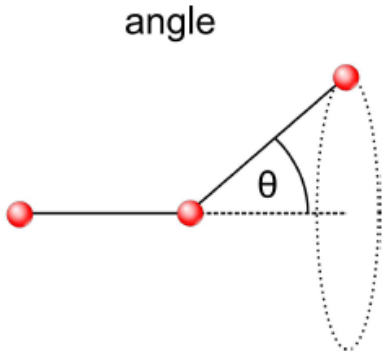
# Basic standard methods



- **Boltzmann inversion**

$$P(r,\theta,\varphi) = \exp\left[-\beta U(r,\theta,\varphi)\right]$$
$$P(r,\theta,\varphi) = P_r(r)P_\theta(\theta)P_\varphi(\varphi)\ .$$




$$U(r,\theta,\varphi) = U_r(r) + U_\theta(\theta) + U_\varphi(\varphi)\ ,$$
$$U_q(q) = -k_\mathrm{B}T \ln P_q(q),\ q = r,\theta,\varphi$$

**Hendersen Theorem: unique correspondence between U(r) and g(r)**

**Potential is state point dependent**

# Basic standard methods

- **Iterative Boltzmann inversion**

$$U^{(1)}(r) = -k_{\mathrm{B}}T \ln g(r)$$

$$\begin{aligned} U^{(n+1)} &= U^{(n)} + \Delta U^{(n)} \\ \Delta U^{(n)} &= k_{\mathrm{B}}T \ln \frac{P^{(n)}}{P_{\mathrm{ref}}} \end{aligned}$$

# Iterative Boltzmann Inversion

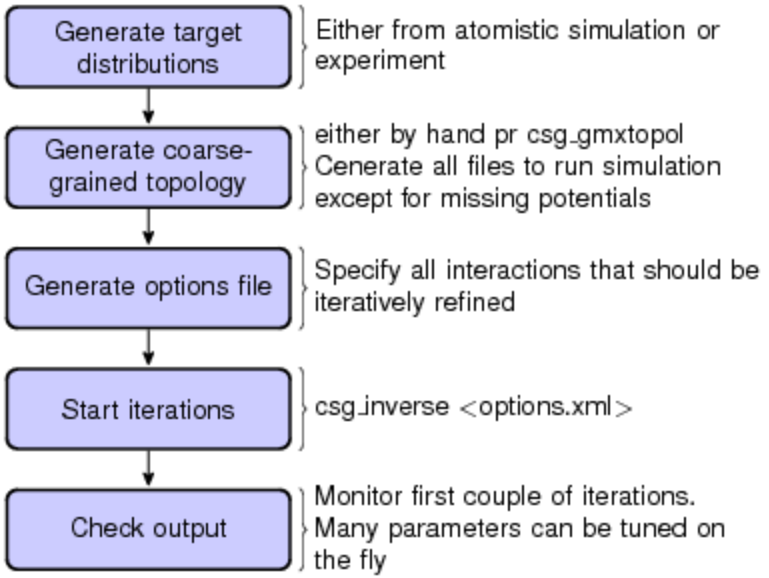
$S_\alpha$ are proportional to the radial distribution function

$$S_\alpha = \frac{N(N-1)}{2}\frac{4\pi r_\alpha^2 \Delta r}{V} g(r_\alpha)$$

$$A_{\alpha\gamma} = \beta\left(\langle S_\alpha\rangle\langle S_\gamma\rangle - \langle S_\alpha S_\gamma\rangle\right)$$

Ignore off-diagonal elements,
and take into account that for an ideal gas

$$\Delta U(r) = k_B T \ln \frac{g(r)}{g^{ref}(r)}$$




IBI: local, no correlations. Robust, but it is not clear how well it performs for mixtures.

D. Reith et al., J. Comp. Chem. 24 (13), 1624 (2003)

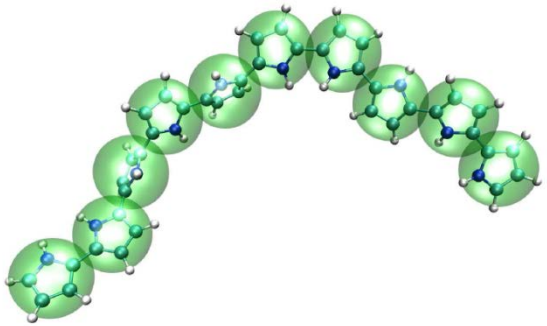
# Basic standard methods

- **Inverse Monte Carlo (Lyubartsev)**

**Similar concept as Boltzmann inversion, however sampling directly on the discretized potential u(r,…)**

**Automatically includes correlations (unlike factorization ansatz for Boltzmann inversion)**

**Numerically more demanding**



# Basic standard methods

- **Iterative Boltzmann inversion**
- **Inverse Monte Carlo (Lyubartsev)**

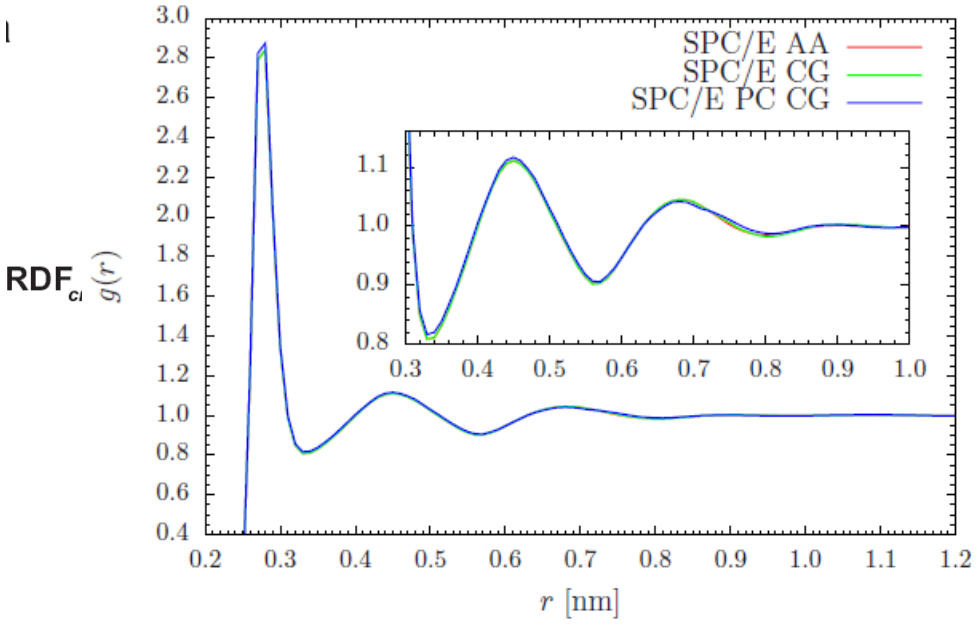
**Both structure based methods**

**Henderson Theorem: Unique relation between g(r) and U(r),**

**but potentials are state point dependent, not generally transferable**

**only g(r) is reproduced and thus the compressibility,**
**but not the pressure (i.e. thermodynamic properties)!**

# Structure based CG - Compressibility




SPC/E water,
cg based on matching g(r)

**Pressure**

$$P = \rho k\,T\; - {}^{2}/_{3}\,\pi\rho^{2}\int_{0}^{\infty} U'(r)g(r)r^{3}dr$$

**Compressibility**

$$\kappa_T = \frac{1}{\rho k_B T}\left(1 + 4\pi\rho\int_0^\infty r^2[g(r)-1]dr\right) = \frac{1}{\rho k_B T}\frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle}$$

# Basic standard methods

- **Iterative Boltzmann inversion**
- **Inverse Monte Carlo (Lyubartsev)**

Structure based
Coarse Graining:

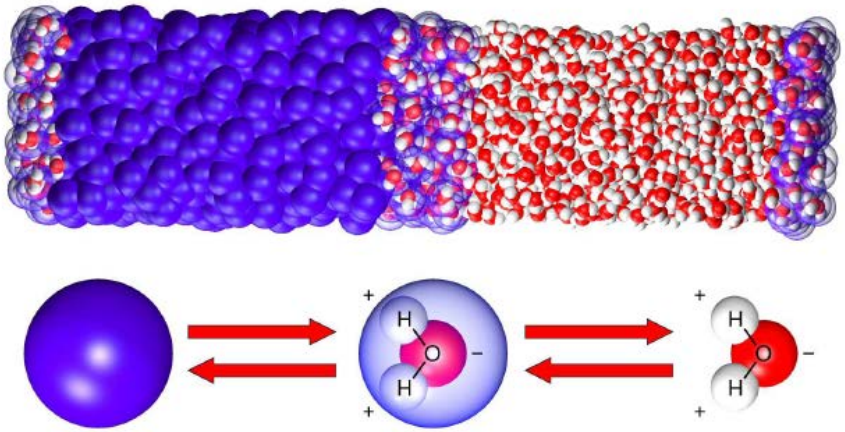
Perfect match of g(r)
all atom – coarse grained

$\kappa_{atomistic} = \kappa_{cg}$

***BUT***

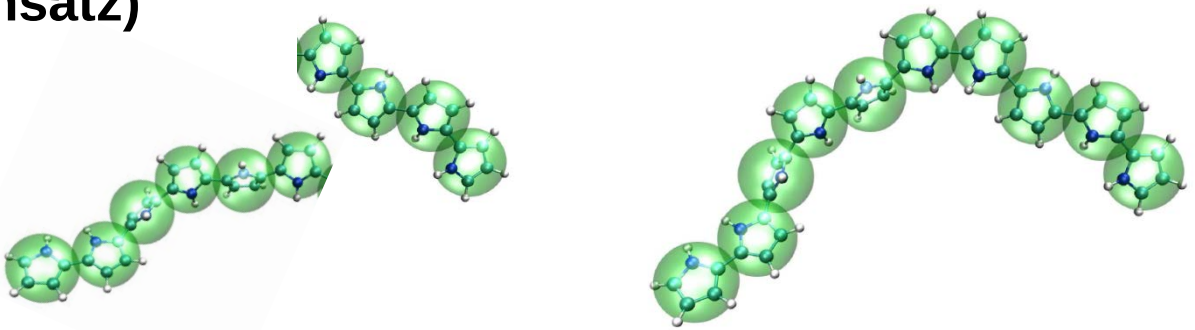
$p_{cg} = 6200 p_{atomistic}$

## Coarse Grained Water: SPC/E



# Basic standard methods: Force Matching

- **Ercolessi&Adams 1993, Noid&Voth et al JCP 2008ff (Martini Force Field follows similar ansatz)**



$$\vec{f}_i^{\,\mathrm{ref}} = M_i \sum_\alpha \frac{w_\alpha \vec{f}_\alpha}{m_\alpha}$$

**cg force** **AA forces**

$$\vec{R}_i = \sum_\alpha w_\alpha \vec{r}_\alpha$$

**Position of cg particle**

$$M_i = \left(\sum_\alpha w_\alpha^2 / m_\alpha\right)^{-1}$$

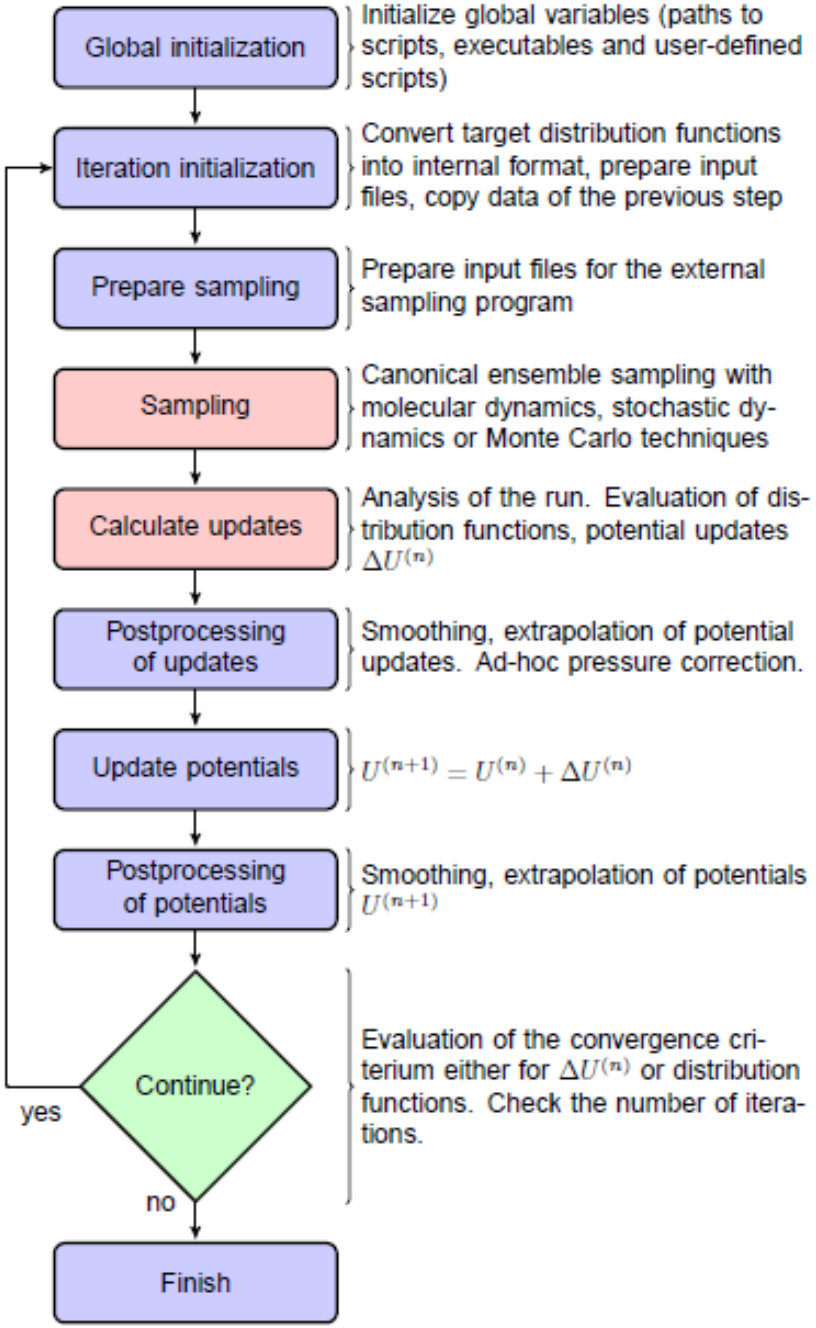
**mass of cg particle**

# VOTCA: Versatile Obj
# for Coarse-grainir

- **General ansatz:**
  - **n “atomistic”,**
  - **N cg particles**

$$\left.\begin{array}{l}\{\boldsymbol{r}_i\},\ i = 1,2,\ldots,n \\ \{\boldsymbol{R}_j\},\ j = 1,2,\ldots,N\end{array}\right\}$$

