Dynamics of Entangled Polymers

Ideas Introduced by de Gennes and Others

Outline

1. Pre-reptation era and the birth of the *tube model*

2. *Reptation* of linear polymers

3. Many-chain effects – *constraint release*

4. Dynamics of entangled stars – *arm retraction*

5. Applications of these ideas

6. Open questions

Polymer Melt

Melt – polymer liquid above its glass and/or crystallization temperatures.

Main feature of a melt – chains are heavily overlapping (overlap parameter $P \sim N^{1/2}$)

Melts with long chains $N > 100$ and $P > 10$ behave as elastic networks at short times.

Elastic properties of melts were attributed to *temporary entanglements between chains*. *Busse 1932, Treloar 1940*

Early models treated entanglements in melts either as *temporary cross-links* (stickers) *Green & Tobolsky '46; Lodge '56; Yamamoto '56* or introduced *entanglement friction* due to snaking circularly motion of chain sliding around entanglements (*Bueche 1952*).
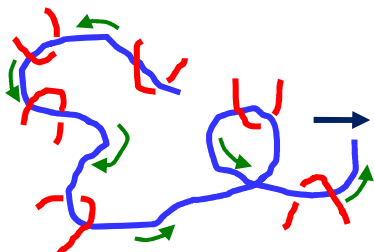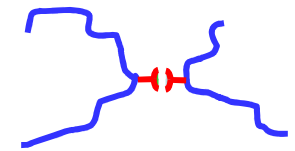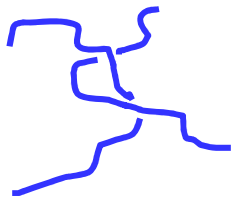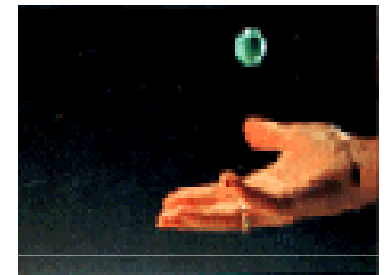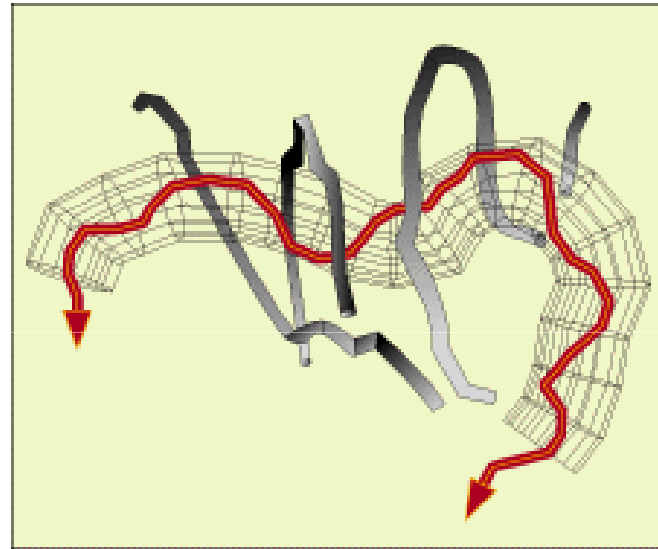
Tube Model

The major breakthrough in the theory of entangled polymers was *Edwards' tube model* of entangled polymer networks.

Edwards 1967

Surrounding chains restrict transverse motion of a polymer.

Each polymer is effectively confined to a tube-like region.

Confining tube potential was defined for polymers with permanent topological interactions (for networks).

