Interdiffusion and polymer dissolution

Jacob Klein, Weizmann Institute

Guidelines for de Gennes Symposium talks

1. Introduction - state of the field before de Gennes' work
   (experimental + theoretical)
2. New ideas introduced by de Gennes
3. Development of the field after de Gennes' paper(s)
4. Current status of the field
5. Future directions

1. Introduction - state of the field before de Gennes' work (experimental + theoretical)

Prior to the 1970's the ideas of polymer interdiffusion were not well developed at the molecular level(only small molecules in polymers, e.g. Crank 1968, Meares 1963)

Interdiffusion for condensed small molecules, however, was reasonably well understood

e.g. metals: Kirkendall (1942), Darken (1948) - first treated case of interdiffusion of metals of different mobilities
or
Simple liquids: e.g. Rowlinson (book 1964, 1969) - reviewed liquid mixing

But the case of highly entangled chains was intrinsically very different: no lattice hopping as in metals, and strong entanglement constraints, unlike liquids

One difficulty was, that there was no adequate model for dynamics of entangled chains.

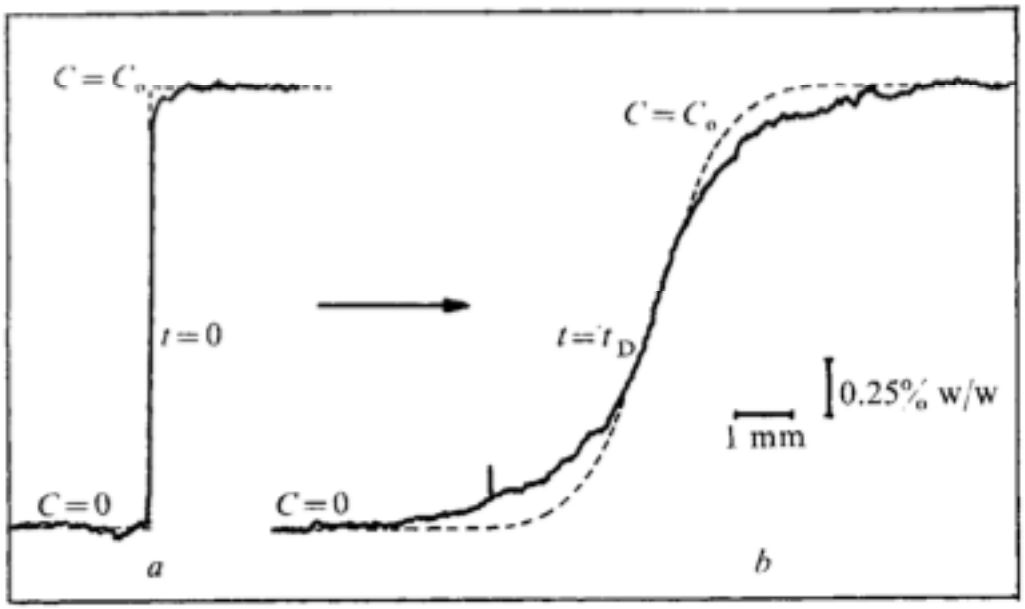
De Gennes reptation model (1971) was one of several proposed mechanisms.

Early experiments on the mechanism of entangled chain diffusion set out to discriminate between the different predictions.

Nature Vol. 271 12 January 1978 (J. Klein)

Evidence for reptation in an entangled polymer melt

ENTANGLEMENTS, their nature and their role in the dynamic properties of concentrated polymer solutions and melts are not well understood[1,2]. The classical molecular view of entanglements has been one of rope-like intermolecular couplings at a number of points along the length of a molecule; molecules in motion would drag past these couplings the essential



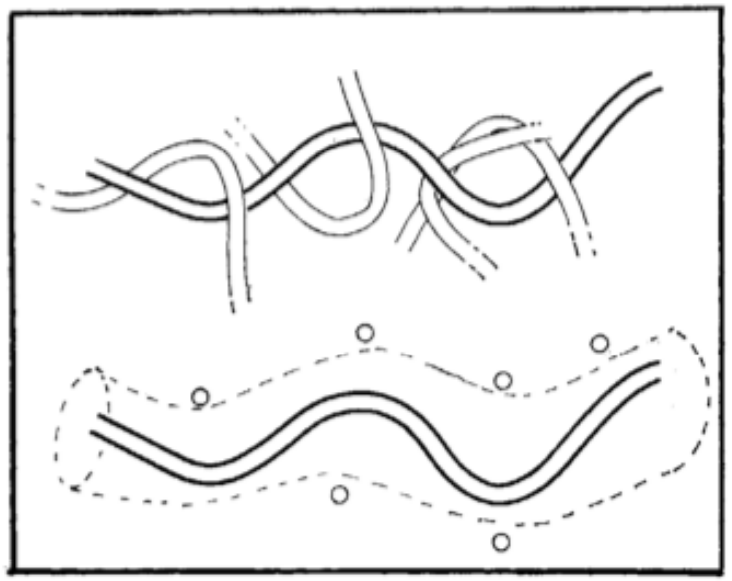


Fig. 1 A polymer chain in an entangled melt (or concentrated

→ $D \sim M^{-2\pm0.1}$

This experimental result supported the reptation model

Following the 1978 experiments and the accompanying 'News & Views' in *Nature*, de Gennes' reptation model took strong hold, providing finally a framework for understanding also of polymer interdiffusion.