$$\Rightarrow \quad \boldsymbol{R} = \hat{M}\boldsymbol{r}$$




D. Andrienko et al, subm. 2009

# *Structure Based Coarse Graining*

**********

## *Coarse Graining (CG) <=> Inverse Mapping*

**Micro-Meso Simulation**

**Interplay Energy ⇔ Entropy**

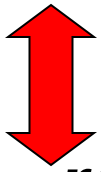
**Free Energy Scale: $k_B T$**

***atomistic model***

**=>** ***parameterize cg model***

**=>** ***run/analyze large system (melt etc)***

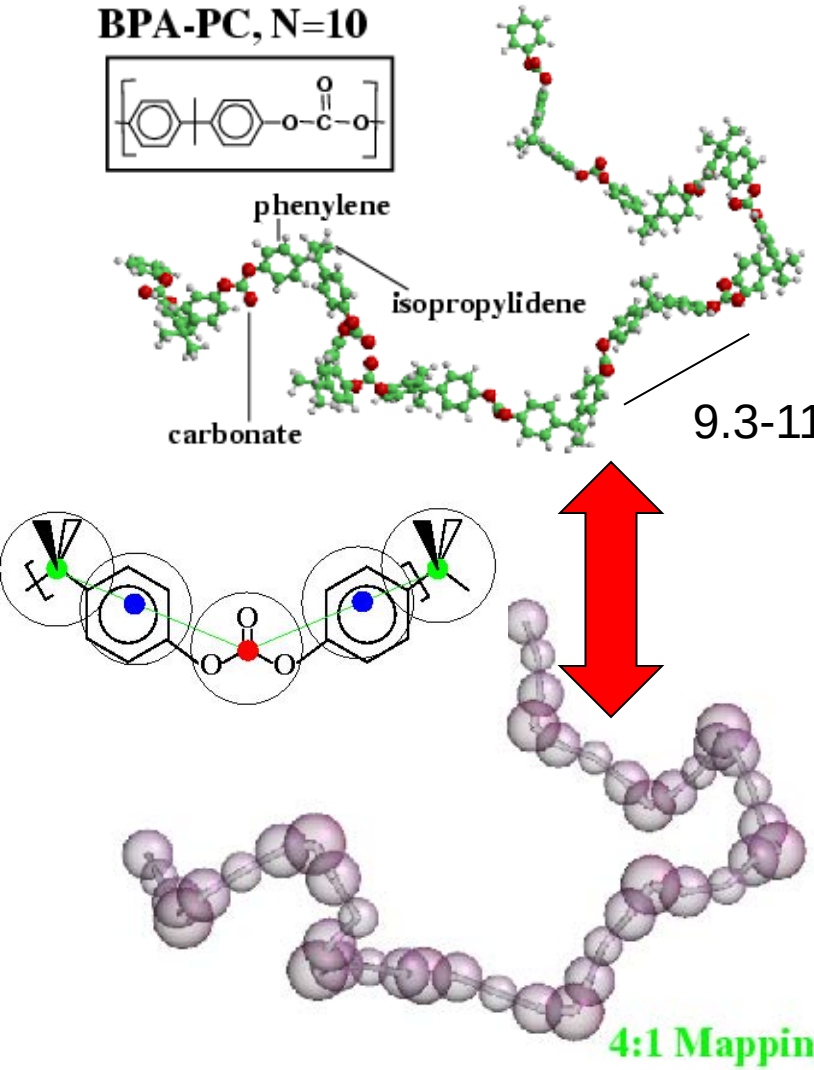
*"measurements" $R^2(N)$…*



***reintroduce details***

**=>** ***run/analyze atomistic system***

# Structure Based Molecular Coarse-Graining: Bisphenol-A-Polycarbonate

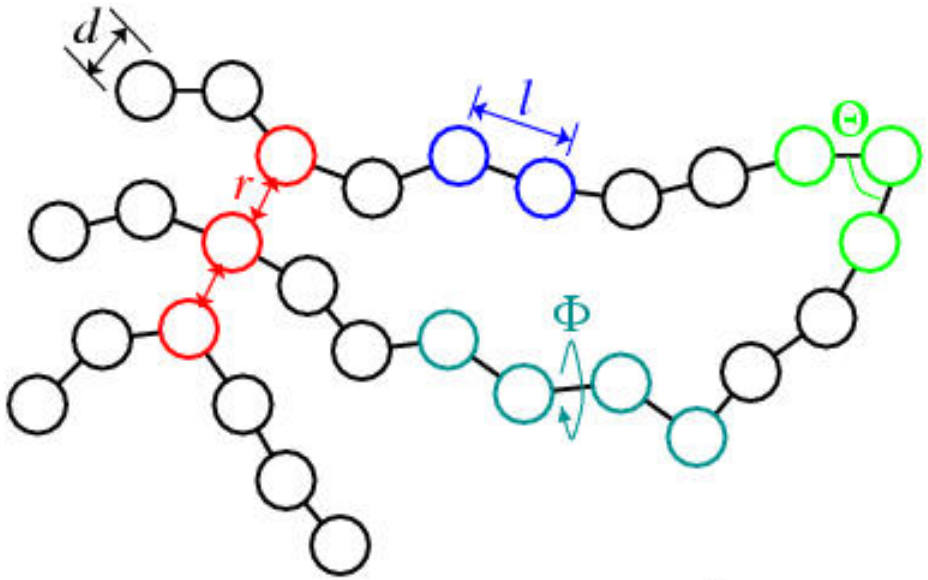



**Coarse-graining**:
map bead-spring chain over molecular structure.
=> Many fewer degrees of freedom

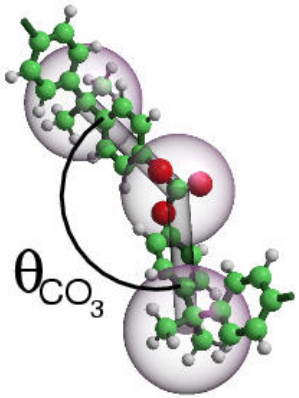
**Inverse mapping:** grow atomic structure on top of coarse-grained backbone
=>Large length-scale equilibration in an atomically resolved polymer

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

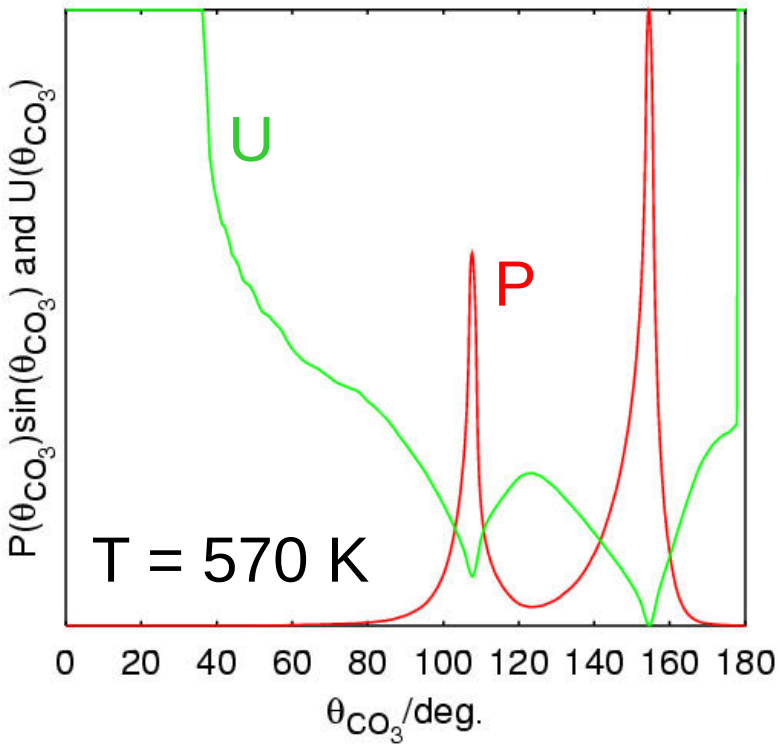
# Interaction Energies in the Coarse-Grained Model




- Excluded volume
- Bonds
- Angles
- Torsions



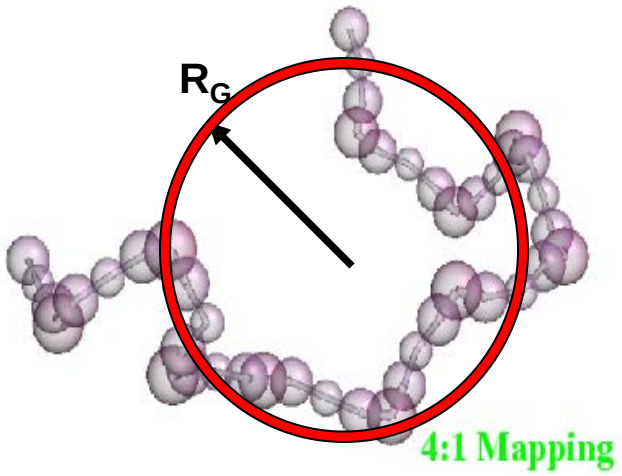

Angle potentials are T-dependent Boltzmann inversions; *e.g.*, at carbonate:



# Results for Melts, N=20….120

## - Molecular Coarse-Grained Melt

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

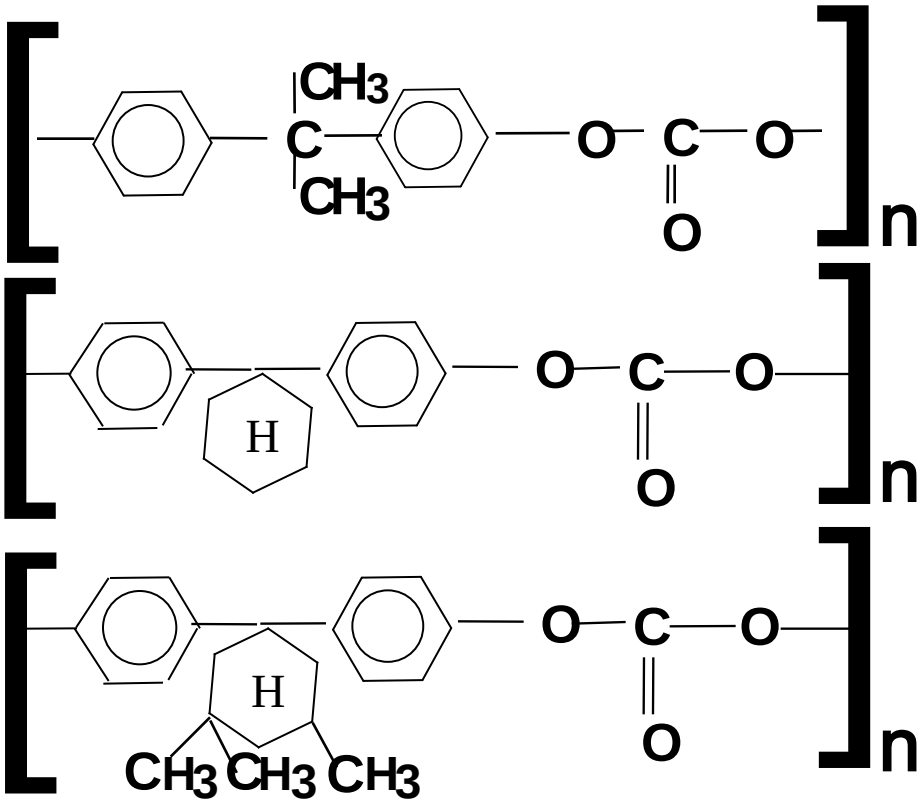



**$R_G$ of coarse grained simulations agrees to n-scattering experiments!**

## - Reintroduce Details: Inverse Mapping

**Speedup ≈ $10^4$ !**

# Polycarbonate




**BPA-PC**

$T_{VF}$ = 390 K  $N_e$ = 7

$T_G$ = 420 K  $M_e$ = 1700

ductile

**BPZ-PC**

$T_{VF}$ = 390 K  $N_e$ = 10

$T_G$ = 420 K

brittle

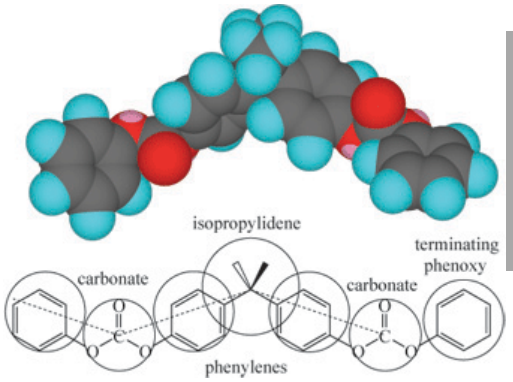
**TMC-PC**

$T_{VF}$ = 480 K  $N_e$ = 15

$T_G$ = 510 K

"somewhat ductile"

($M_e$ Entanglement molecular weight $M < M_e$ , $T_{VF}(M) \approx T_{VF} - 50$ K)

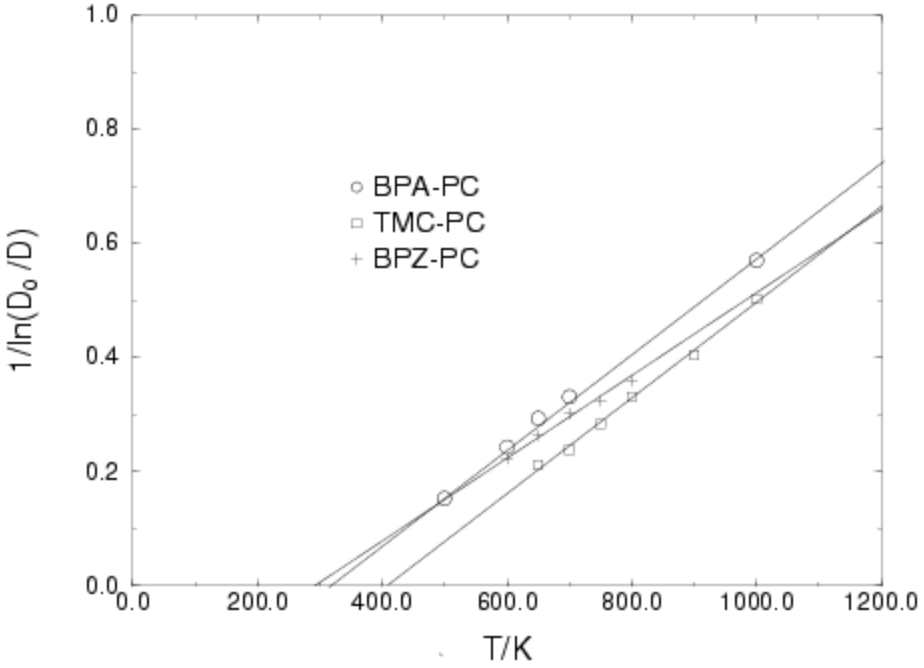



# Dynamics: Vogel-Fulcher La

## Simulation vs Experiment

$$D = D_O \exp\left( -A_o / T - T_{VF} \right)$$

| BPA | BPZ | TMC |
|---|---|---|
| 323K | 292K | 407K |
| 387K | 392K | 477K |




Simulation: N=10
Experiment: N≈200

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

# Viscosity => Time Mapping

$$\eta = \rho R_N^2 k_B T / s^3 (N-1)^2 36 D$$

- Melt simulation
- Viscosity from chain diffusion coefficient (Rouse)
- Property of entire chains

$$\tau \approx 22\,ps$$

(T=500K, new data 2005)

