Molecular modeling of polymers: An introduction

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Content

- Introduction to polymers
- Chemical structure of polymers
- Polymer models
- Polymer statistics
- How to simulate polymers
- Simplifications, counterion condensation

History

- Polymers ≙ many particles
- H. Staudinger (1881-1965), Nobel Price for Chemistry 1953: suggested the existence of covalent bounded monomers (1920)→ Polymers

  So far people believed that Polymers were disordered conglomerates of small molecules
- 1928: Proof of the existence of Polymers
  - Structure revealed via X-Ray scattering by P. Debye (1884-1966), Nobel Prize for chemistry in 1936
  - Other important people:

W. Kuhn (1899-1963)	
P. Flory (1910-1985)	1974 Nobel Prize for Chemistry
S. F. Edwads (1928-)	Feynman Path Integrals for Polymers
P.G. de Gennes (1932-2007)	1991 Nobel Prize for Physics (LC and Polymers)

History up to Modern Times

Within 10 years of polymer science attitude changed from:

Impossible → maybe it’s true → “Oh well, that’s well known!”

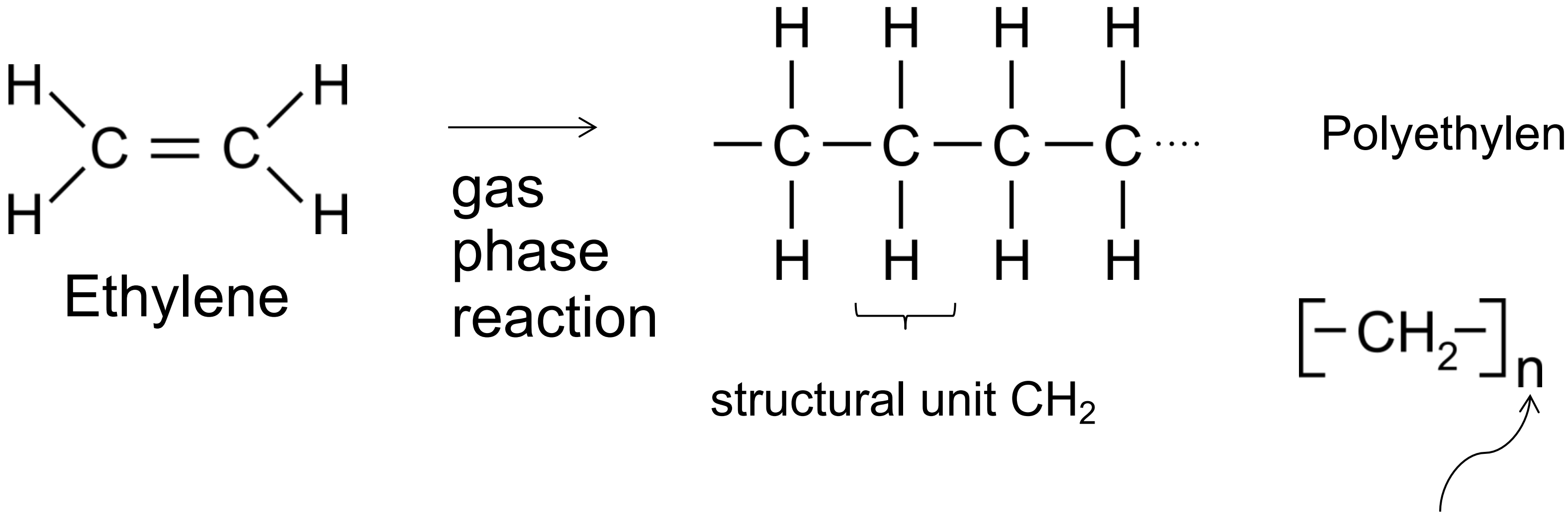
1928: Du Pont → Nylon
1930: PVC, Teflon, polyurethane, polystyrene

Plastics means “able to be modelled”

Now we have more promising fields:
organic electronics, solar cells, polymer batteries….

Semi-conducting polymers, Electrochemical Transistors

Examples for Polymers



Ethylene

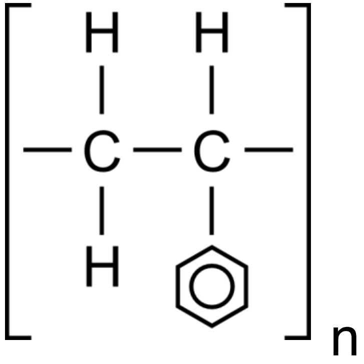
gas phase reaction

structural unit CH_2

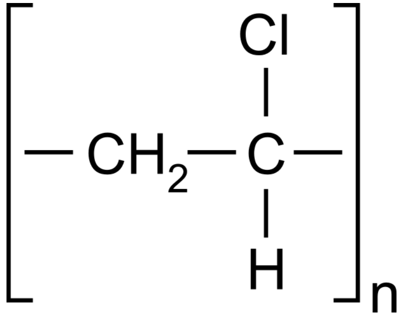
Polyethylene

$[-CH_2-]_n$

degree of polymerization



polystyrene



polyvinylchloride, PVC

If more than one group is attached to a main C atom, different spatial arrangements are possible (e.g. see Polystyrene)

<u>Tacticity:</u>	atactic	no regularity in the chemical structure
	isotactic	completely regular attachment pattern
	syndiotactic	regular and alternating attachment pattern
<u>Homopolymer</u>	single type of repeat unit	
<u>Copolymers:</u>	more than one type of repeat unit, i.e. A, B	

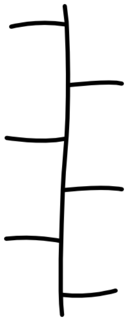
random copolymer: ABBAABAB	random arrangement of blocks (quenched)
block copolymer: AAAABBBB	Different monomers are arranged in blocks of homopolymers: di-, tri-, multiblock copolymers

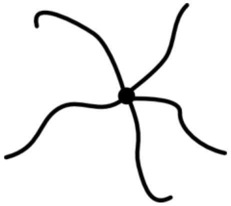
Polymer Architectures

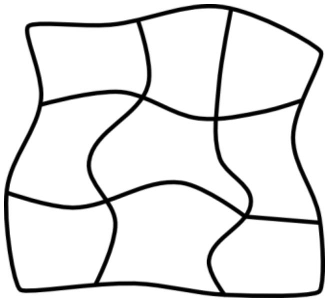
Linear Polymers: completely characterized by the degree of polymerization **n**

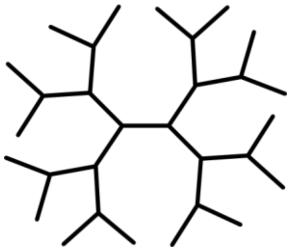
Branched polymers:

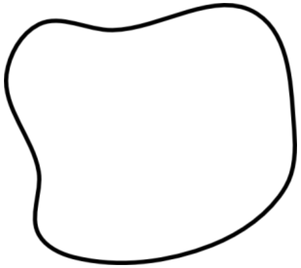

Polymer with short and long chain branches

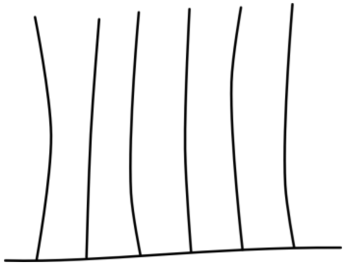

Polymer with grafted oligomeric side chains

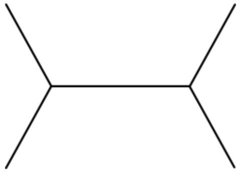

Star polymers

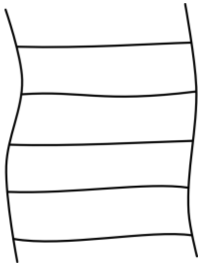

Network of cross-linked chains (rubber)


Dendrimers


Ring polymers


Combs


H-branched


Ladder

Polymer Solutions

For uncharged polymers one normally needs organic solvents

charged polymers are soluble in water

V_{mon}: monomer volume
$V \approx R^3$, R size of polymer

Overlap volume fraction $\phi^* = \frac{NV_{mon}}{V}$

ϱ: polymer density

Overlap concentration $c^* = \varrho\phi^* = \frac{\varrho N\, V_{mon}}{V}$

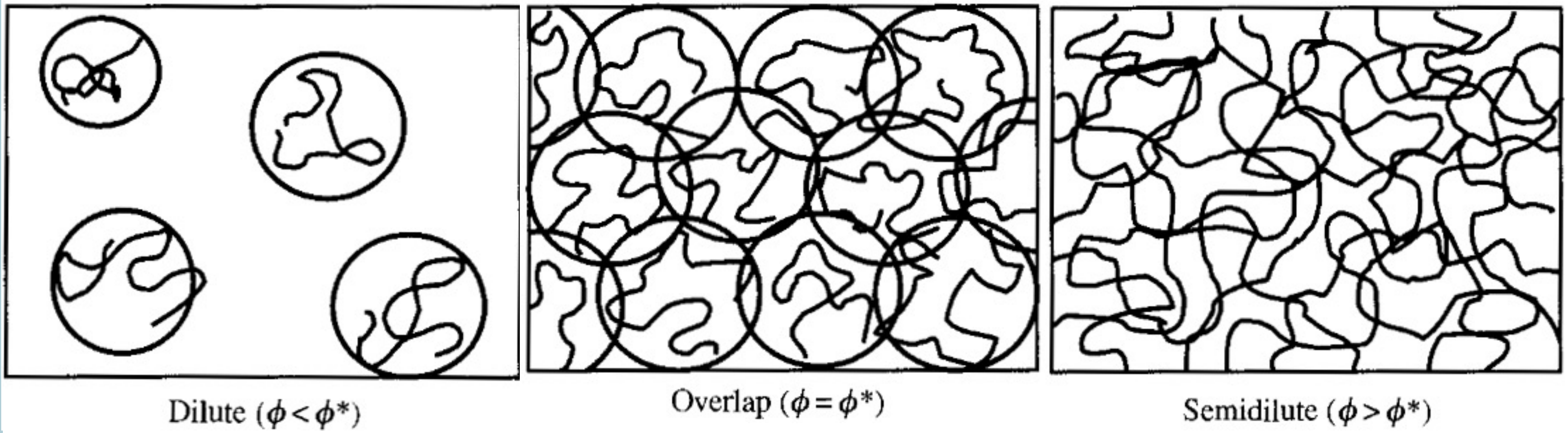
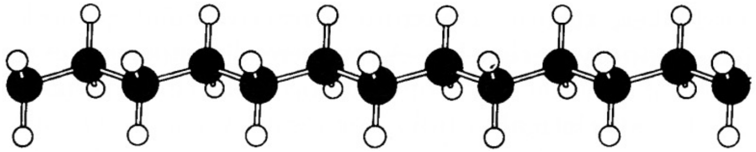