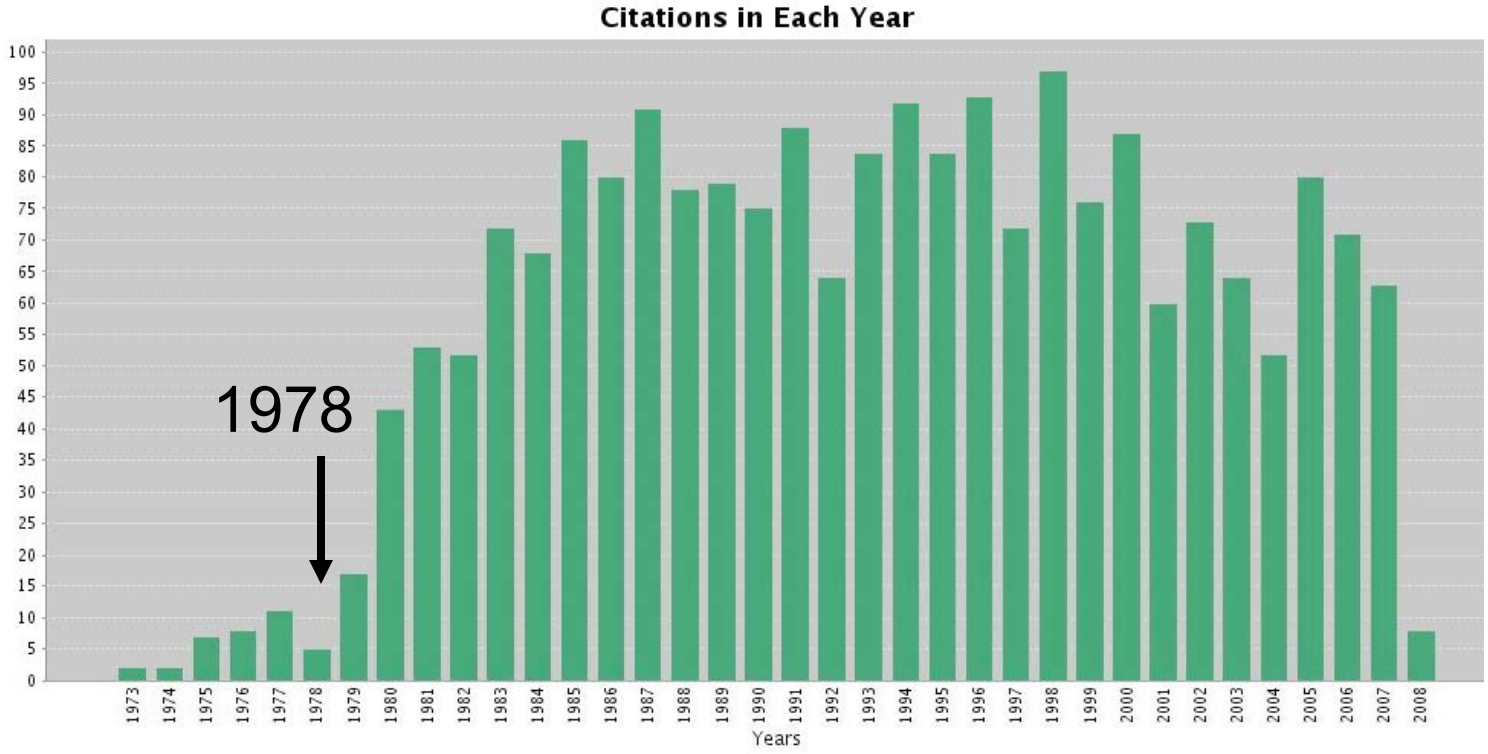
News & Views *Nature Vol. 271 12 January 1978* 113

Polymer diffusion disentangled

from P. D. Calvert

IN 1971 de Gennes predicted that the diffusion coefficient of a polymer chain in a gel would be proportional to the inverse square of the molecular weight (M) and with some reserva- unconvincing routes.

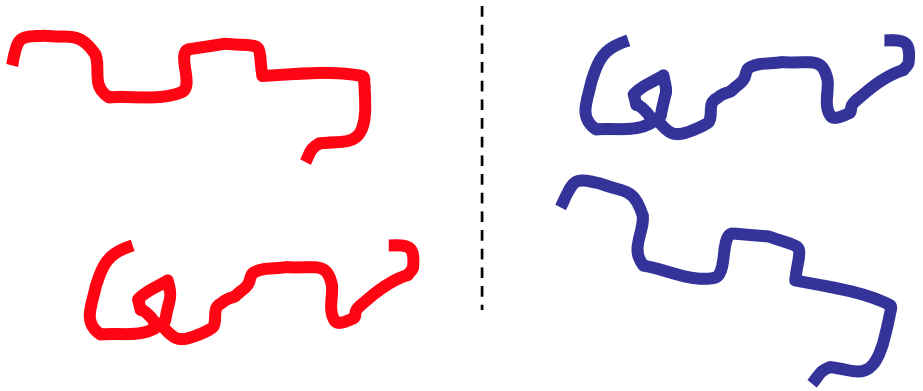
De Gennes approached this problem by considering a chain molecule moving through a cross-linked network so that the moving chain must



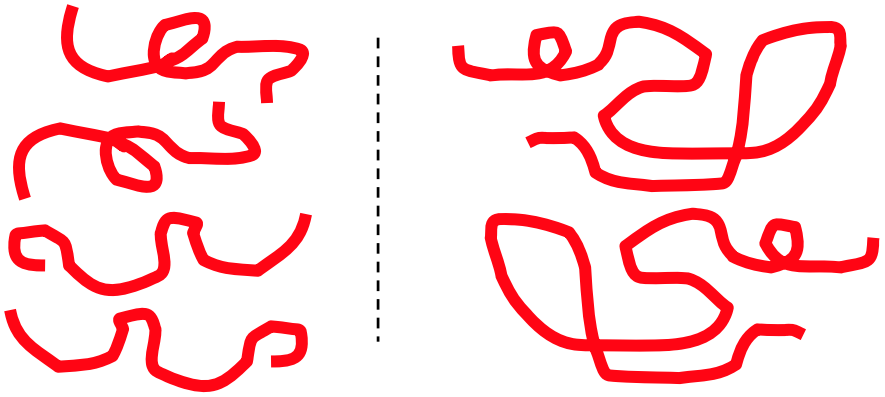
Title: REPTATION OF A POLYMER CHAIN IN PRESENCE OF FIXED OBSTACLES
Author(s): DEGENNES PG
Source: JOURNAL OF CHEMICAL PHYSICS
Volume: 55 Issue: 2
Pages: 572-& Published: 1971
Total citations: 2,137

In this talk we trace the development of an interdiffusion process intrinsic to polymers: how bulk polymers composed of chemically identical chains of <u>different lengths</u> interdiffuse.