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

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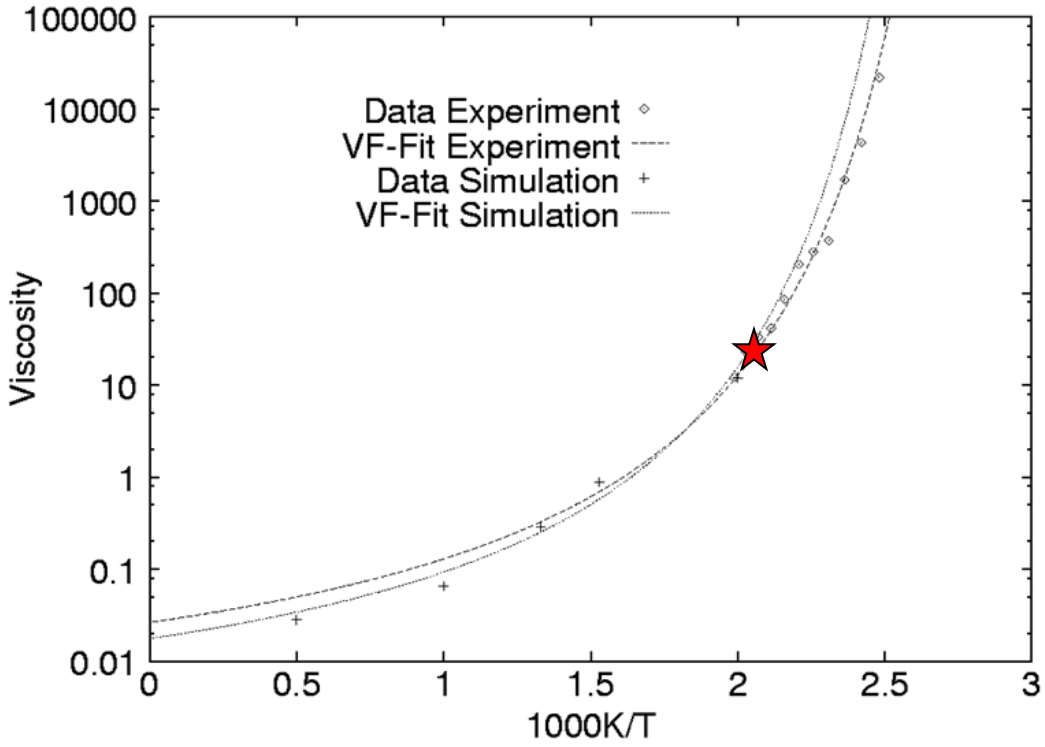
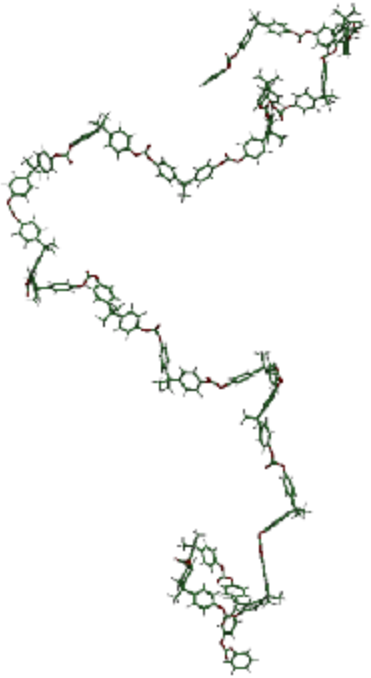



[W. Tschöp, K. Kremer, J. Batoulis, T. Bürger, O. Hahn, Acta Polym. **49**, 61 (1998); ibid. **49**, 75].

# How good are generated conformation?

## Inverse Mapping:
## Reintroduce Chemical Details



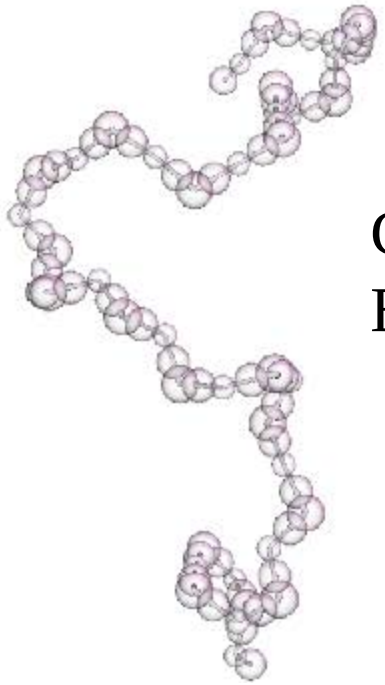
All atom model

⇐

⇐

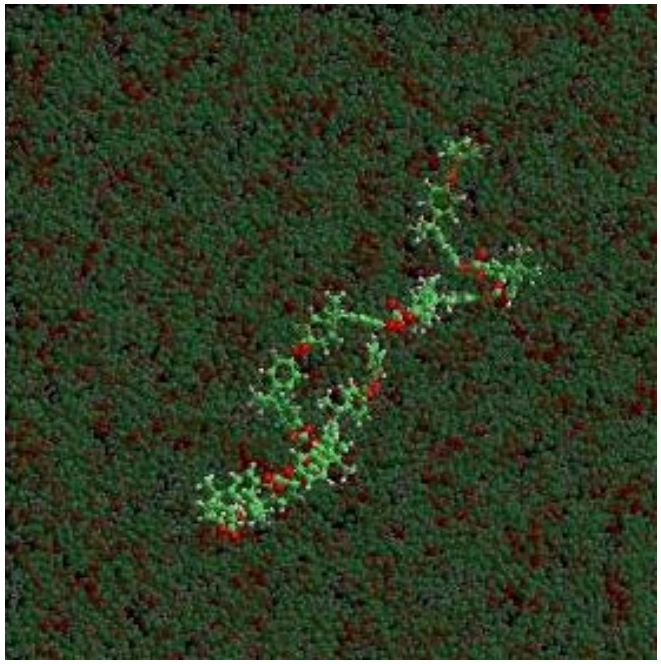
⇐

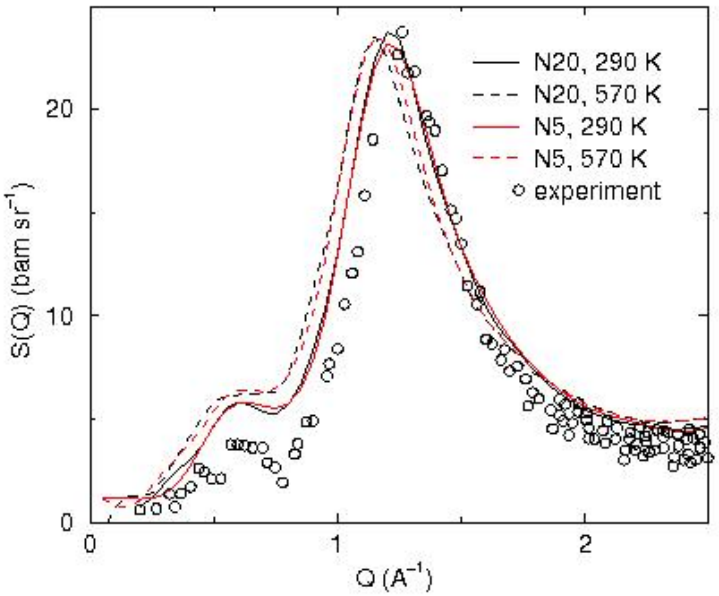
⇐



Coarse grained
BPA-PC chain

# Comparison: Simulation vs n-Scattering






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

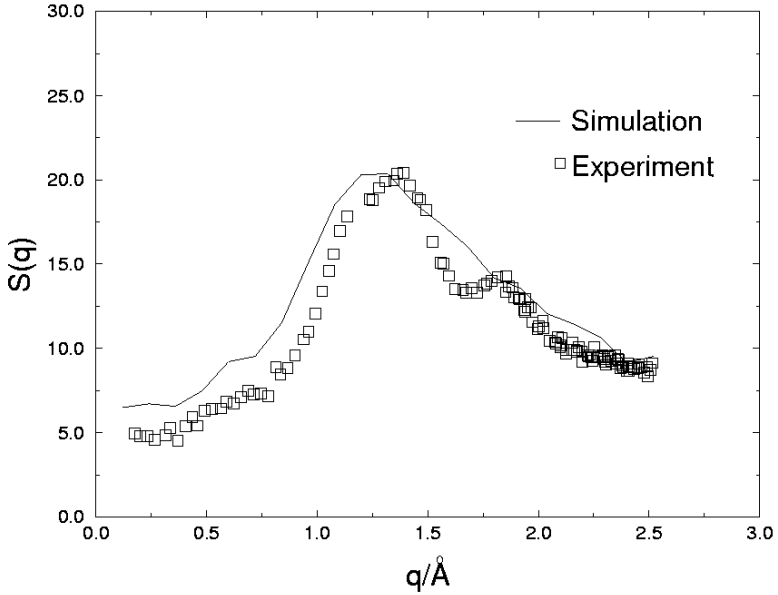
J. Eilhard et al, J. Chem. Phys. **110**, 1819 (1999)
B. Hess et al, Soft Matter 2006

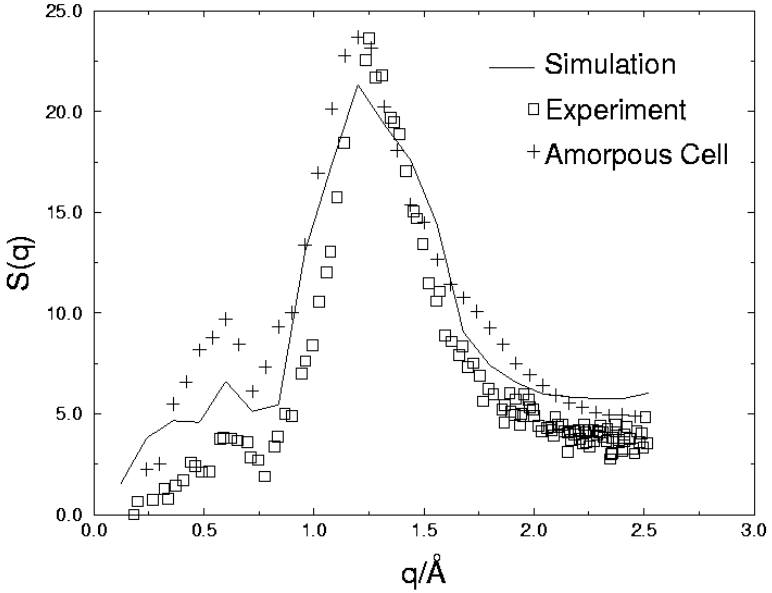
**Well equilibrated coarse grained AND all atom melt configurations!**

# Comparison: Simulation n-Scattering

**Structure factors of (deuterated) BPA-PC**

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

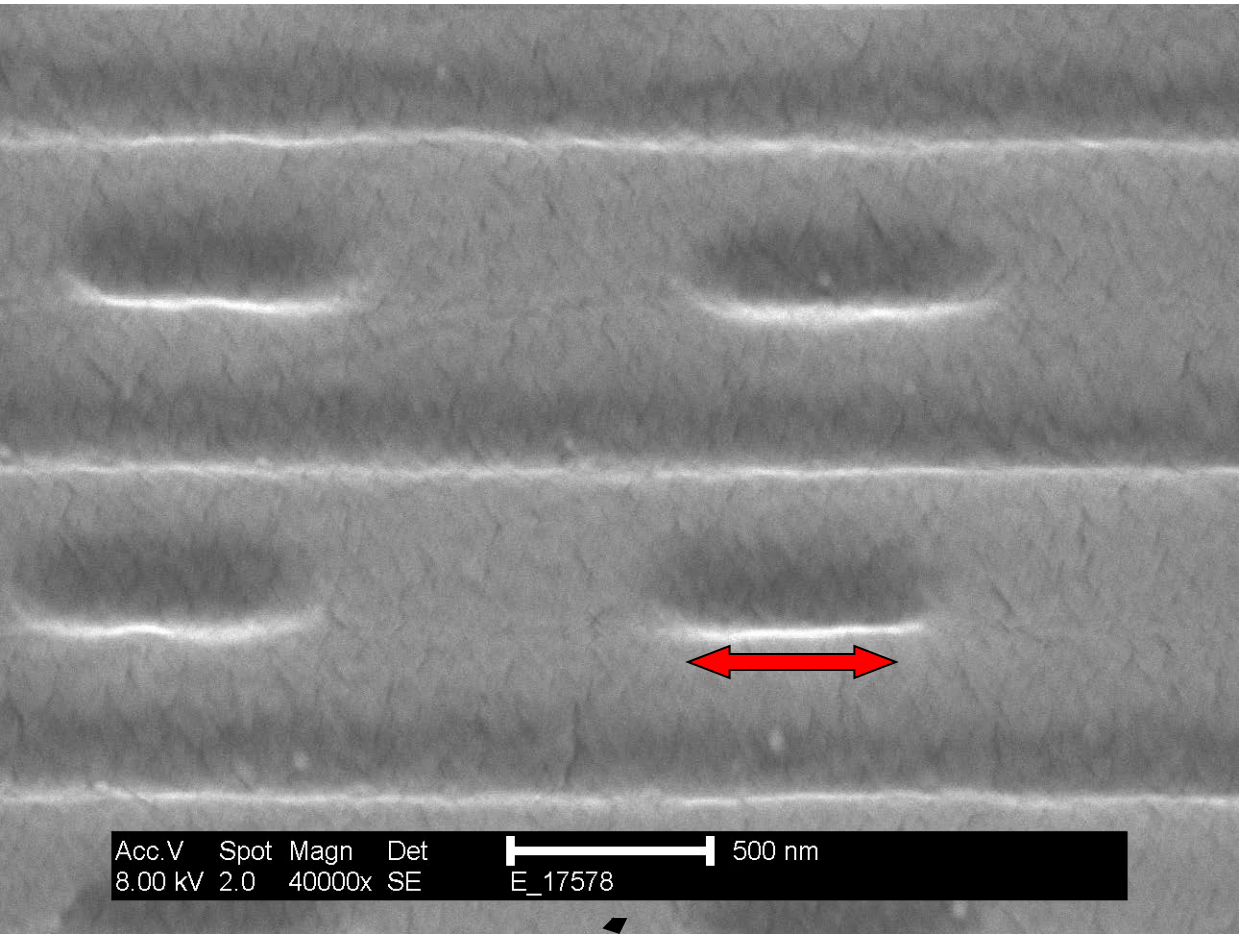


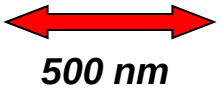




[J. Eilhard, A. Zirkel, W. Tschöp, O. Hahn, K. K., O. Schärpf, D. Richter,U. Buchenau, J. Chem. Phys. **110**, 1819 (1999)]