Dilute ($\phi < \phi^*$)
Overlap ($\phi = \phi^*$)
Semidilute ($\phi > \phi^*$)

Fig. from M. Rubinstein, R. Colby, *Polymer Physics*

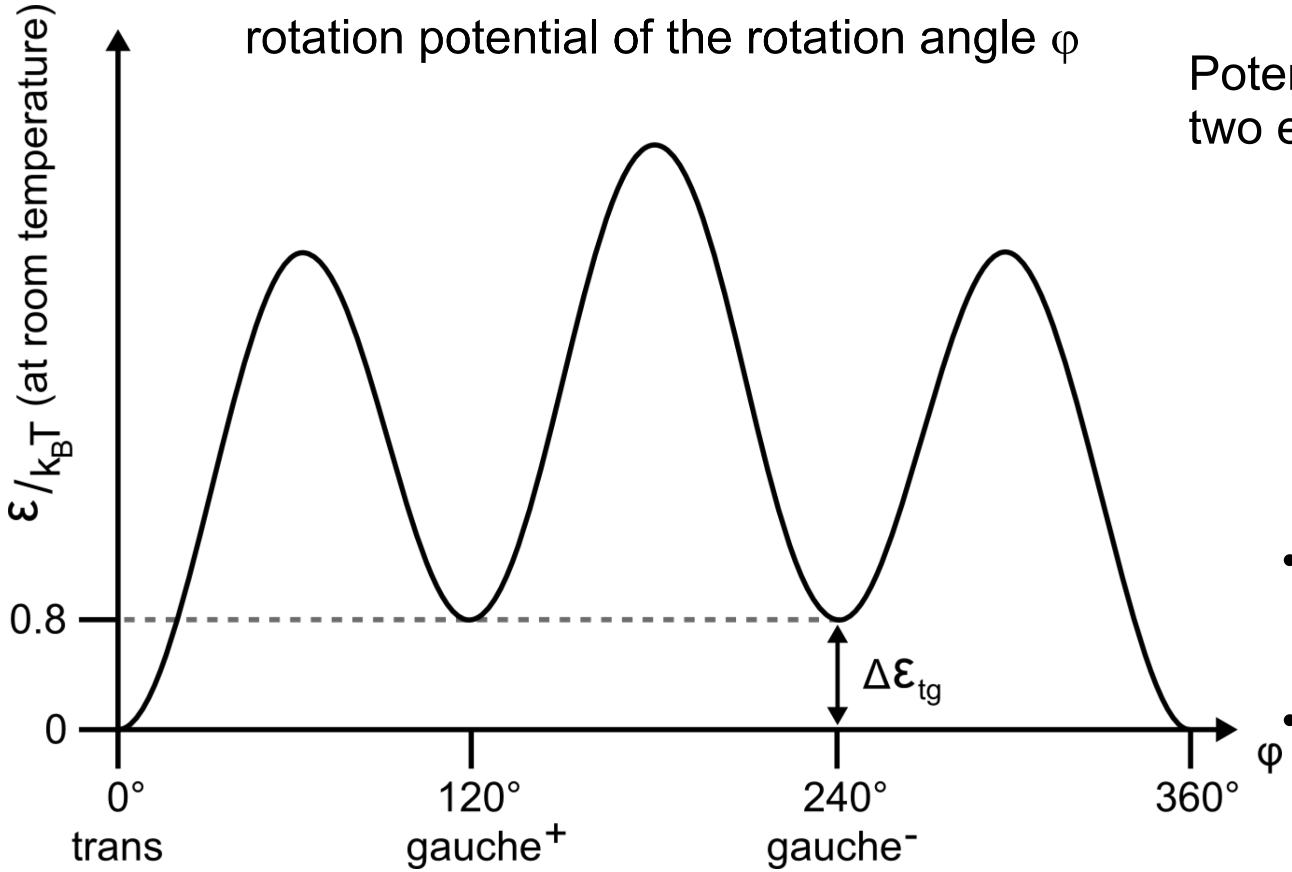
Origin of Flexibility of Polymers

Polyethylene:



all carbons lie in one plane!

bond length l ~ $1.54\ \dot{A}\ (\text{const!} \pm 0.05\ \dot{A})$
tetrahedral angle $\Theta = 68°$ almost const.
$R_{max} = nl \cos(\Theta/2)$


rotation potential of the rotation angle φ

Potential energy shows two equal minima at

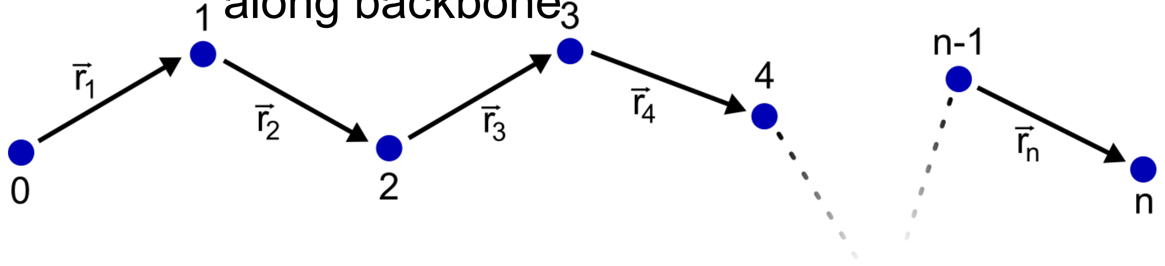
120° gauche$^+$
240° gauche$^-$
$\Delta\varepsilon_{tg} = 0.8\ k_B T$

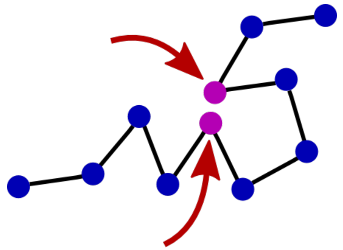
- all different rotational isomeric states can be occupied
- large conformational state space

Ideal Chain Conformations

- only local interactions between monomers

close in space along backbone





non-local in backbone
→ leads to non-ideal behavior
SAW

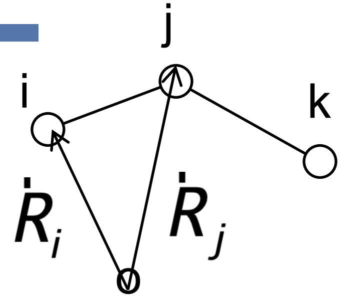
$\vec{R}_n = \sum_{i=1}^{n} \vec{r}_i$ “End-to-End vector”

$\langle \vec{R}_n \rangle = 0$ no preferred orientation in each step

$= \sum_{i=1}^{n} \langle \vec{r}_i \rangle$ mathematically described as a random walk

$\langle \, \rangle$ ensemble average over all possible states of the system (i.e. many chains or many realizations of one chain)

Radius of Gyration



$\vec{R}_j$ position vector of monomers

$$\vec{R}_{CM} \equiv \frac{1}{N}\sum_{j=1}^{N}\vec{R}_j \quad \text{(set all masses to unity)}$$

$$\langle R_G^2\rangle = \frac{1}{N}\left\langle\left(\vec{R}_i - \vec{R}_{CM}\right)^2\right\rangle = \frac{1}{N}\left\langle\sum_{i=1}^{N}\left(\vec{R}_i^2 - 2\vec{R}_i\vec{R}_{CM} + \vec{R}_{CM}^2\right)\right\rangle$$

$$= \frac{1}{N^2}\left\langle\sum_{i,j}^{N}\left(\vec{R}_i^2 - 2\vec{R}_i\vec{R}_j + \vec{R}_i\vec{R}_j\right)\right\rangle = \frac{1}{2N^2}\sum_{i,j}^{N}\left\langle\vec{R}_i^2 - 2\vec{R}_i\vec{R}_j + \vec{R}_j^2\right\rangle$$

$$= \frac{1}{2N^2}\sum_{i,j}^{N}\left\langle\left(\vec{R}_i - \vec{R}_j\right)^2\right\rangle$$

Following relations can be proven:

ideal chain: $\frac{\langle R_n^2\rangle}{\langle R_G^2\rangle} = 6$

rod: $\frac{\langle R_n^2\rangle}{\langle R_G^2\rangle} = 12$

uniform sphere : $\frac{\langle R_n^2\rangle}{\langle R_G^2\rangle} = \frac{5}{3}$
of radius R

