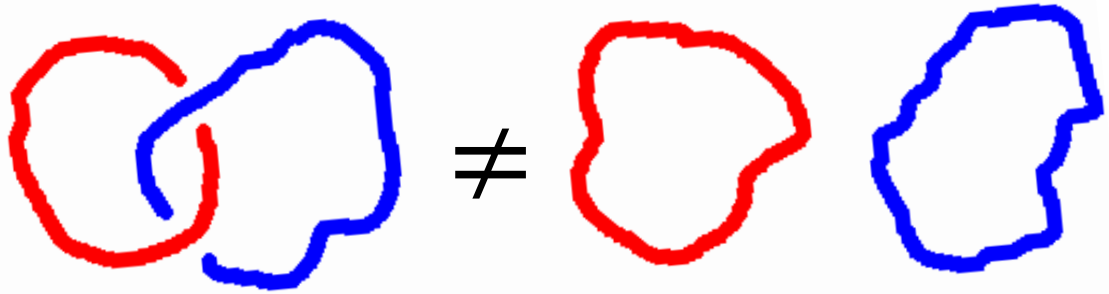
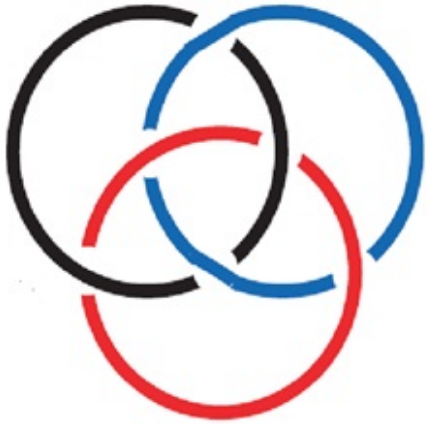


- **Expect tremendous experimental differences**
- **Mathematically extremely difficult to consider**
- **Option for computer simulations**



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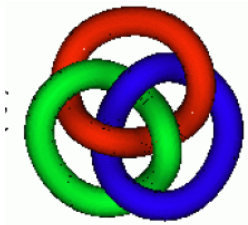
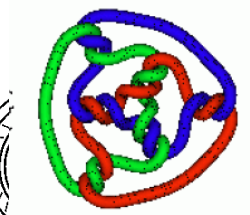
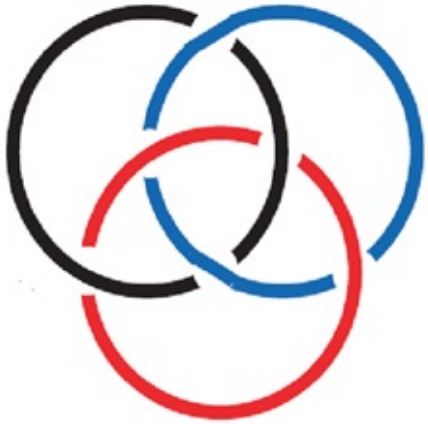




Borromean rings

DNA rings, Nad Seeman, NYU

Door of an Italian church



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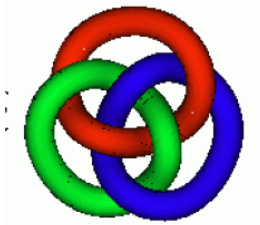
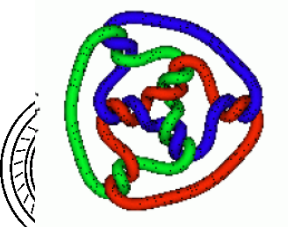




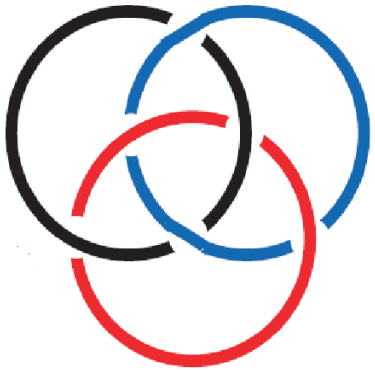
Borromean rings

DNA rings, Nad Seeman, NYU

Door of an Italian church

Topological Constraints Matter

- **Tube concept**
  - **R. Everaers, G. S. Grest, M. Pütz, …**
- Gels etc.
  - **R. Everaers, G. S. Grest, C. Holm, …**
- Melt of non concatenated rings, melt of globules
  - **T. Vettorell, J. Halverson, A. Yu Grosberg**
- Questions



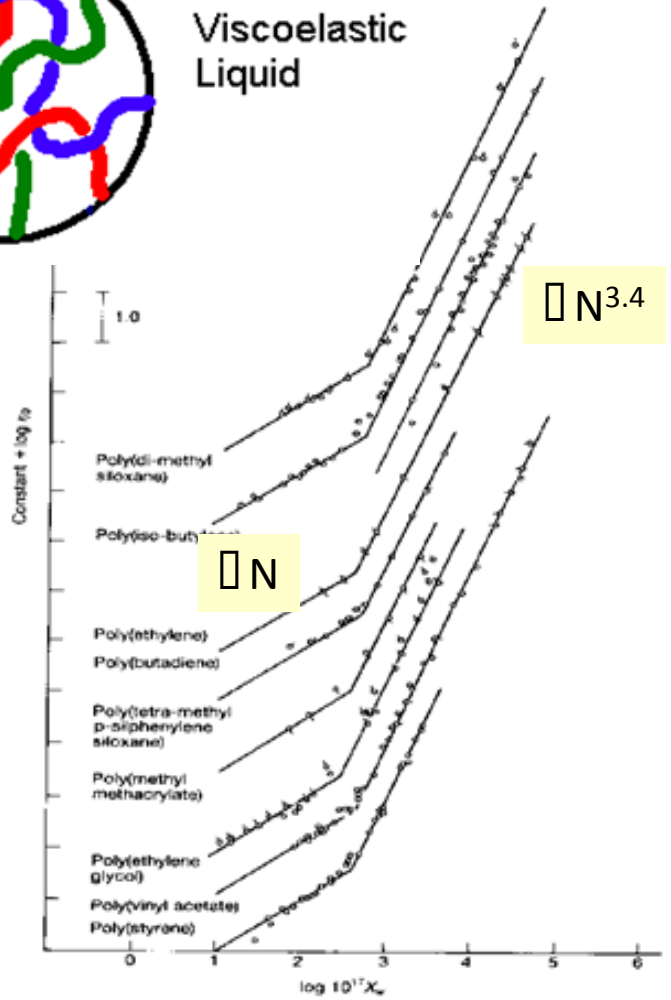
Elastic modulus of network vs 1/N, N chain length

Soft Solid

(Moore & Watson 1956
Mullins 1959)

Melt viscosity vs N

Viscoelastic Liquid

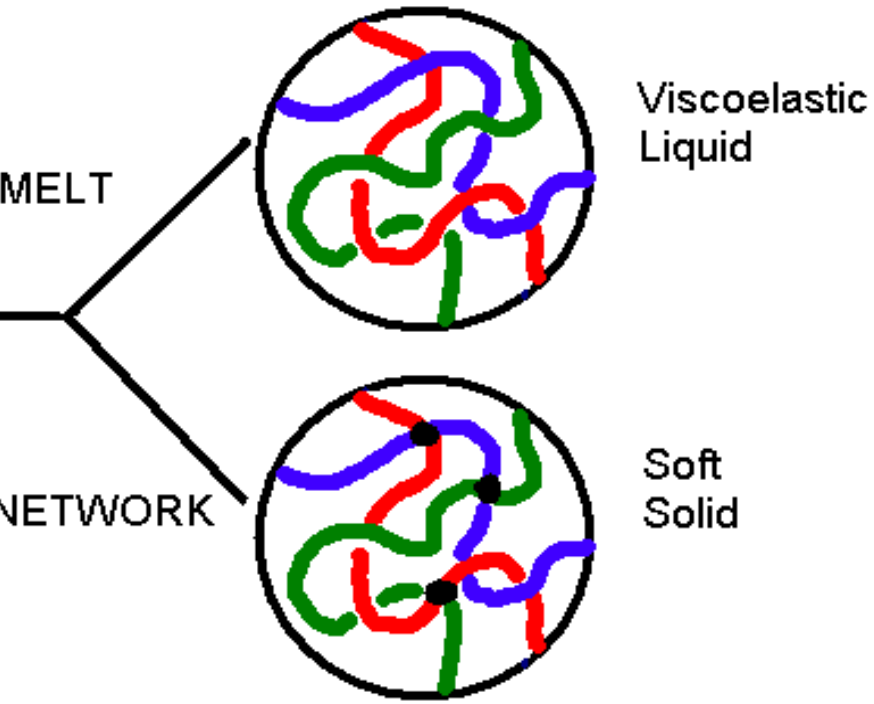


$\propto N^{3.4}$

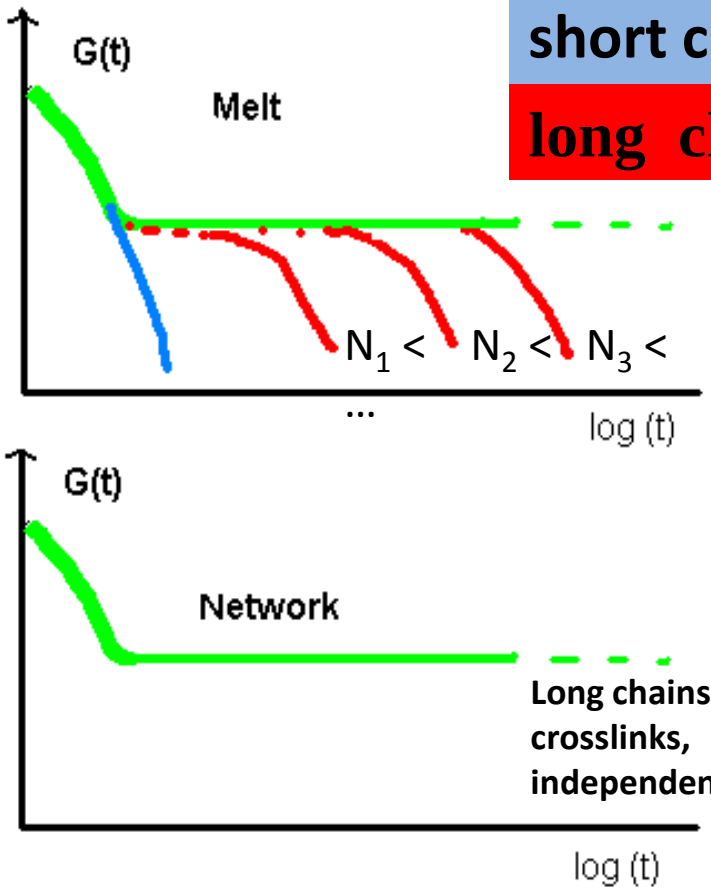
$\propto N$

From Doi and Edwards

Classical Problem: MELT ↔ NETWORK



 quenched

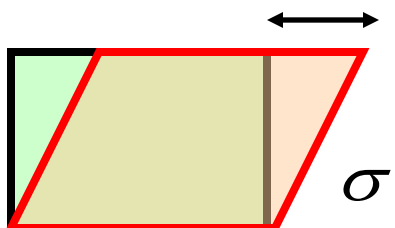


short chains

long chains

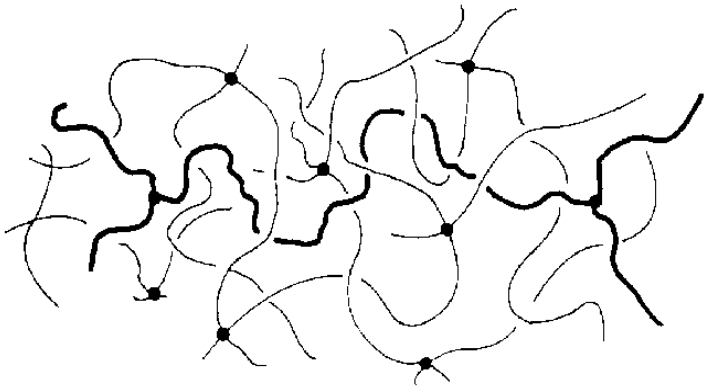
Long chains between crosslinks, independent of N

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

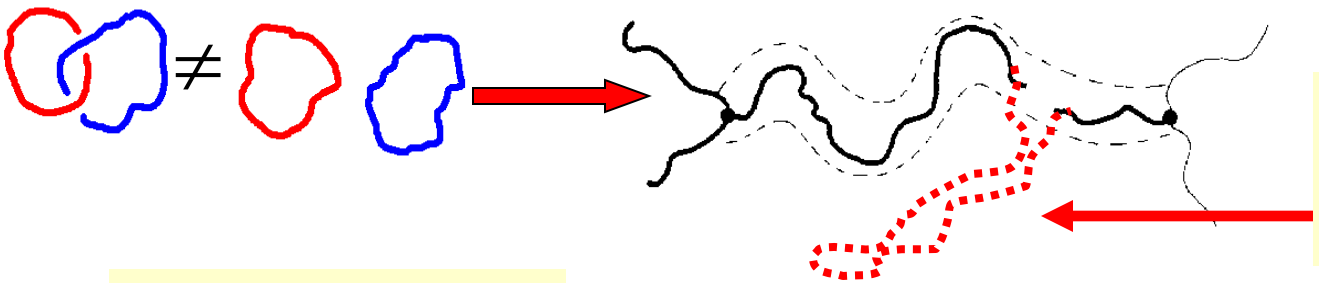


$$\sigma(t) = G(t)(\lambda - 1)$$

Tube Model



Edwards `67



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

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

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

$$\tau_e \propto N_e^2$$

De Gennes `71

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 `67

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

De Gennes `71

d_T

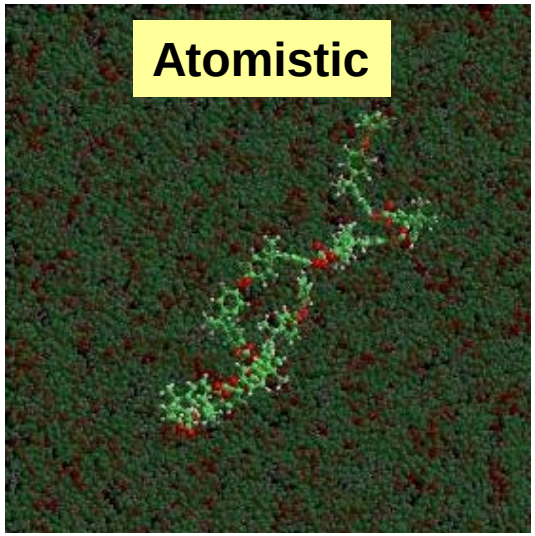
$\tau_e \propto N_e$

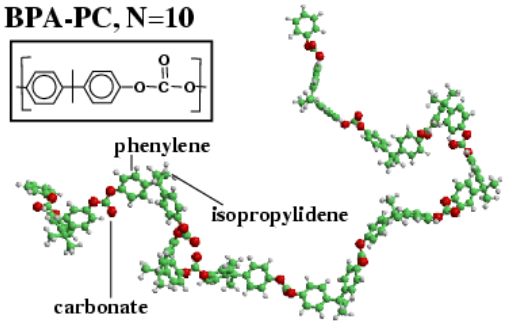
Unique length d_T

Polymers: Simulation

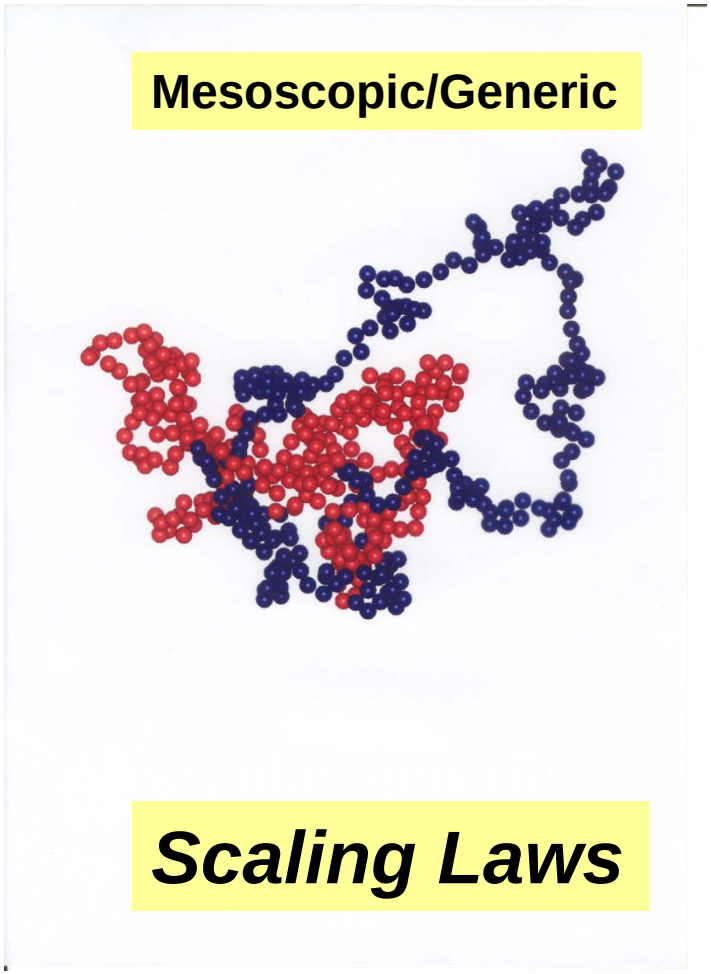
Structure Property Relations

...





versus



...

Polymers: Simulation

Structure Property Relations

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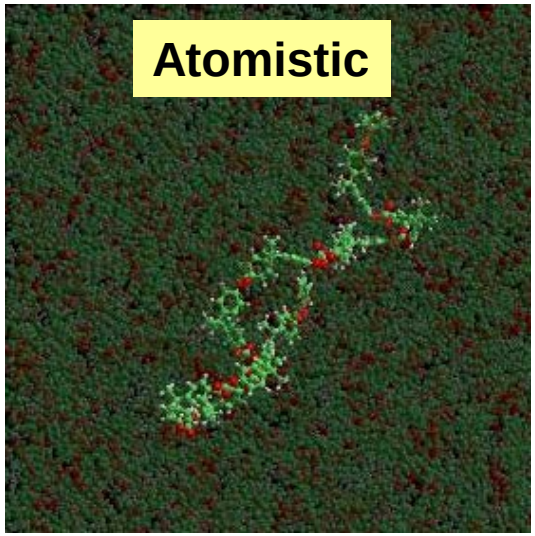

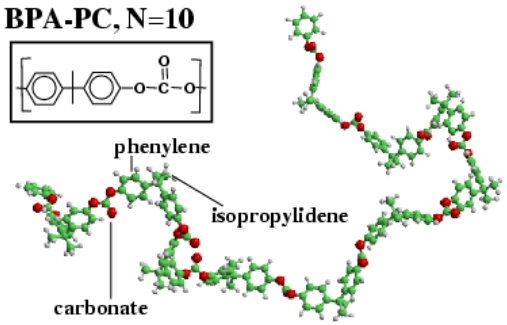

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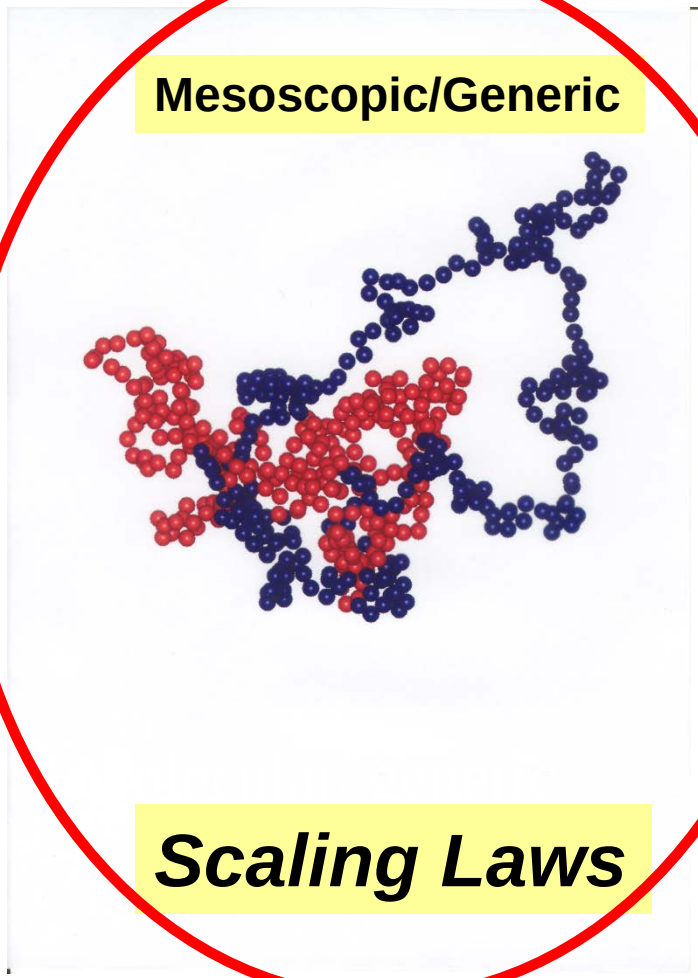
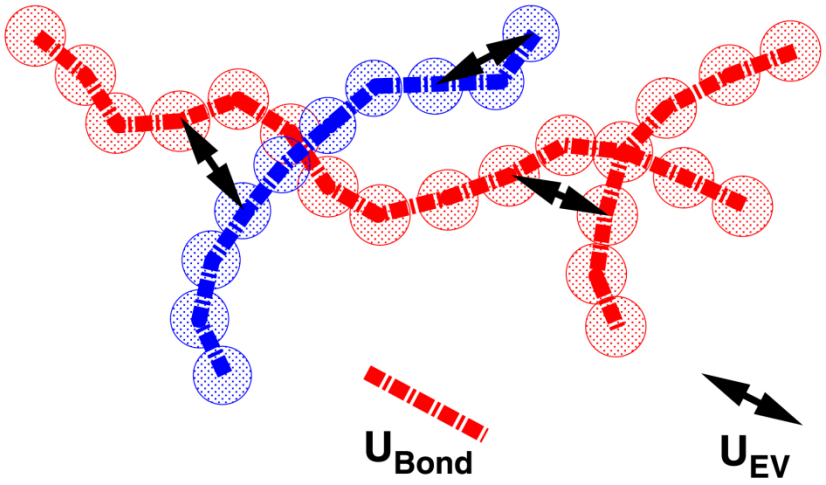
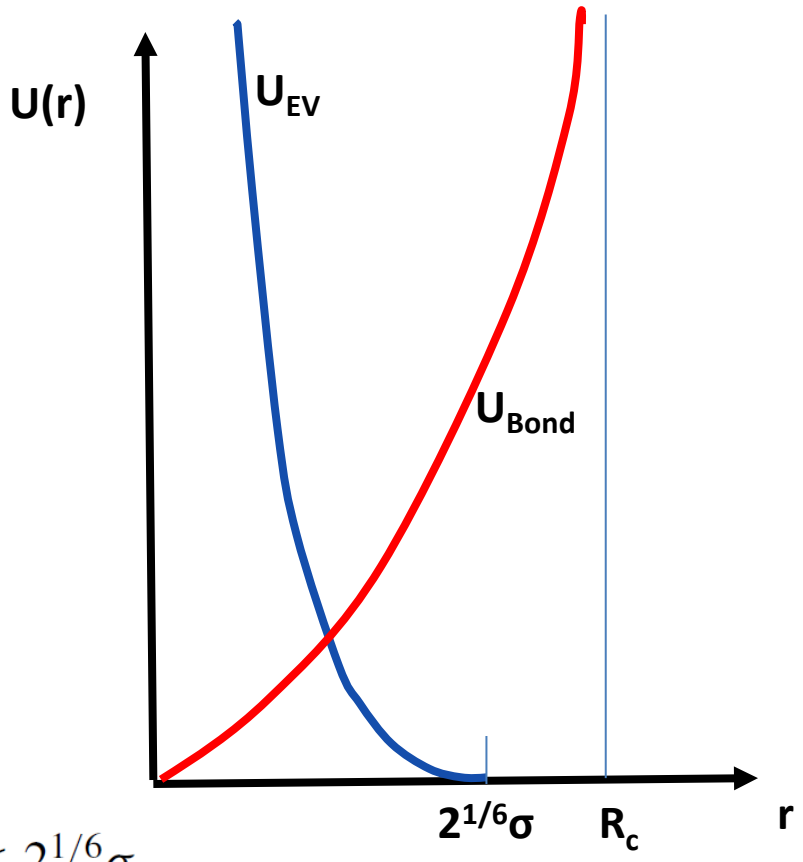


...