# Polycarbonate (PC) and the PC/Ni interface

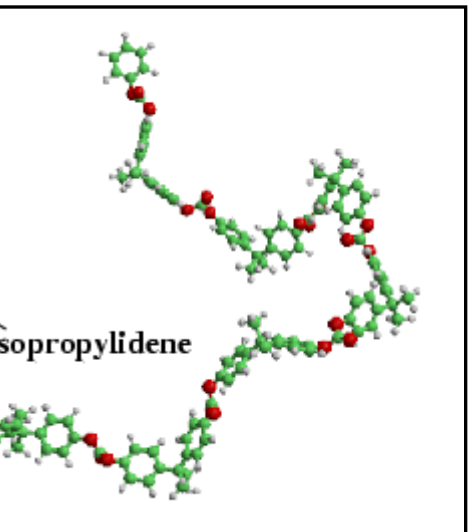
Grooves and address pits of a die cast sample of polycarbonate for a high storage density (**blue laser**) optical disc

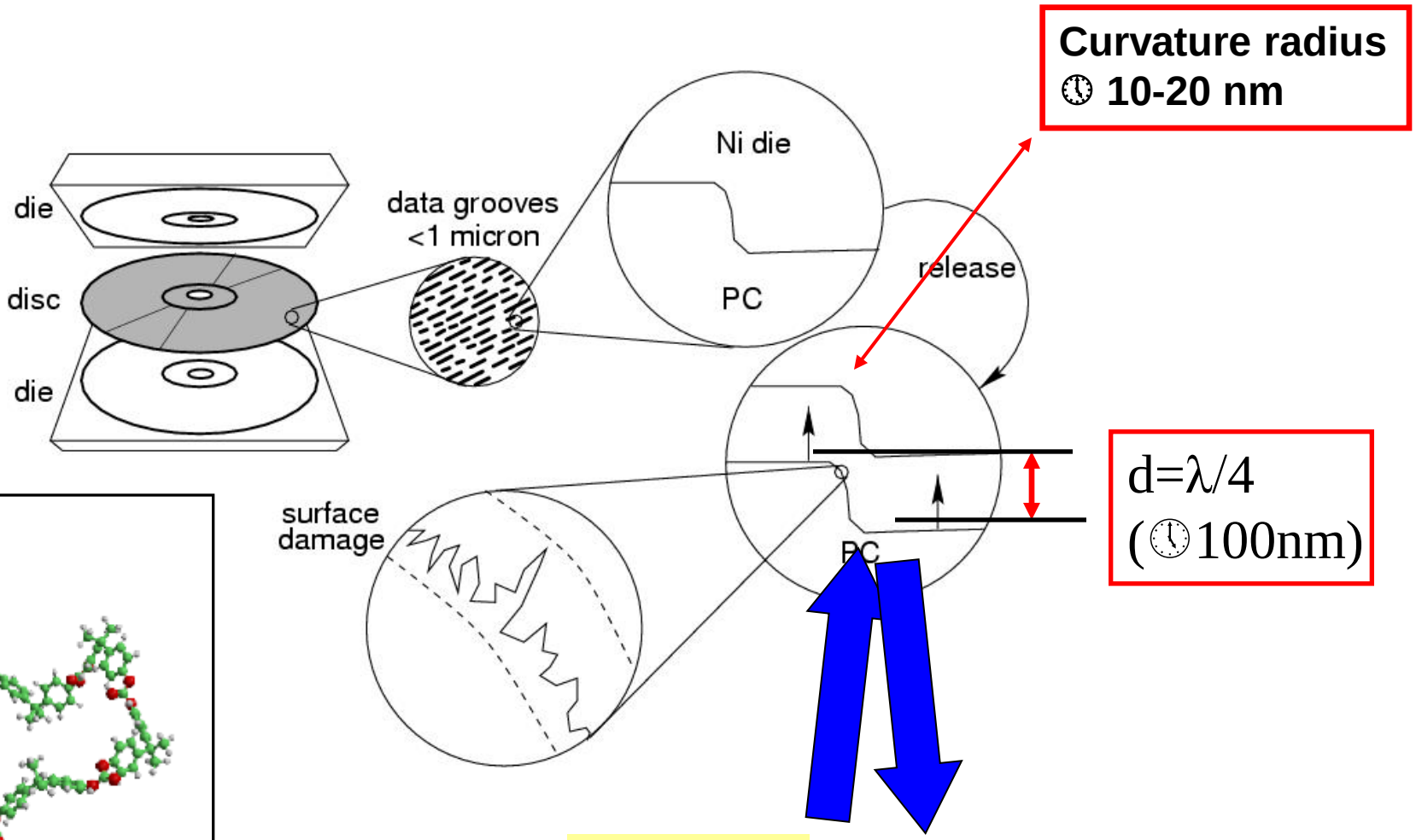


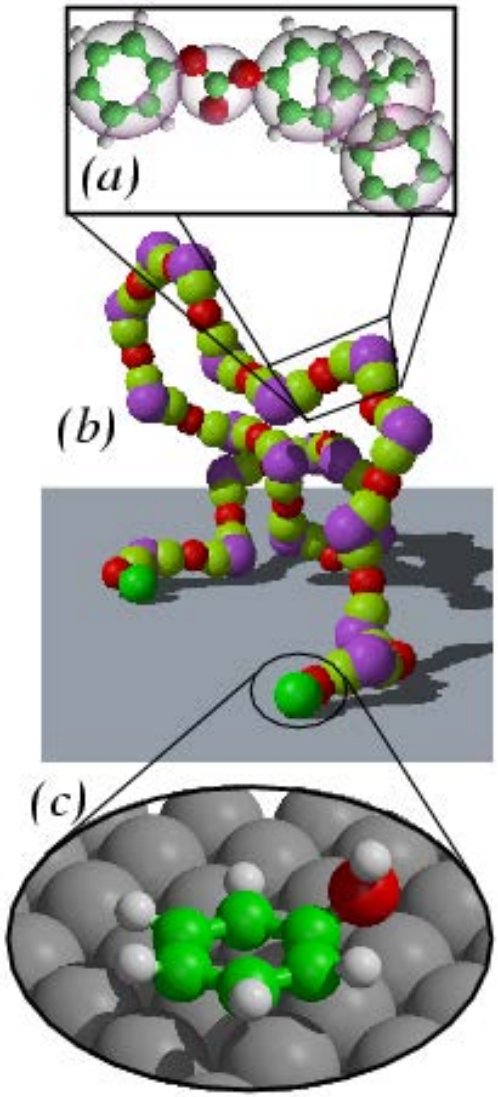

Bayer Materials

# Why study Polycarbonate and the PC/Ni interface?



# Simulating BPA-PC/Metal Interfaces




Molecular structure coarse-grained onto bead-spring chain

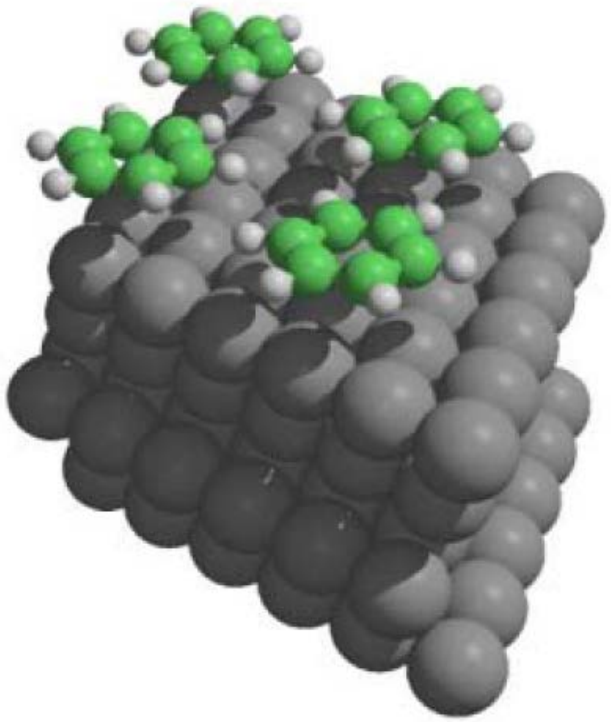
↓

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

↑

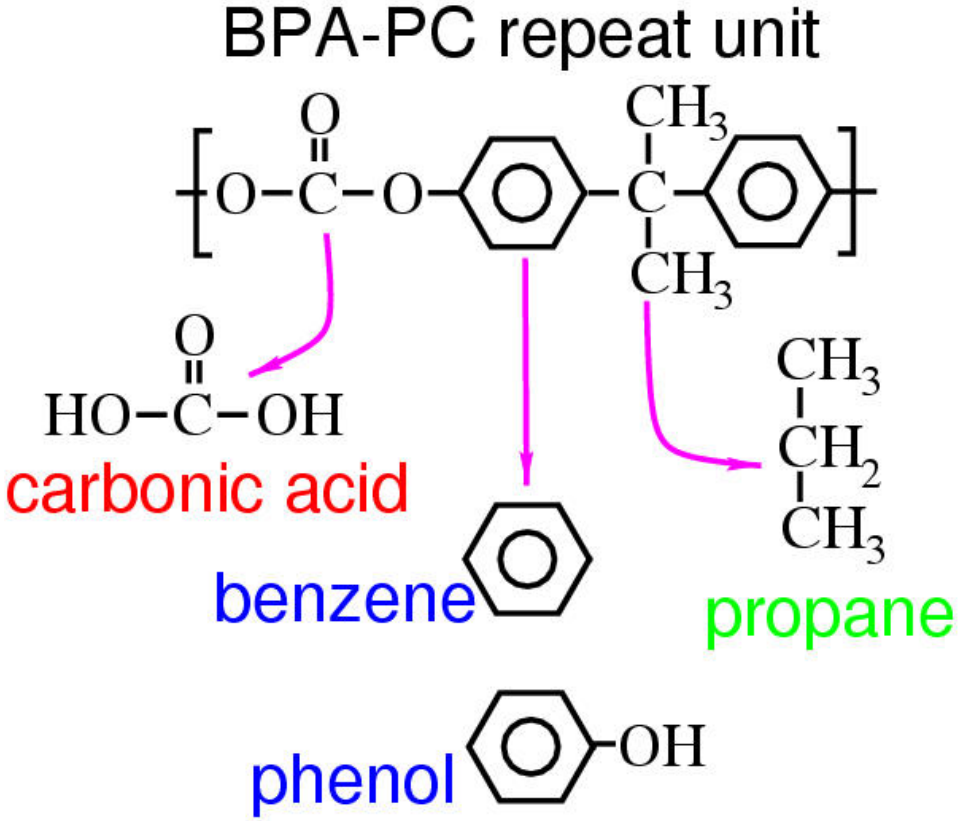
Specific surface interactions investigated via *ab initio* calculations

# Ab initio Investigations of Comonomeric Analogues on Nickel

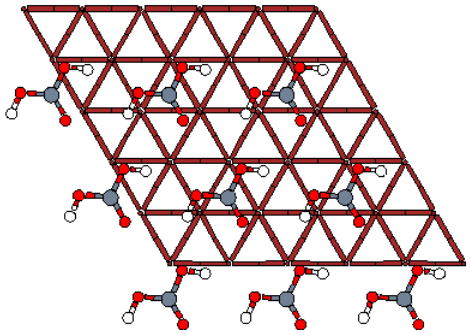


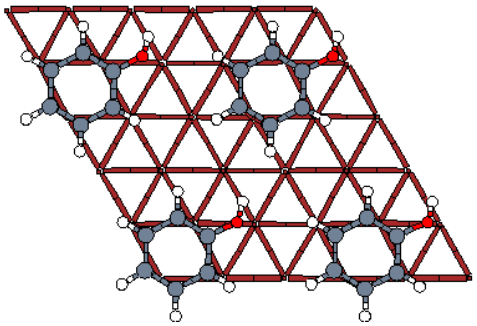
Snapshot: CPMD simulation of benzene chemisorbed on nickel (111)