Reptation of Linear Chains

Main new idea – *"free" chain* in an array of topological constraints, such as linear polymer diffusing through a gel, *is also confined to a tube*, although a temporary one.
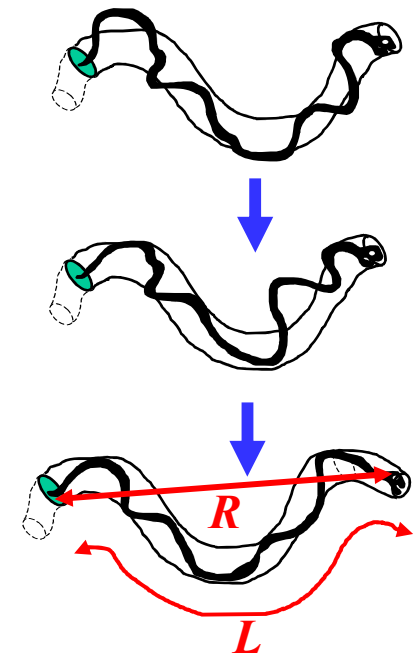
de Gennes 1971

The polymer has hard time moving tangentially to the direction of its tube (exponentially unlikely leakage of loops) and moves predominantly along the tube – *reptates*.

Motion of chain along the contour of the tube is unhindered by topological constraints with curvilinear diffusion coefficient $D_c \sim N^{-1}$
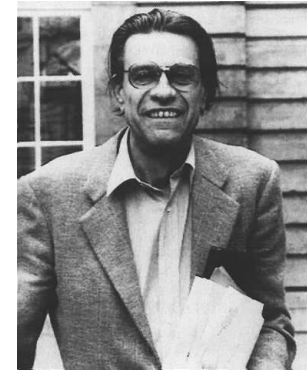
Time it takes chain to diffuse out of its original tube is reptation time $\tau_{rep} \sim L^2/D_c \sim N^3$

de Gennes' reptation model prediction for diffusion coefficient is $D_{3d} \sim R^2/\tau_{rep} \sim N^{-2}$
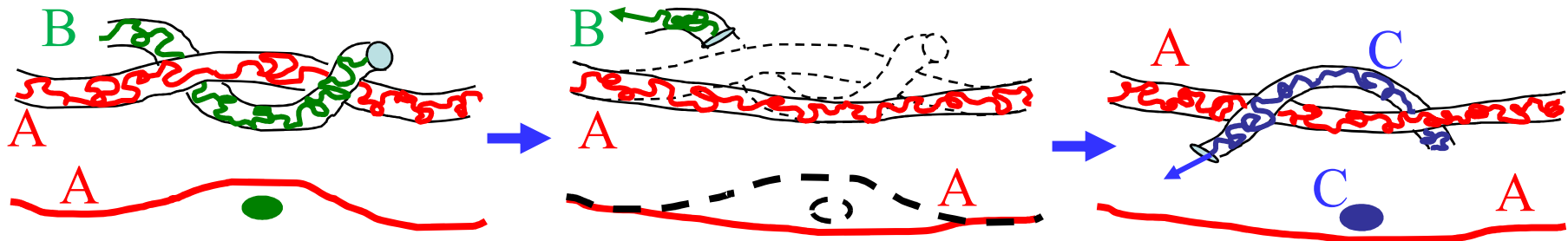
Constraint Release

Motion of surrounding chains
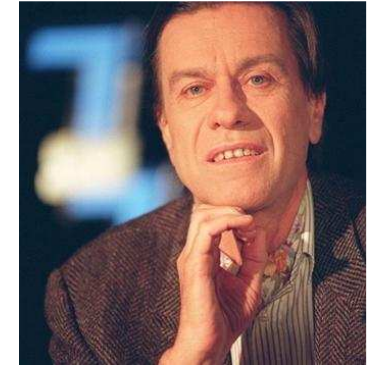leads to *tube reorganization.*

de Gennes 1975

de Gennes proposed to model constraint release by Rouse motion of tube,
but assumed the rate to be proportional to the fraction of chain ends.

The rate of Rouse constraint release motion
is determined by reptation of surrounding chains.