Generally one expects two generic cases:



a) Chemically different, driven by mobility and χ (segmental interaction)



b) Only physically different (i.e. in length): driven by mobility alone ($\chi = 0$)

In 1980 de Gennes presented a good starting point for interdiffusion :

Dynamics of fluctuations and spinodal decomposition in polymer blends

P. G. de Gennes

Collège de France, 75231 Paris Cedex 05, France
(Received 3 December 1979; accepted 11 January 1980)

J. Chem. Phys. 72, 4756 (1980)

Treated chemically different chains of same mobility (I.e. N equal, monomer friction coefficients equal), basic equation for chemical potential μ

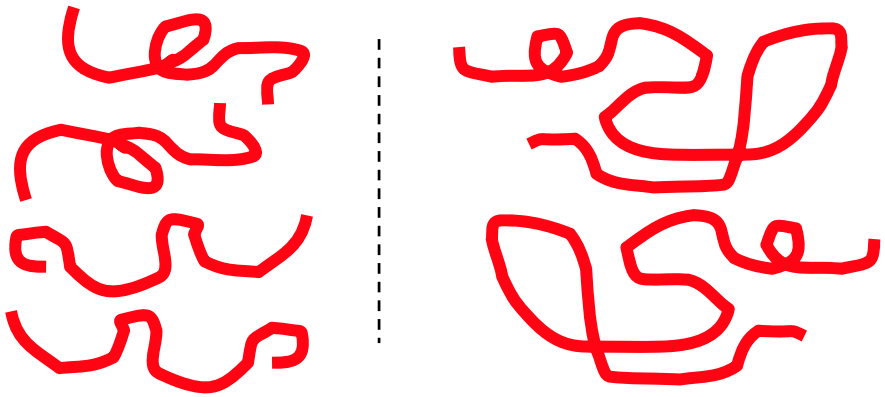
$$\frac{\mu}{kT} = N^{-1}\ln\frac{\phi}{1-\phi} + \chi(1-2\phi) - \frac{a^2}{36\phi(1-\phi)}\nabla^2\phi$$

(where ϕ is the volume fraction)
We are interested more in the other generic limit: chains of same chemistry but different lengths and hence different mobilities

This was first extended by Brochard and co-workers in 1983 to interdiffusion of short vs. long chains:
F. Brochard-Wyart, J. Jouffray, P. Levinson, (BJL)
J. de Physique 1983, Macromolecules 1983

The issue is:

D_s, N_s



D_L, N_L

the constraint of constant density - i.e. equal monomer fluxes in both directions - led to strong coupling of the motion of short and long, and to mutual diffusion

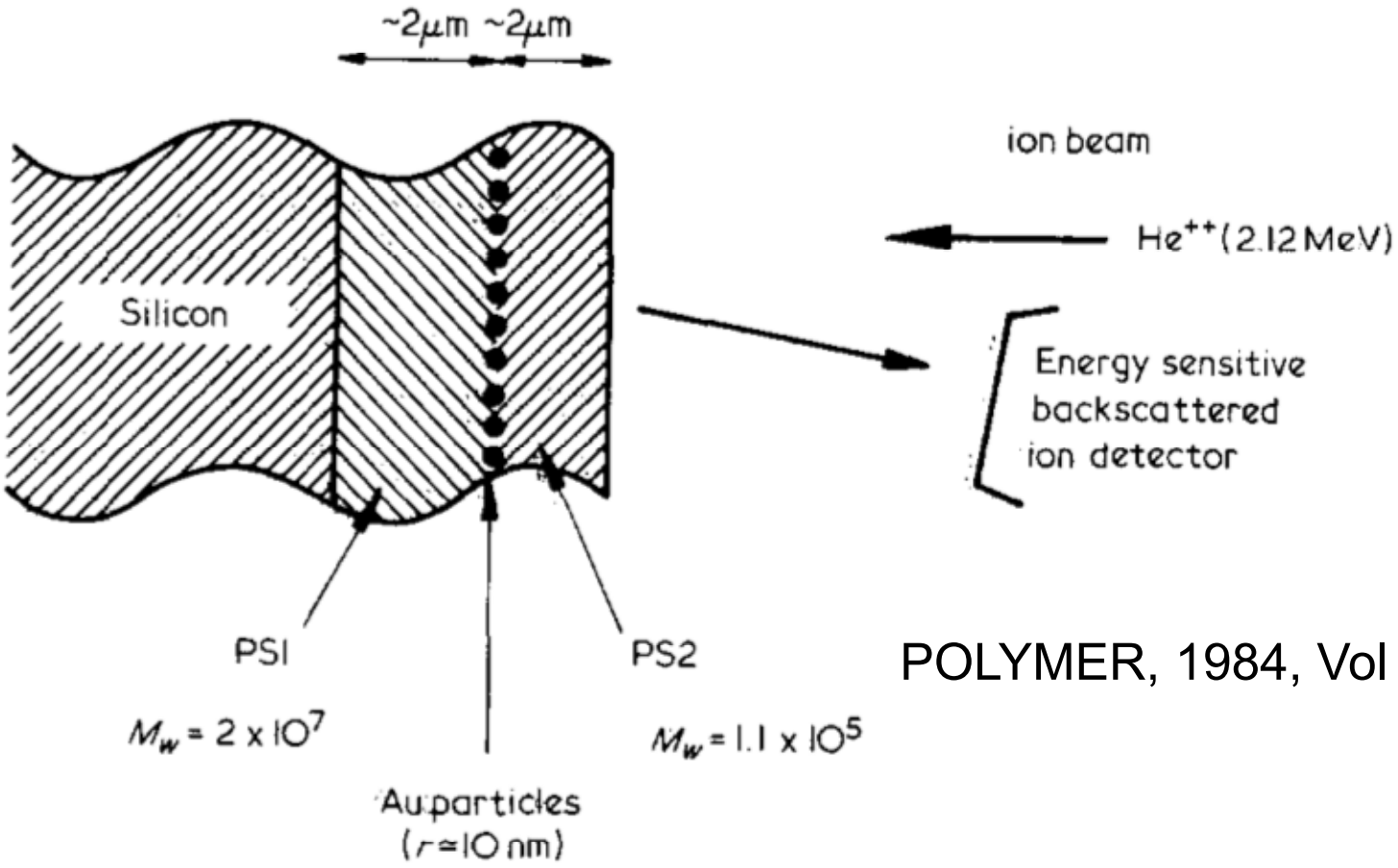
<u>The BJL prediction</u>:

$D \sim (D_s D_L)^{1/2}$ - dominated by <u>slower</u> species since $D \sim N^{-2}$

What of interdiffusion experiments?

Pioneering experiments by Kramer, Green and Palmstrom (Cornell) showed that the fast mode apparently dominated, in contrast to the BJL prediction

Movements in polymer–polymer diffusion couples: E. J.



POLYMER, 1984, Vol 25, April 473

Figure 2 Configuration of Rutherford backscattering experiment to determine gold marker movements

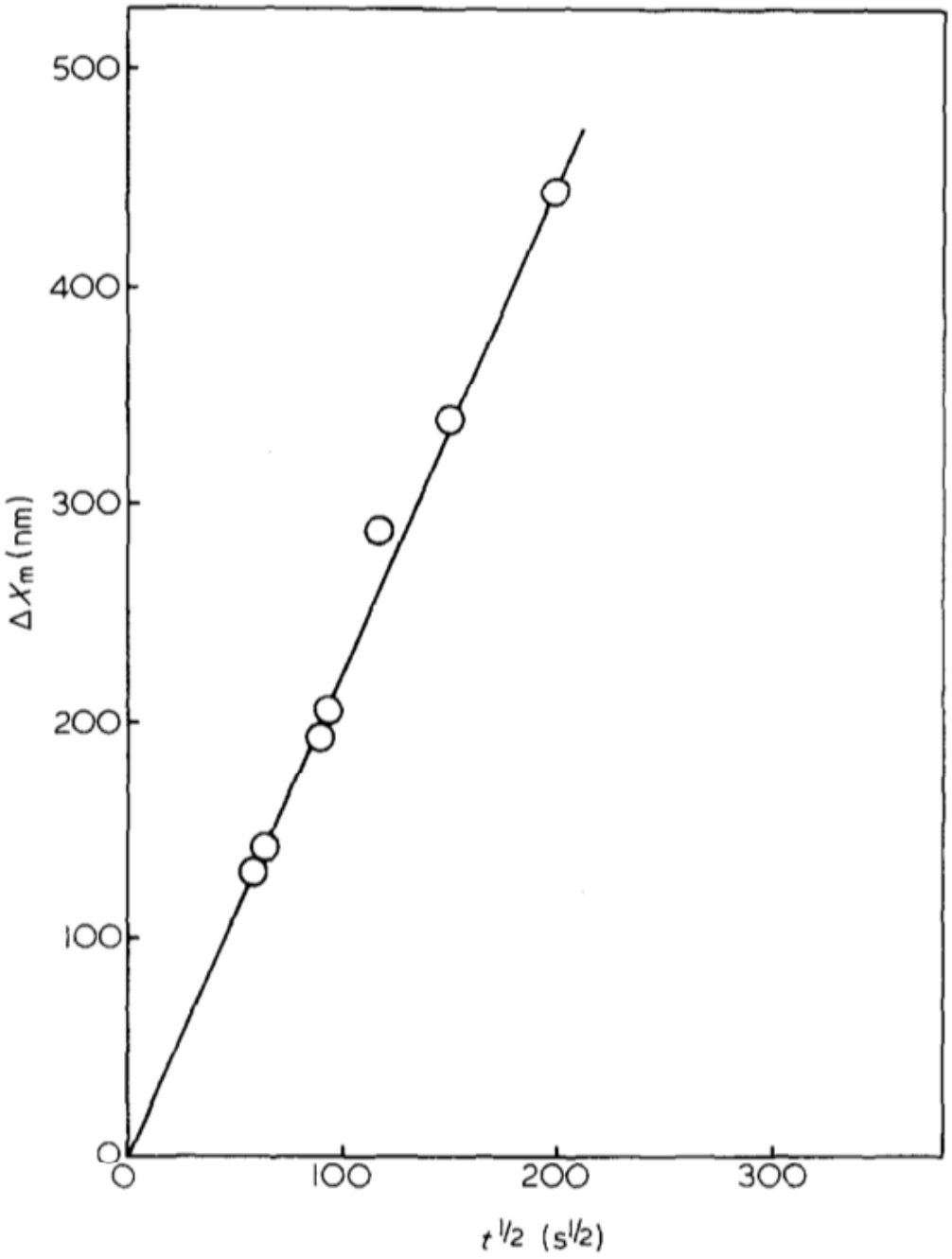


Figure 4 Gold marker movement Δx_m to the free surface (toward

They found that marker movement obeyed $x^2 \sim D_s t$

i.e. dominated by faster moving chains!

This was explained in terms of vacancy flux which allowed a decoupling of the short and long chain motion

(Sillescu (1984) used a different convection type explanation to account for the 'fast mode' interdiffusion)

Polymer-Polymer Interdiffusion.

F. BROCHARD and P. G. DE GENNES
Collège de France - 75321 *Paris Cedex* 05

Europhysics Letters, 1986

In response, Brochard & de Gennes suggested that the Kramer et al. vacancy flux argument might lead to unacceptable density anomalies.