“Simplest Model” Bead-spring model

K.K & G.S. Grest



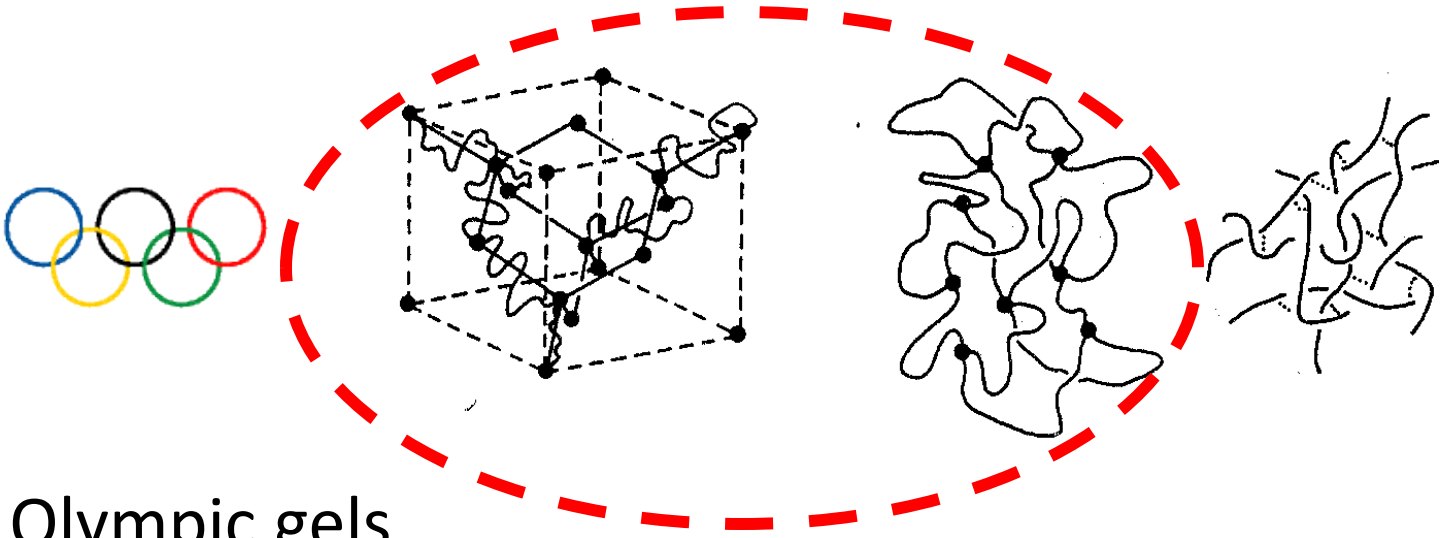


$$U_{Bond} = -30\ k_B T \ln\{1-(\frac{r}{R_c})^2\}$$

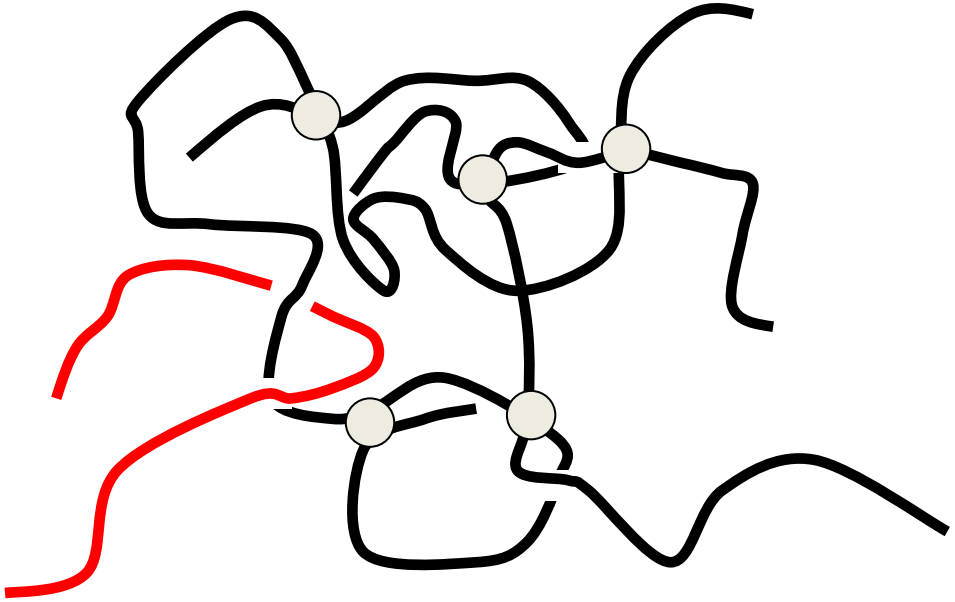
$$U_{\text{pair}}(r_{ij}) = \begin{cases} 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}] + \epsilon, & r_{ij} \le 2^{1/6}\sigma \\ 0, & r_{ij} > 2^{1/6}\sigma \end{cases}$$

- **Topology conservation**
- $U_{Cross} \approx 70 k_B T$

Model Networks



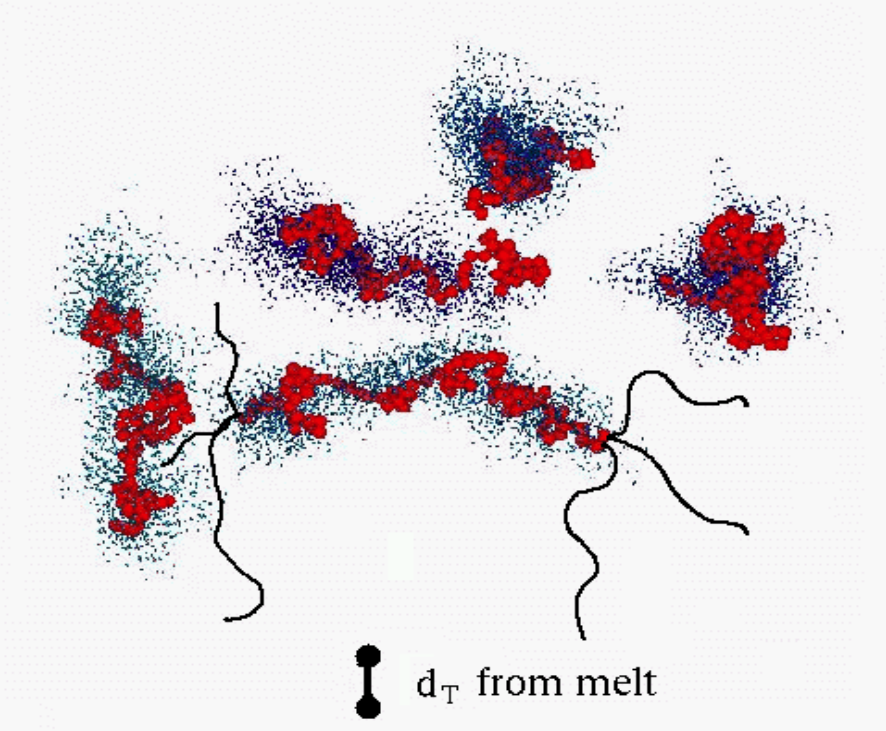
- Olympic gels
- Lattice Networks
- Endlinked melts
- Crosslinked melts

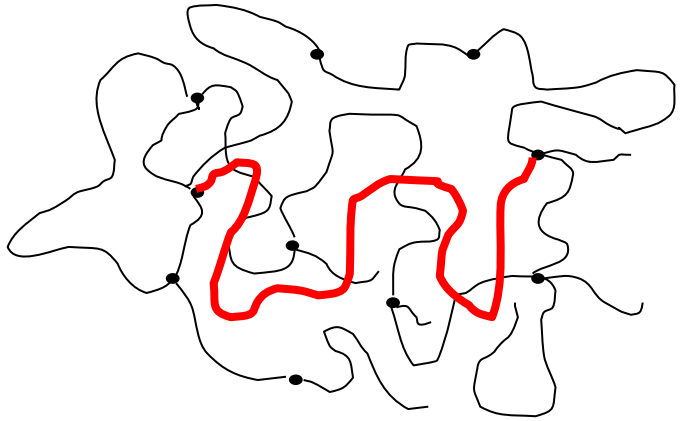


- ~~Polydispersity~~
- ~~Dangling ends~~
- ~~Self loops~~

- Entanglements

Confinement of network chains to a "tube"





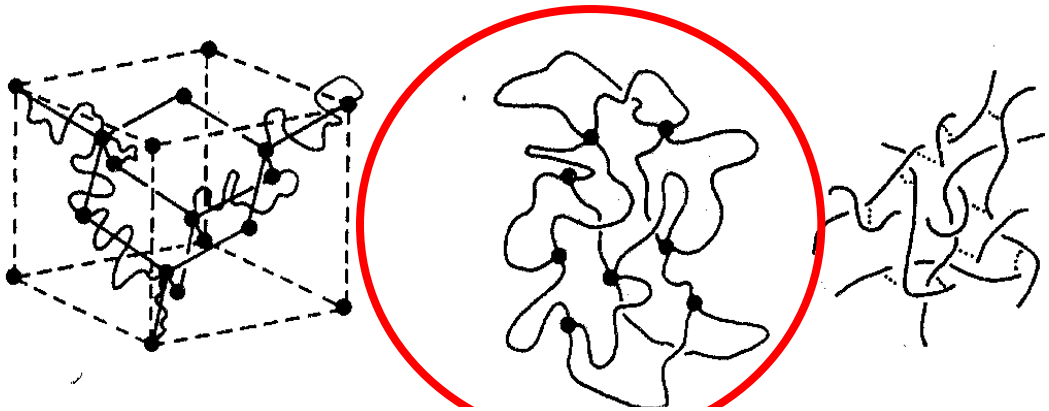
$N = 100 \qquad N_e \approx 70$

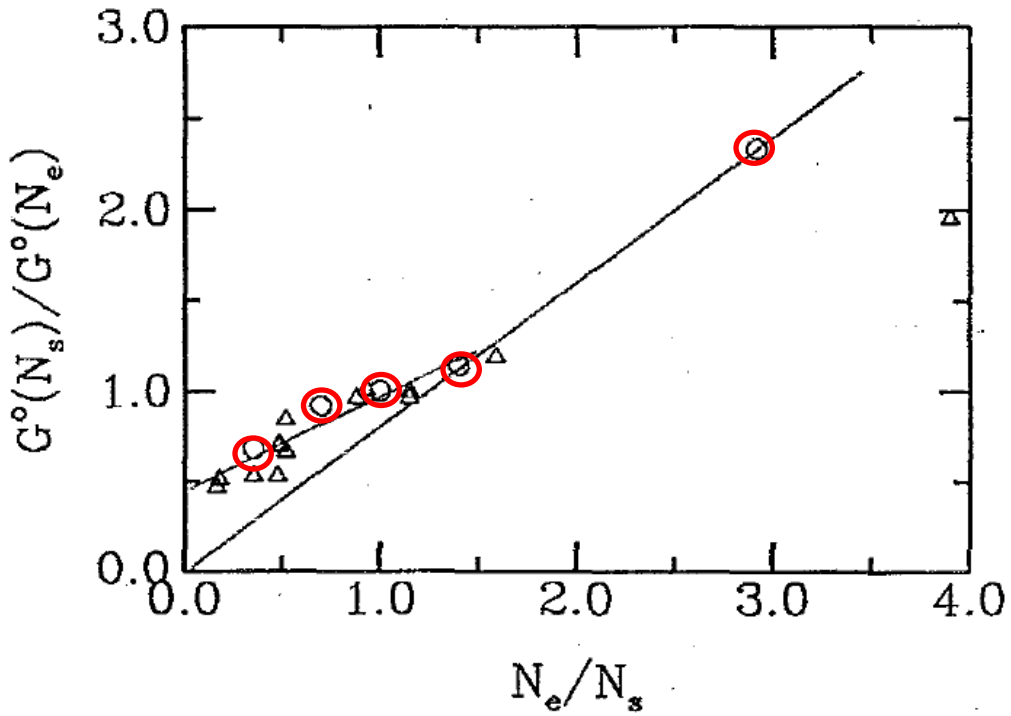
initial conformations

all subsequent positions

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

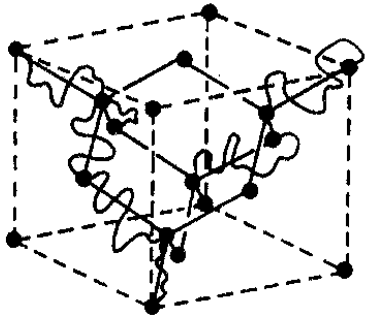
Elastic Modulus

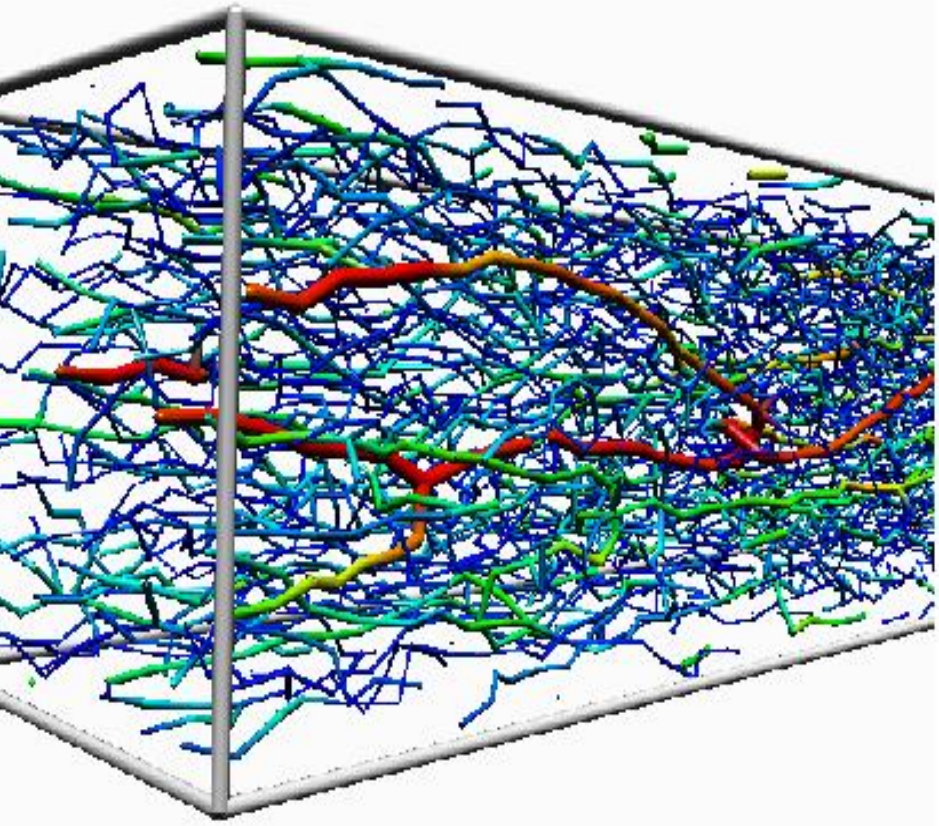




Comparison to PDMS (Colby & Cohen et al.)

Links &Stress randomly interpenetrating networks



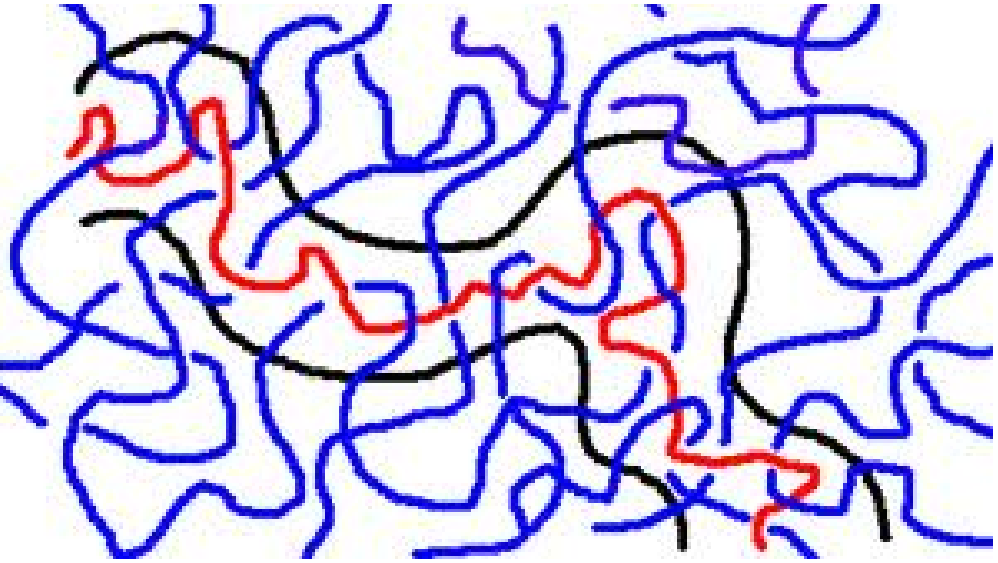


Local stress distribution

- SMALL STRESS
- **LARGE STRESS**

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

Entangled
Melts



and Solutions

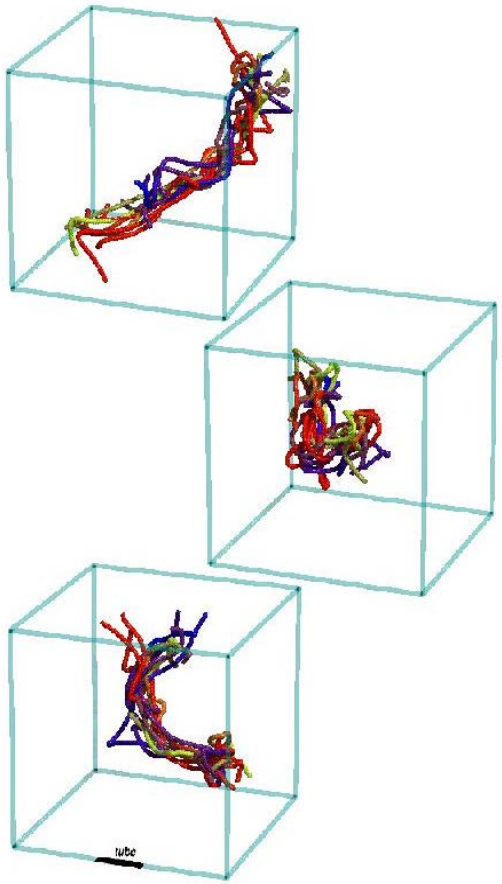
fulanofiles.blogspot.com

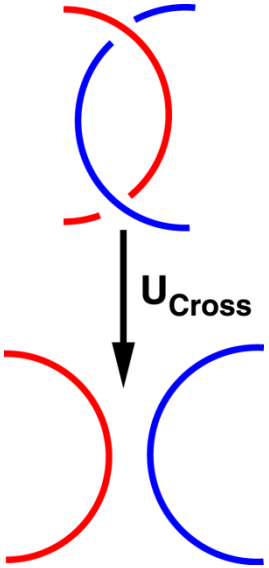
M. Puetz
PhD Thesis 2000

Time Evolution of Melt Chain Conformation

(primitive chain in melt)