Klein 1978

Dynamics of Entangled Stars

The concept of arm retraction for entangled stars
was introduced by *de Gennes in 1975*

The arm retraction potential was assumed to be linear
- section with **K** monomers is retracting along
its primitive path $U \sim kT \, K/N_e$

Retraction time for arm section
with **K** monomers $\tau \sim exp(K/N_e)$

Exponential dependence
of arm retraction time
on number of entanglements
$\tau_{arm} \sim exp(N_a/N_e)$
was estimated correctly.
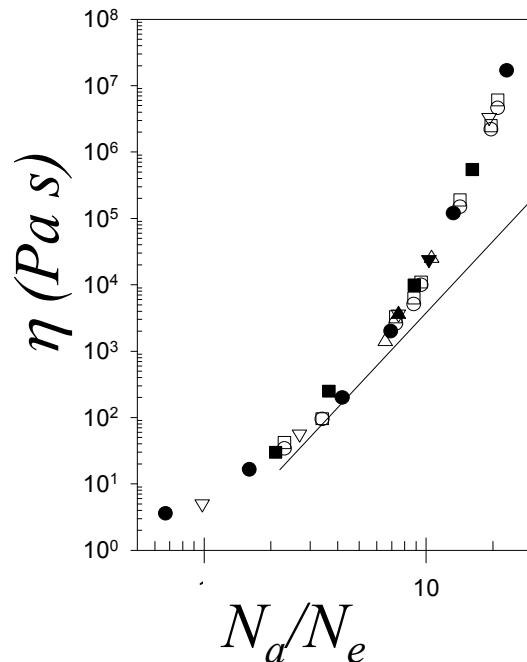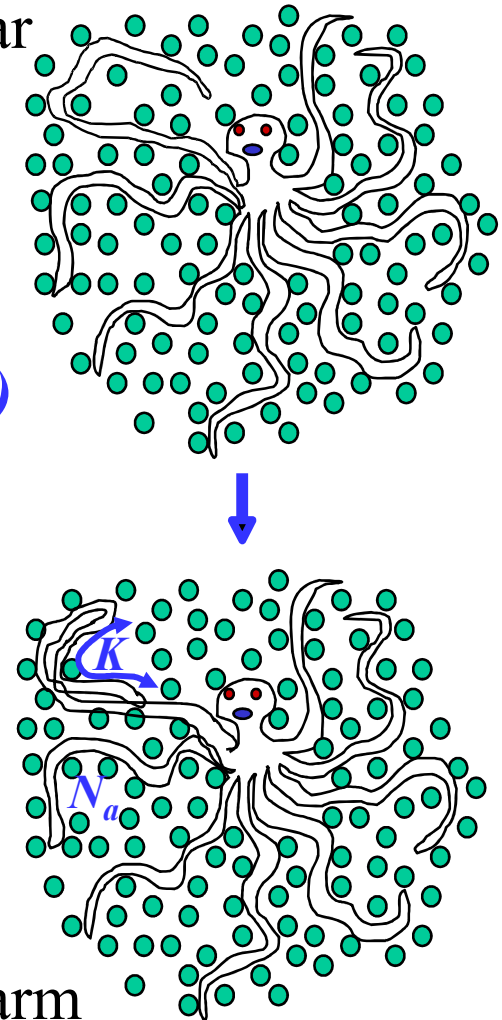
N_a - number of monomers in an arm