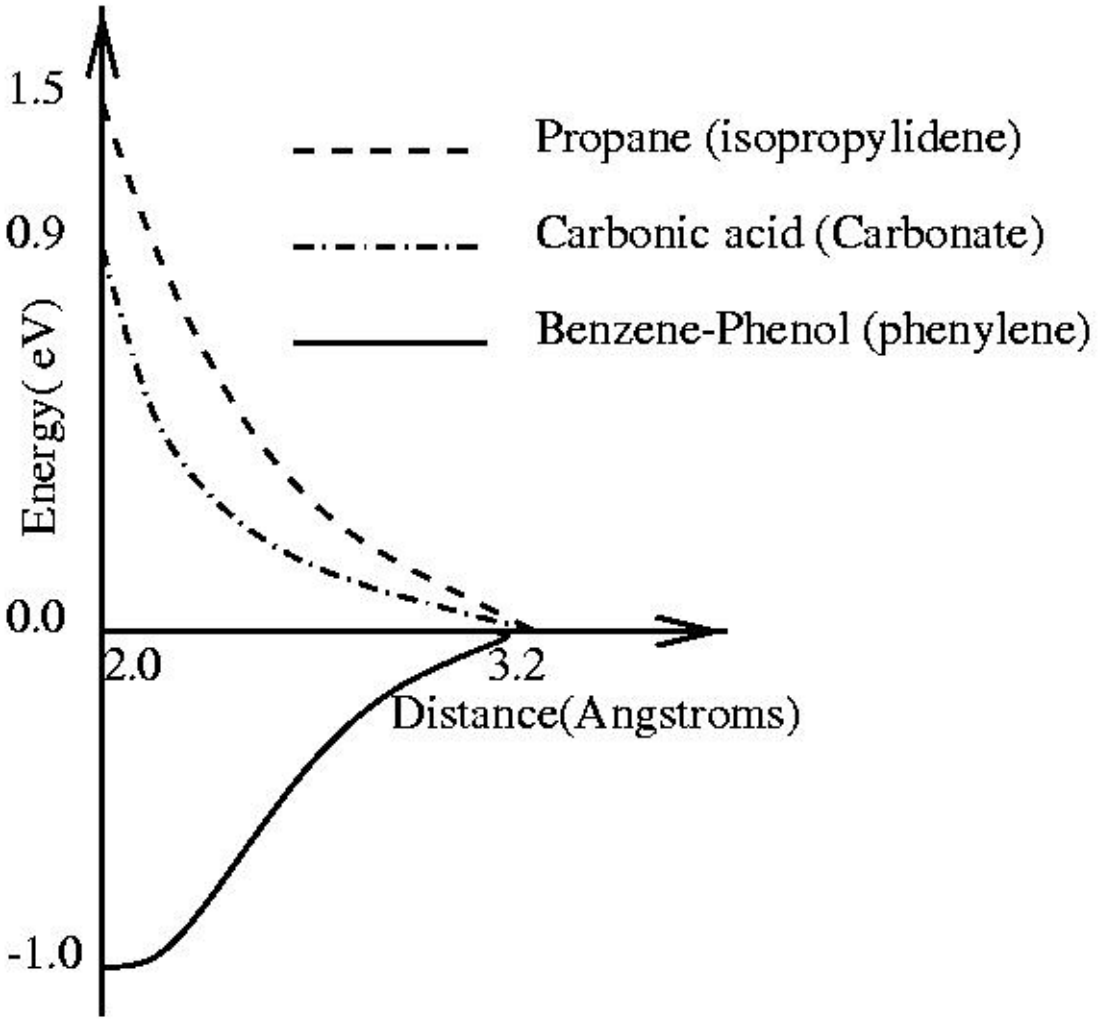
(CPMD Program: M. Parrinello)



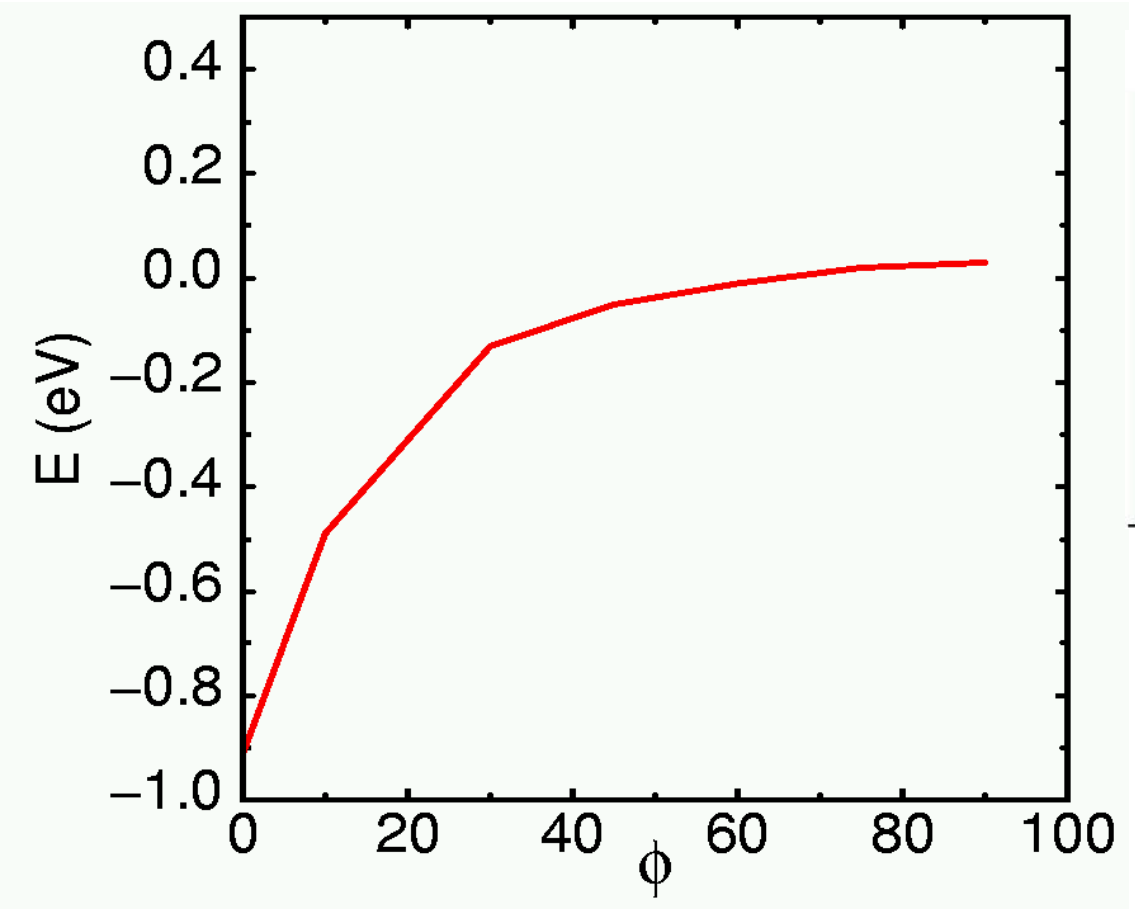
# Adsorption energies of BPA-PC fragments

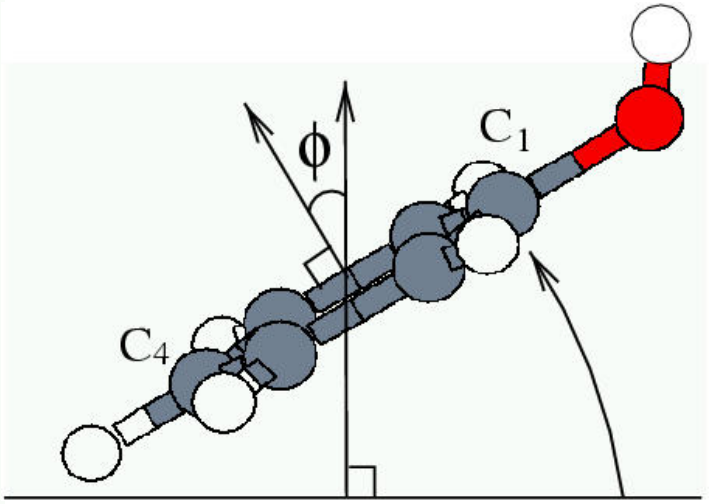






# *CPMD*: Dependence of Phenol-Ni Interaction on Ring Orientation




Interaction very sensitive to orientation!

# *Ab Initio MD:* Conclusions

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

  with Ni {111}

  ➔

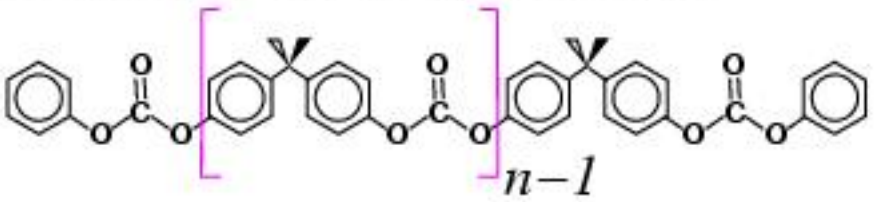
  **Internal phenylene comonomers in BPA-PC are sterically hindered from adsorbing on Ni {111}.**

  ➔

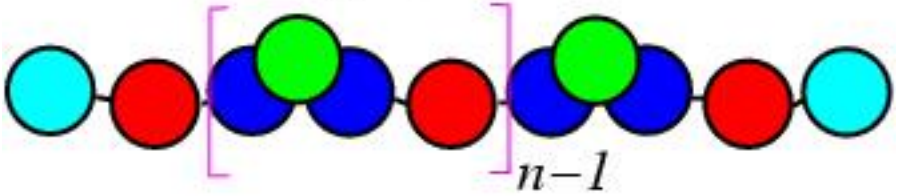
  **Torsional freedom in carbonate group allows for terminal phenoxy groups to adsorb**

# Coarse-Grained BPA-PC with End-Group Resolution (*Dual Scale MD*)

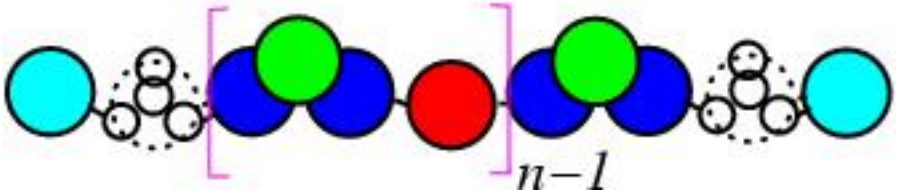
Bisphenol–A–polycarbonate




4:1 Coarse–grained

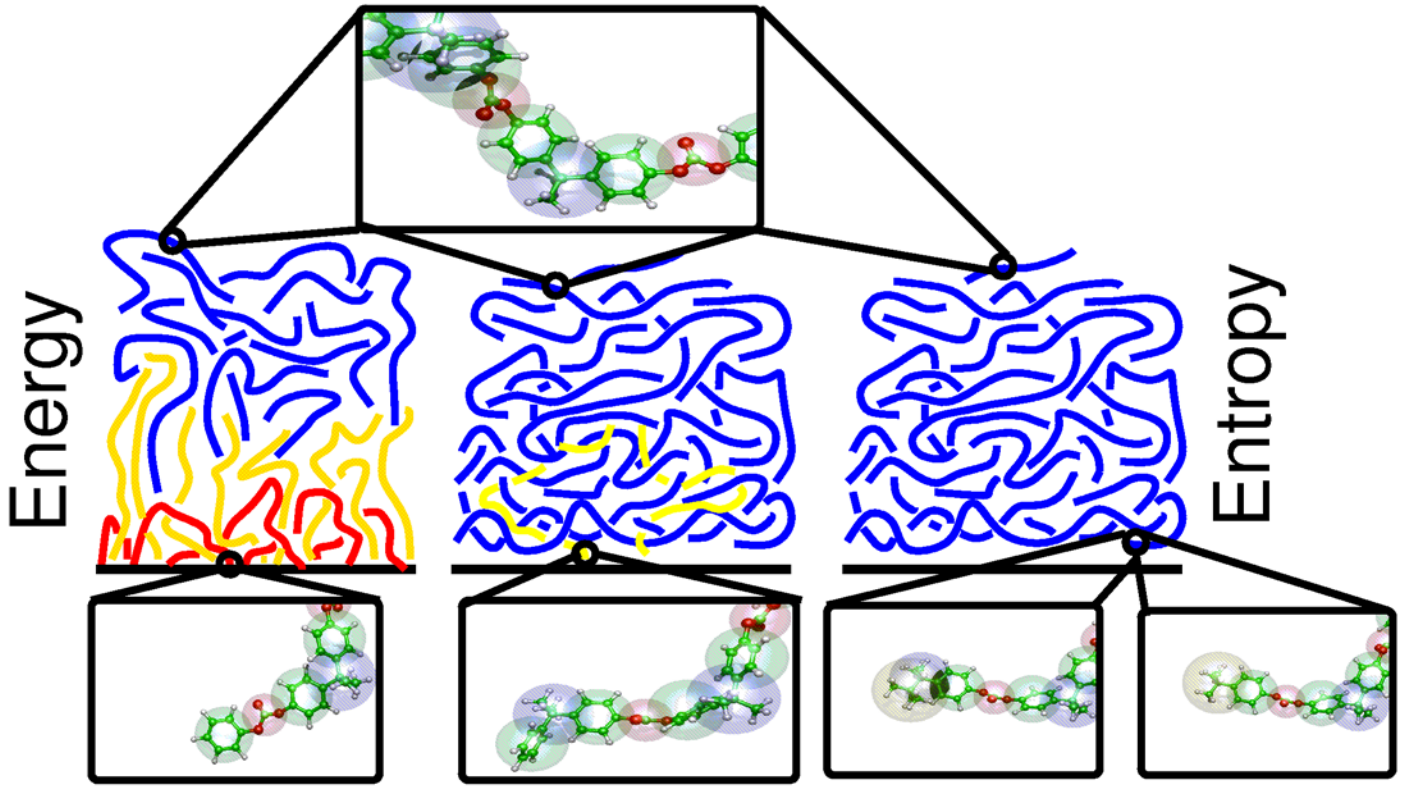



4:1 with end–group resolution



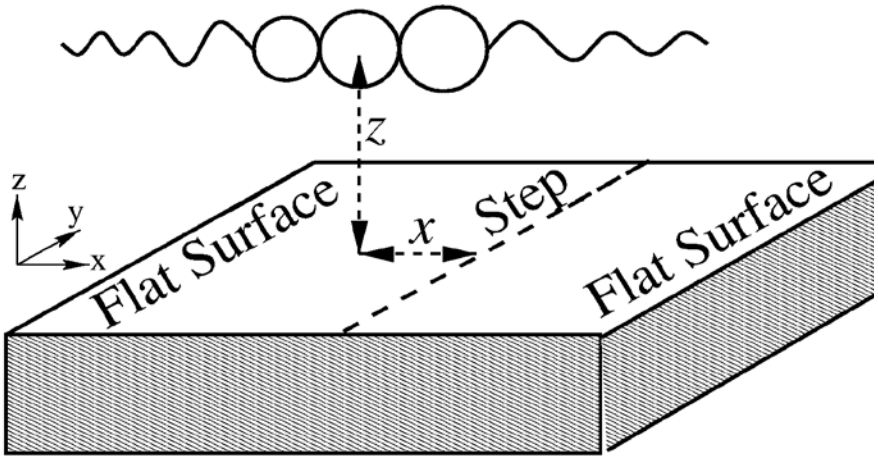

- Phenol-Ni interaction strongly dependent on $C_1$-$C_4$ phenol orientation
- In standard 4:1 model, phenoxy end orientation not strictly accounted for
- Resolving only the *terminal* carbonates specifies 1-4 orientation and is inexpensive