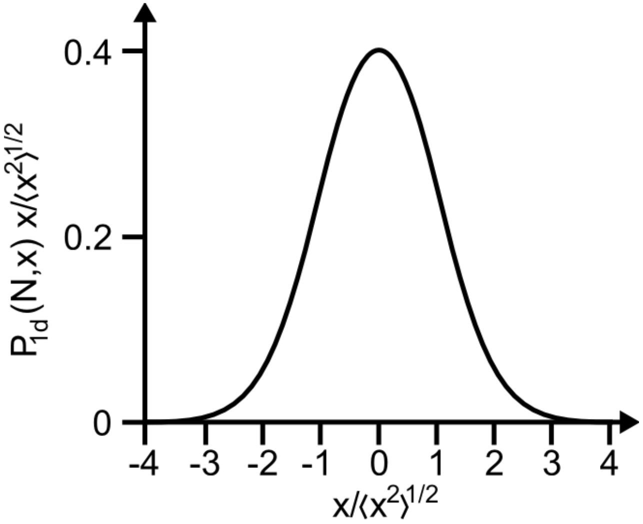
End-to-End Distance Distribution

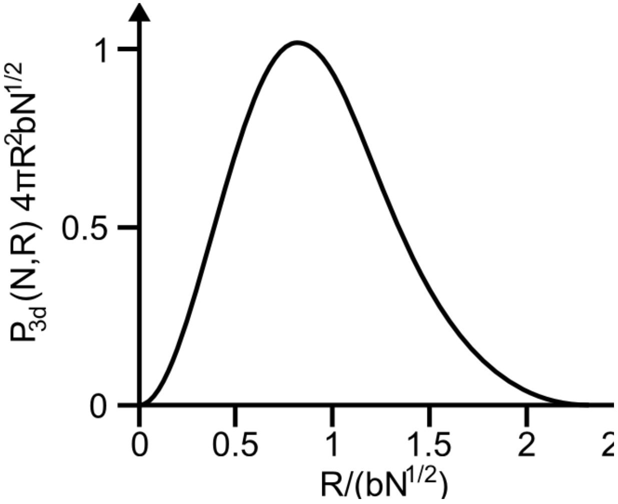
$$\boxed{P(\vec{R},N) = \left(\frac{2\pi N b^2}{3}\right)^{-3/2} \exp\left(-\frac{3R^2}{2Nb^2}\right)}$$

equivalent to a RW distribution

In spherical coordinates it can be written as: here $|\vec{R}| = R$

$$P_{3D}(R,N)4\pi R^2 \mathrm{d}R = 4\pi \left(\frac{2\pi N b^2}{3}\right)^{-3/2} \exp\left(-\frac{3R^2}{2Nb^2}\right) R^2 \mathrm{d}R$$





Be aware: For $R > R_{max}$ the Gaussian approximation predicts a finite probability, which is unphysical

Free Energy of an Ideal Chain

Entropy $S = k_B \ln \Omega$

$\Omega(N,\vec{R})$: number of conformations of a freely jointed chain with N monomers and $\vec{R}$

$$\hookrightarrow \; P_{3D}(N,\vec{R}) = \frac{\Omega(N,\vec{R})}{\int \Omega(N,\vec{R}) \mathrm{d}R}$$

$$\begin{aligned}
\hookrightarrow S(N,\vec{R}) &= k_B \ln P_{3D}(N,\vec{R}) + k_B \ln\left[\int \Omega(N,\vec{R})\right] \\
&= -\frac{3}{2} k_B \frac{R^2}{Nb^2} + \underbrace{\frac{3}{2} k_B \ln\left(\frac{3}{2\pi N b^2}\right) + k_B \ln\left[\int \Omega(N,\vec{R}) \mathrm{d}R\right]} \\
&= -\frac{3}{2} k_B \frac{R^2}{Nb^2} \qquad\qquad + S(N,0)
\end{aligned}$$

$\hookrightarrow \max\left(S(N,\vec{R})\right) = S(N,0)$ Helmholtz-Free energy:

$$F(N,\vec{R}) = \underbrace{U(N,\vec{R})}_{\text{ideal chain has no long range interaction, independent of } \vec{R}} - TS(N,\vec{R}) = \frac{3}{2} k_B T \frac{R^2}{Nb^2} + \underbrace{F(N,0)}_{U(N,0) - TS(N,0)}$$

Free Energy of an Ideal Chain

Ideal chain free energy increases $\sim\vec{R}^2$

Hooke's law of a spring!

To stretch the chain ends by a distance R_x in x-direction requires a force

$$f_x = \frac{\partial F(N,R_x)}{\partial x} = \frac{3k_BT}{Nb^2}R_x, \text{ or in general } \boxed{\vec{f} = \underbrace{\frac{3k_BT}{Nb^2}}_{\text{entropic spring constant}}\vec{R}}$$

For large N, large b, lower T a polymer becomes easier to stretch

Entropic elasticity

Metals and ceramics become soft as T is raised energetic elasticity

Rubber contracts if one raises T [or heats up when one extends it!]

www.youtube.com/watch?v=GUY1w2WX2tc

$$F(N,\vec{R}) = \frac{3}{2}K_BT\frac{R^2}{Nb^2}$$

Scaling of the Polymer Extension

For polymers different scaling regimes exist
in the limit of large N:
$R \sim N^{\nu}$
where ν is called the Flory exponent

Ideal (RW, Gaussian) chain or Θ – solvent:	$\nu = 1/2$
SAW, real chain, polymer in good solvent:	$\nu = 0.63\ldots$ (Flory $\nu = 3/5$)
Polymer in poor solvent:	$\nu = 1/3$
Polyelectrolyte:	$\nu = 1$

Flory Scaling Theory (Real Chains)

In reality, chains can not intersect, have excluded volume. ↷ Self-Avoiding Walk (SAW)

The energy of excluded volume interaction is $k_B T$ per exclusion $v\frac{N}{R^3}$, for N monomers we have $F_{Rep} \sim k_B T v \frac{N^2}{R^3}$ (second virial interaction)

Minimization:

$$\curvearrowright \frac{F^{Flory}}{k_B T} \sim \frac{R^2}{Nb^2} + v\frac{N^2}{R^d} \quad \Bigg\| \quad \frac{\partial F^{Flory}}{\partial R} = 0 \Rightarrow \frac{R}{Nb^2} - v\frac{N^2}{R^{d+1}} = 0$$

up to pre-factors

$$\Rightarrow \boxed{R \sim N^{\frac{3}{d+2}}}$$

ν Flory exponent

d	ν^{Flory}	ν_{exact}
1	1	1
2	$\frac{3}{4}$	$\frac{3}{4}$
3	$\frac{3}{5}$	0.588…
4	$\frac{1}{2}$	$\frac{1}{2}$

$d \geq 4$ no correction in chain statistics due to excluded volume "upper critical dimension"

Blobology (left out more or less)

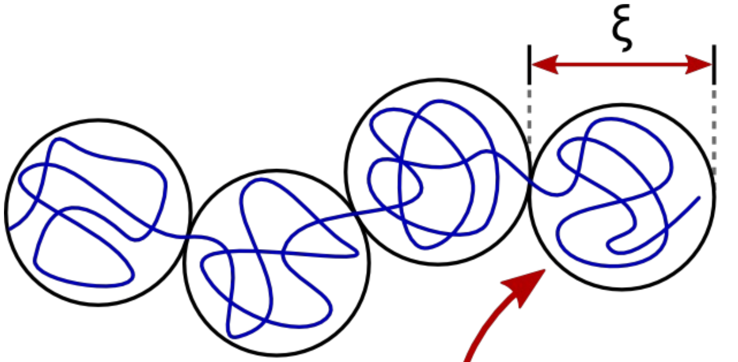
deGennes scaling theory…

P.G. deGennes, Scaling Concepts in Polymer Physics, Cornell University Press, Ithaca (1979).

Sufficiently small parts of the chain are unperturbed (blobs)

Chain ~ sequence of blobs

Yielding simple power law scaling relations



g monomers/blob

Hydrodynamics of polymers

Hydrodynamic radius of a polymer $$\langle \frac{1}{R_H} \rangle = \frac{1}{N} \sum_{i \neq j} \langle \frac{1}{|\vec{r}_i - \vec{r}_j|} \rangle$$

Einstein relation $$D_0 = \frac{k_B T}{\Gamma_0}$$

Stokes relation $$\Gamma_0 = 6\pi\eta R$$

Stokes-Einstein $$D = \frac{k_B T}{6\pi\eta R}$$

Single monomer Γ_0

Rouse dynamics $$\Gamma_R(N) = \sum_i^N \Gamma_i = N\Gamma_0 \qquad D_{Rouse}(N) = \frac{k_b T}{\Gamma_0} N^{-1}$$

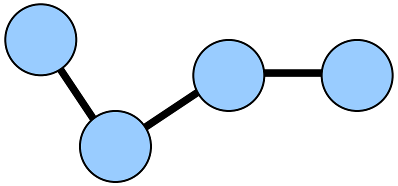
Zimm dynamics $$\Gamma_Z(N) \sim 6\pi\eta R(N) \sim 6\pi\eta R^\nu \qquad D_{Zimm} = \frac{k_B T}{\Gamma_Z(N)} \sim \frac{k_B T}{6\pi\eta b} N^{-\nu}$$

Chain as a coil

Kirkwood-Zimm Theory $$D_{KZ}(N) = \frac{D_0}{N} + \frac{k_B T}{6\pi\eta} \langle \frac{1}{R_H} \rangle$$

Ex: Gaussian Polymer in a Θ-Solvent

- Conformational properties of a Gaussian polymer in a Θ-solvent are that of a random walk
- ➔ Basis for bead-spring model of a polymer!



- Use a harmonic potential for the bonds:

$$V_{\mathrm{h}}(r) = \frac{k}{2}\left(r - r_0\right)^2$$

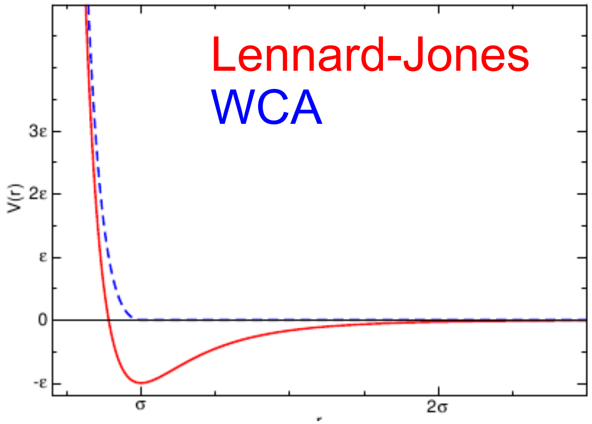
- We can compute the partition function exactly

$$H_0 = \frac{1}{2}\underbrace{\frac{3k_BT}{b^2}}_{k}\sum_{i=0}^{N-1}\left|\vec{r_i} - r_{\vec{i+1}}\right|^2$$

- Random walk and bead-spring model generate the same partition function!