Extensions of Arm Retraction Idea

The arm retraction potential is closer to parabolic as double-folded loops raise entropy by branching out.
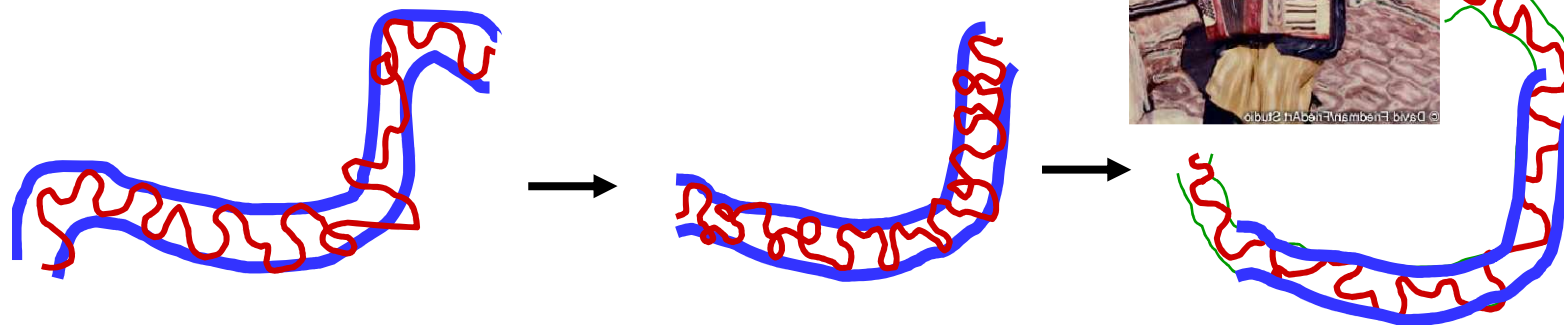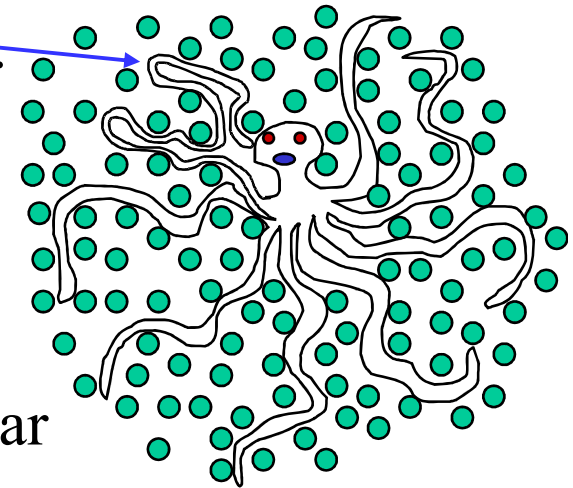
Doi et al 1980

$$\tau \sim exp[K^2/(N_a N_e)]$$

No barrier for tube length fluctuations of sections containing $\dfrac{K}{N_e} \sim \sqrt{\dfrac{N_a}{N_e}}$ entanglements for both star arms and linear chains (accordion modes).

Doi 1981

Tube length fluctuation modes modify molecular weight dependence of relaxation time, diffusion coefficient and viscosity of polymer melts.
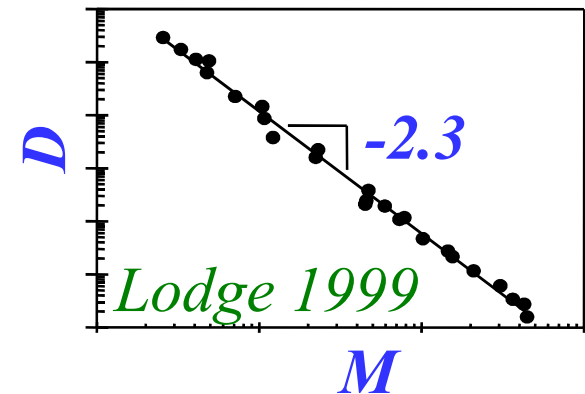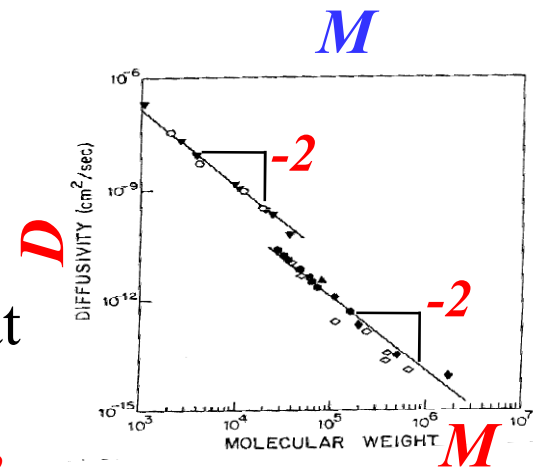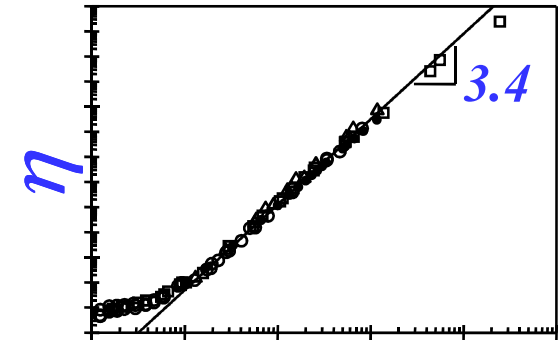
Reptation vs. Experiments