$$U_{Cross} \approx 70 k_B T$$





$$t_{\max} \approx \tau_{Rouse}$$

M. Puetz
PhD Thesis 2000

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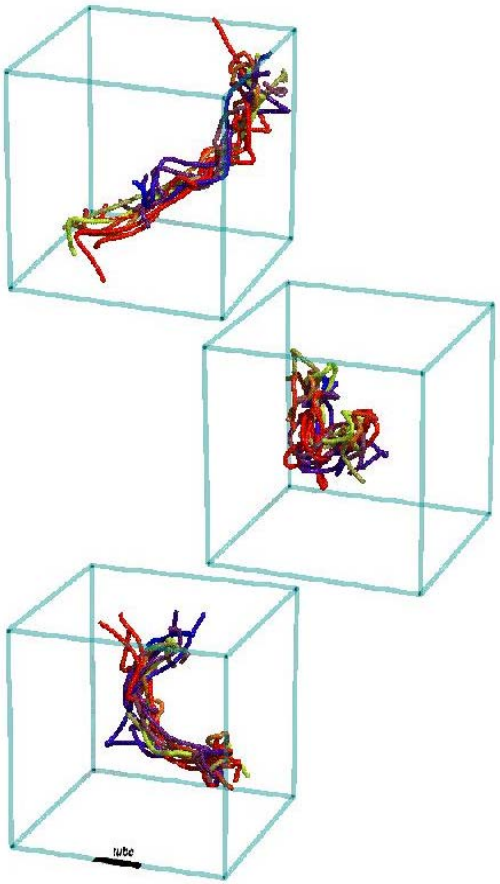
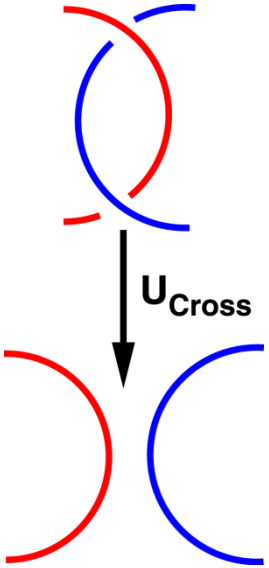
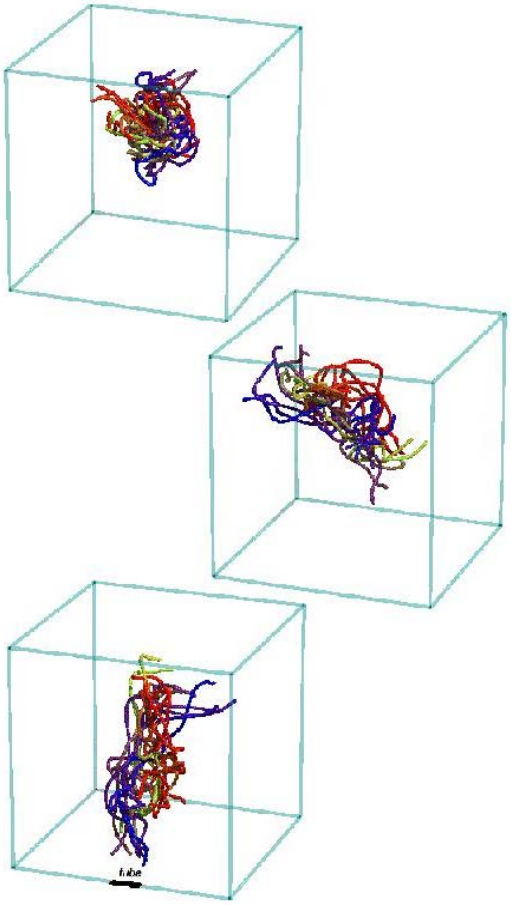




$U_{Cross} \approx 4 k_B T$



Crossing barrier CAN be switched OFF

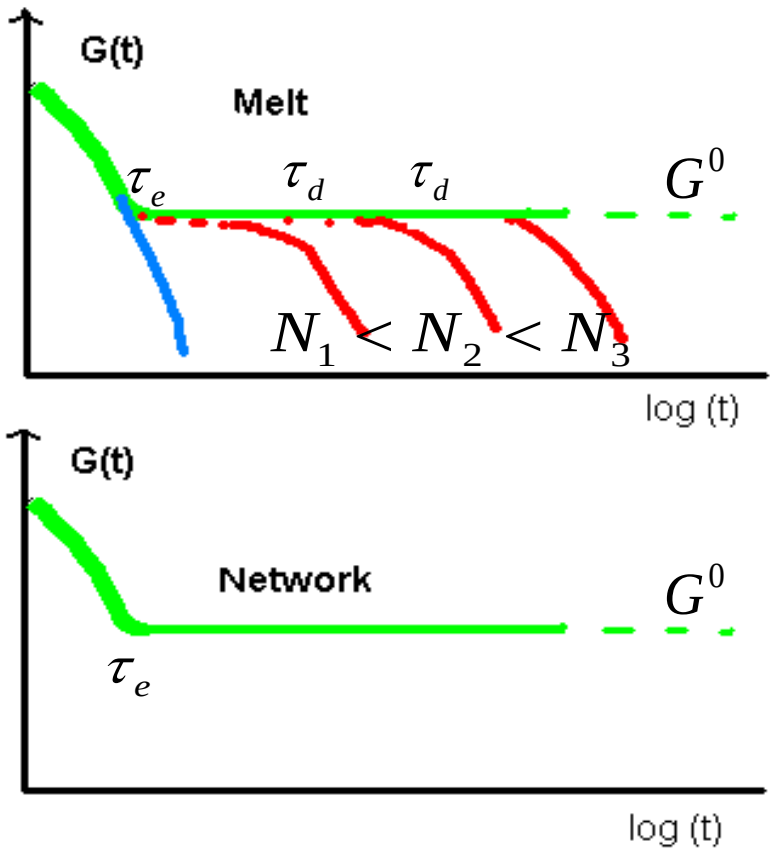
Without changing $\langle R^2 \rangle$

$t_{\max} \approx \tau_{Rouse}$

Dynamic Response: Restoring modulus G^I after step strain

short chains

long chains



$$\tau_d \sim N^{3...}$$

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

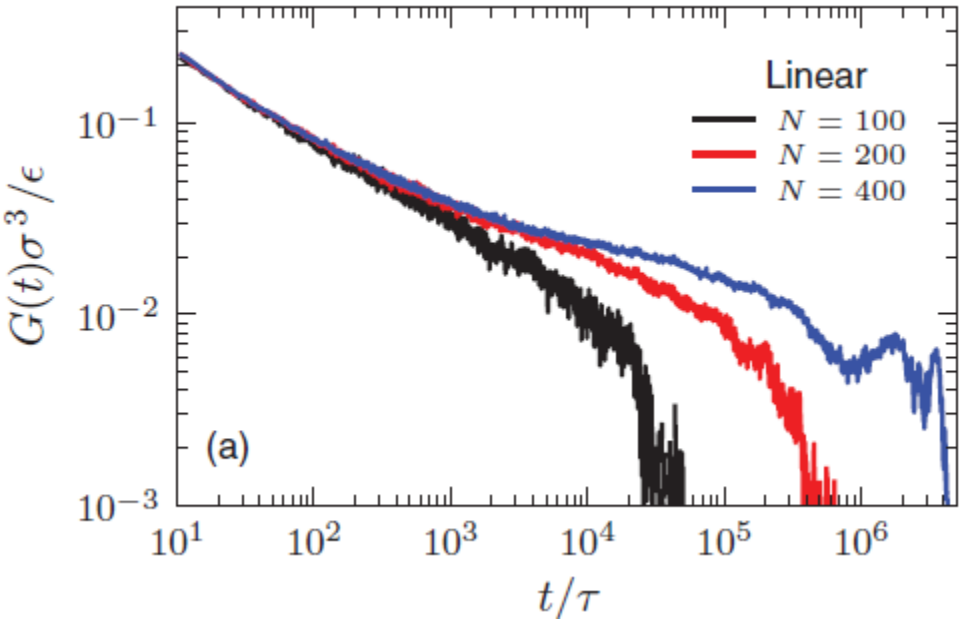
$$G^0 \propto \frac{1}{N_S}, \quad N_S \leq N_e$$

$$\propto \frac{1}{N_e}, \quad N_S \gg N_e$$

N, N_s: chain length
G^0 independent of N, if N >> N_e

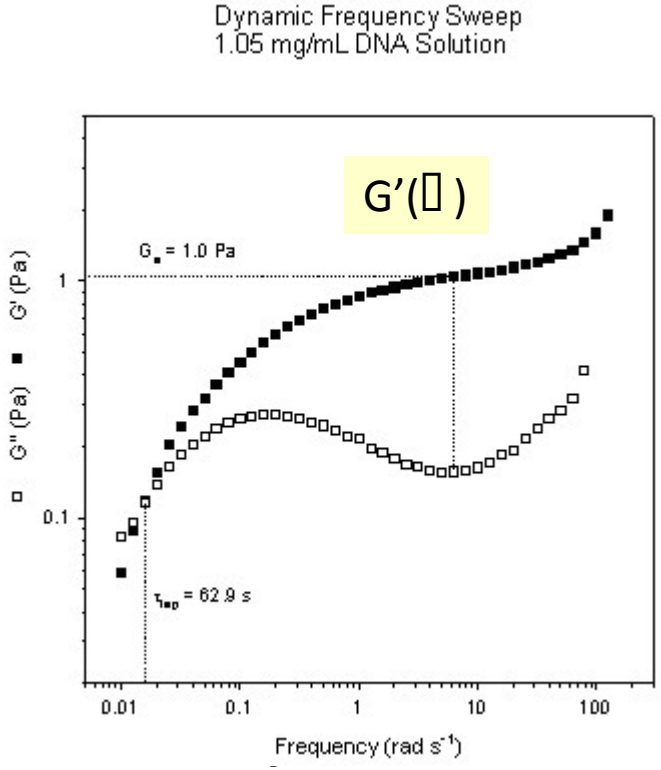
Dynamic Response: Restoring modulus G′(t)

Simulation, $N \lesssim 15N_e$



Halverson et al, 2011

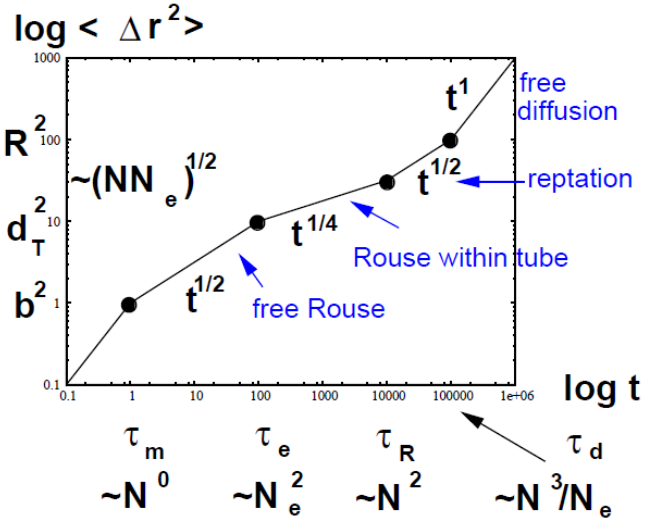
Dense DNA solution

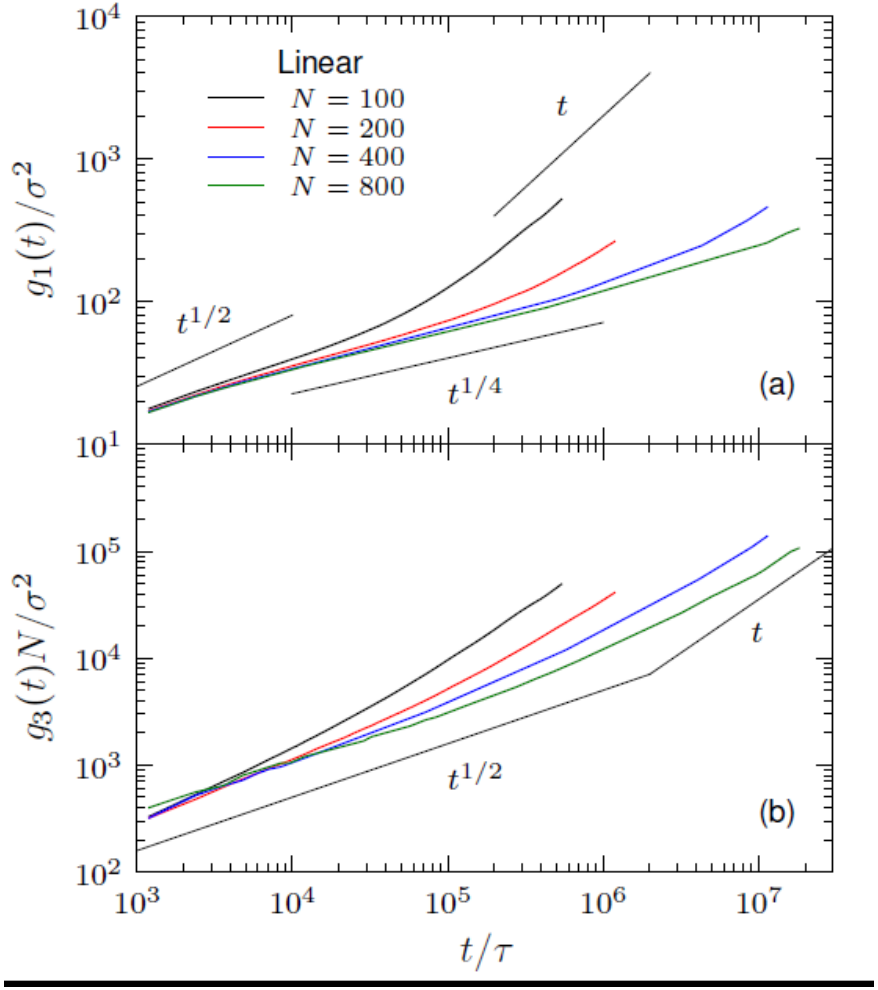


http://everydayscientist.com/research.html

Dynamic Response: mean square displacement

Simulation, N_e= 28





Halverson et al, 2011

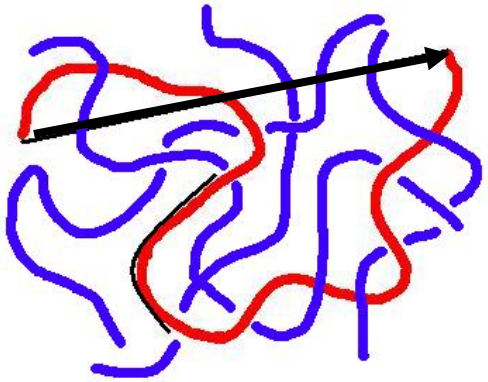
How to determine N_e?

So far: Experiment and simulation measure dynamical quantity and fit N_e.

Original Edward's argument is only based on conformational statistics of the network strands.

Specific Polymers?

Melt: Polymer Conformations, d=3



N: number of bonds per chain

Polymer melt:
Excluded volume screened,
chains are random walks

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

$$P(\vec{r}) \propto \exp(-3r^2/2\langle R^2(N)\rangle)$$

$$\rho_{self} \propto N/\langle R^2(N)\rangle^{3/2} \propto N^{-1/2}$$

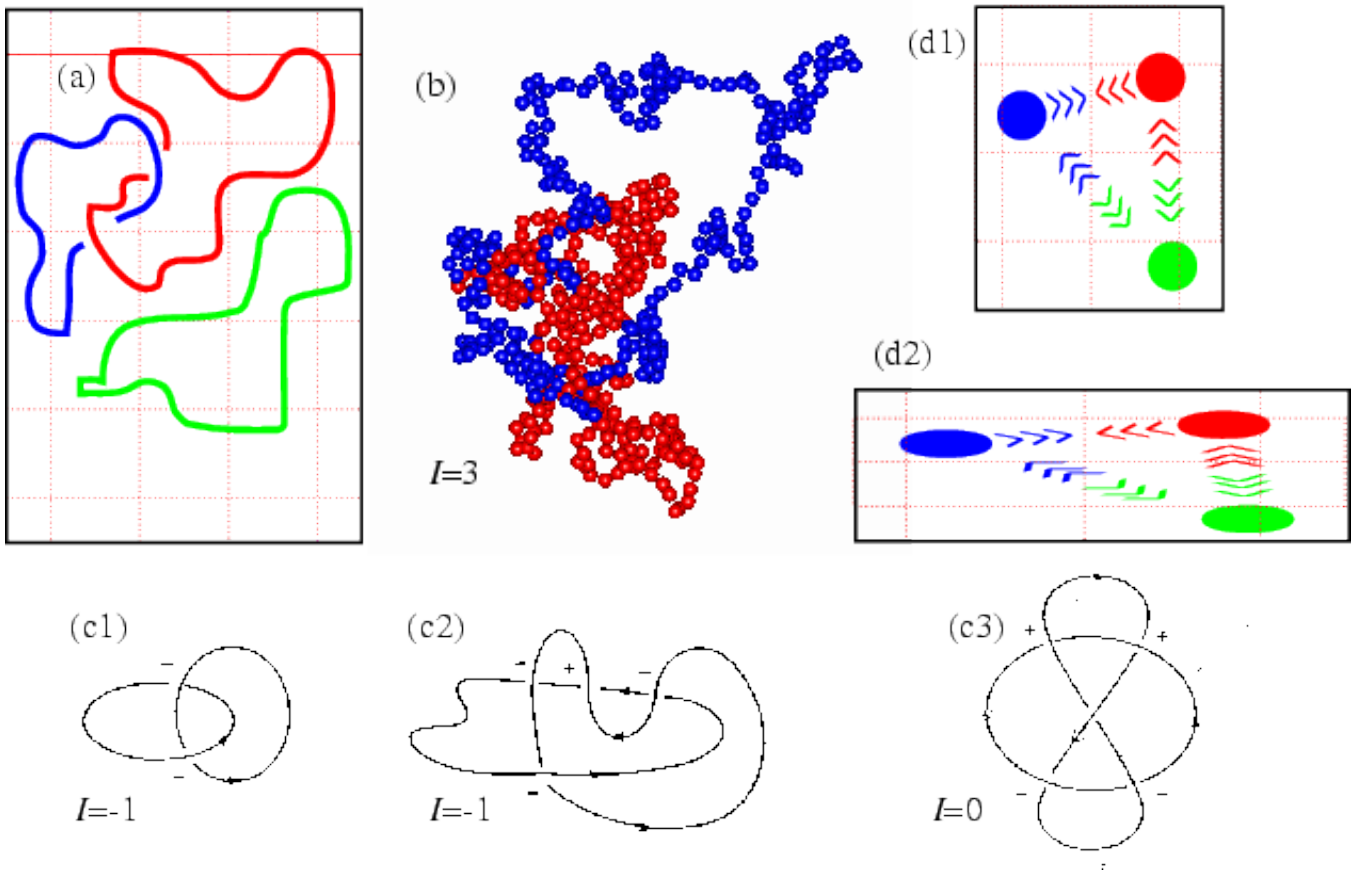
Melt density: ρ_{melt}=const

⇒ **Volume of each chain is shared by $N^{1/2}$ other chains**

⇒ **These $N^{1/2}$ other chains have to impose O(N) constraints to form a tube!**

Same holds for networks and gels

Entanglements: Melts
Back to topology arguments



RE&KK (1996)

S. F. Edwrads, Edwards & Iwata, ….

Entanglements/Primitive Path (Large N)

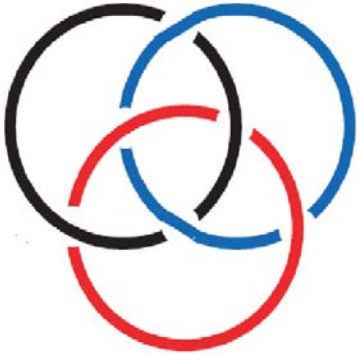
- **O(N) constraints per chain needed**

  $\Rightarrow$ **$O(N^{1/2})$ chains sharing same volume!**

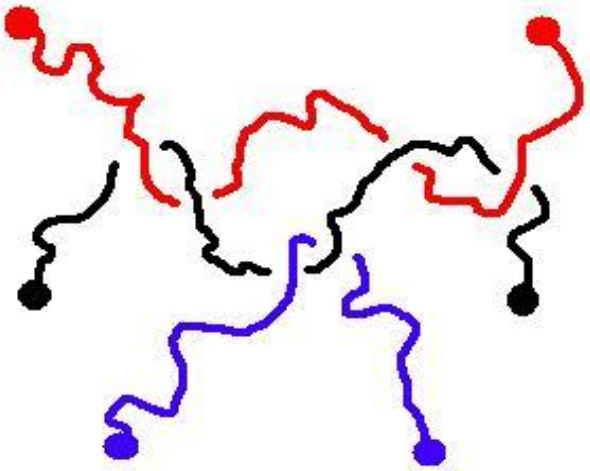
- **Pairwise (Gaussian) linking number in ring melts:**

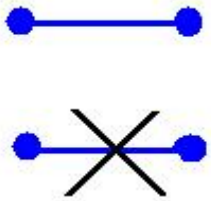
  $O(N^{1/2+1/4})$ NOT SUFFICIENT!