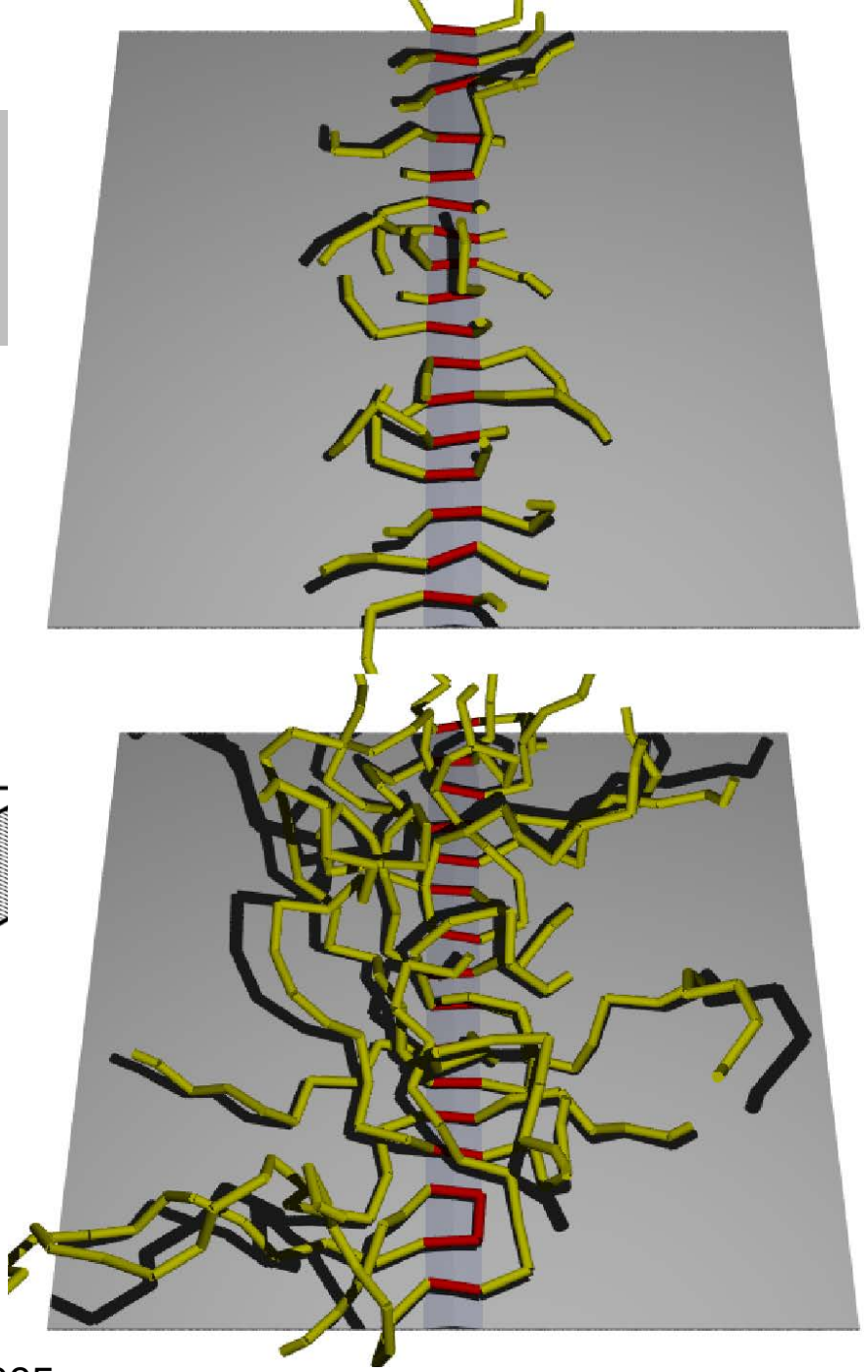
# Competition Energy-Entropy
# Other Chain Ends




L. Delle Site et al., *J.Am.Chem.Soc.*; 126; **2004**; *2944*

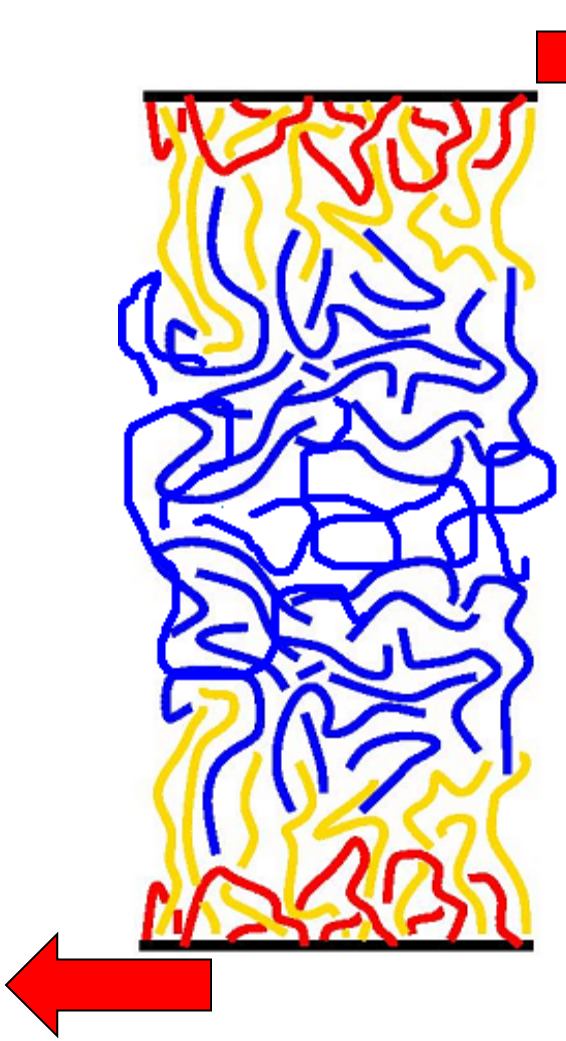
# Line Defect Induced Ordering



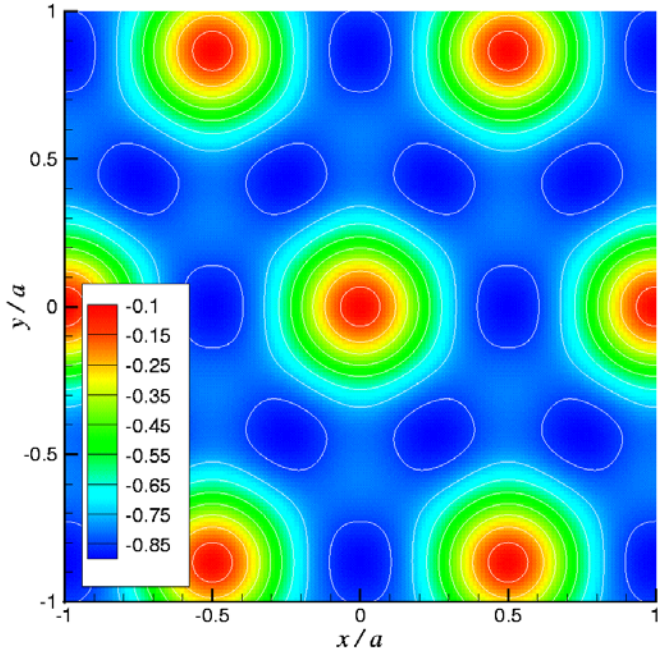
L. DelleSite, S. Leon, KK, J. Phys. Cond. Matt. 2005

# Shearing a Melt



end adsorption energy dominated case:
**phenolic** chain ends

Surface Potential for Ends

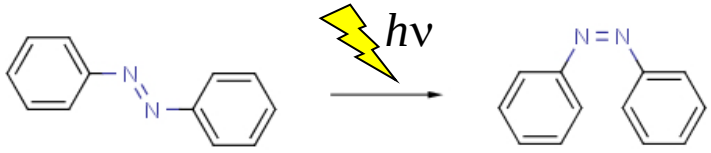


# Photoswitchable Azobenzene Structure Developing Liquid

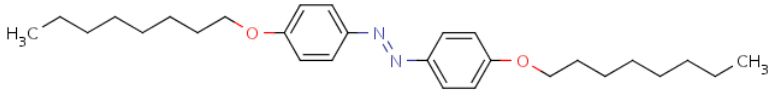
## VW Stiftung, C. Peter,L. Delle Site, KK - D. Marx (Bochum)

QM scale

Photoisomerization of azobenzene




*trans* azobenzene as a mesogen 8AB8

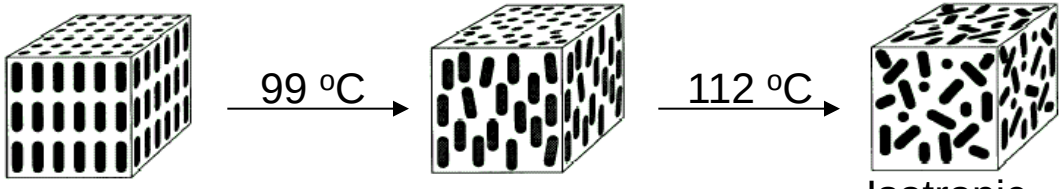



isomerization mechanism ?!?
(particularly in polymer or anisotropic environment)

light induced phase transition

hν

mesoscale



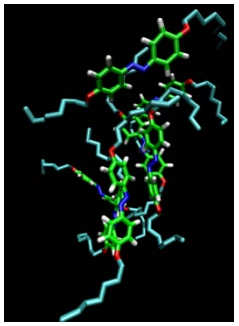

Ikeda & Tsutsumi, Science 1995

phenomena on wide range of time and length scales mutually influencing each other

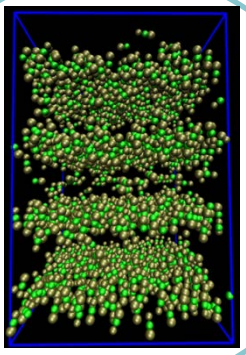
⇨ **multiscale approach**

# Example LC phase transitions

Disordered @ 480 K

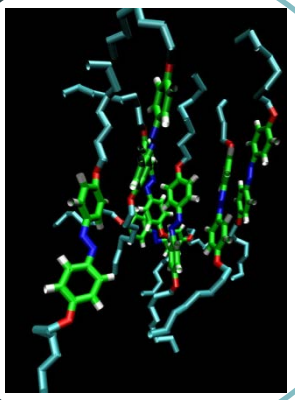


SmA @ 460 K



CG model should reproduce this transition !

Super-cooled fluid @ 460 K



CG model should reproduce structure

Parametrisation impossible here: (layering built into potentials)

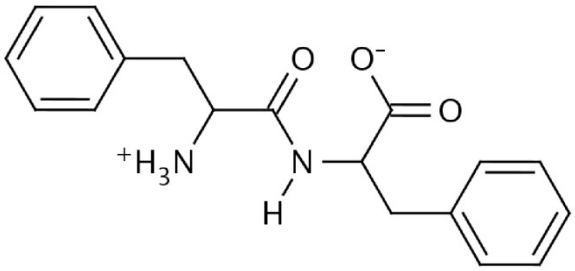
overall isotropic

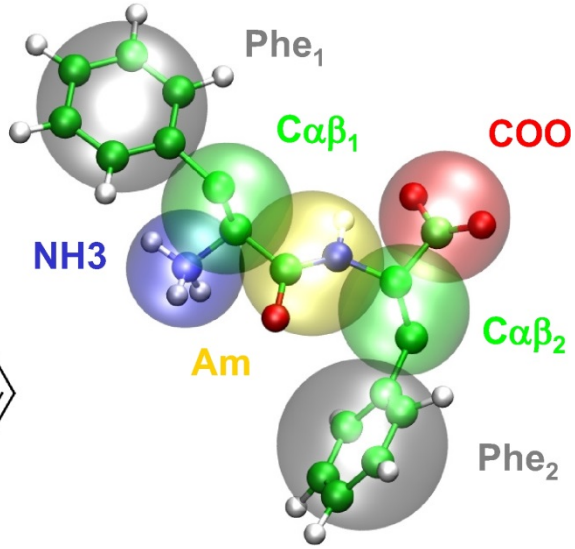
residual nematic order

Parametrise HERE !!