Polymer Chains in Good Solvent

- Θ-solvent is a special case!
- Solvents are good or poor w.r.t. to the polymer
- Good solvent can be modeled via a repulsive potential
  - Use the repulsive part of Lennard-Jones (aka Weeks-Chandler-Anderson)

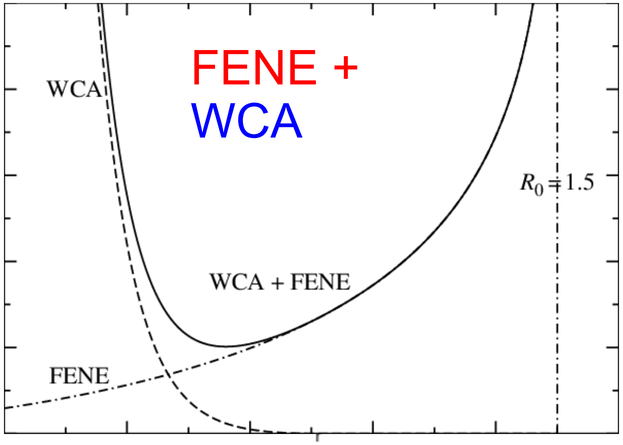


$$V_{\mathrm{WCA}}(r) = \begin{cases} V_{\mathrm{LJ}}(r) + \varepsilon & , \text{if } r < 2^{1/6}\sigma \\ 0 & , \text{otherwise} \end{cases}$$

- FENE (Finite Extensible Nonlinear Elastic) bond

$$V_{FENE}(r) = -\frac{1}{2} k R_0^2 \ln(1 - \frac{r}{R_0})$$

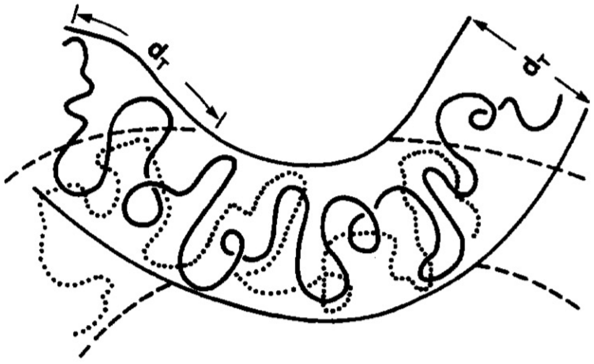
  - Has a maximal extension/compression
  - Sufficient to avoid bond crosssing



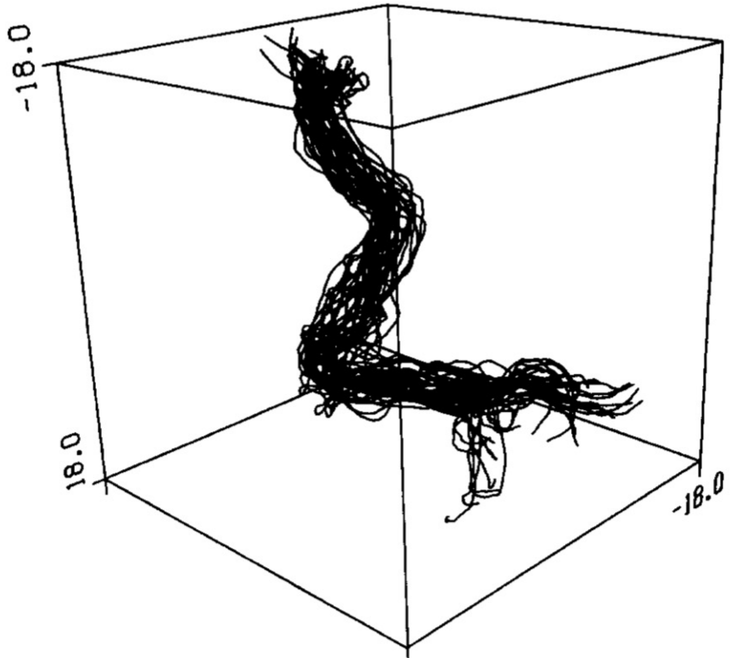
Kremer-Grest Model

K. Kremer, G. Grest, J. Chem. Phys. **92**, 5057 (1990)

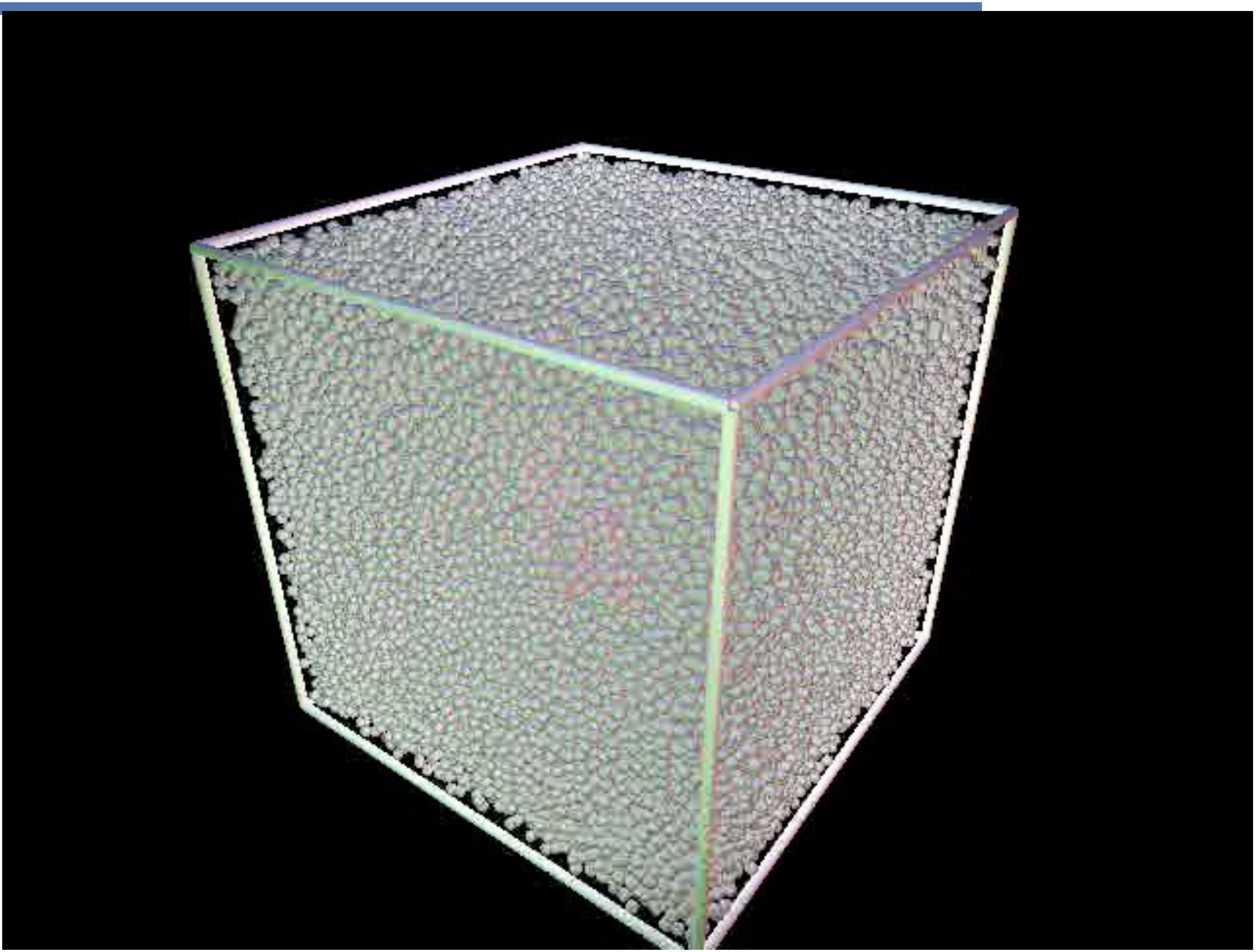
- The standard model for polymer melts!
- Langevin-MD with a bead-spring model: FENE bonds plus WCA potential for beads with Kremer-Grest parameters:
  $R_0 = 1.5\sigma$ and $k = 30\varepsilon/\sigma$
- Very efficient. Sizes can be pushed up to a few hundred chains of 300-400 beads