- **Multi chain effects needed, to give sufficient O(N) local constraints!**



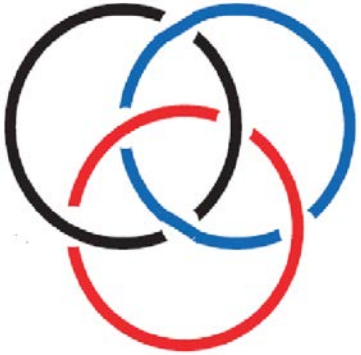
Constraints: Multi-Chain Effects
Constraints red-black





2 Constraints (links)

0 Constraints

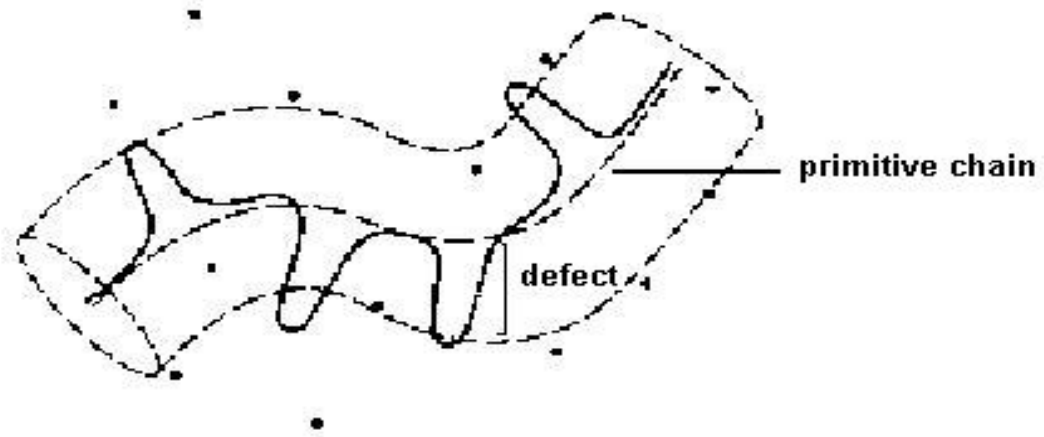


Origin of the Tube: Primitive Path Analysis
for equilibrated long chain polymer melts

Need O(N) constraints per chain (distributed along the backbone of the polymer)!

- **Length of primitive path**

  ⇒ tube diameter



"The primitive path is the shortest connection between the tube ends, which does not violate any constraint."

(Edwards '69, Doi & Edwards '78ff)

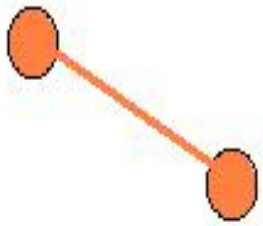
Primitive Path Analysis
for equilibrated long chain polymer melts

Free chains

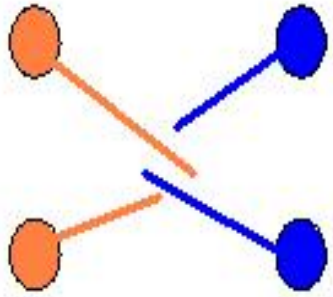
→ Fixed chain ends

Fixed contour length

→Line tension



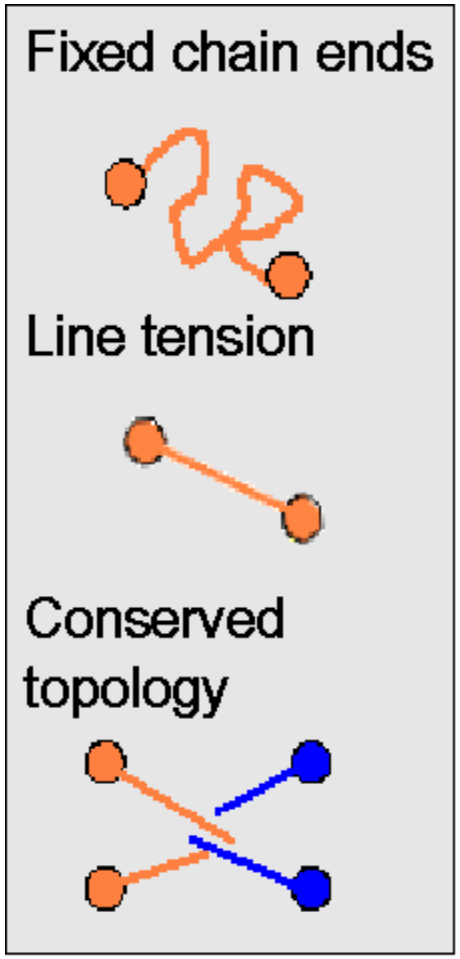
Conserved topology

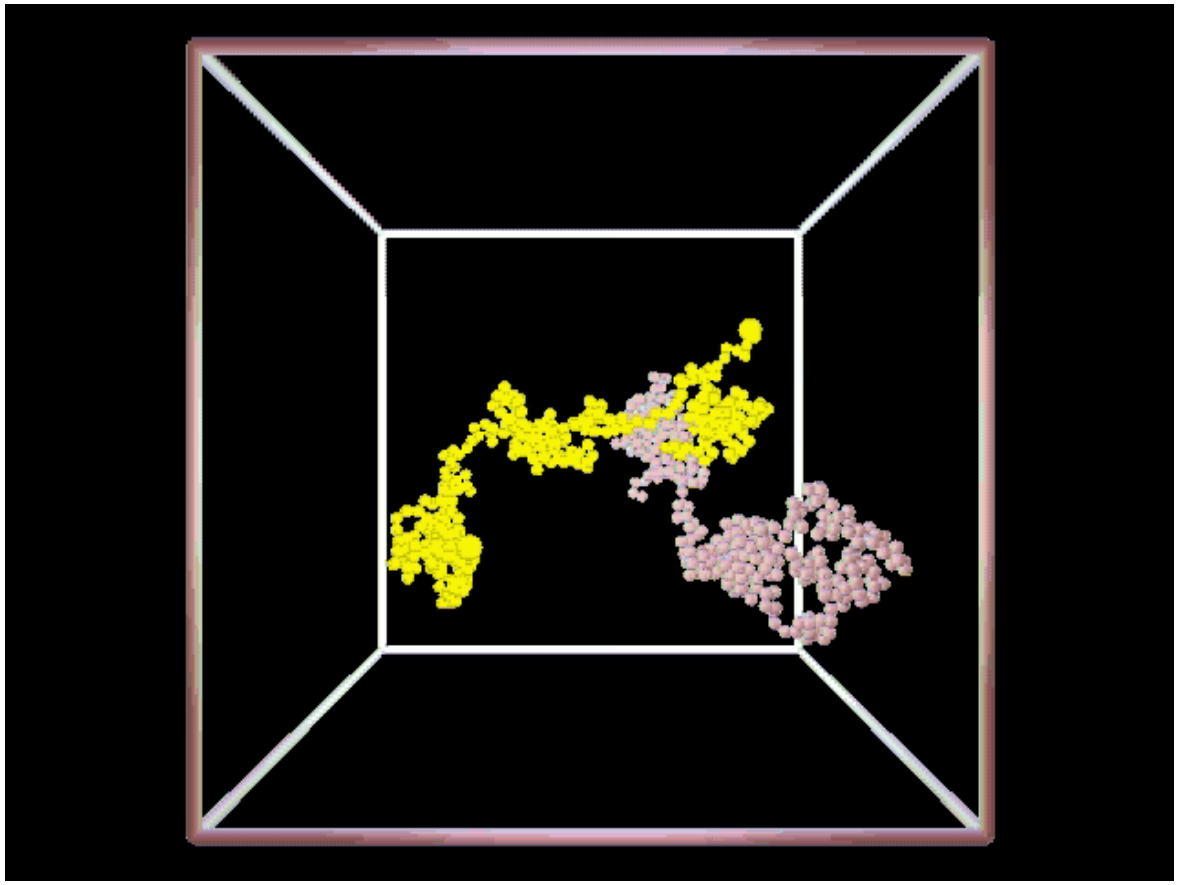


Problem: Obstacles are not fixed but other chains →primitive path determination needs to be simultaneous for all chains!

Similar Idea: M. Rubinstein and E. Helfand, JCP 82, 2477 (1985)

Primitive Path Analysis: Two chains





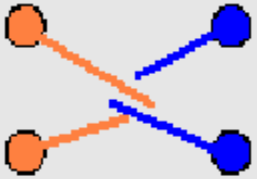
Related work: Milner, Theodorou, Kröger, Larson, Briels,…

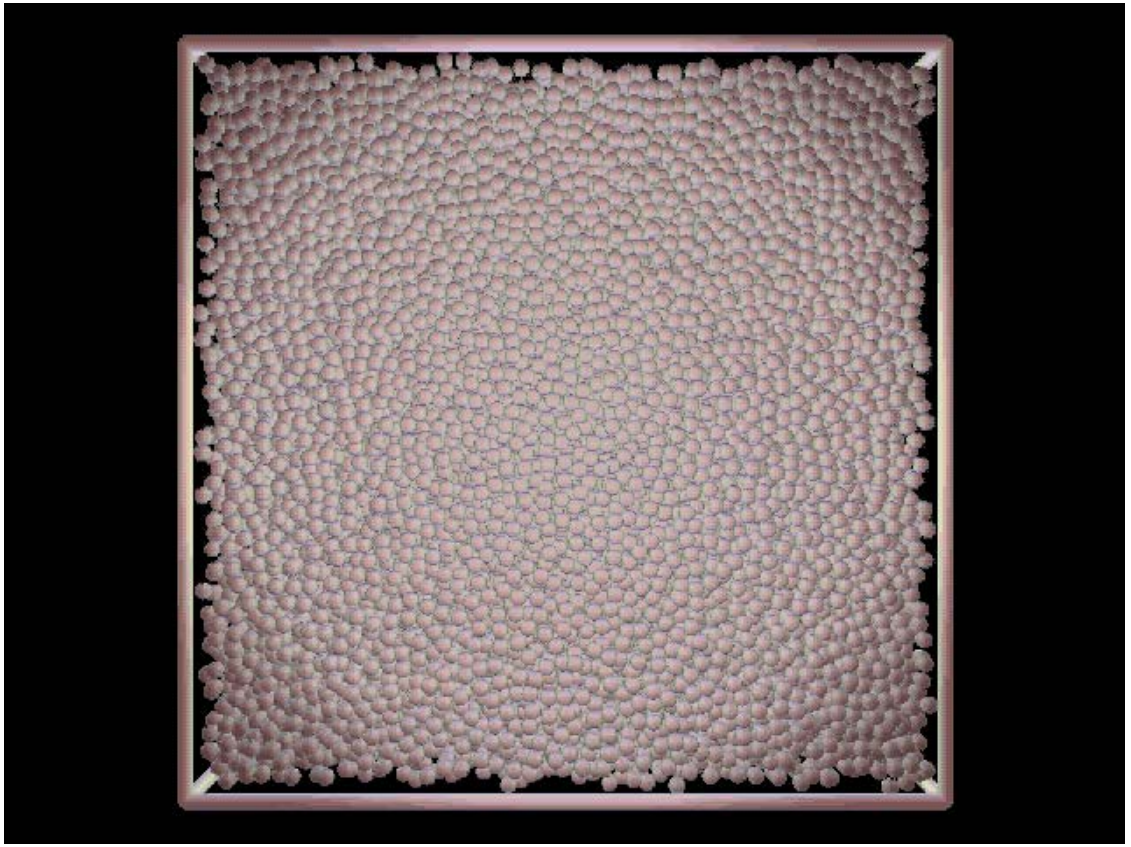
Primitive Path Analysis: All chains

Fixed chain ends

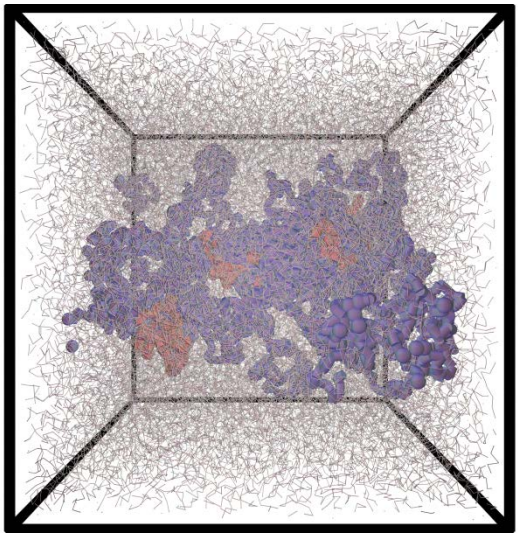
Line tension

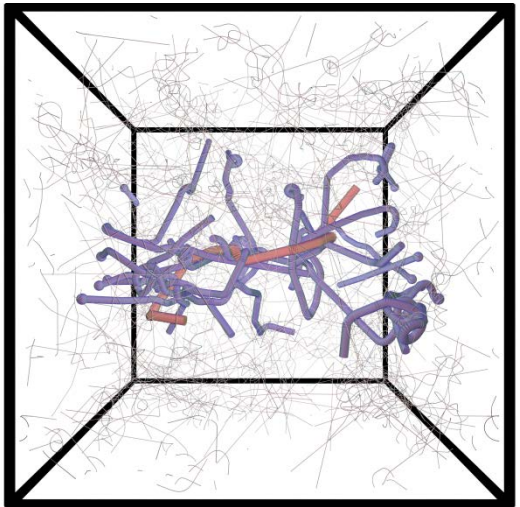
Conserved topology



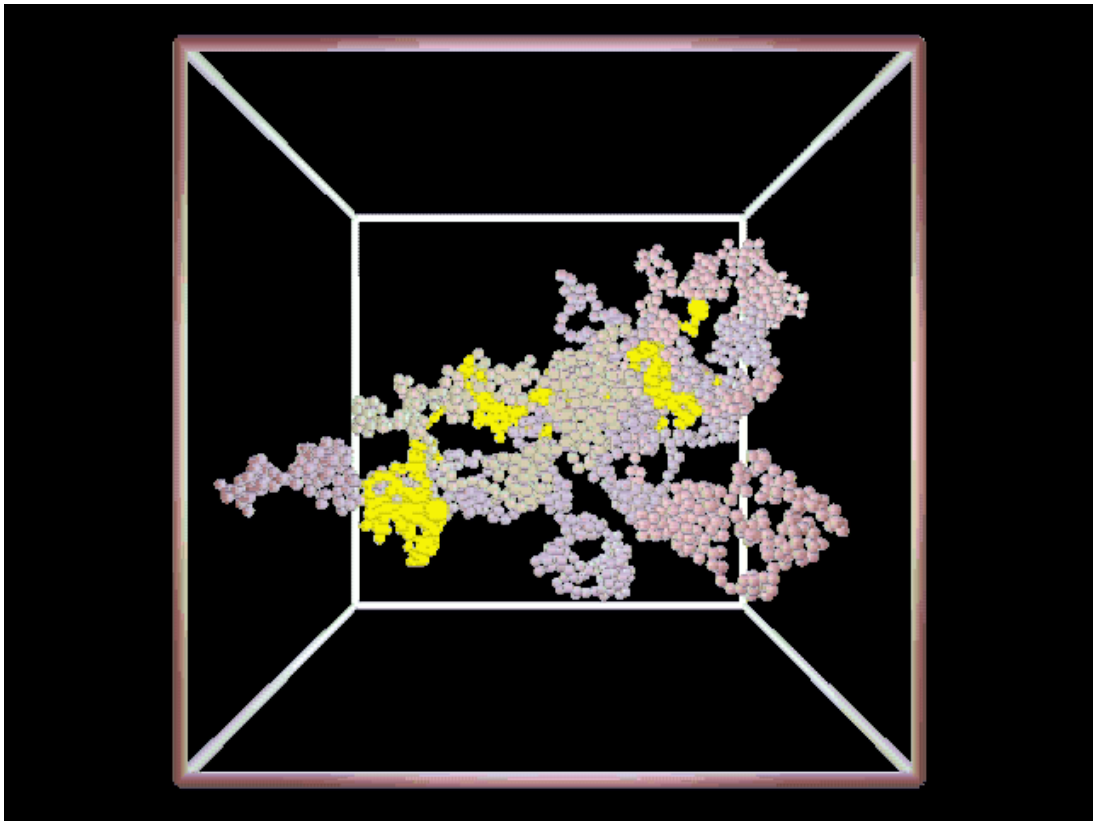


Entanglements: Primitive Path Analysis





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



Related work: Milner, Theodorou, Kröger, Larson, Briels,…

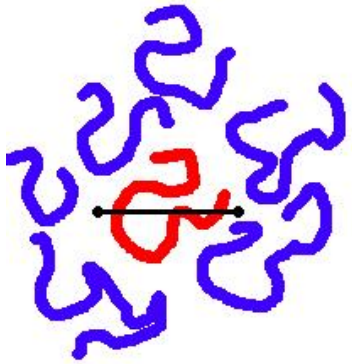
Characteristic Lengths: l_K and p

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

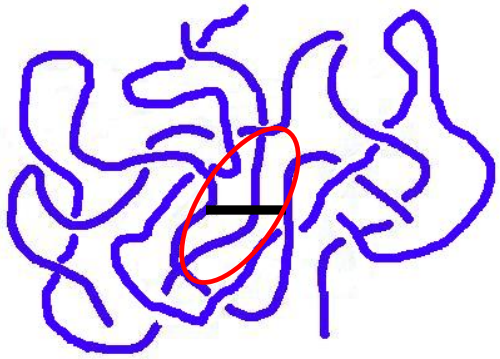
□/N = chain density

Packing Length *p*

Solution at □□: ***p*** □ ***R***



Melt: ***p*** □ strand-strand distance

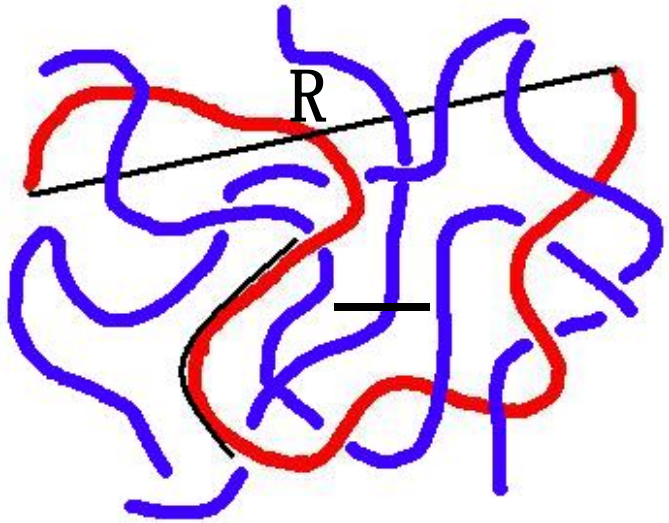


Packing Length *p* and Modulus *G*

Fetters et al

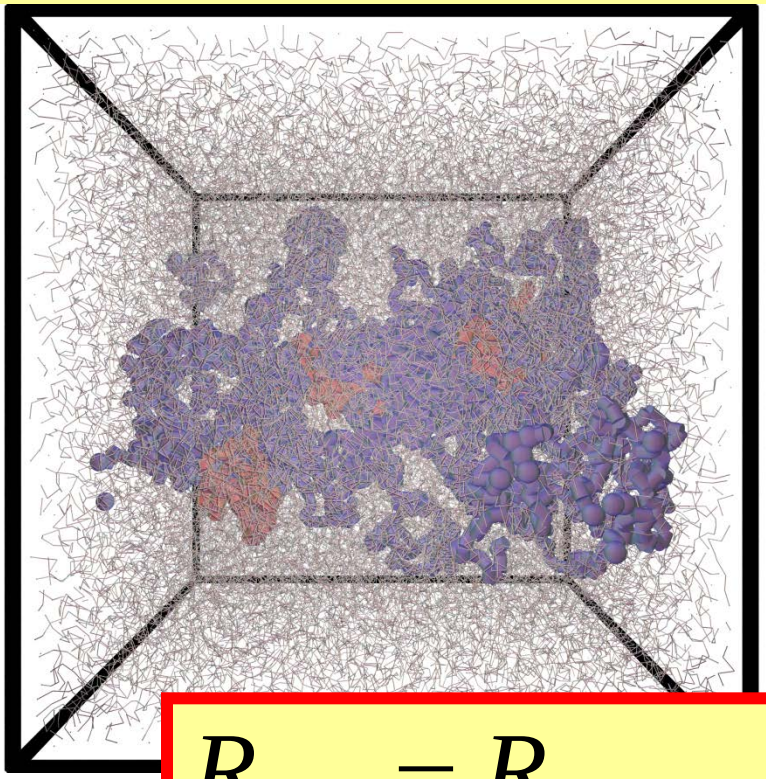
$$G_N \propto p^{-3}$$

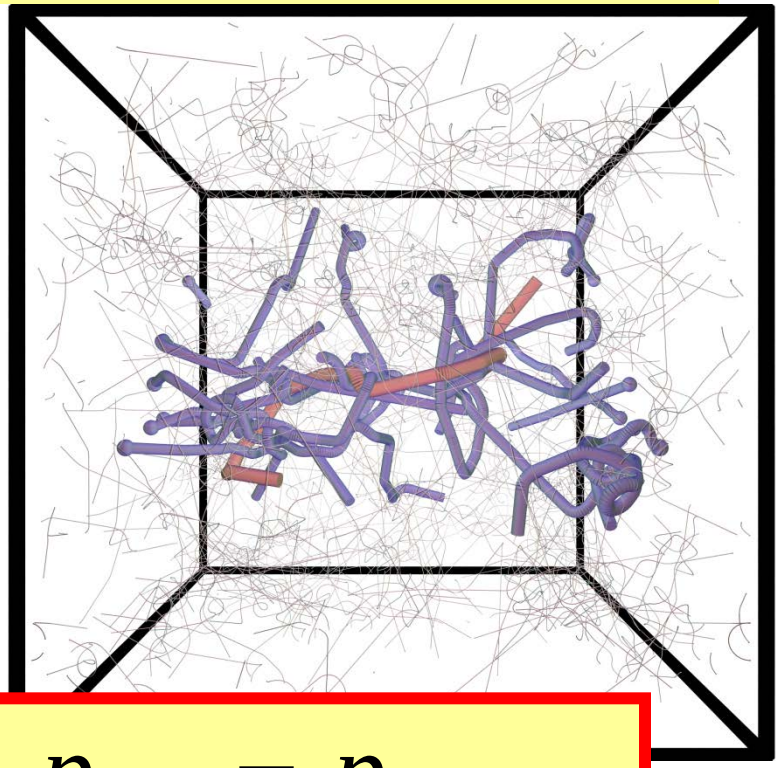
$$p = \frac{N}{\rho} \frac{1}{\left\langle R^2(N) \right\rangle}$$



Experimental observation for many polymer melts

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





$$R_{melt} = R_{primpath} \Rightarrow p_{melt} = p_{primpath}$$

$$l_k L = a_{pp} L_{pp}$$

Plateau Modulus:

Modulus (Doi-Edwards):

$$G^0 = 0.8\,\rho kT / N_e$$

$$G = \frac{4}{5}\frac{kTN}{pR^2 N_e}$$

..