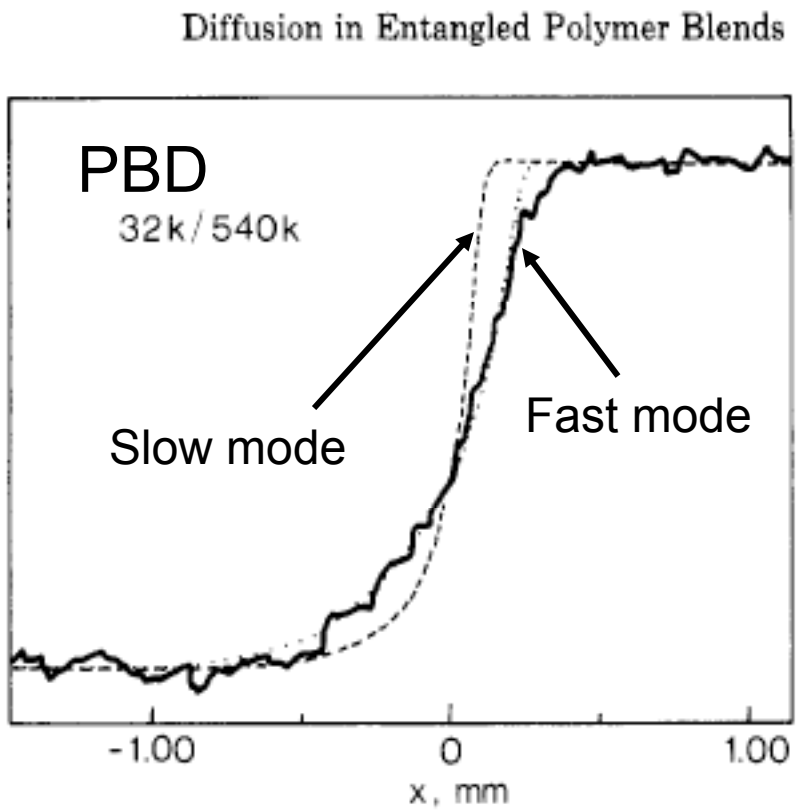
Rather, they accounted for the 'fast mode' observed thus: at the short length scales (O(1 μm)) involved in the gold marker experiments, the longer chains were merely being swollen - like a gel - by the shorter ones, and that at longer length scales than L,

$L \approx (D_s \tau_L)^{1/2}$, (cf. polymer/solvent dissolution) ~ 1 - 10 μm

(where τ_L is the reptation time of the longer chains)
the 'slow mode' interdiffusion should prevail, as predicted.

However, experiments were then carried out at much longer length scales (mm) to check this fast vs. slow mode controversy

Jordan et al, Macromolecules 1988



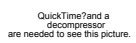
i.r. microdensitometry profiles

These showed conclusively that interdiffusion between long and short chains (but both N_s, N_L >> N_e) was dominated by the faster N_s chains.

Reconciliation of the theory and experiment resulted when analysis by Brochard (1988) showed that correct picture involved reptation of chains in ‘tubes’ that were themselves in motion: recovered ‘vacancy flux’ and ‘convection’ predictions

In a review of polymer-polymer interdiffusion, *Science* **260**, 640 (1990), it was finally concluded that:

“



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So where is this area going now ?

Answer: in many directions, often application-driven - welding, adhesion, advanced composites, nanosystems and nano-confinement, lubrication

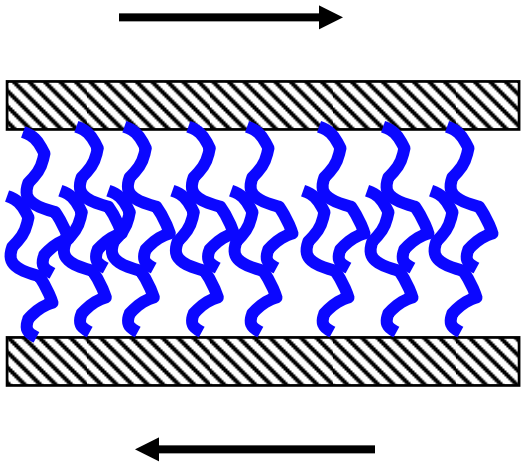
But one of the main threads that runs through PGG work: a toolbox containing a few powerful concepts that turn up again and again

e.g. ‘Blobs’ (in solution); reptation; entropy of stretching; simple modelling and free energy minimization; …

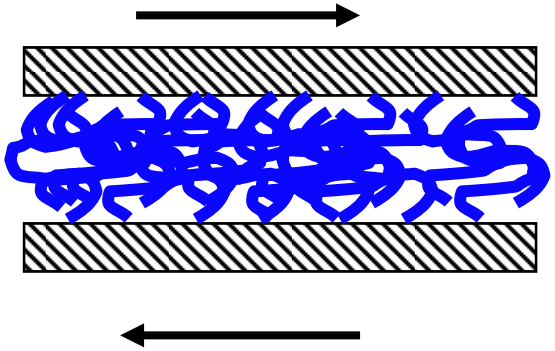
Using this toolbox it is often possible to understand situations (in interdiffusion) not previously envisaged

One example which we discuss in more detail: interdiffusion between surface-attached polymer layers, such as brushes, which affect their friction and lubrication properties