Idea of Reptation

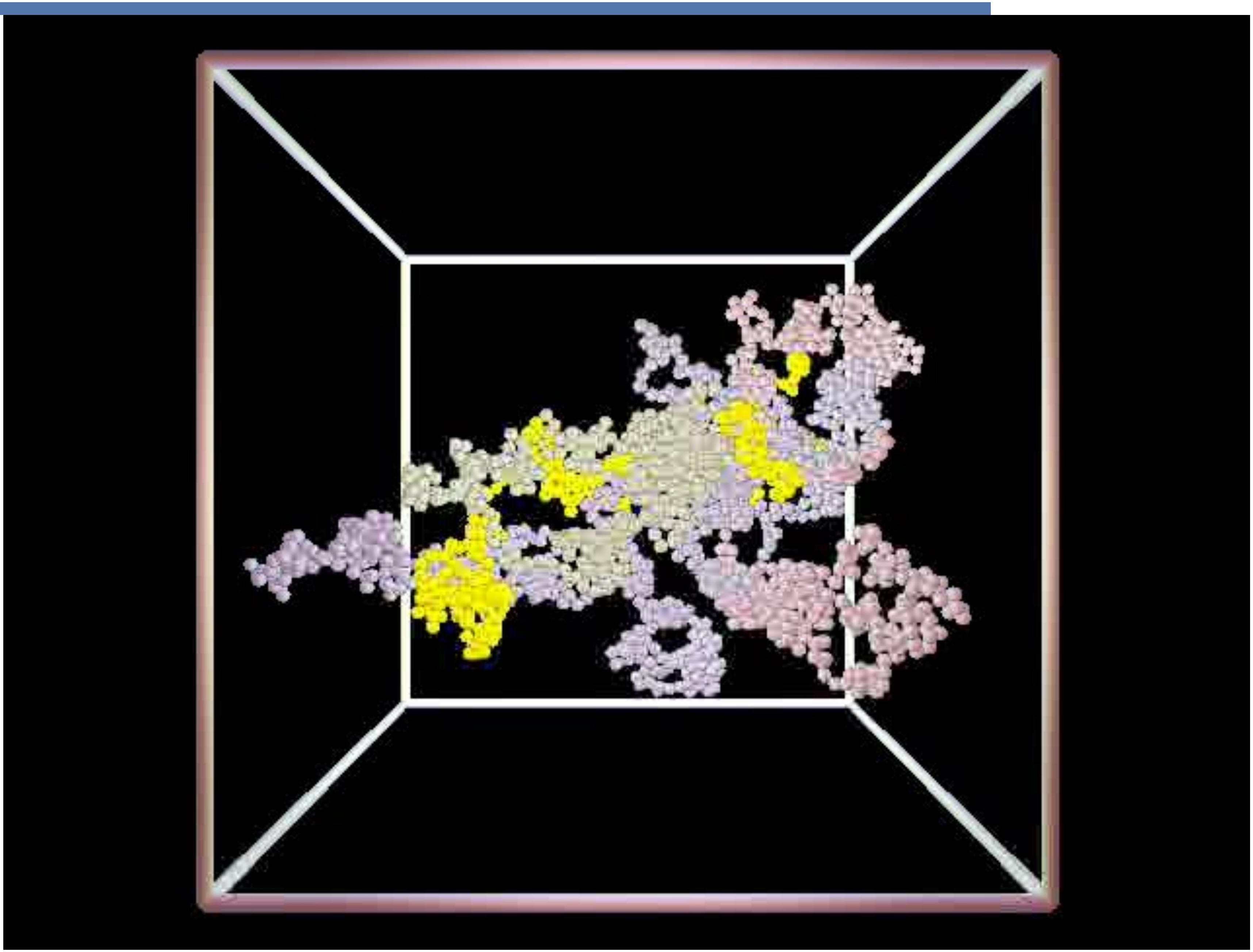


Kremer-Grest Polymer Melt



Ralf Everaers, *et al. Science* **303**, 823 (2004); DOI: 10.1126/science.1091215

Primitive Path Analysis ->



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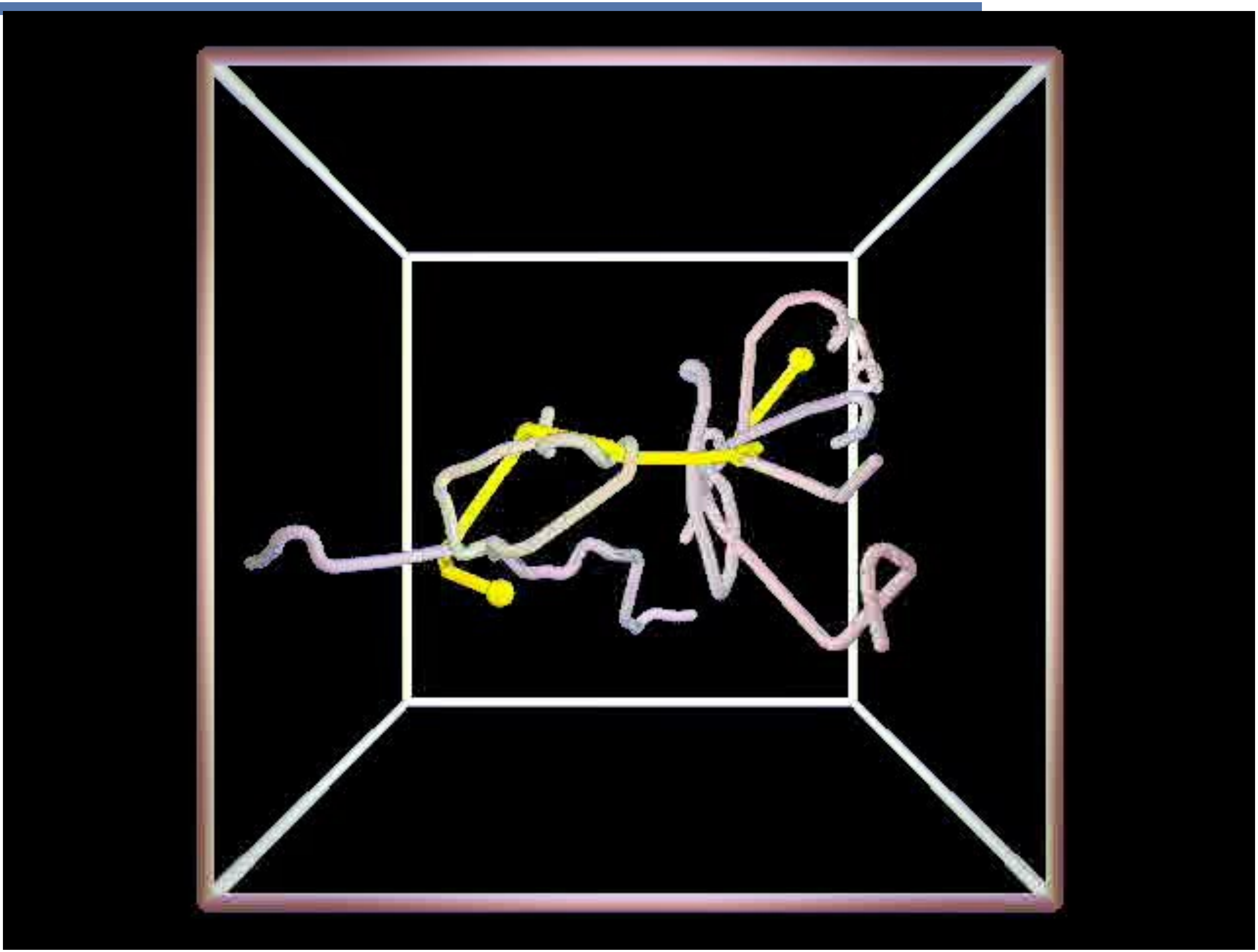
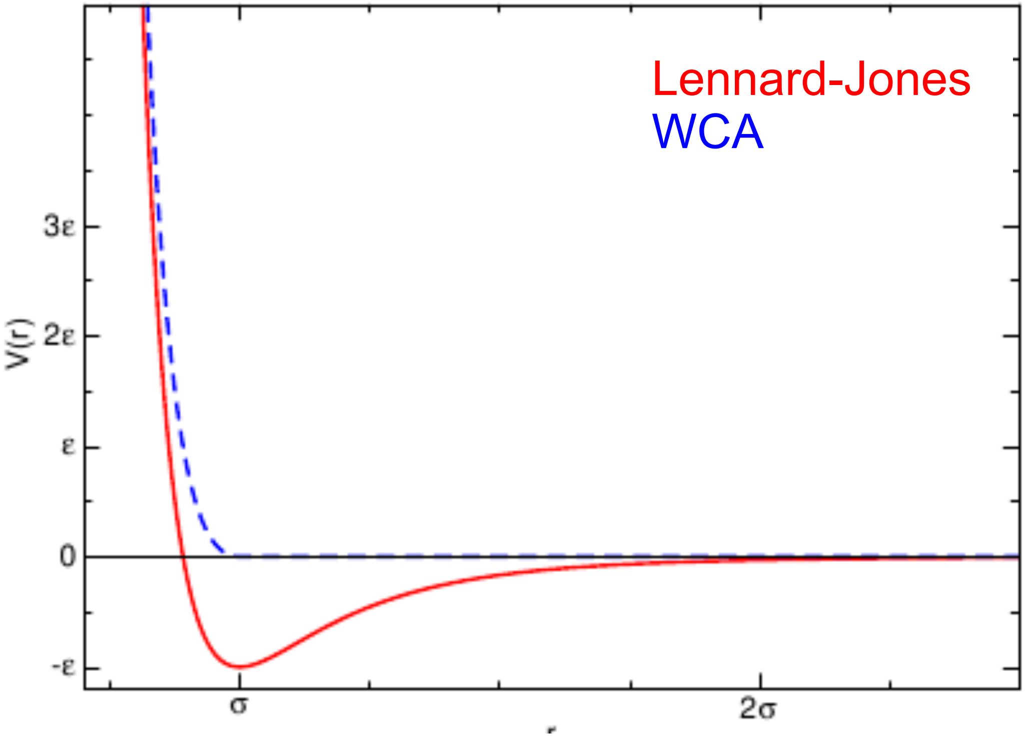
Entanglements



Ralf Everaers, *et al. Science* **303**, 823 (2004); DOI: 10.1126/science.1091215