Experimental molecular weight dependence of relaxation time and viscosity was established well before reptation model $\tau \sim \eta \sim M^{3.4}$

Difference between experimental *3.4* and reptation model exponent *3* is primarily due to tube length fluctuations (*Doi 1981*)

de Gennes' reptation model was so influential that diffusion experiments made and analyzed after reptation model confirmed its prediction $D \sim M^{-2}$

More recent diffusion experiments observed expected tube length fluctuation corrections to reptation $D \sim M^{-2.3}$

η vs M, slope *3.4*

D (DIFFUSIVITY (cm²/sec)) vs M (MOLECULAR WEIGHT), slopes *-2* and *-2*

D vs M, slope *-2.3*, *Lodge 1999*

Comments on 1971 Reptation Paper

Looking back at this paper, I am amazed at the slow course which we followed after. The first active reaction was through the group of J. Ferry, who succeeded in trapping some chains in a compatible gel, and measuring their contribution to complex elastic modulus. But in fact there was a much simpler way to operate: integrating test chains in a melt of (chemically identical) longer chains: the latter are so slow that they behave as a gel on the time scale of interest. It took us about four years to realize this simple point. Finally, the most delicate step is to go to a monodisperse melt, and to see if one chain is still trapped in an "effective gel" by its neighbors: The first detailed justification for this idea (with long enough chains $N \geq 10 N_e$) came from Doi and Edwards. There are still, however some unresolved disputes between them and J. des Cloizeaux on "double reptation".

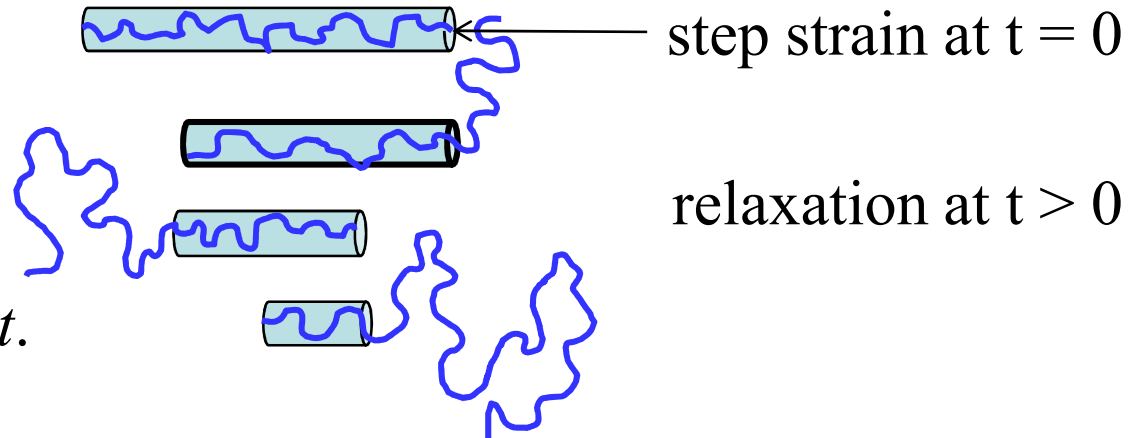Pierre Gilles de Gennes, 1992
"Simple Views on Condensed Matter"
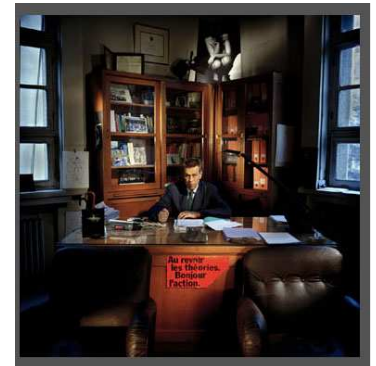
Applications of Reptation