..

$$\boxed{N_e/N = a_{pp}/L_{pp}}$$

$$G = \frac{4}{5}\frac{kT}{pa_{pp}^2} \propto p^{-3}$$

=> Experiments Fetters et al

Plateau Modulus:
rescaled plot – dimensionless units: Å⇔σ

Modulus (Simulation): $G^0 = 0.8\rho kT / N_e$

Plot of Experimental data by Fetters et al. ’99ff:

$$G_N^0 \quad vs \quad p^{-1}$$

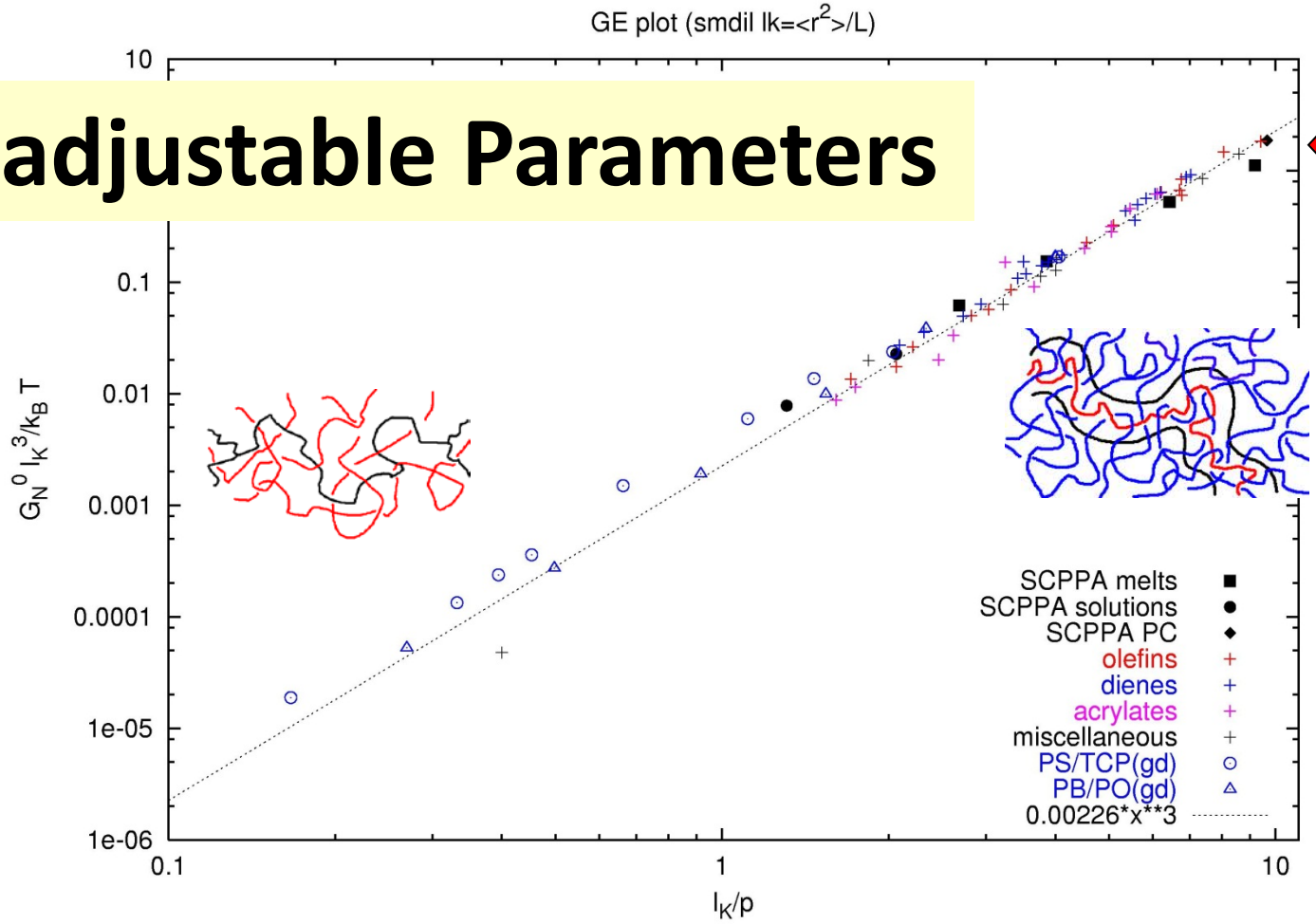
Simulation + Experiment => Length, energy scaling needed:

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

Plateau Modulus Different Polymers

Melts and Solutions: Tological analysis and experiment

NO adjustable Parameters

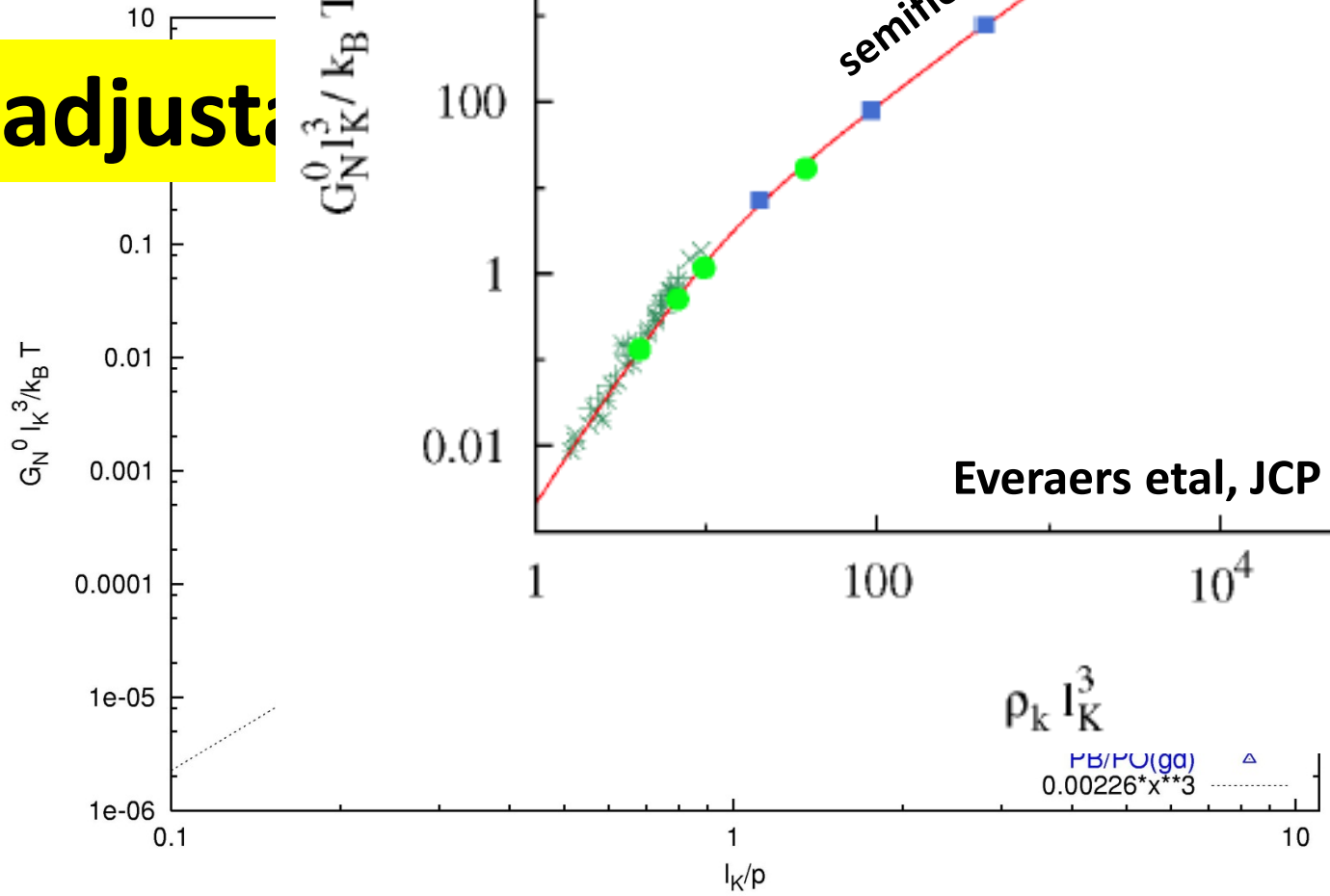


BPA-PC

Everaers et al Science 2004, J.Pol.Sc. B 2005, Leon et al Macrom. 2005

Pla
Melts and S

NO adjusta

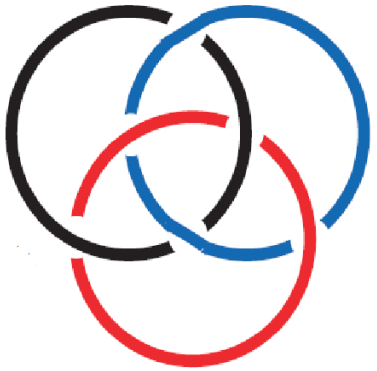


Everaers et al Science 2004, J.Pol.Sc. B 2005, Leon et al Macrom. 2005

Topological Constraints Matter

- **so far:** topological constraints relevant for dynamics,relaxation
- for melts, solutions no general consequences for conformational statistics (RW character of chains)

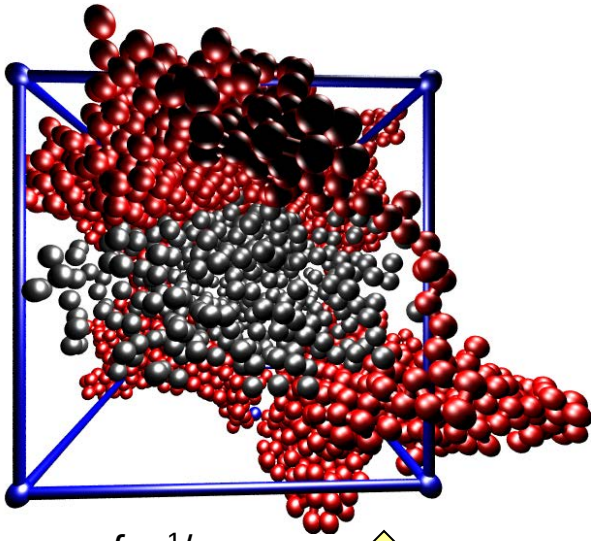
- **Now:** constraints on conformations: gels, rings



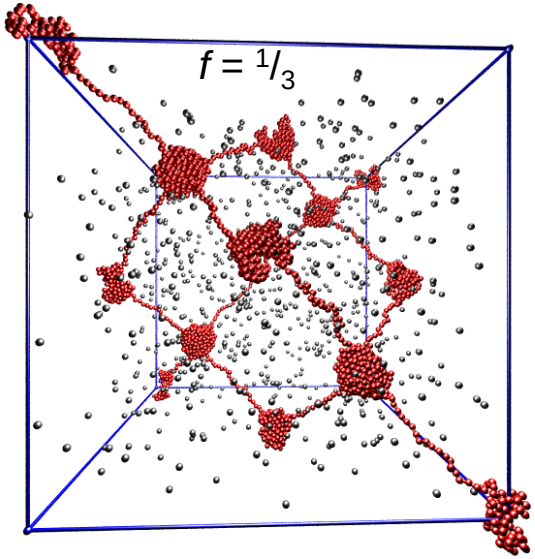
Shrinking Gels: Poor Solvent Hydrogels

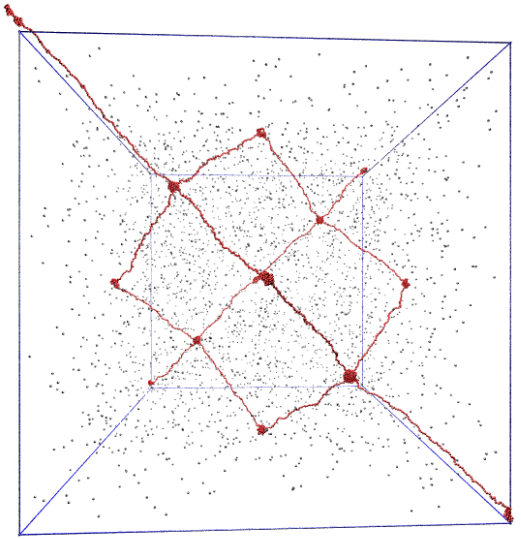
high salt … **low salt**

Low charge fraction … **high charge fraction**



$f = {}^1/_8$





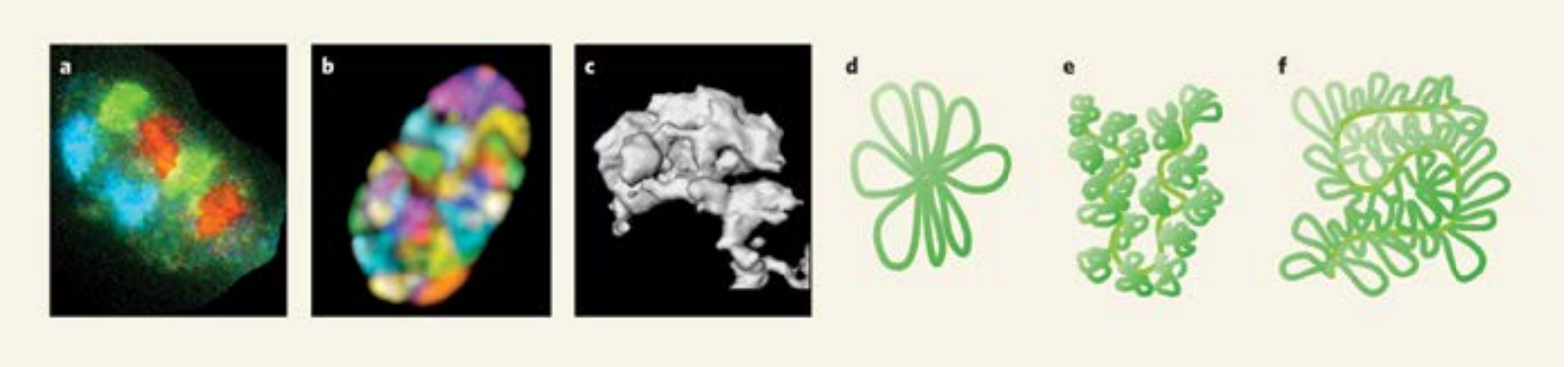
$f = {}^1/_1$

Segregated strands?

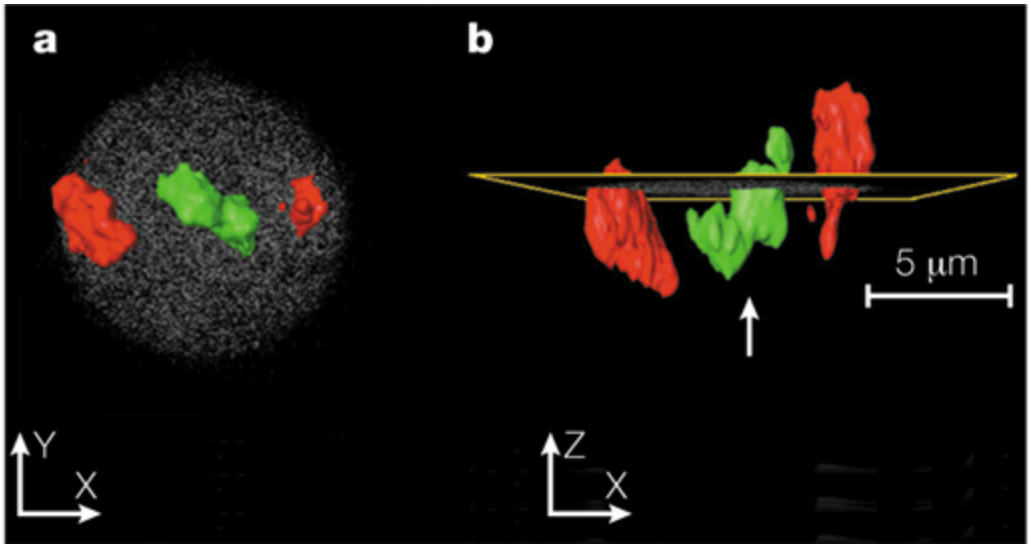
- **osmotic pressure of "counterions" enforces swelling (↔ good solvent picture)**
- **nodes act as condensation nuclei**
- **"pearls" form due to balance with surface tension (↔ Rayleigh instability)**

Chromosome Territories

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

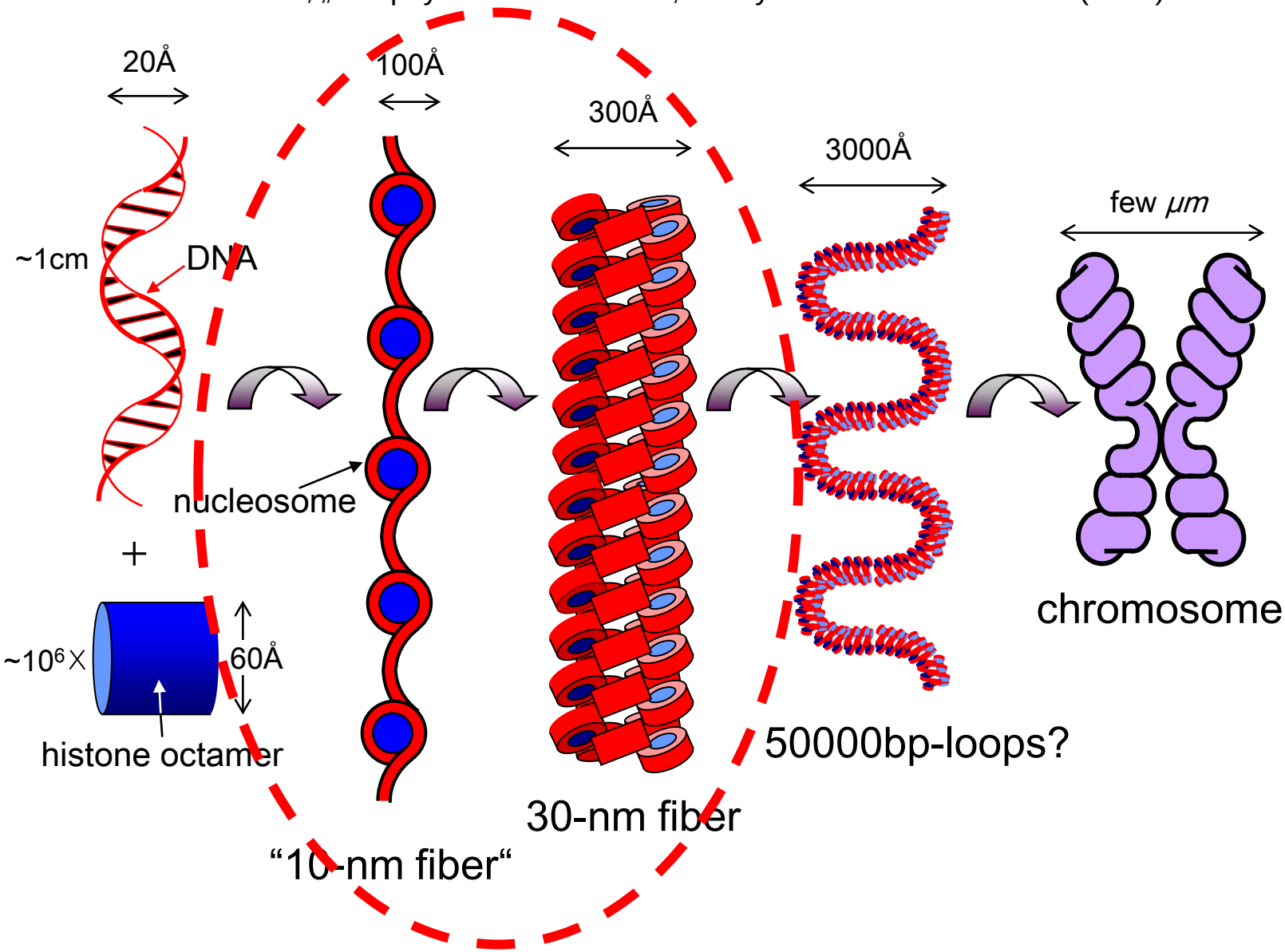


T. Cremer, C. Cremer, Nature Reviews Genetics vol. 2, pp. 292-301 (2001)



structure of chromatin

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

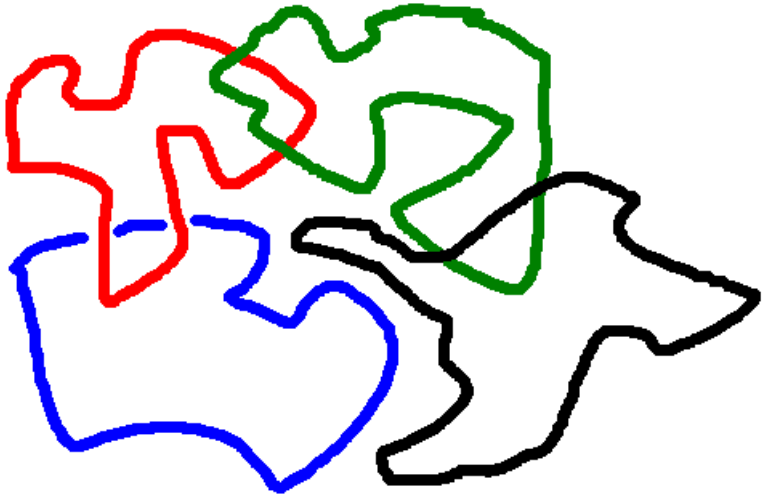


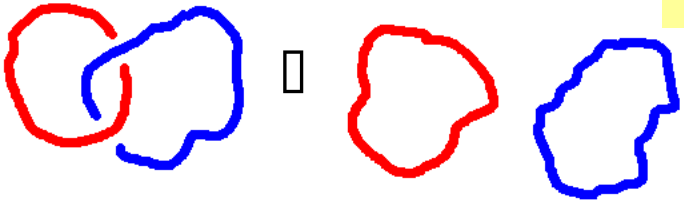
Questions

- Why do chains in a collapsed model (polyelectrolyte) gel not interpenetrate?
- Human DNA about 2m contour length, few cm of 10nm fiber in a nucleus of a few μm, how can they pack?
- Why seem DNA (10nm fibers) not to entangle, but segregate?