Moderate compressions



High compressions

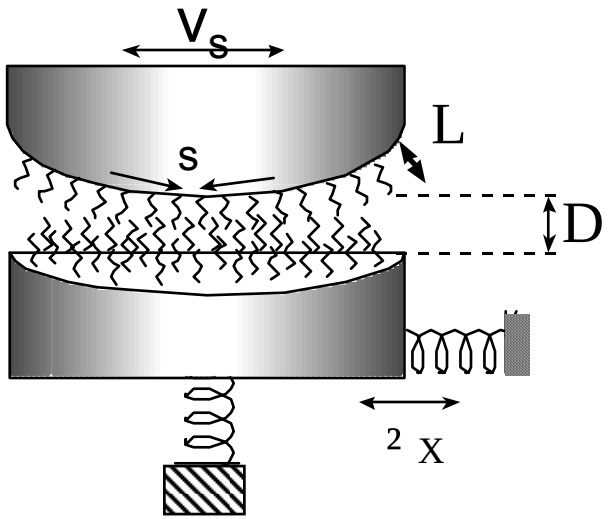


This was examined experimentally by compressing and shearing polymer brushes at different compressions and shear-rates

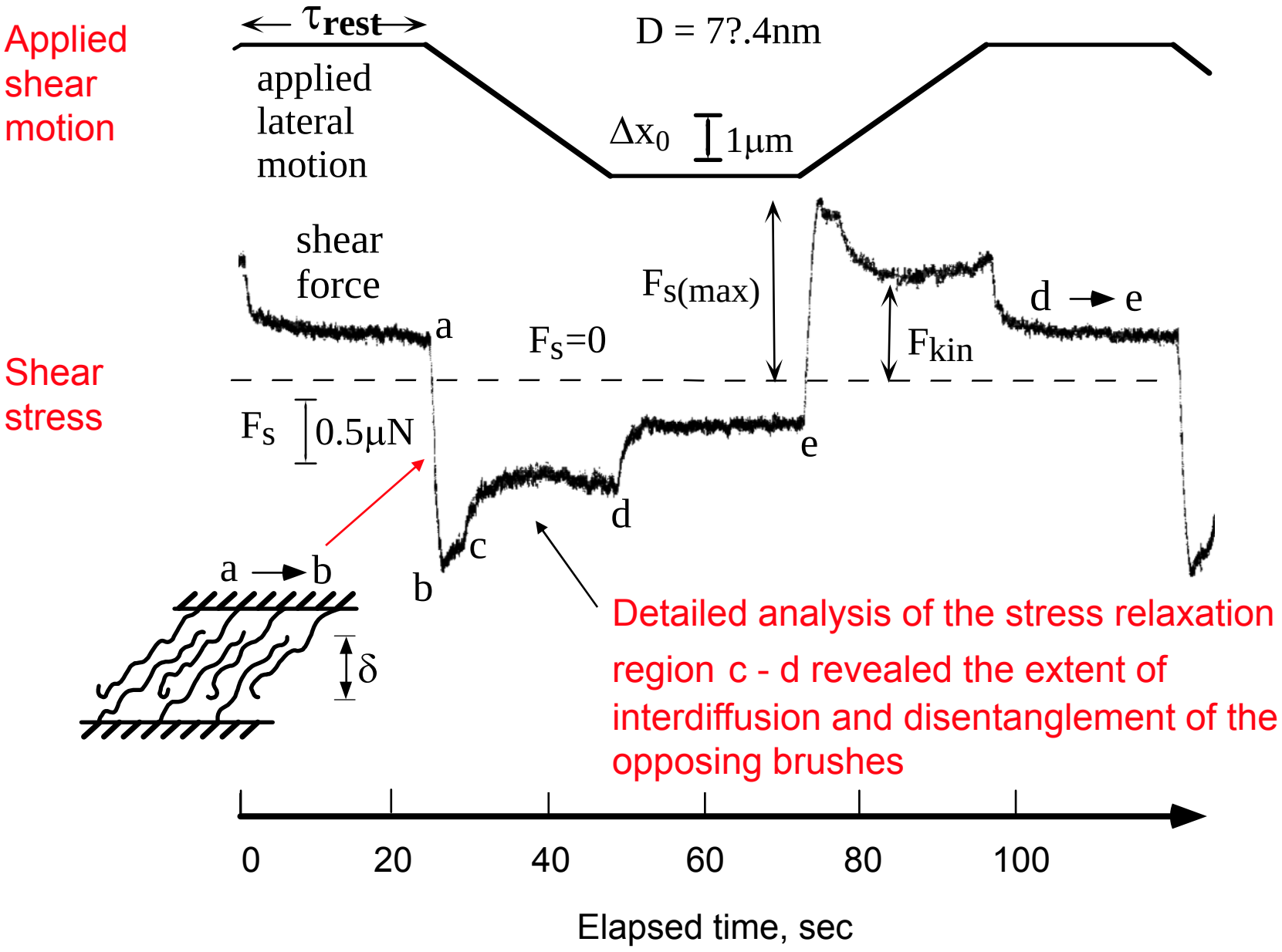
Probing of dynamics in shearing chains using Polystyrene chains: failed due to onset of glassy concentration ($T_g \approx 100^0C$) (e.g. Klein et al., *Nature* 1994).

So use low T_g polymer brushes: poly(ethylene propylene)*, PEP, $-[CH_2-CH_2-CH(CH_3)CH_2]_N-$, terminated with zwitterion (PEP-X),

for which $T_g = -60^0C$.

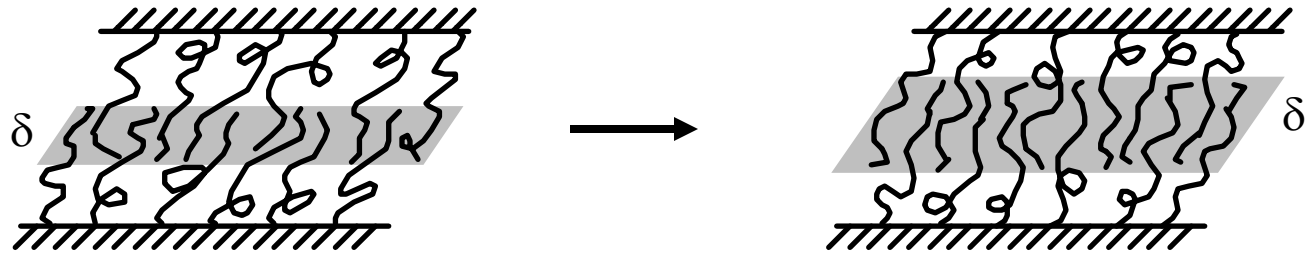


*Rafael Tadmor, Joanna Janik, Lew Fetters, JK (PRL 2003)