# CG model for di-phenylalanine with/without explicite water

⇨ Mapping

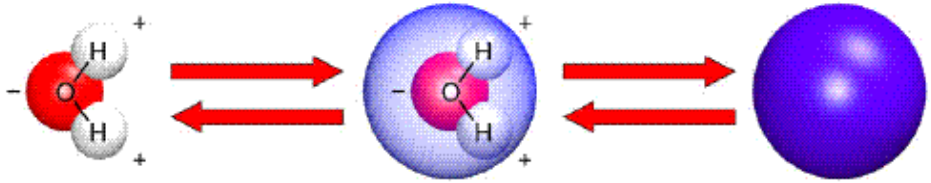


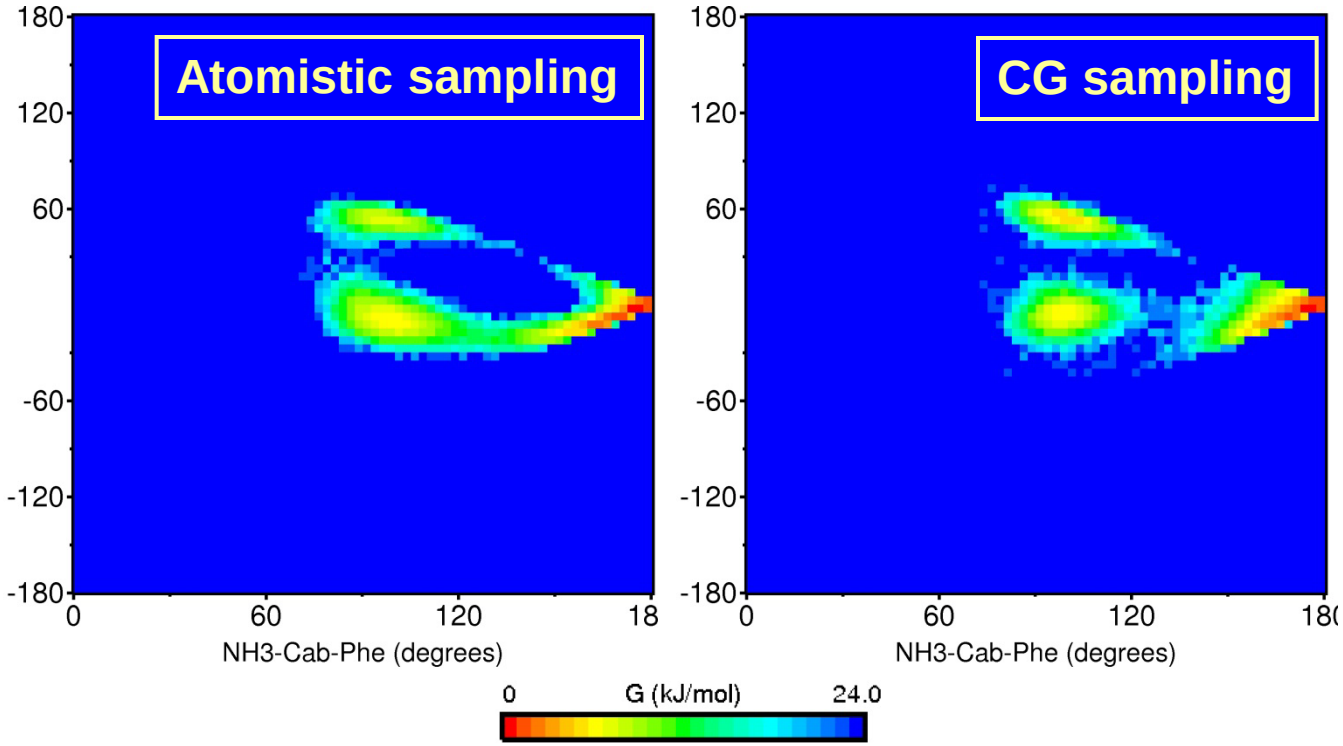

⇨ Intramolecular degrees of freedom

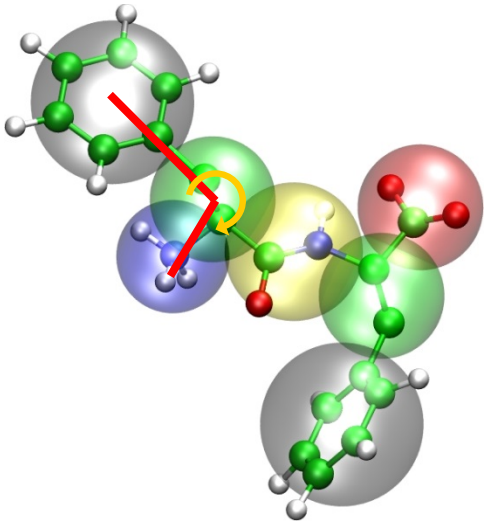
⇨ Nonbonded interactions

1. solvent free model
2. model w. explicit (CG) solvent representation



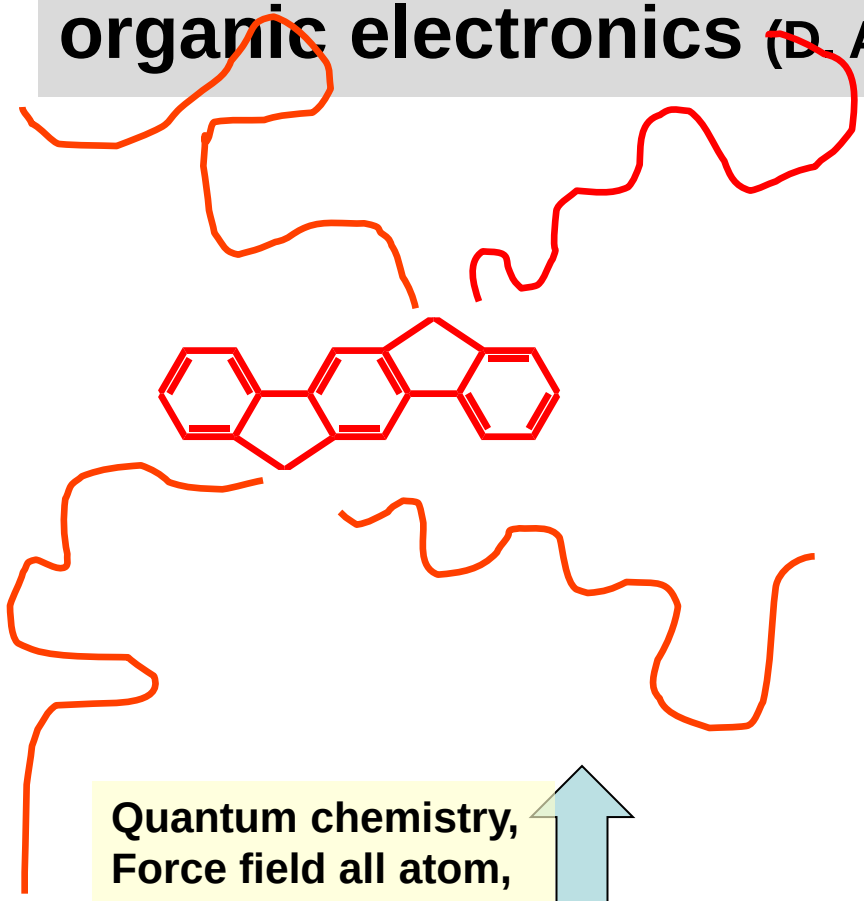
# Intramolecular (bonded) degrees of freedo...

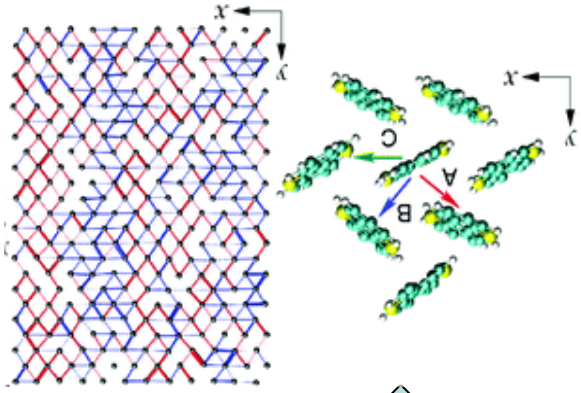


⇨ Correlations between degrees of freedom are well represented in the CG description

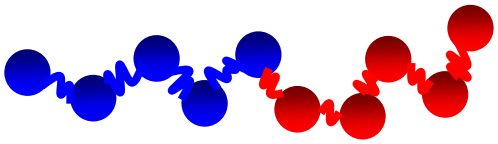
# Simulation and Modeling: (ideal) Work Flow organic electronics (D. Andrienko, K. Daoulas)





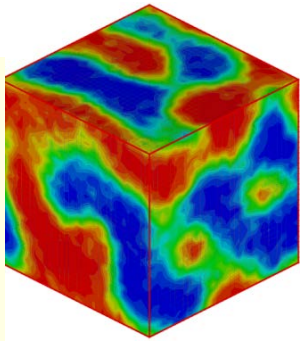

**Kinetic MC**
**Quantum Chemistry**

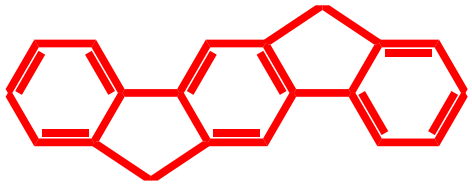
**Quantum chemistry,**
**Force field all atom,**
**coarse grained**
**MD simulation**



**MD, SCMF**

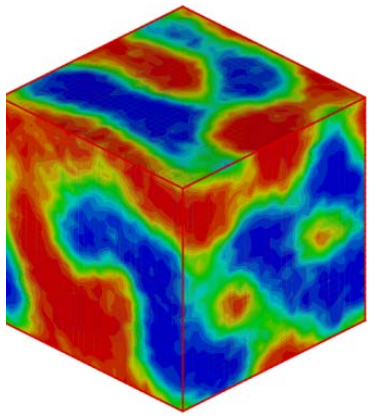
**Processing**
**Nonequilibrium**





**MD, SCMF**

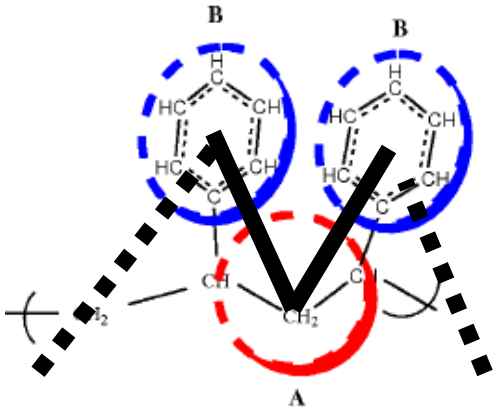
**Processing**
**Nonequilibrium**



# *Structure Based Coarse Graining*

- **Dynamics -- Melts, Rheology**
  **-- Diffusion of Additives**

# Time scale, PS, BPA-PC




$M_{mon}$ = 104

$M_{sphere} \approx 52$

$\sigma \approx 3$ Å

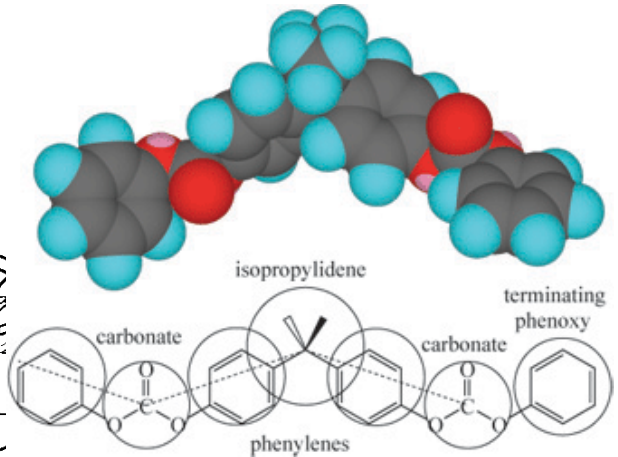
$N_e^{primpath} \approx 150$

T=463K

=====> $\tau_{LJ} \approx$ 1*ps*

$$\tau_{LJ} = (M_{sphere}\sigma^2/\varepsilon)^{1/2}$$

**Time scaling: $\tau^{cg}_{LJ}$ = physical time *x* constant**




$M_{mon}$ = 254

$M_{sphere} \approx 63$

$\sigma \approx 5$ Å

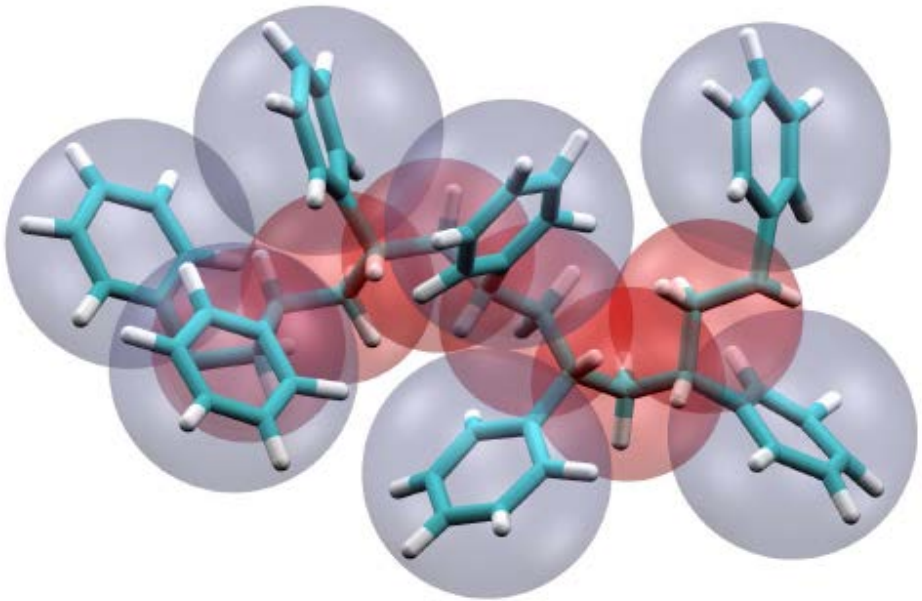
$N_e^{primpath} \approx 5.5$

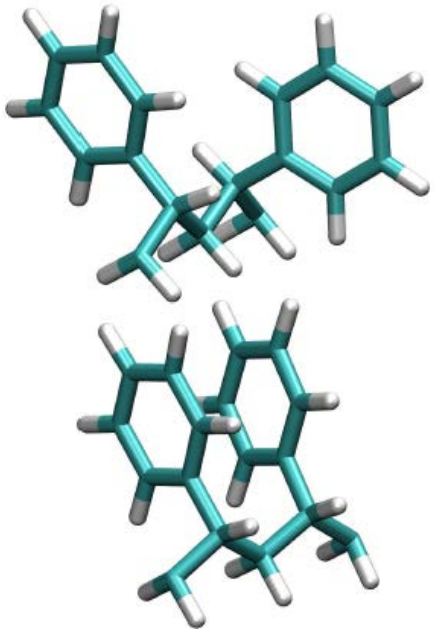
T=570K

=====> $\tau_{LJ} \approx$ 1.7*ps*

# PS: Polystyrene

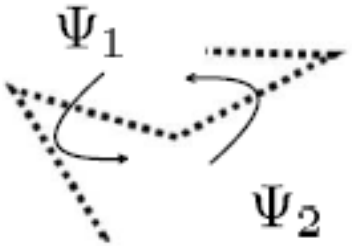
**D. Fritz, V. Harmandaris, G. Floudas, N. Van der Vegt**