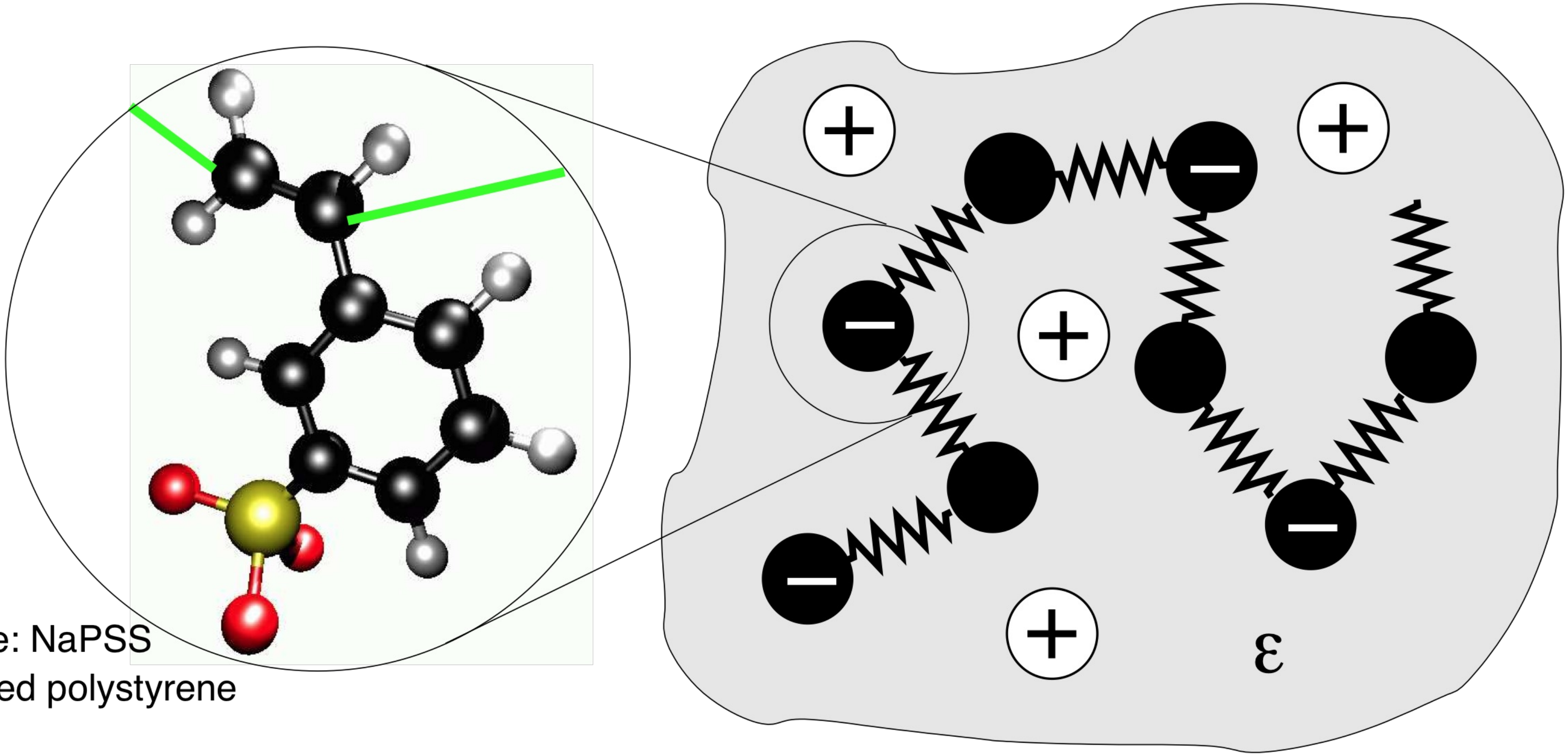
Polymer Chains in Poor Solvent

- Poor solvent can be modeled via a full Lennard-Jones potential
- Polymer monomers experience an attraction, since they want to minimize contact with solvent
- the quality of the solvent can be changed by varying the attraction via the interaction parameter ε and the cut-off



Charged Polymers

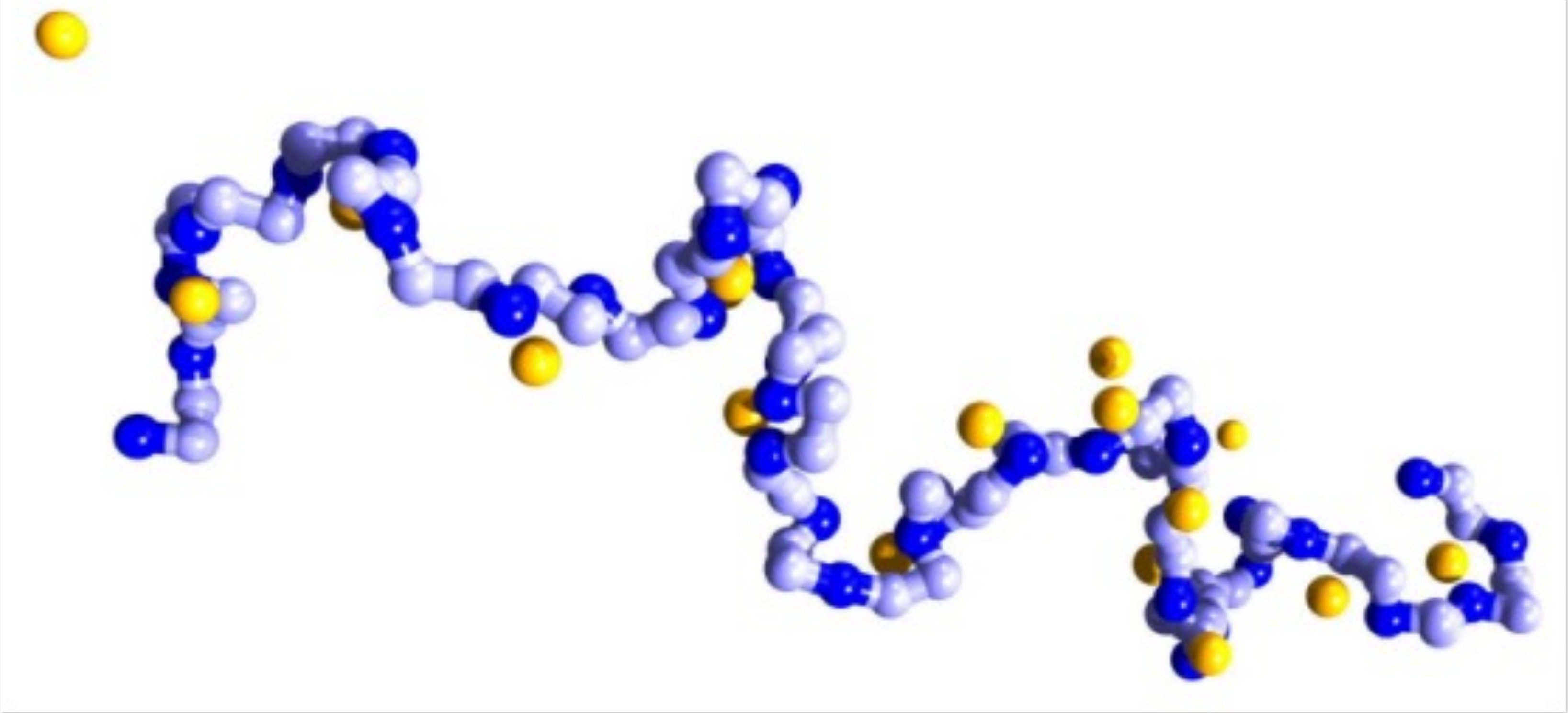
Mapping onto a bead–spring model



Example: NaPSS
sulfonated polystyrene

monomers, ions	→	beads with charge fraction f
bond potential	→	nonlinear springs
solvent	→	dielectric background ε
solvent quality τ	→	effective bead–bead interaction

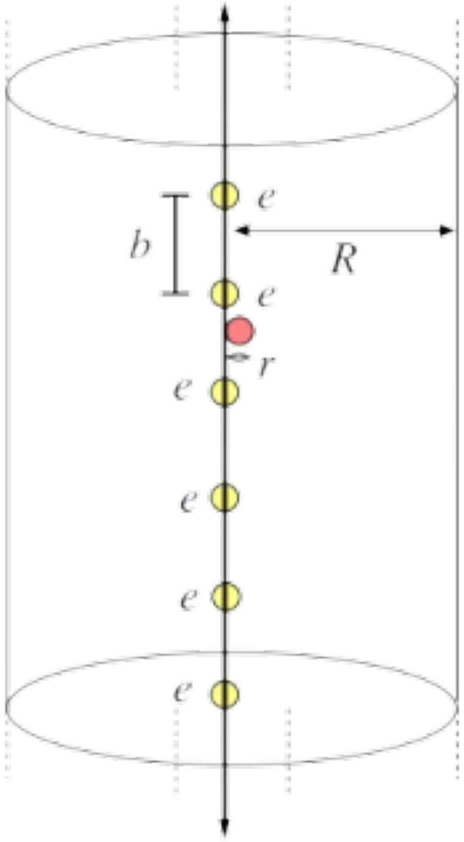
Polymer simplification



complex interaction: ion distribution ↔ polymer conformation

stiff, stretched polymer conformation ⟶ uniformly charged rod.

Onsager Argument for Condensation



$\lambda = e_0/b$ $\qquad$ $\ell_B := e_0^2/4\pi\varepsilon k_B T$

$\phi(r) \approx \frac{\lambda}{2\pi\varepsilon}\ln(r)$

question: $\Delta F = \Delta E - k_B T \Delta S$?