*Doi and Edwards* applied reptation model to rheology of entangled polymer liquids in *1978*.

step strain at t = 0

Stress relaxation function is calculated as the fraction of the tube that has not been vacated between times *0* and *t*.

relaxation at t > 0

Predictions of Doi-Edwards theory are in reasonable agreement with dynamic-mechanical measurements in entangled polymer melts.
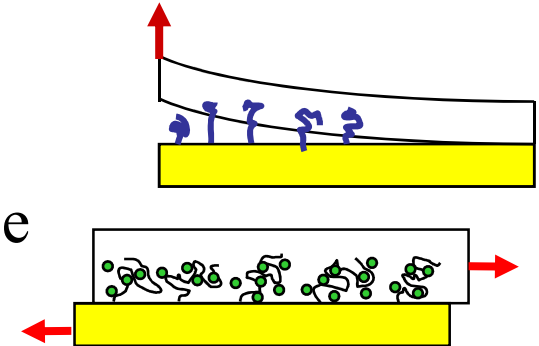
Especially if modes due to tube length fluctuations

and tube reorganization are taken into account as well.
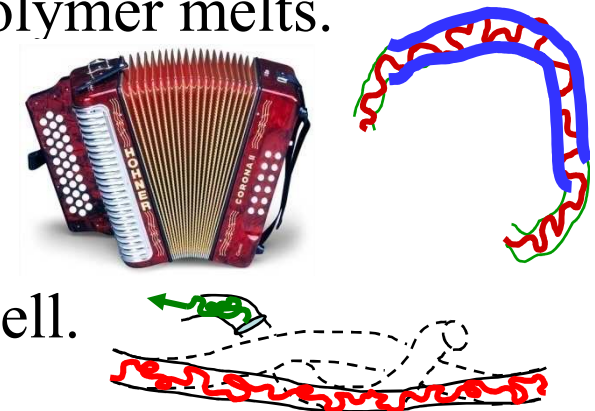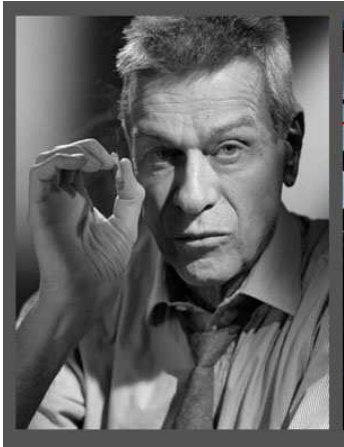
Applications of Arm Retraction

In *1992* de Gennes extended this idea to chain pull-out in crack propagation and to slippage of polymer over surface with grafted chains.

He predicted 3 regimes for friction of an entangled chain pulled by its end through a polymer matrix.
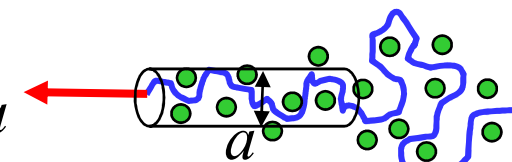
1. Linear regime ($v < v_1 = a/\tau_a$) with friction determined by star-like arm retraction because one end of chain is attached
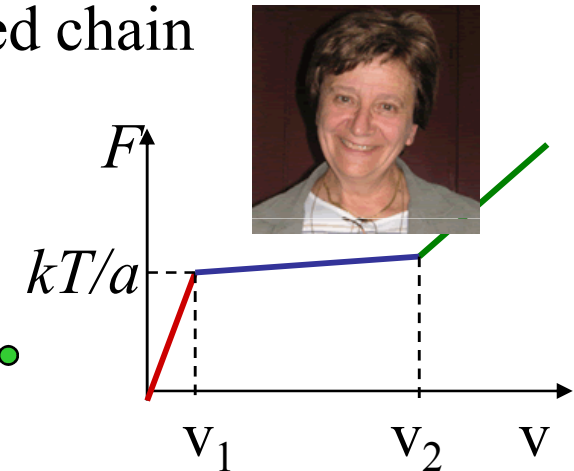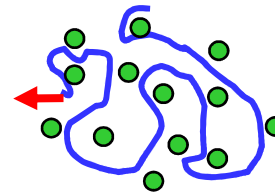
2. Intermediate regime $v_1 < v < v_2 = kT/(\zeta_1 a)$

Not enough time for chain to fully retract.