- **Look for a most simple model system**

Melt of non concatenated ring polymers





Conformation of the rings?

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

=> Rings interpenetrate each other

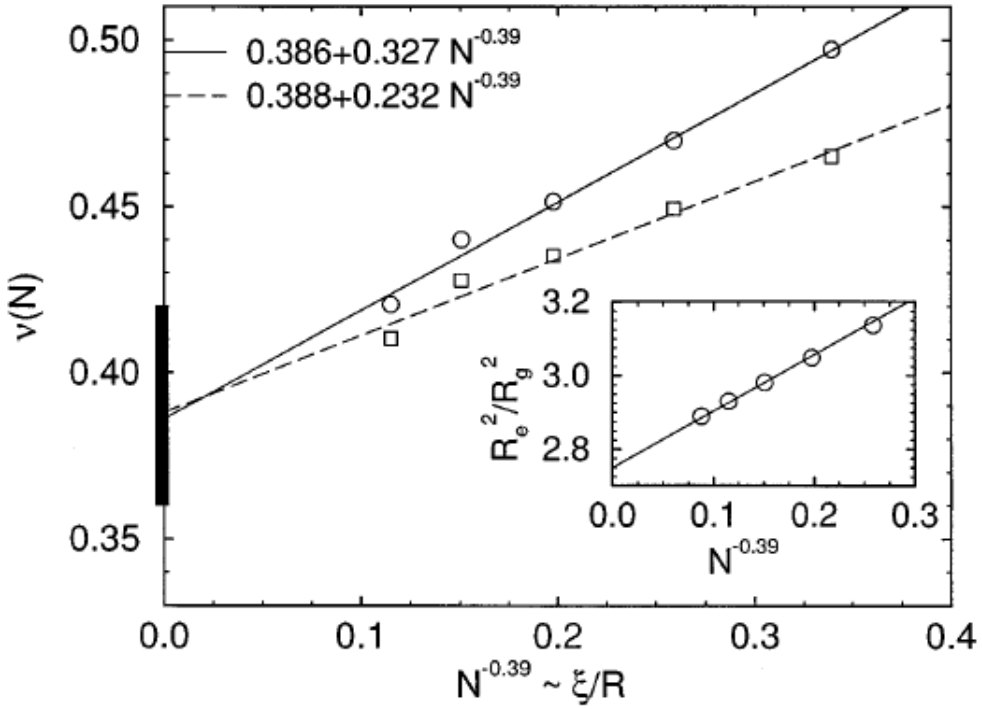
Collapsed ring: $R^2(N) \sim N^{2\nu}$, $\nu=1/3$

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

PHYSICAL REVIEW E VOLUME 53, NUMBER 5 MAY 1996

Topological effects in ring polymers: A computer simulation study

M. Müller,* J. P. Wittmer,† and M. E. Cates



Contributions to Flory free energy (Deutsch & Cates)

'osmotic pressure' of other chains:

$$F \propto kTR^d/N$$

Surface term of EV interaction:

$$F \propto kTN/R^2$$

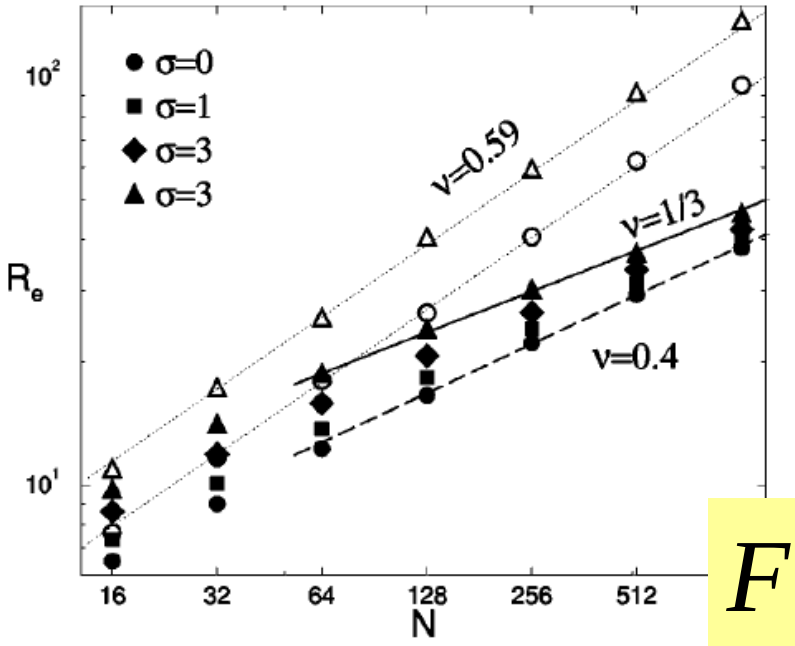
$$\nu = 2/(d+2)$$

$$\nu = 2/5$$

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

$$F \propto kT(R^d / N)^\alpha + kTN / R^2$$

$$\Rightarrow$$

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

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

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

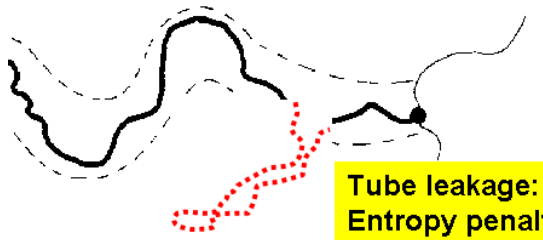
(preliminary) Physical picture

Grosberg, Vettorel, KK

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

$d_T \sim N_e$

(first simple picture)

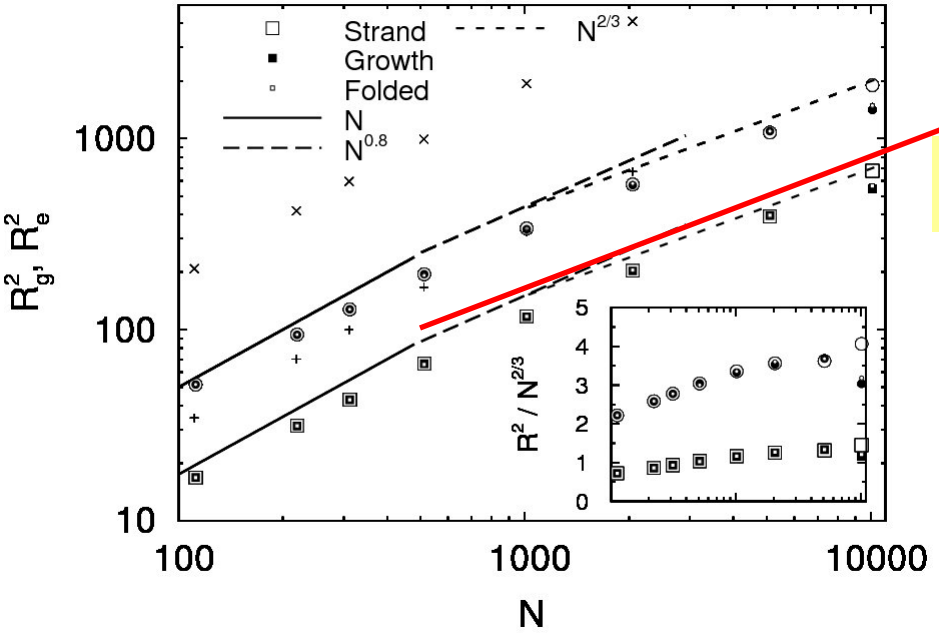


$N \le N_e$ **No effect, random walk**

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

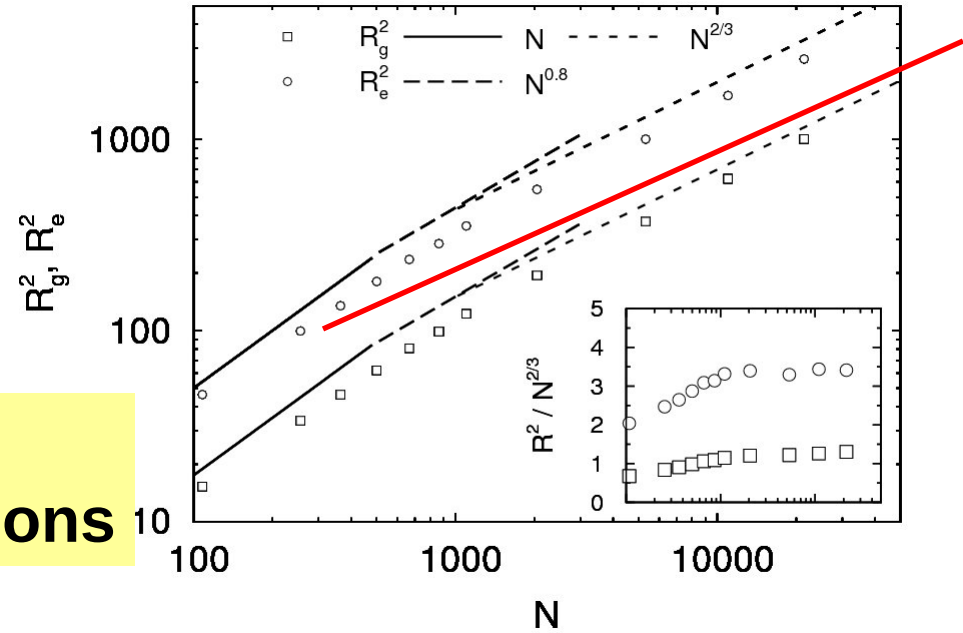
$N \ge O(\approx 10 N_e)$ **Segregation regime**

Ring extensions: MC and MD



<= melt of many rings

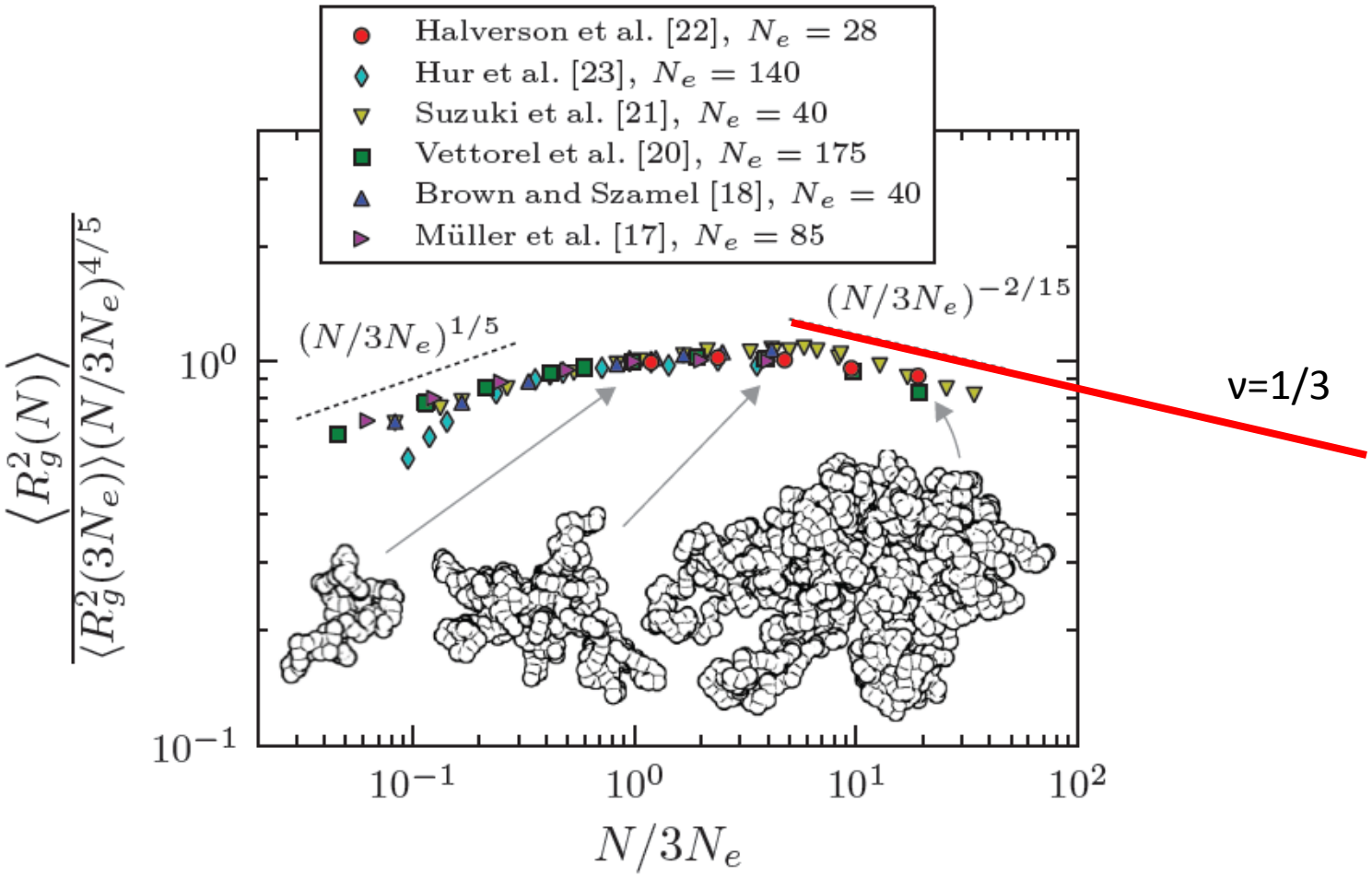
ν = 1/3



melt of one ring, seeing itself via periodic boundary conditions

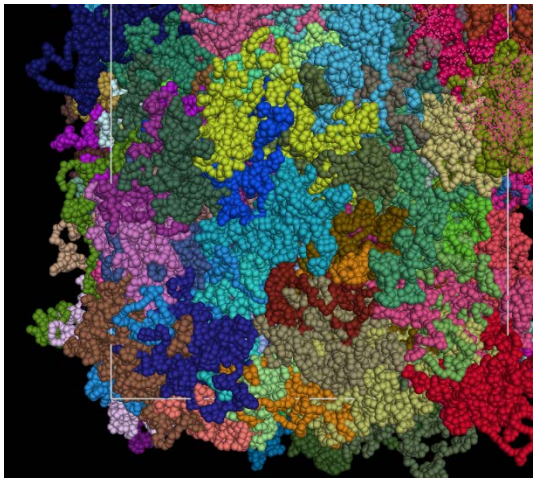
Ring extensions: Collection of data

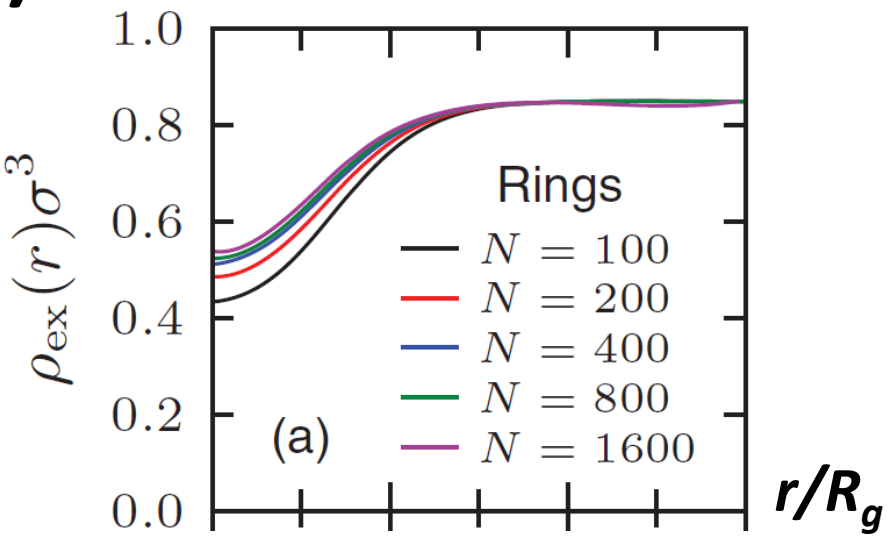
$R_g^2(N)/R_g^2(3N_e)(N/N_e)^{4/5}$ vs N/N_e

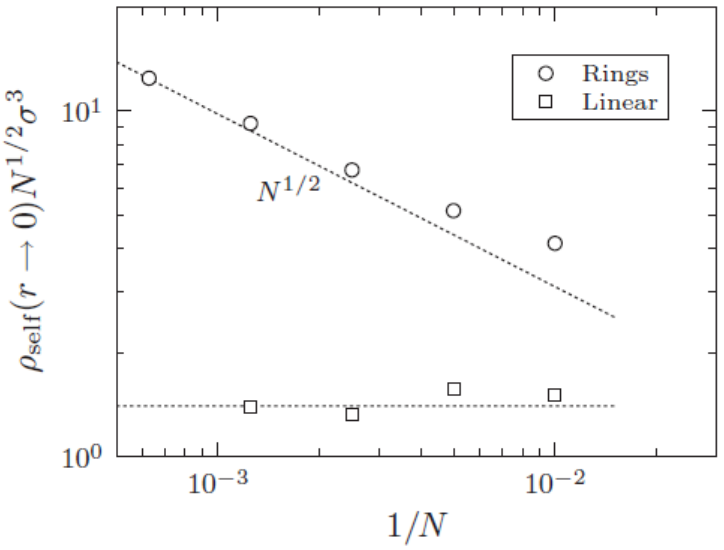


J. Halverson, G.S. Grest,
A. Grosberg, KK, 2011

Melt of Ring Polymers: Core Density $\rho_{self}(r)$







Self density

ρ_{intra} ($N \to \infty$) ≈ 1/3 ρ_{melt} (!)

≈ ρ_{intra} (N_e)

Volume shared be several rings

 # sharing rings $\propto N^0$,
but incomplete segregation!

T. Vettorel, A. Grosberg, KK,
J. Phys. Biology, 2009
J. Halverson, W. B. Lee, G.S. Grest,
A. Grosberg, KK, JCP, 2011

Melt of Ring Polymers

#"surface" beads ∝ N^{β}

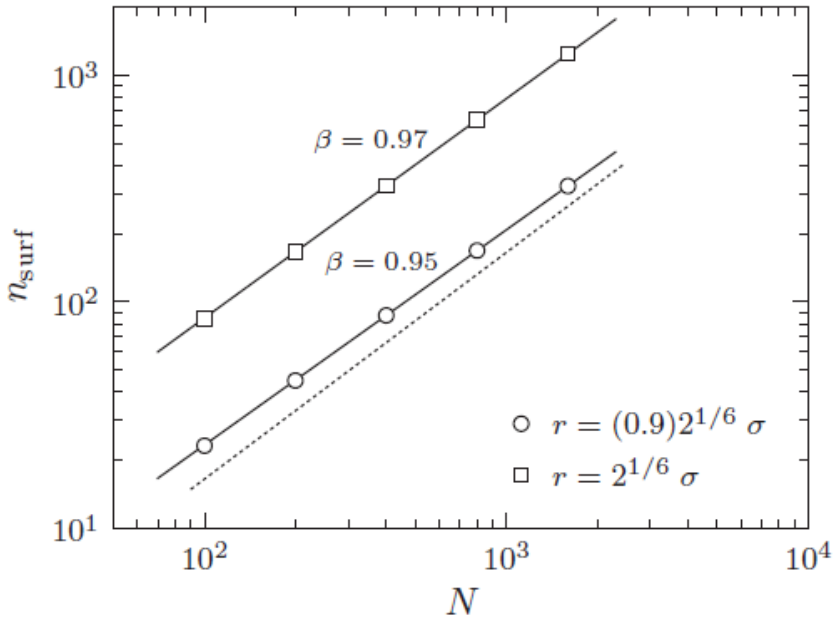
ring form factor S(q)

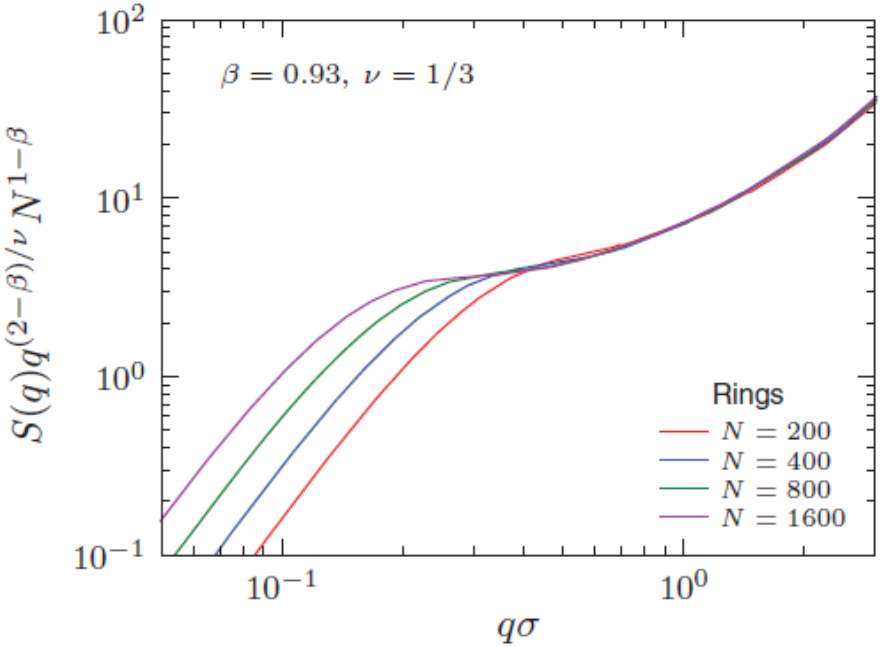
Without surface correction

$S(q) \propto q^{-1/\nu}$

With surface correction

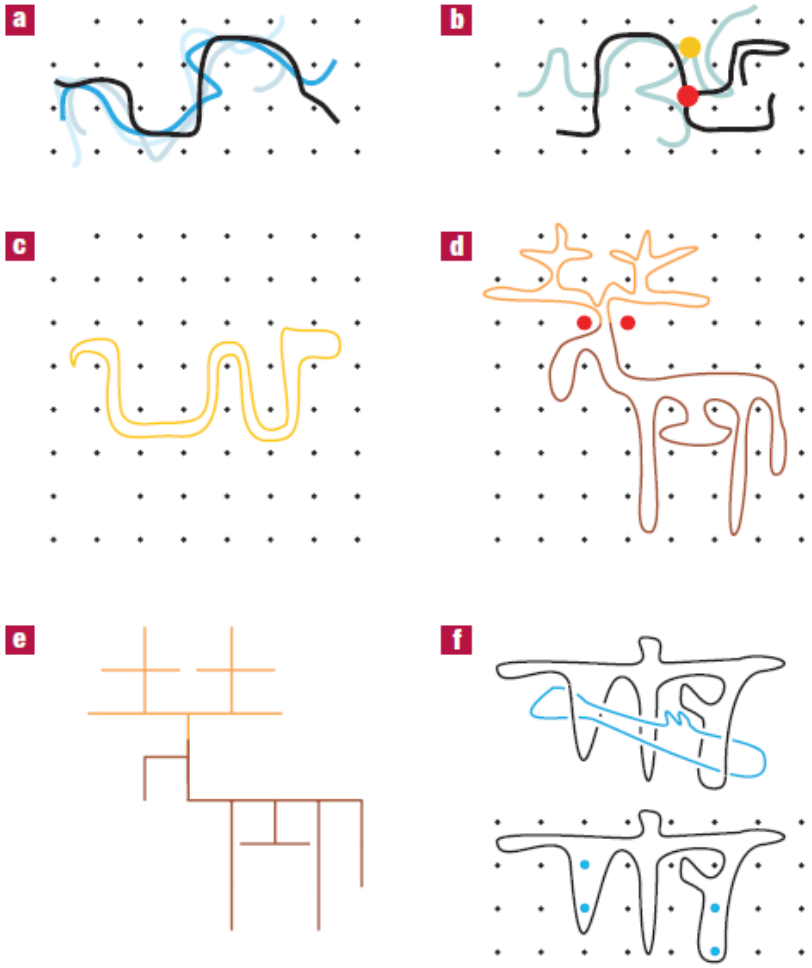
$S(q) \propto q^{-(2-\beta)/\nu} N^{-(\beta-1)}$