$\Delta E \sim e_o \frac{\lambda}{2\pi\varepsilon} \ln\frac{R}{r}$ $\qquad$ $\Delta S \sim \ln\frac{V_R}{V_r} \sim 2\ln\frac{R}{r}$

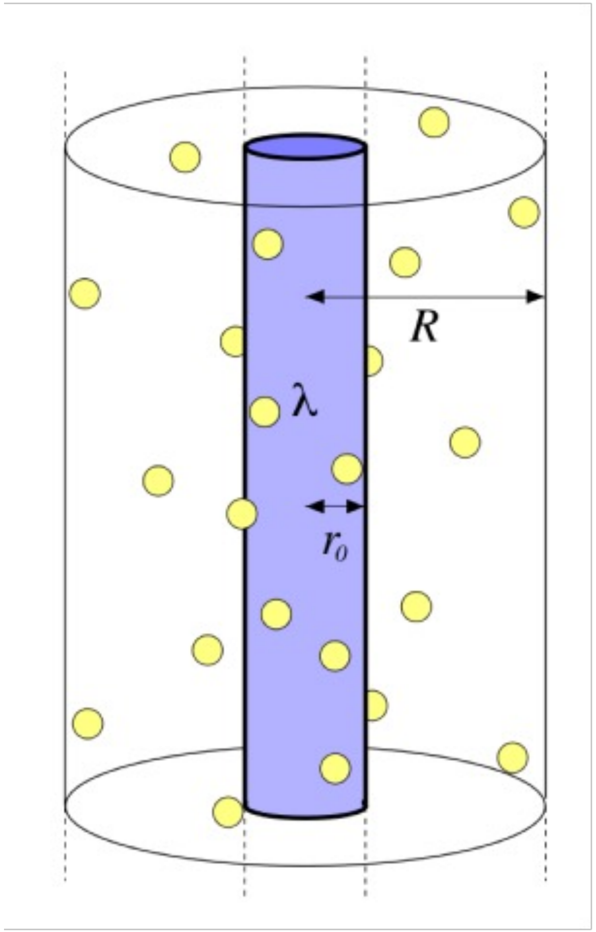
$$\Longrightarrow \Delta F = \left(\frac{\ell_B}{b} - 1\right) 2k_B T \ln\frac{R}{r}$$

$\xi := \frac{\ell_B}{b} < 1$, entropy dominated, $\xi := \frac{\ell_B}{b} > 1$, energy dominated

$\Longrightarrow$ The charged plane is energy dominated

$\Longrightarrow$ The charged sphere is entropy dominated

PB for a cylindrical cell model



Bjerrum length $\ell_\mathrm{B} := e_0^2/4\varepsilon k_\mathrm{B}T$

Manning parameter $\xi := \lambda\ell_\mathrm{B}/e_0$

Reduced potential $y(r) := e_0\Psi(r)/k_\mathrm{B}T$

$$\boxed{\begin{aligned} y'' + \frac{1}{r}\,y' &= 4\pi\ell_\mathrm{B}\,n(r) \\ n(r) &= n(R)\,\mathrm{e}^{y(r)} \end{aligned} \quad ; \quad \begin{aligned} y'(r_0) &= -2\xi/r_0 \\ y'(R) &= 0 \end{aligned}}$$

$$y(r) = -2\ln\left\{\frac{r}{R}\sqrt{1+\gamma^{-2}}\cos\left(\gamma\ln\frac{r}{R_\mathrm{M}}\right)\right\}$$

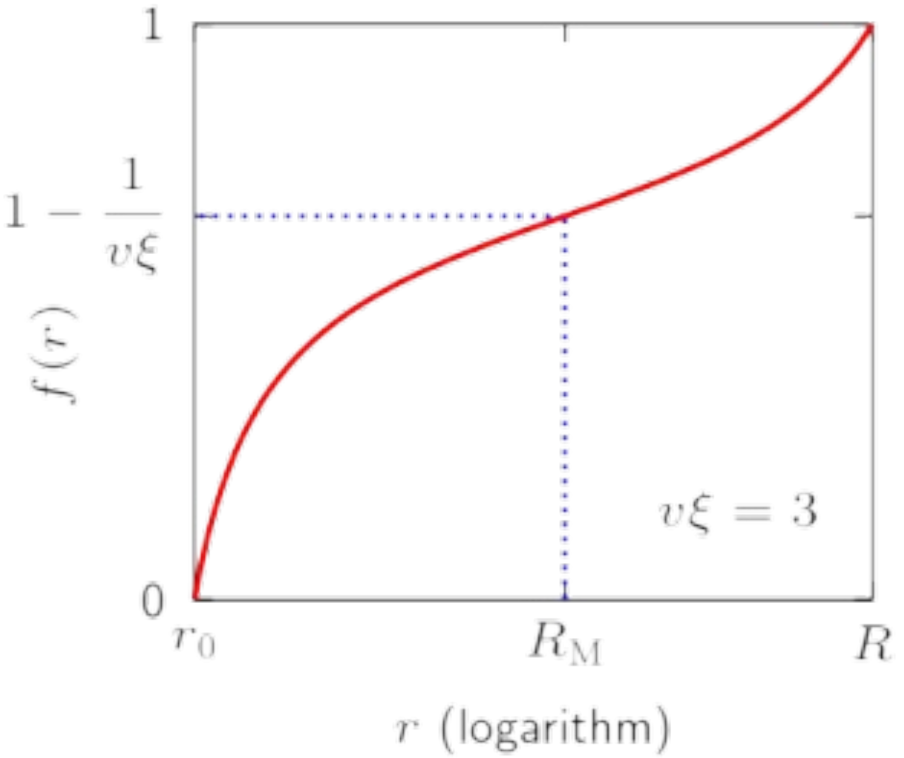
where the integration constants γ and R_M are obtained from the boundary conditions

[Deserno, Holm, & May, *Macromolecules* **33**, 199–206 (2000).]

Counterion Condensation

the fraction of counterions within a distance $r \in [r_0, R]$ is given

$$f(r) = 1 - \frac{1}{\xi} + \frac{\gamma}{\xi} \tan\left(\gamma \ln \frac{r}{R_M}\right)$$



Manning condensation at $\xi > 1$:

$$f < 1 - \frac{1}{\xi} \iff \lim_{R\to\infty} r(f) < \infty$$

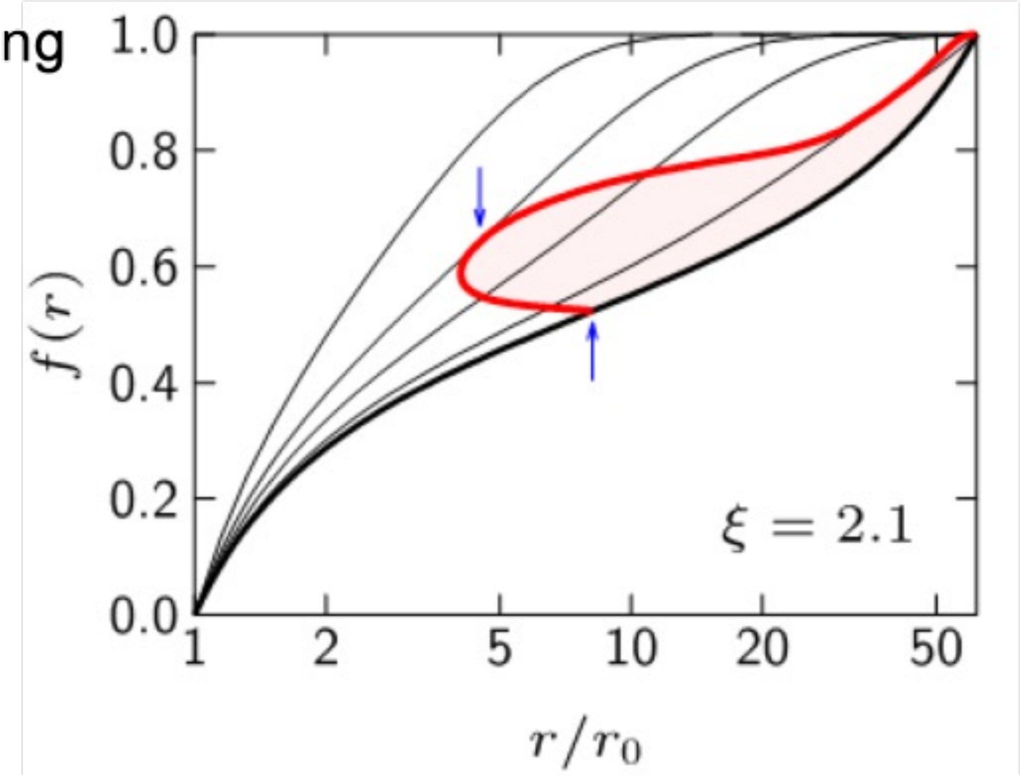
Inflection point criterium:

$$\left.\frac{d^2 f}{d(\ln r)^2}\right|_{r=R_M} = 0 \quad \Rightarrow \quad R_M$$