Tension in the front part of chain is constant kT/a
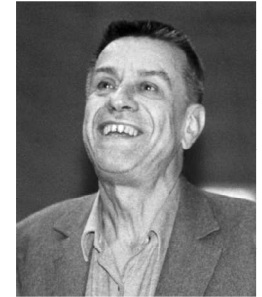
Parachute - part of the chain that relaxes by arm retraction

3. High velocity regime with tension dominated by monomeric friction

Microrheology

2000

Diffusion of a Particle in Polymer Melt

If particle size is smaller than tube diameter ($R < a$), topological interactions between chains do not affect particle motion.

Number of monomers in a chain section of particle size $g = (R/b)^2$

Rouse modes of these sections contribute to effective viscosity "felt" by the particle.
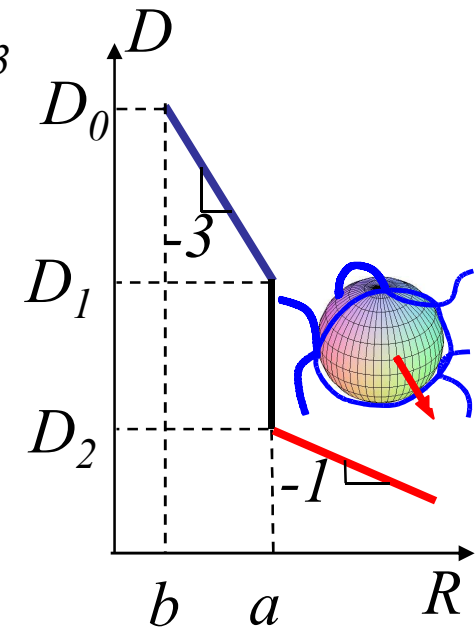
$$\eta = \eta_0 g = \eta_0 (R/b)^2$$

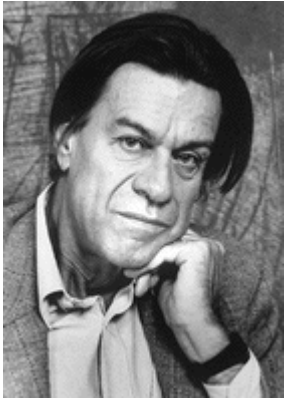Particle diffusion coefficient $D \approx kT/(\eta R) \sim D_0 b^3/R^3$

If particle is larger than tube diameter, $R > a$, it becomes trapped and has to wait for chains to reptate away before it can diffuse further.

Diffusion of particles with $R > a$ is determined by melt viscosity.

$$D = \frac{kT}{6\pi\eta R} \sim R^{-1}$$

Drop of diffusion coefficient at $R = a$ is the ratio of melt and local $\eta_0 N_e$ viscosity: $D_1/D_2 = (N/N_e)^3$
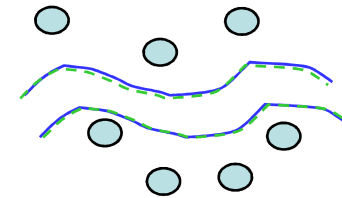
Open Questions

Constraint Release vs. Tube Dilation

De Gennes 1975

Marrucci 1985

Alternative tube reorganization mechanism – tube dilation
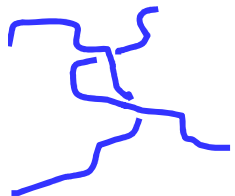
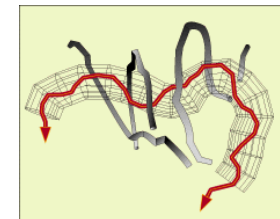Reptation of surrounding chains leads to widening of a tube.