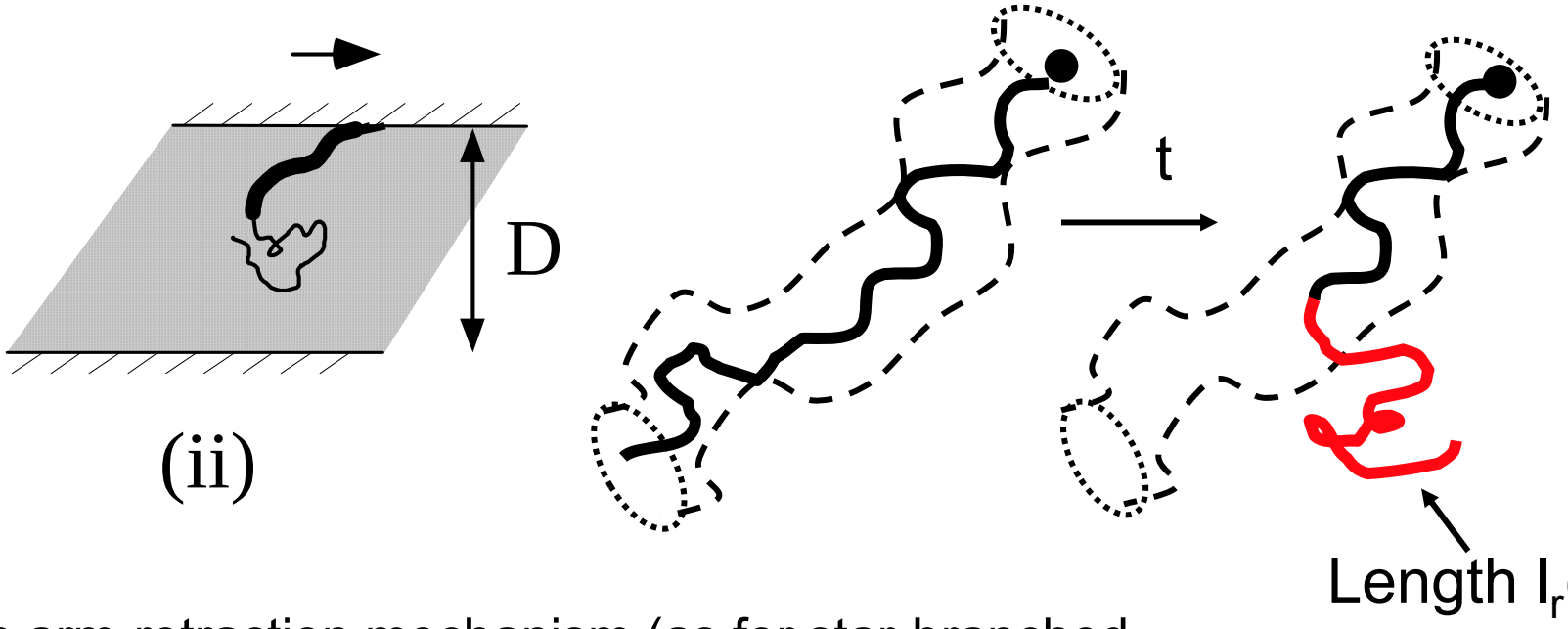


Tadmor et al. PRL 2003

Varying the ‘rest time’ during which interdiffusion occurred enabled a delicate probe of the growth of the interpenetrated region via the shear stress on sliding



Longer rest time



From arm-retraction mechanism (as for star-branched chains)

$$t(l_r) = \tau_1 \exp(\alpha l_r / l_e),$$

where $\alpha \approx 0.6$, l_e is (concentration-dependent) entanglement length, τ_1 varies weakly with l_r.