Condensation with Added Salt

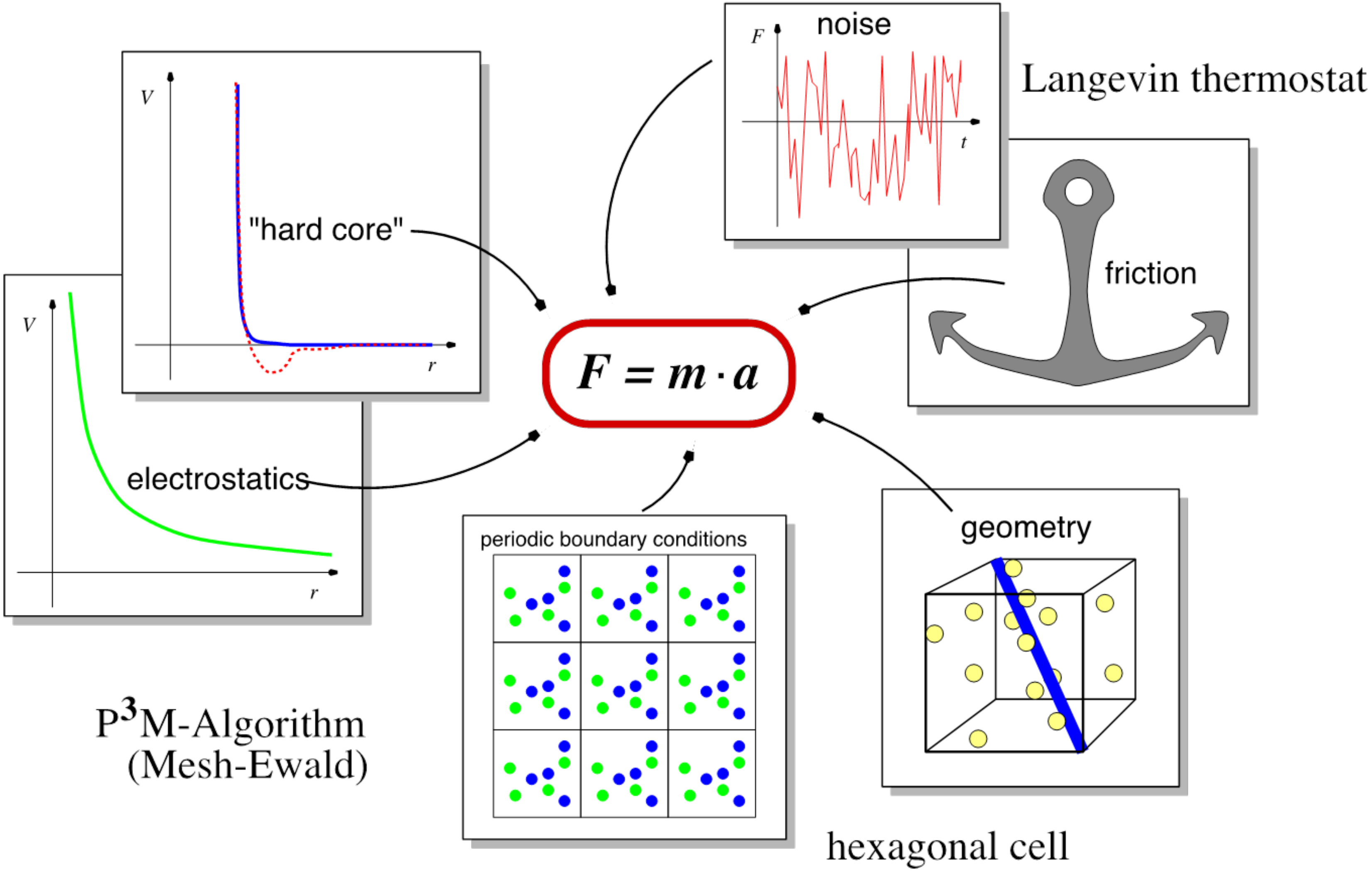
- Inflection points of f(r) → Manning radius & fraction
- Ion fraction → charge fraction
- More salt → more screening: condensed layer contracts

- $\lambda_D < R$: new inflection points for increasing concentration
- $\lambda_D < R_M$: no inflection points (screening dominates)



Exchange of the relevant length-scale: $R_M \to \lambda_D$.
If screening dominates the concept of condensation looses its meaning!

Simulations…



"hard core"

electrostatics

P^{3}M-Algorithm
(Mesh-Ewald)

$F = m \cdot a$

noise

Langevin thermostat

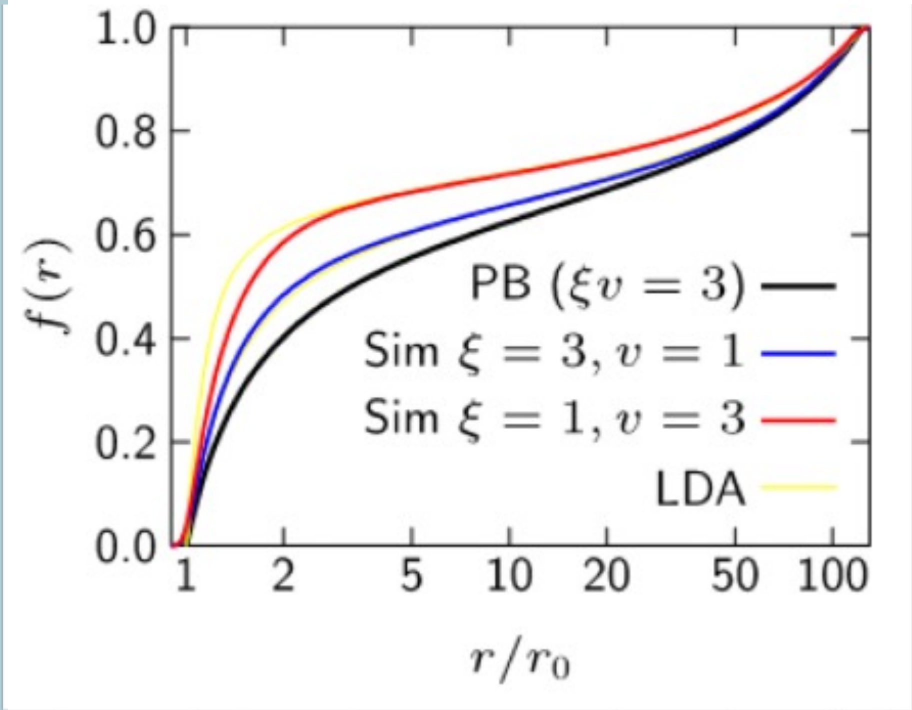
friction

periodic boundary conditions

geometry

hexagonal cell

Manning Parameter versus Valence



- Counterion condensation is stronger than in Poisson-Boltzmann theory.
- Product ξv is no longer universal.
- Discrepancy increases with valence.

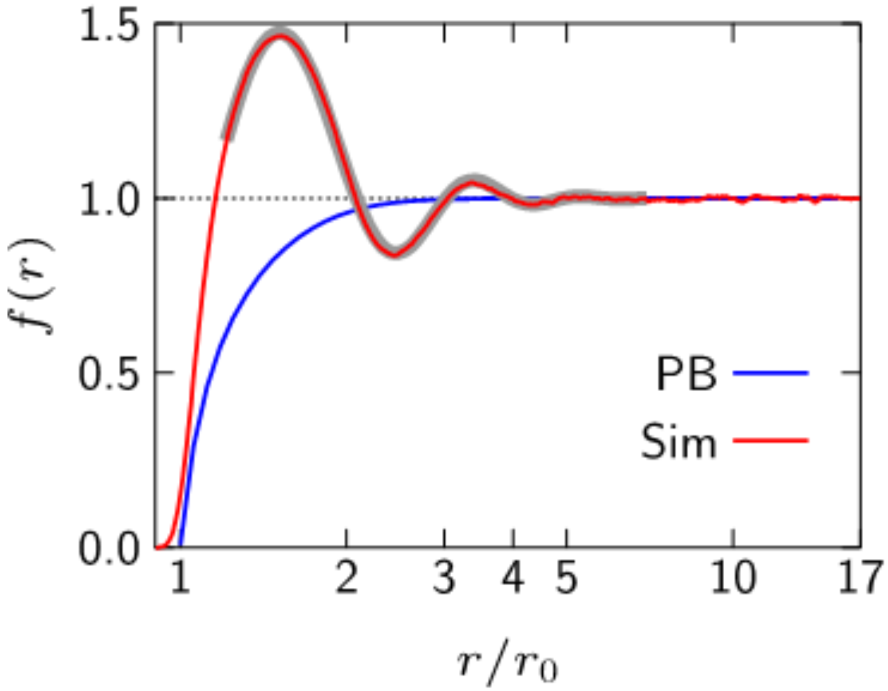
- Local density approximation(LDA): local correction to the PB free energy functional (~first correction on correlation effects)

Poisson-Boltzmann theory neglects correlations; these enhance counterion condensation, especially for multivalent counterions.

Overcharging for Multivalent Salt

$\xi = 4$; 2:2-Salt; $\bar{n} = 2.1 \times 10^{-2}\sigma^{-3}$

- The rod charge gets repeatedly overcompensated.
- Reversed charged layers.
- Charge oscillations are exponentially damped.

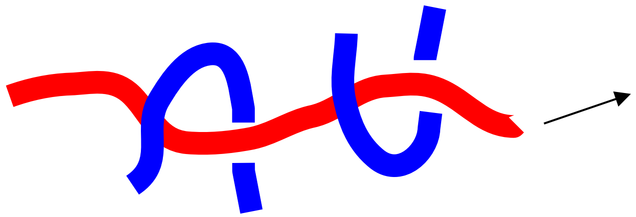


PB fails if:
1) Strong electrostatic interactions (large λ)
2) Multivalent ions (correlation effects)
3) High density (excluded volume becomes important)

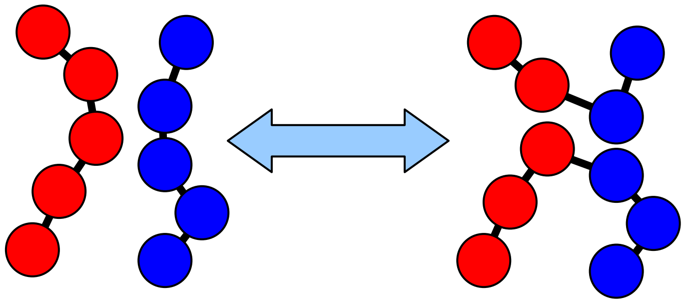
MC moves in molecular simulations

- Single particle moves ensure irreducibility
- Other moves can be invented to faster sample the possible states
- Examples for polymer simulations: pivot, double pivot, or...

Reptation moves



Crossover moves



Summary

- Basic polymer chemistry facts
- Basic polymer physics concepts
- Theoretical description of polymers
- Polymeric diversities and statistics
- How to simulate polymers
- Concept of counterion condensation

Good text books on polymers

- Gert Strobl, *Condensed Matter Physics*, Springer, 2004
- M. Rubinstein, R. Colby, *Polymer Physics*, Oxford University Press, 2003
- Richard A.L. Jones, *Soft Condensed Matter*, Oxford Master Series in Condensed Matter Physics, Vol. 6, 2002