Does constraint release or tube dilation provide a better description of tube reorganization of linear and branched entangled polymers?
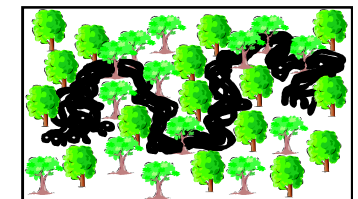
Is there any coherence in tube reorganization – the same chain releases several constraints for a given tube?

Are constraints pairwise or collective?

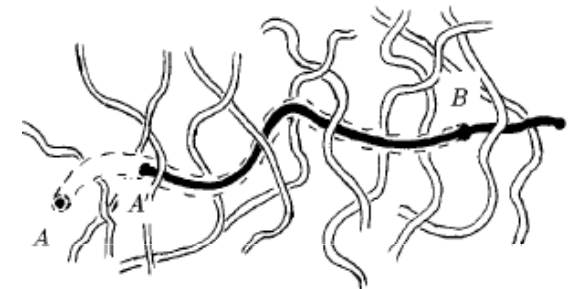What is the precise definition of confining tube and its axis (primitive path)?

Open Questions

What is the asymptotic molecular weight dependence of relaxation time and viscosity for ultra-high molecular weight polymer melts?
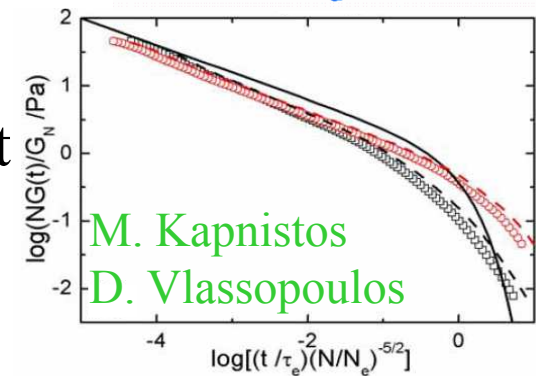
Is it ~ M^3 as predicted by de Gennes reptation theory or ~ $exp(M^{2/3})$ due to chain trapping in their tubes as predicted by J. Deutsch in 1985?
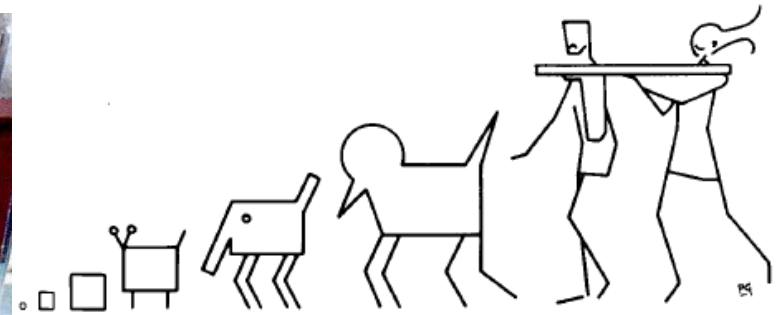
Why don't non-concatenated rings trap themselves in a melt (as suggested by Obukhov in 1994)
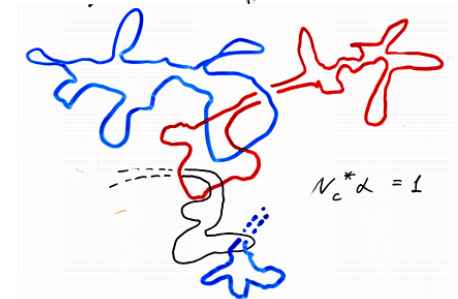
and instead relax as self-similar power law without a rubbery plateau?

M. Kapnistos
D. Vlassopoulos

Personal Remarks

Various animals attempting to follow a scaling law.

Pierre-Gilles de Gennes was the *most inspiring scientist* *in polymer physics during the last 4 decades.*

He had the *most original ideas* *that* *redefined the field* *of modern polymer physics.*

De Gennes with his "impressionist" style and approach to science *influenced my own research* *more than any other scientist.*

PGG will be missed dearly both as a scientist and as a person.