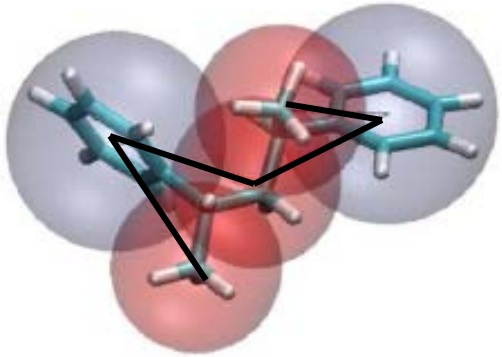


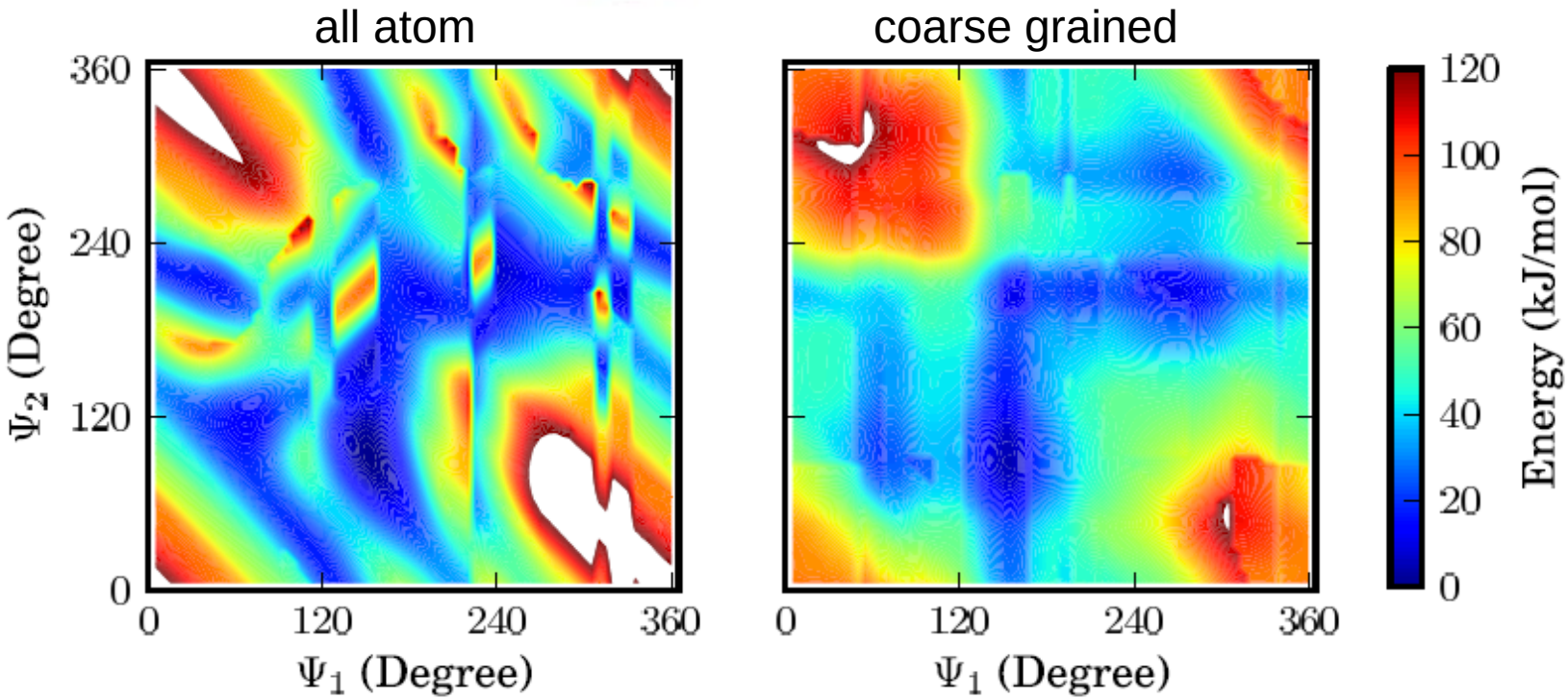


# Dynamics

- **Too complicated already for PS!**

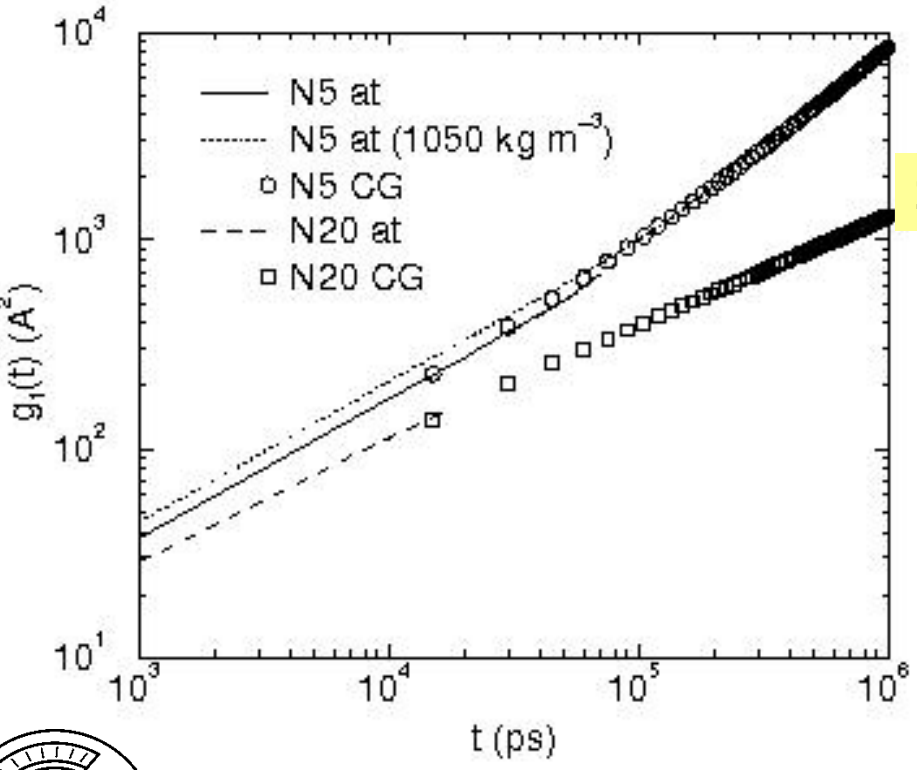




# Atomistic vs cg Simulation: Time Mapping

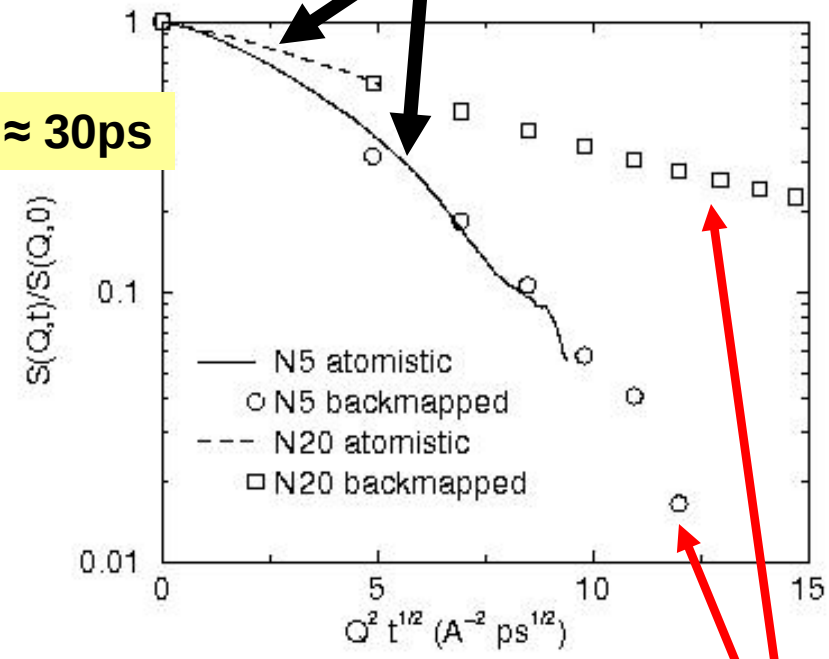
**mean square displacements atomistic vs coarse grained**




**1 τ ≈ 30ps**

**BPA-PC**

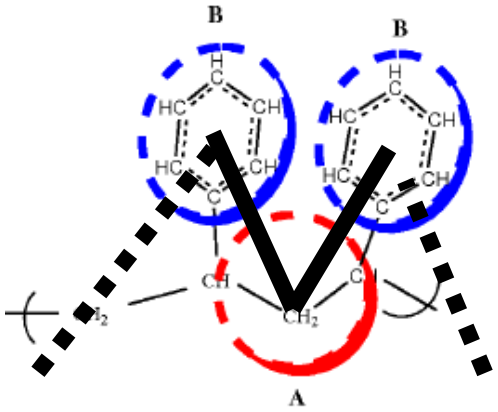
**All atom sims**




**CG sims Back mapped**

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

# Time scale, PS, BPA-PC

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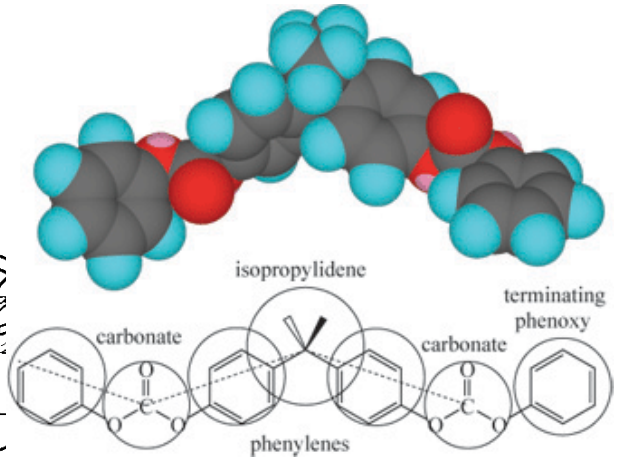
T=463K

=====> $\tau_{LJ} \approx$ 1*ps*

$\tau_{sim} \approx 400ps$

$$\tau_{LJ} = (M_{sphere}\sigma^2/\varepsilon)^{1/2}$$

**Time scaling: $\tau^{cg}_{LJ}$ = physical time *x* constant**

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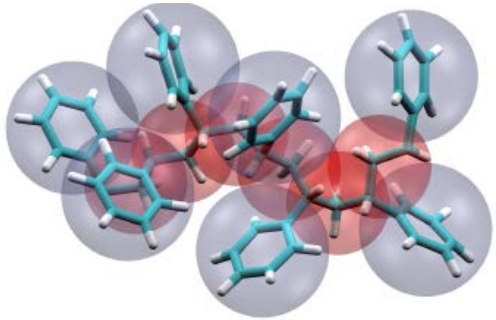
=====> $\tau_{LJ} \approx$ 1.7*ps*

$\tau_{sim} \approx 30ps$

# Application: Diffusion Constant of PS

**(two step approach AA->UA->CG)**





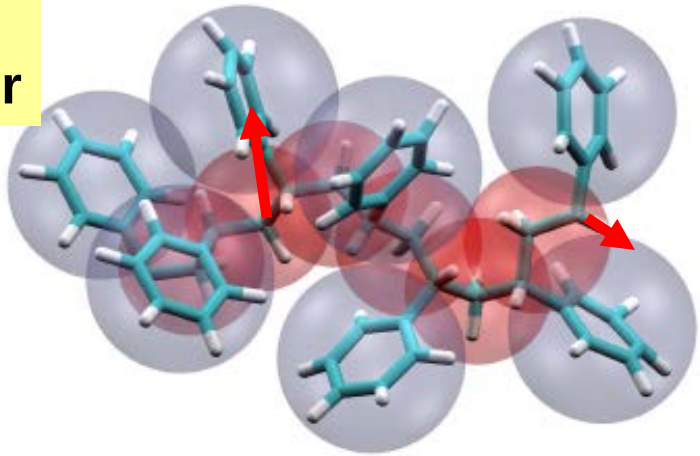

**Simulation:**
**NO adjustable parameter**
**$M_W \leq 50$kD**

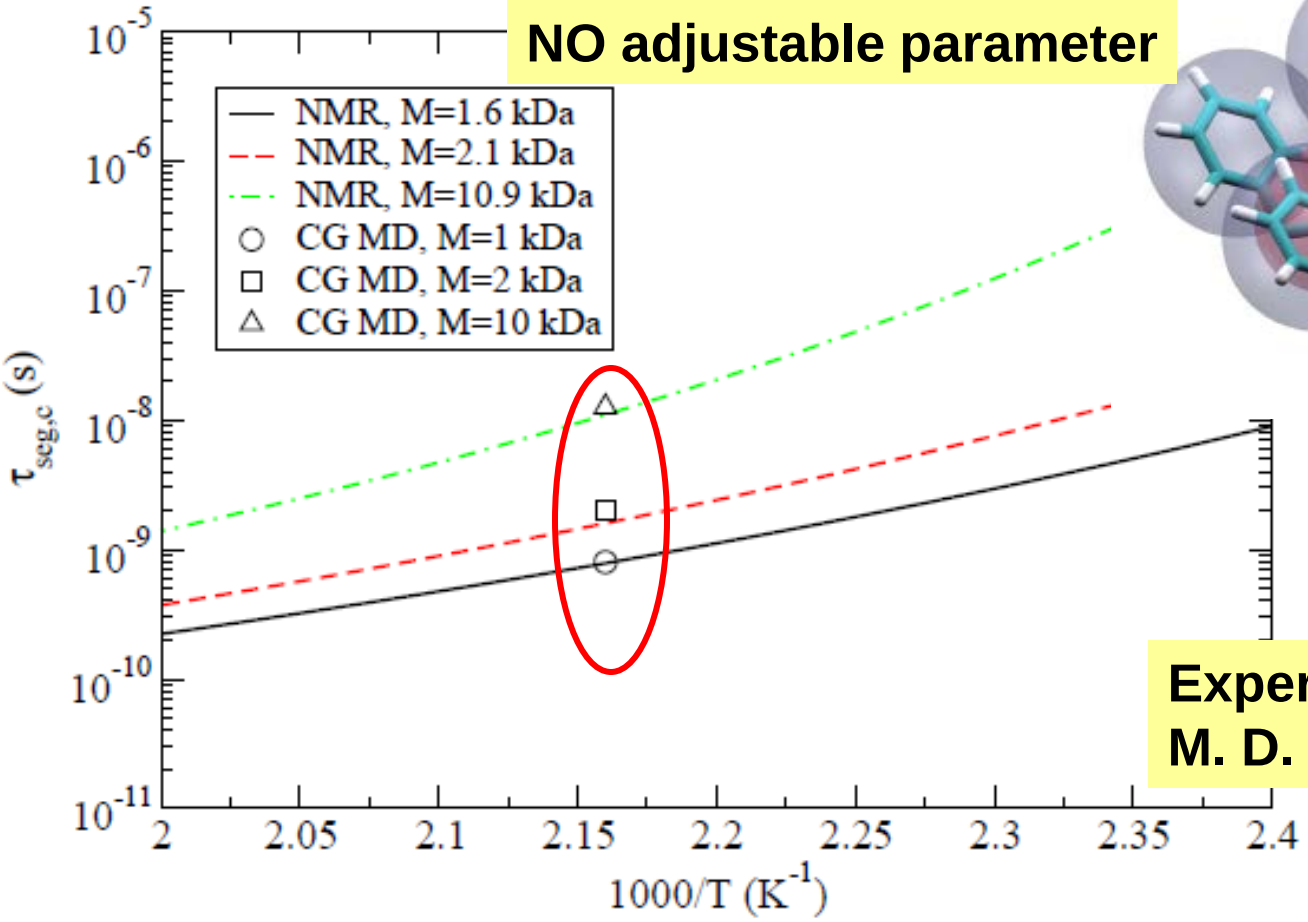
**Experiment:**
**Raw FRS data, Sillescu**

**V. Harmandaris, KK, Soft Matt. 2009**

# Application: NMR data of PS

**Simulation:**
**NO adjustable parameter**






**Experiment:**
**M. D. Ediger et al, MM 2004**

Figure 5: Segmental correlation times from NMR experiments [30] and CG MD simulations for three different molecular weights.

# Conclusion preliminary

- **Soft and Nanostructured Matter**
  - **Finite size effects crucial**
- **Coarse Graining**
  - **Bonded, nonbonded interactions, transferability**
  - **Inverse mapping => link to details**
  - **Dynamics**

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# Force Field Bias in Protein Folding Simulations

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**Force field errors can be very significant for large molecules**

**For proteins easily sum up to size of basin off attraction**

**Can CG be used to refine underlying force fields?**

# Conclusion preliminary

- **Soft and Nanostructured Matter**
  - **Finite size effects crucial**
- **Coarse Graining**
  - **Bonded, nonbonded interactions, transferability**
  - **Inverse mapping => link to details**
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- **Adaptive Resolution Simulation: AdResS**
- **Conclusion/Outlook**