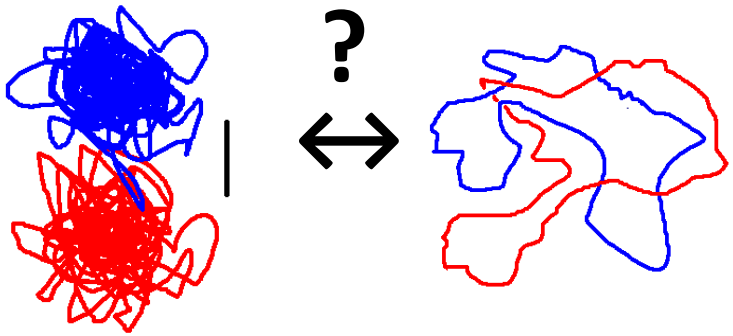




$\beta \approx 0.95 < 1$

Melt of nonconcatenated rings: N=100, 200, 400, 800, 1600 (≈58N_e)



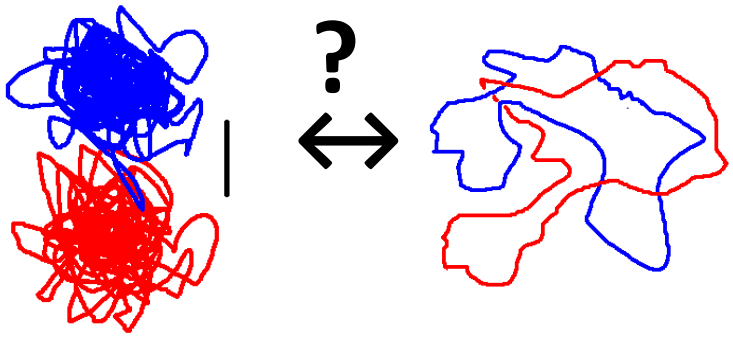


significant entropy barrier?

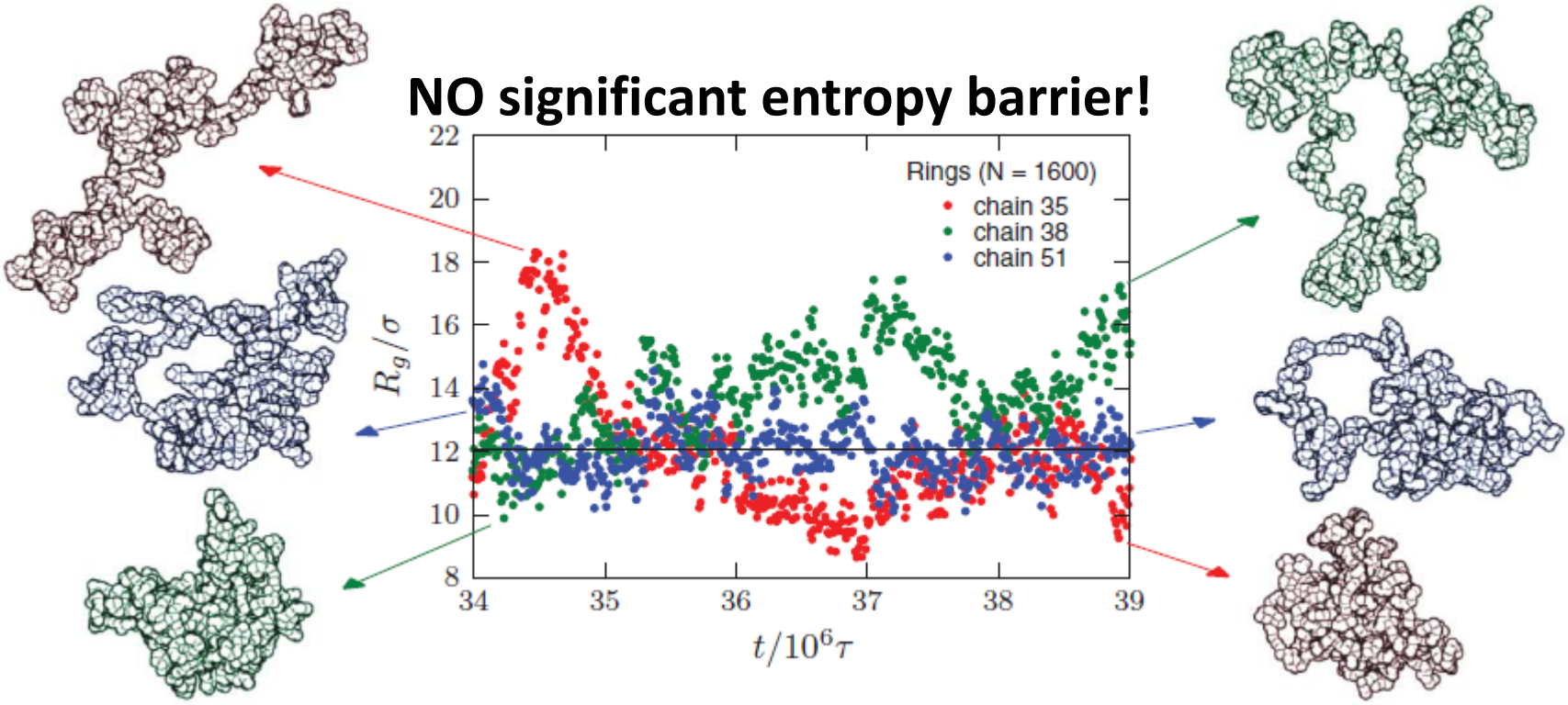
significant entropy barrier!

Rubinstein et al, Nature Mat. 2008

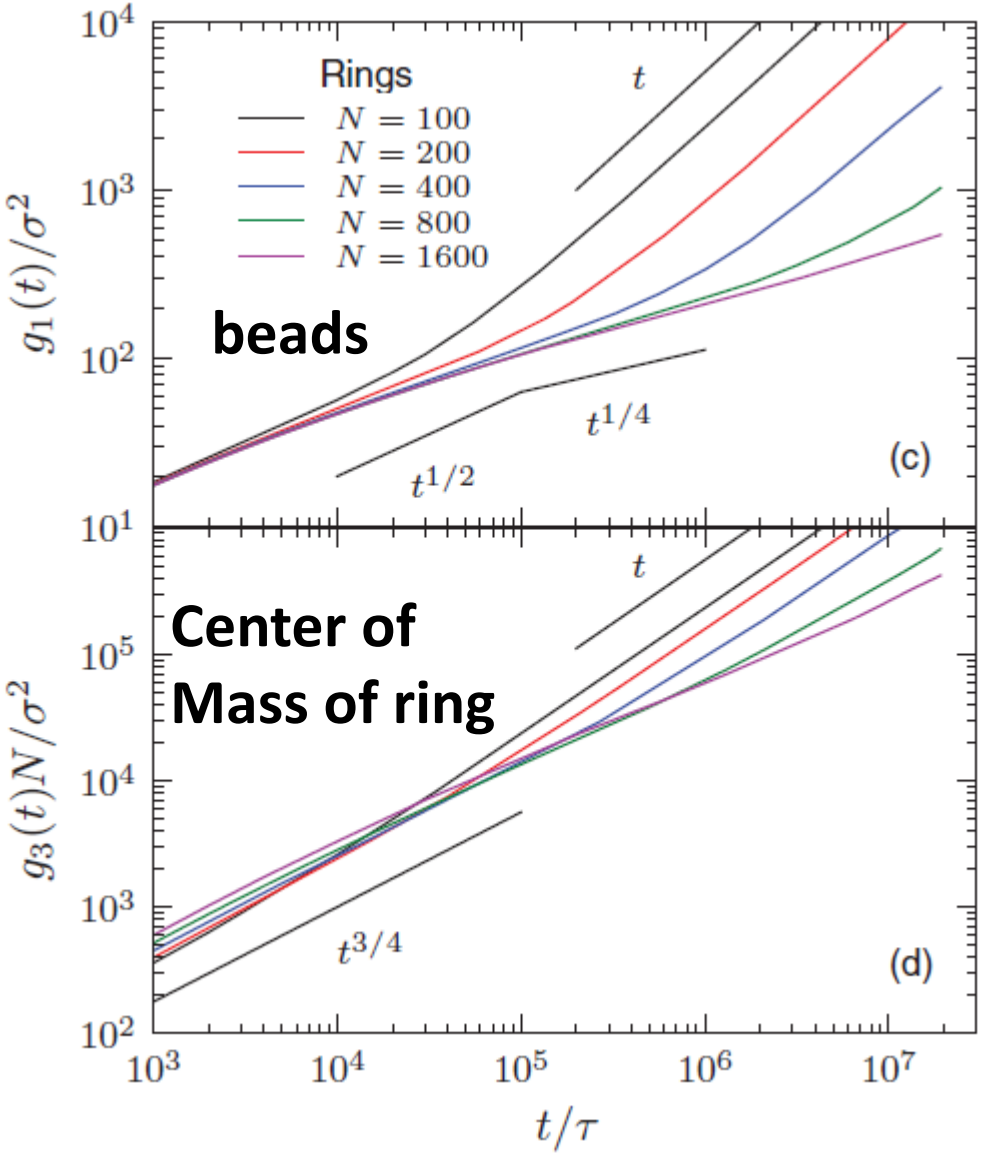
Melt of nonconcatenated rings: N=100, 200, 400, 800, 1600 (≈58N_e)



NO significant entropy barrier!



Melt of nonconcatenated rings: N=100, 200, 400, 800, 1600 (≈58N_e)



Mean square displacements

Slowing down

$g_1 \sim t^{1/4}$

and slower for large N

Subdiffusive

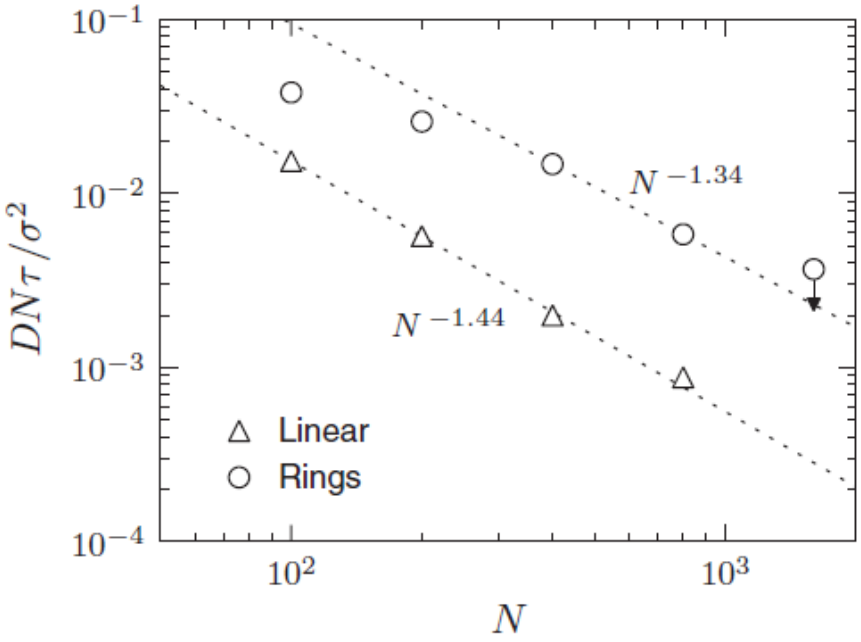
$g_3 \sim t^x$, x=0.75 …0.65(N=1600)

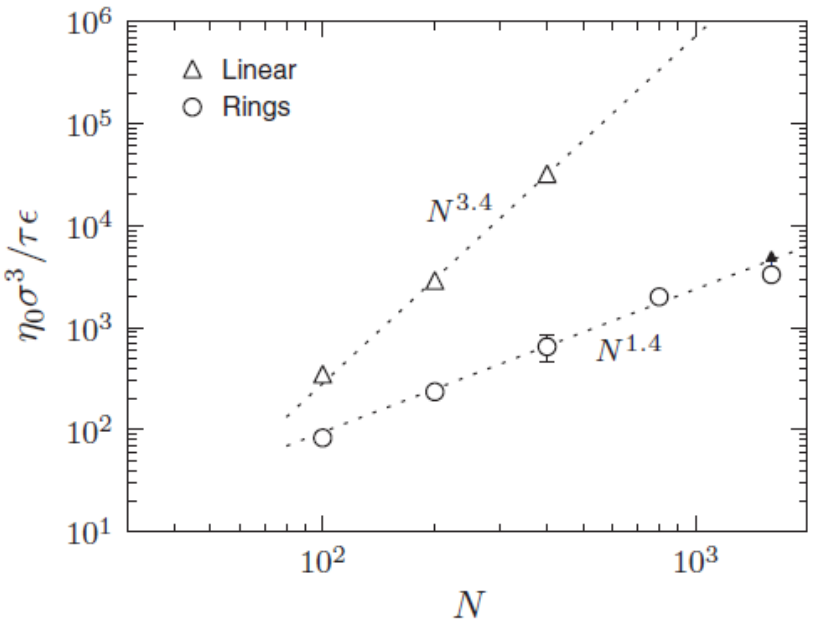
For distances

larger than RG!

Melt of nonconcatenated rings: N=100, 200, 400, 800, 1600 (≈58N_e)

Diffusion **vs** **viscosity**

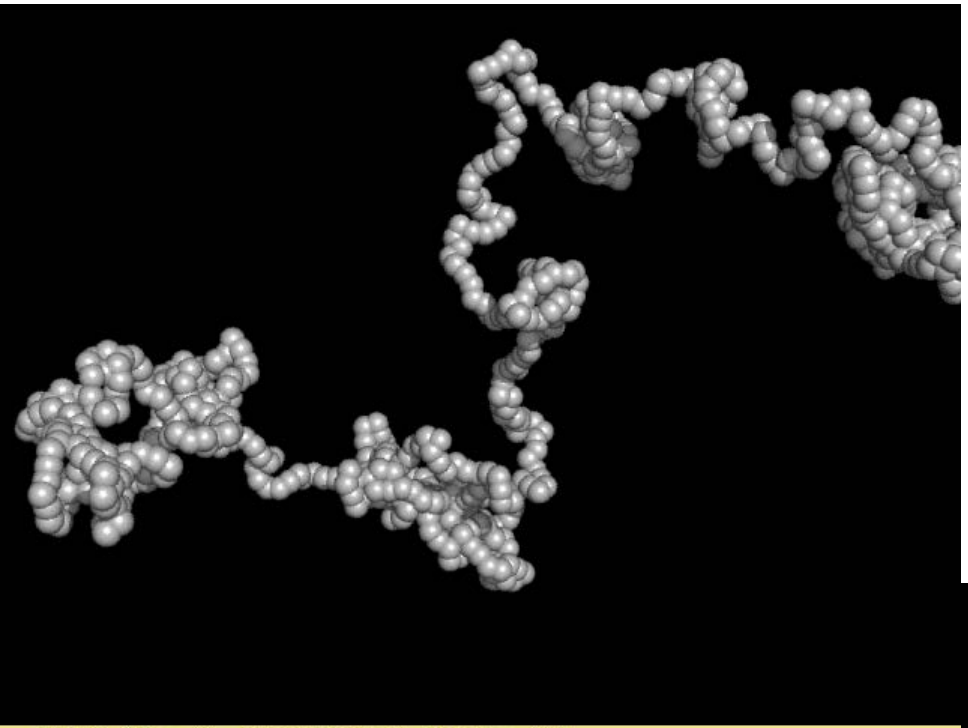




Mean square displacement of center of mass of ring and viscosity seem to decouple!

NO well established theoretical model
Problem of few linear polymers in rings and few rings in linears

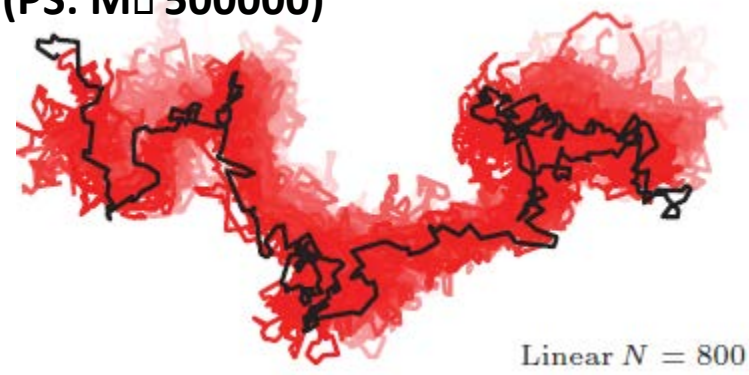
Halverson, Lee, Grest, Grosberg, KK JCP, 2011

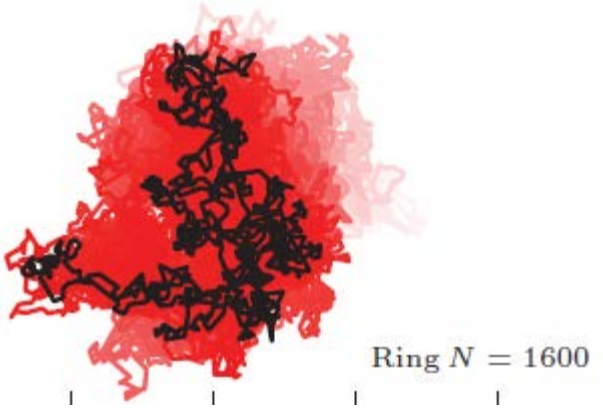


chain id = 78, monomers per chain = 800

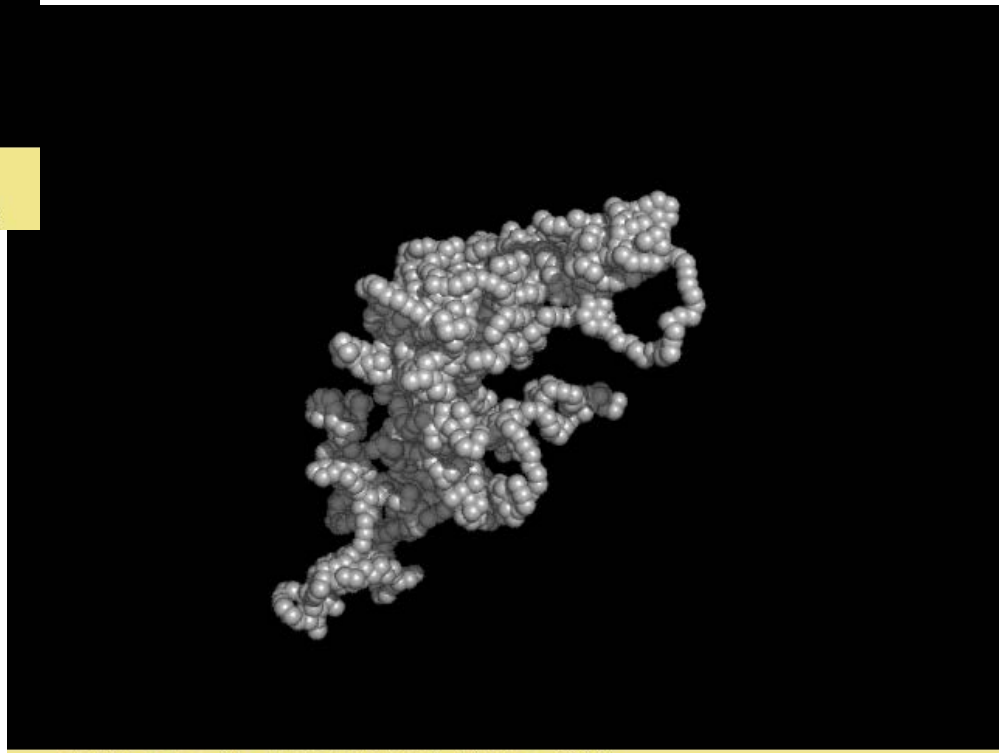
time = 5.664e+06 tau Rg(t)/<Rg> = 1.22 sqrt[g3(t)]/<Rg> = 0.00

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





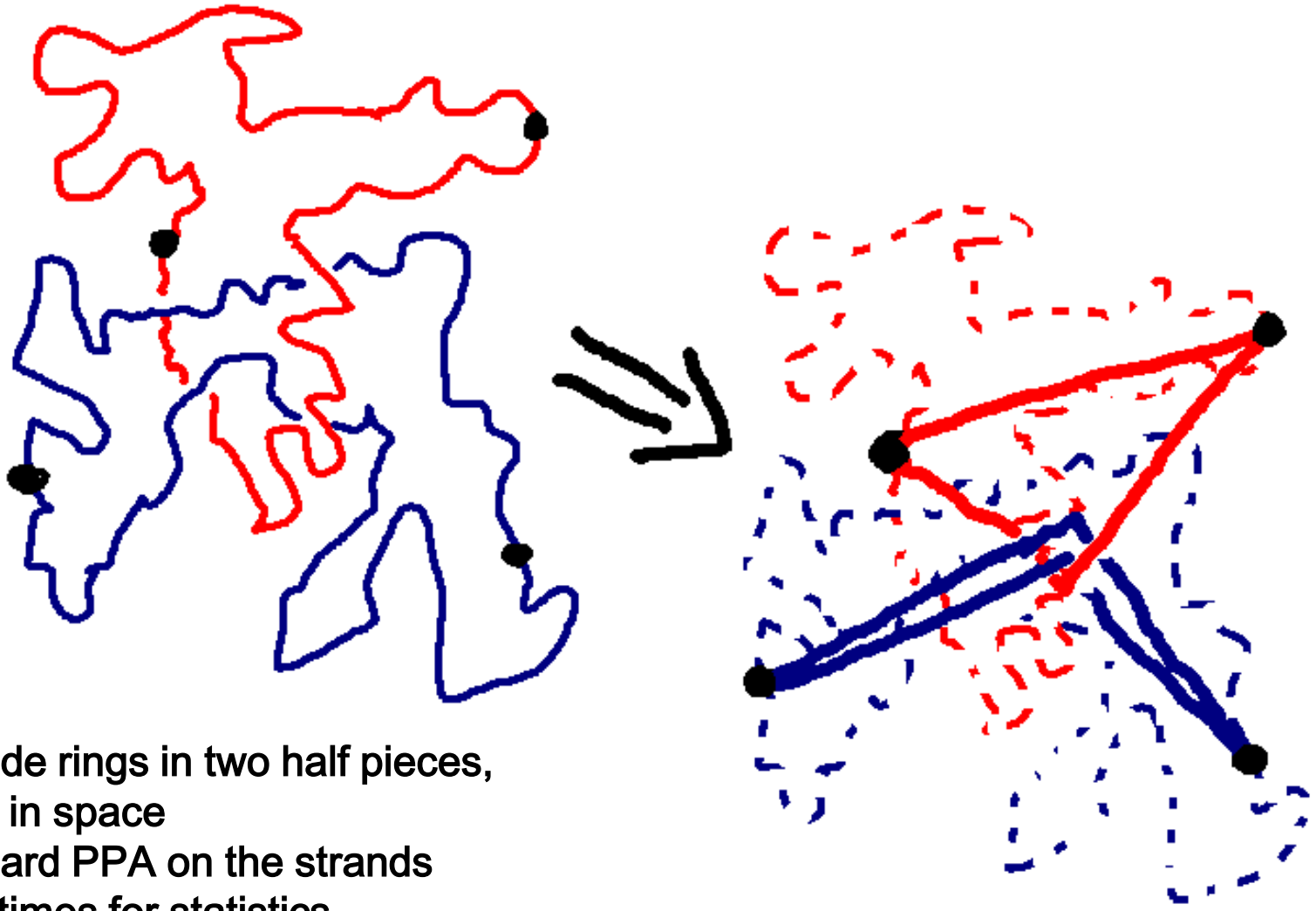
Ring, N=1600
(PS: M≈ 1000000)



chain id = 29, monomers per ring = 1600

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

Melt of Ring Polymers: Dynamics, Primitive Path Analysis

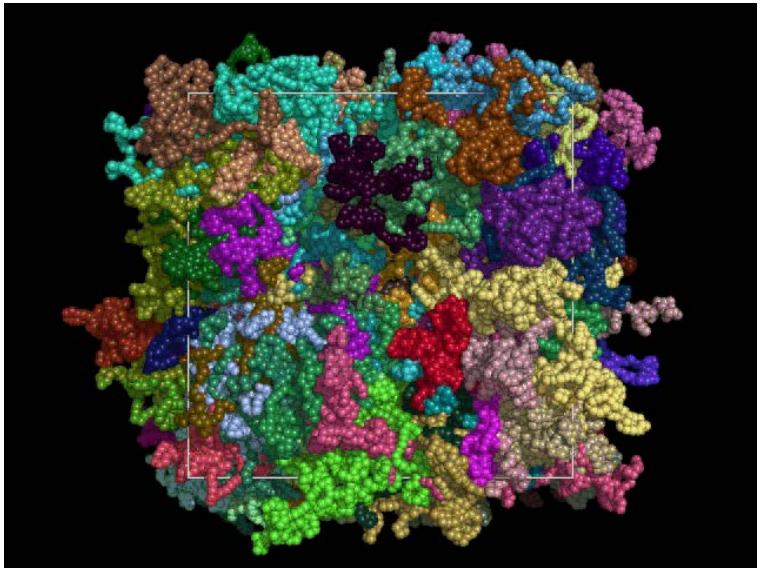


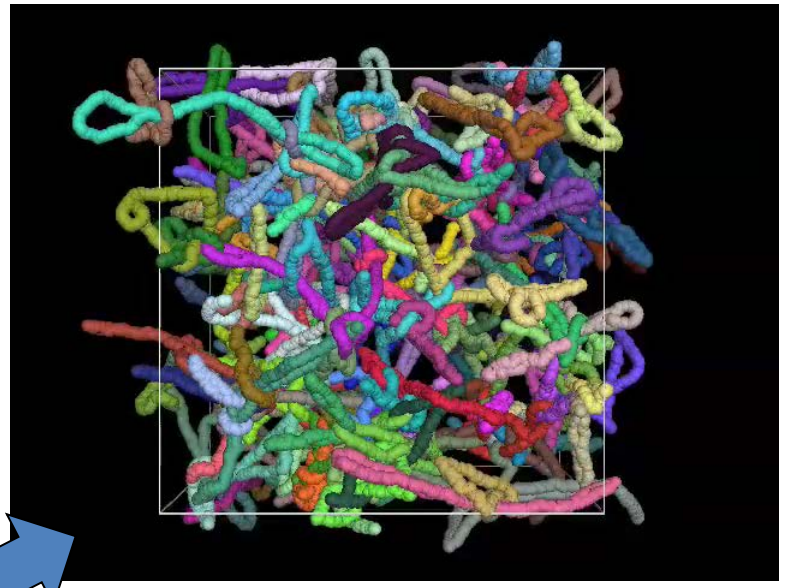
Randomly divide rings in two half pieces,
Fix end points in space
Perform standard PPA on the strands
Repeat many times for statistics

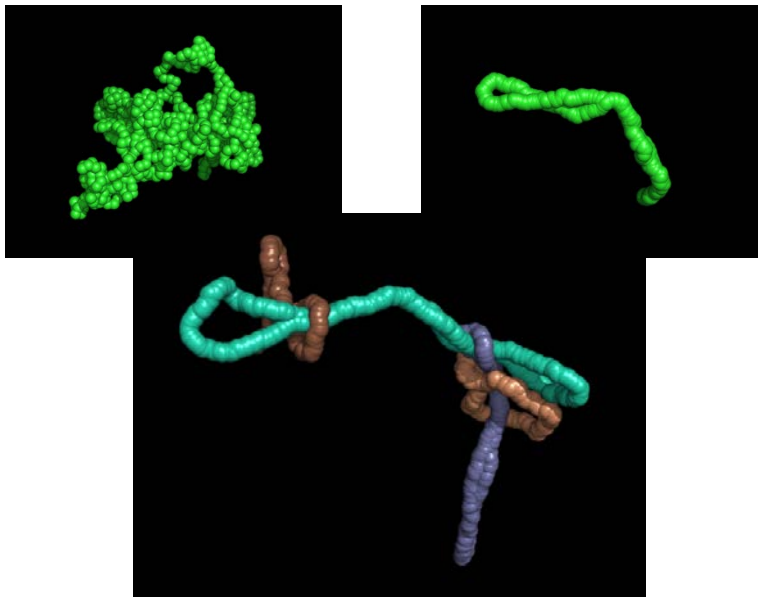
Melt of Ring Polymers:Dynamics

Primitive Path analysis
(similar to linear polymers)

Rings are somewhat
entangled







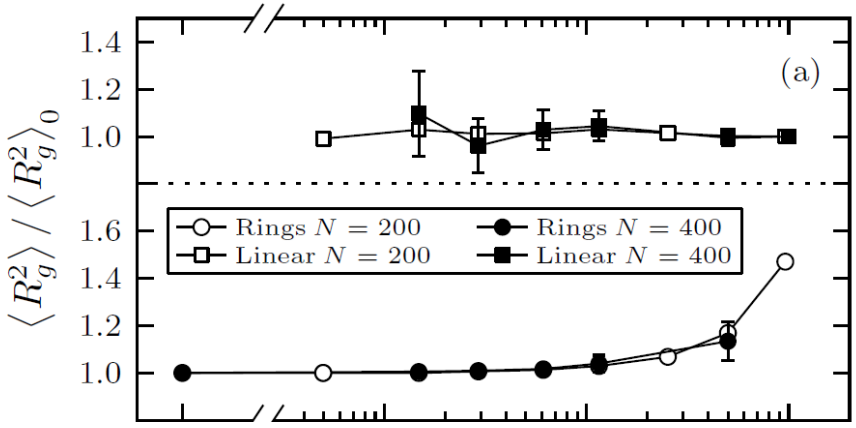
$N_{e,ring} \approx 3\, N_{e,linear}$

N=800, # of rings 200

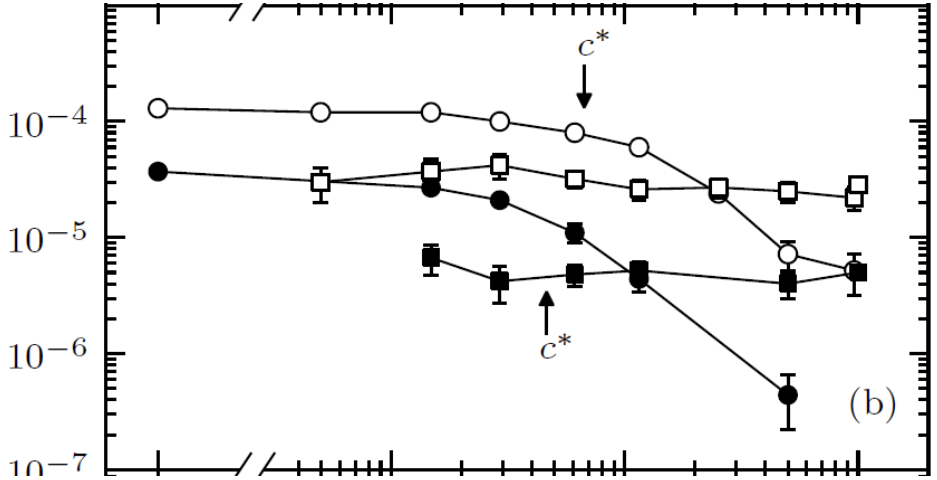
Another Puzzle: Rings plus linear Polymers

J. Halverson, et al, 2011

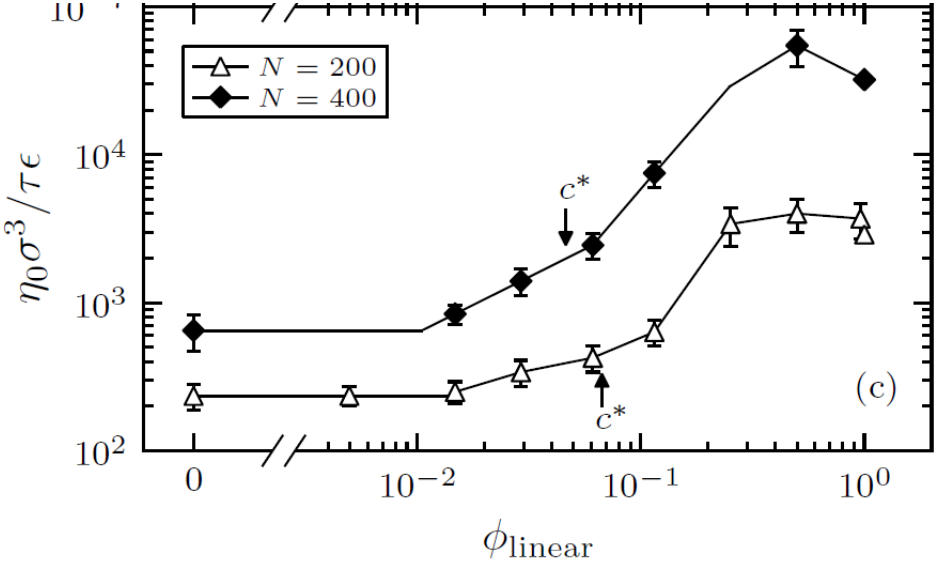
Radius of Gyration

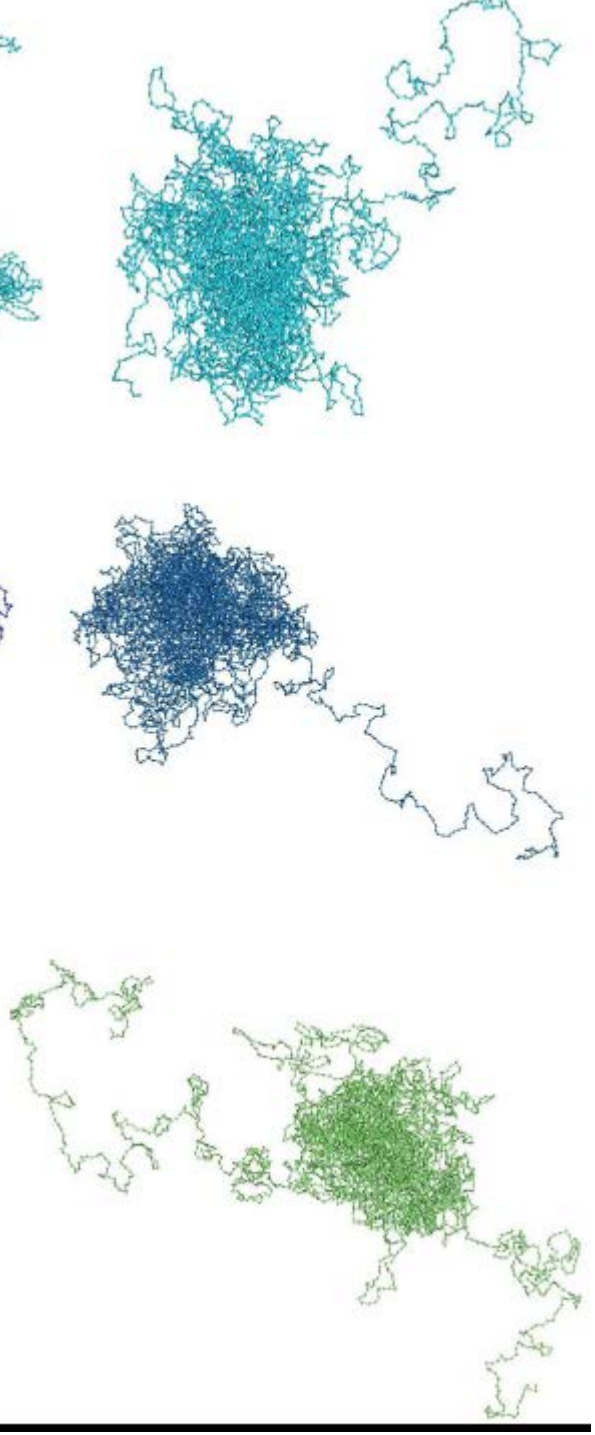


Diffusion

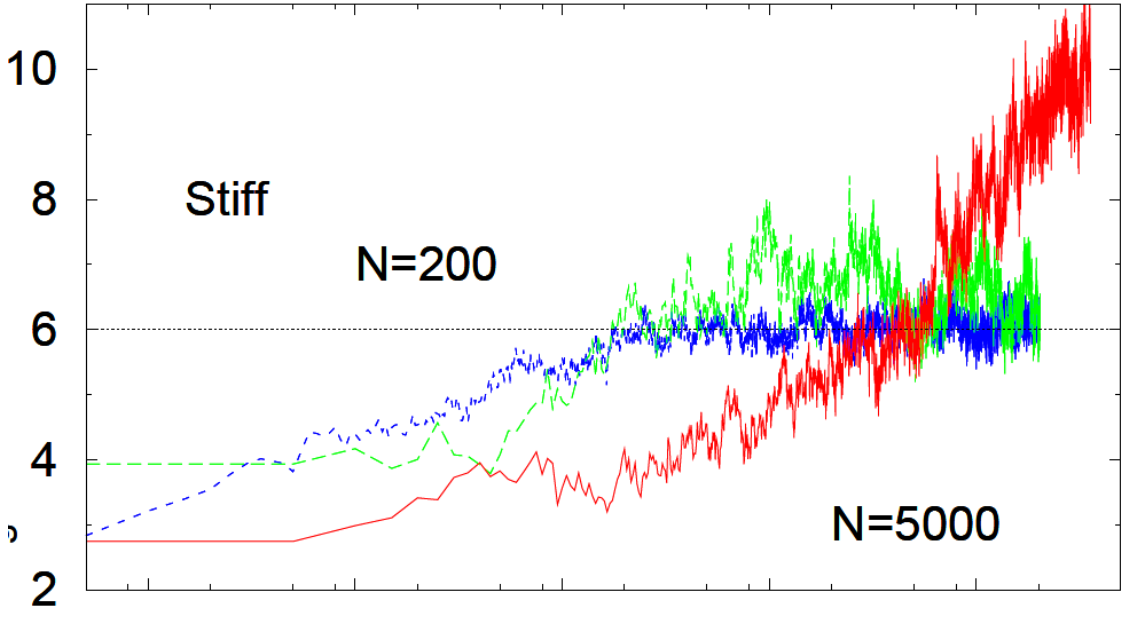


Viscosity



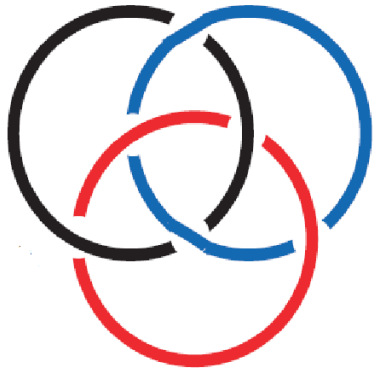


“Use” topological constraints: Melt of collapsed linear polymers

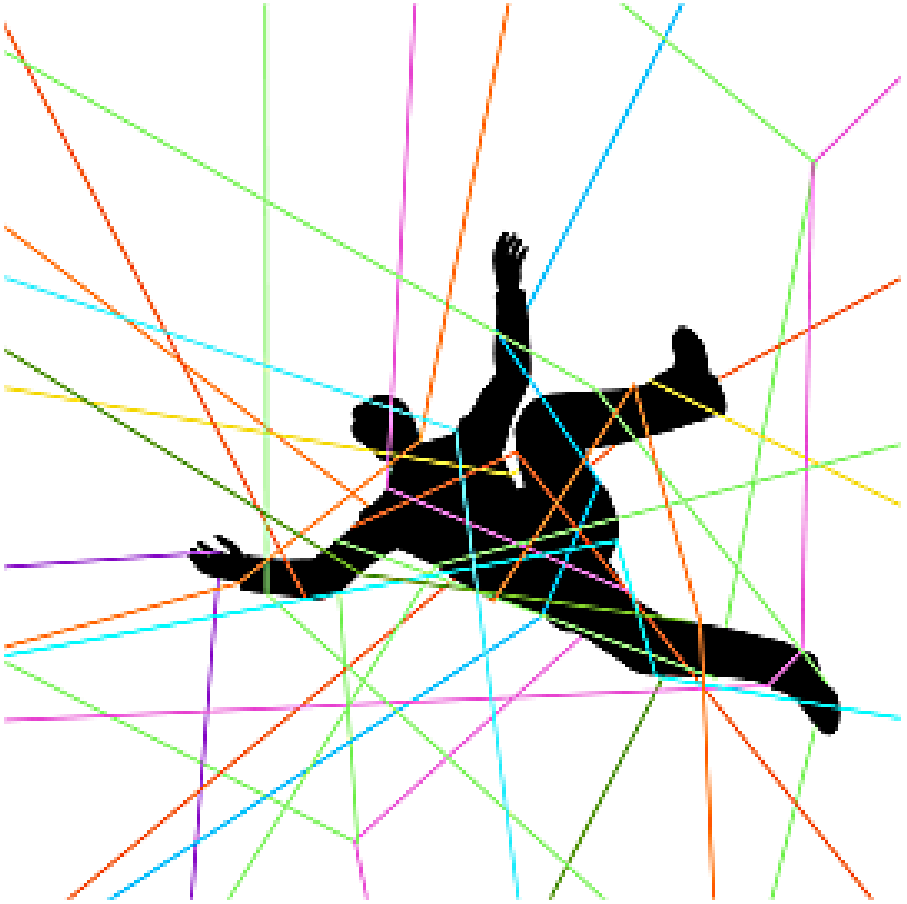


Topological Constraints Matter

- **Tube concept**
  - N_e derived from conformational statistics
  - Good agreement between simulations and experiment, both for melts and networks
- **Melt of non concatenated rings, melt of globules**
  - Still many open questions about conformations
  - Dynamics poorly understood so far
  - Mixtures, composites, applications beyond model system for chromosome territories…



Thank you for your attention



http://news.cnet.com/8301-31114_3-20030591-258.html