This gives tension in unrelaxed portion of chain

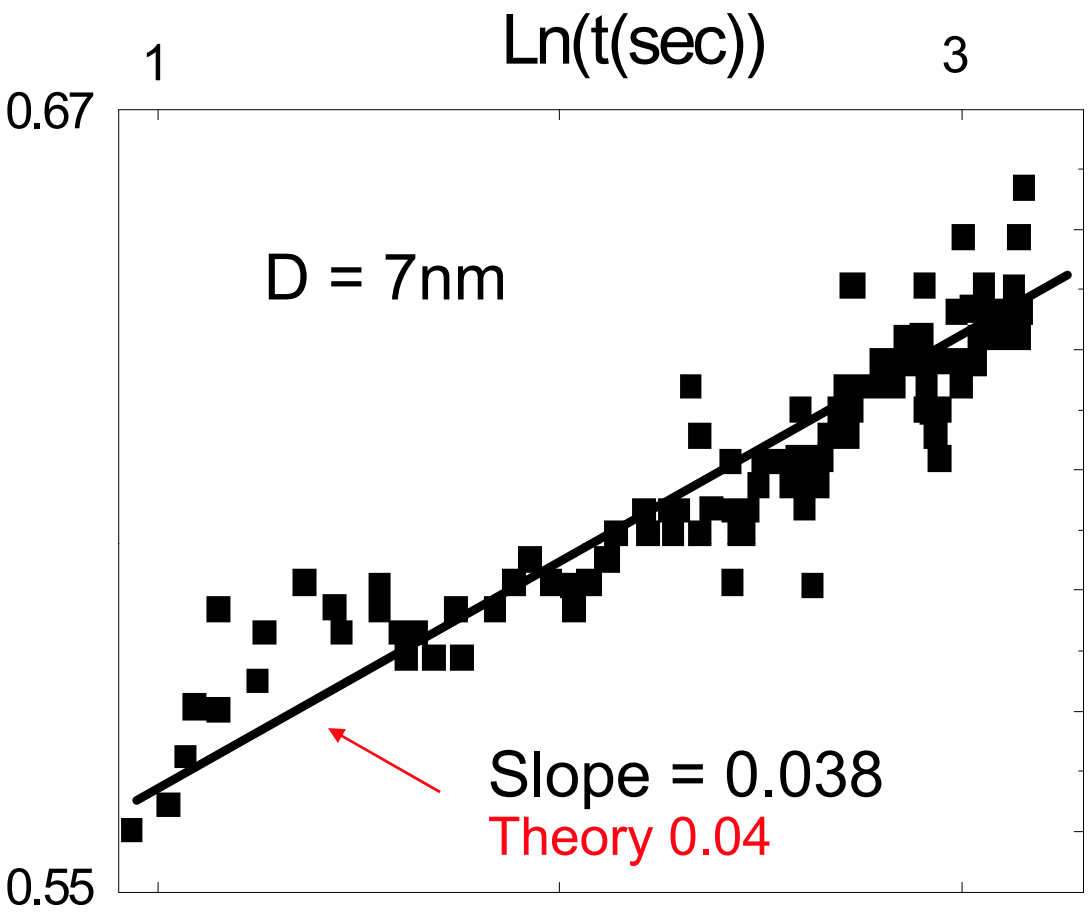
$$f_s(t) \propto [L_0 - l_r(t)],$$

and finally, for overall shear force $F_S(t)$

$$\frac{F_S(0) - F_S(t)}{F_S(0)} \cong \frac{l_r(t)}{L_0} = \frac{l_e}{\alpha L_0} \ln\left(\frac{t}{\tau_1}\right)$$

Analysis using concepts from PGG toolbox - arm retraction - predicted logarithmically slow stress relaxation of sheared, inter-diffused brushes

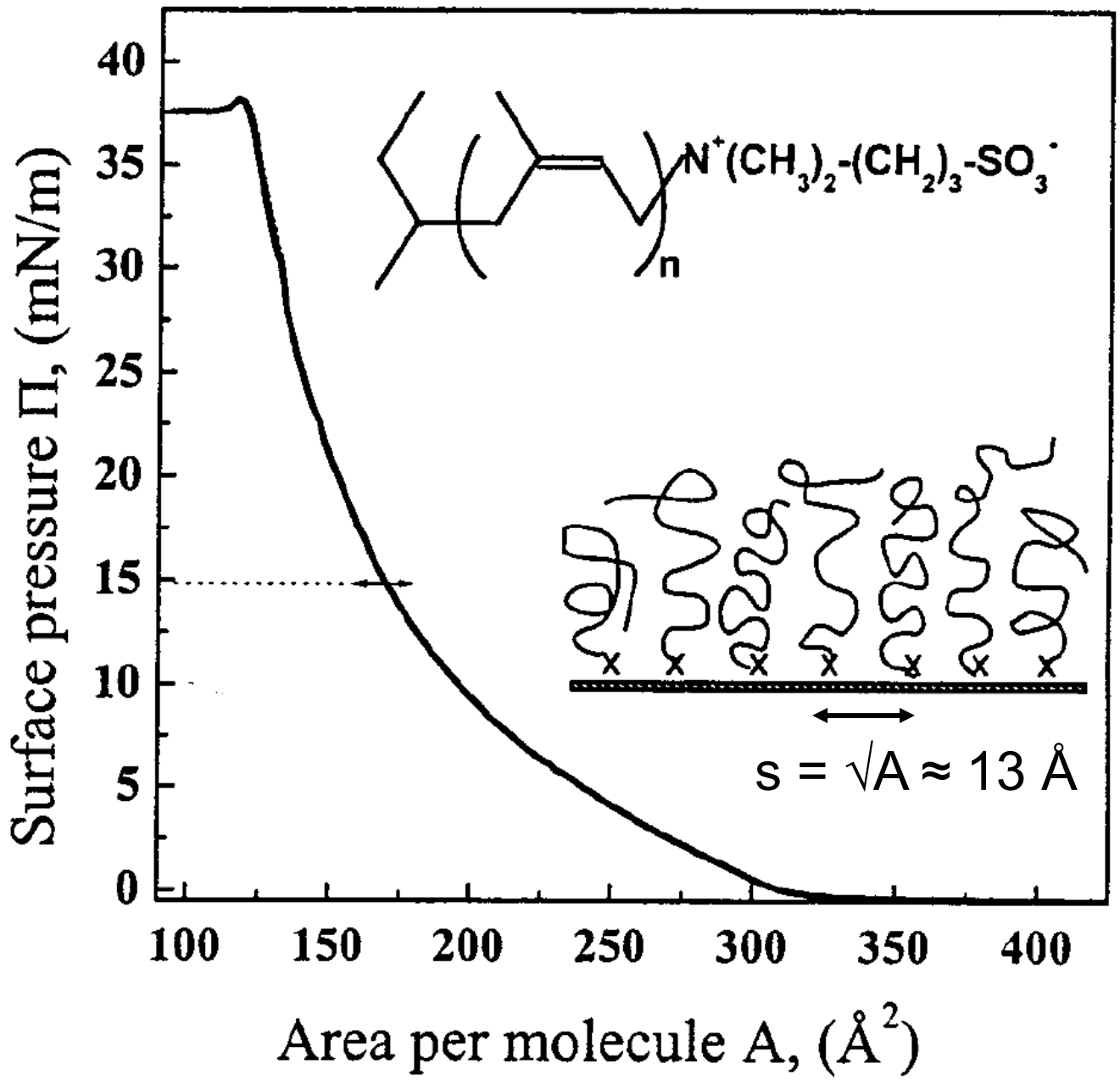
(Note $\frac{l_e}{\alpha L_0} \approx 0.04$ for D = 7nm)



This prediction was quantitatively confirmed for PEP-X brushes

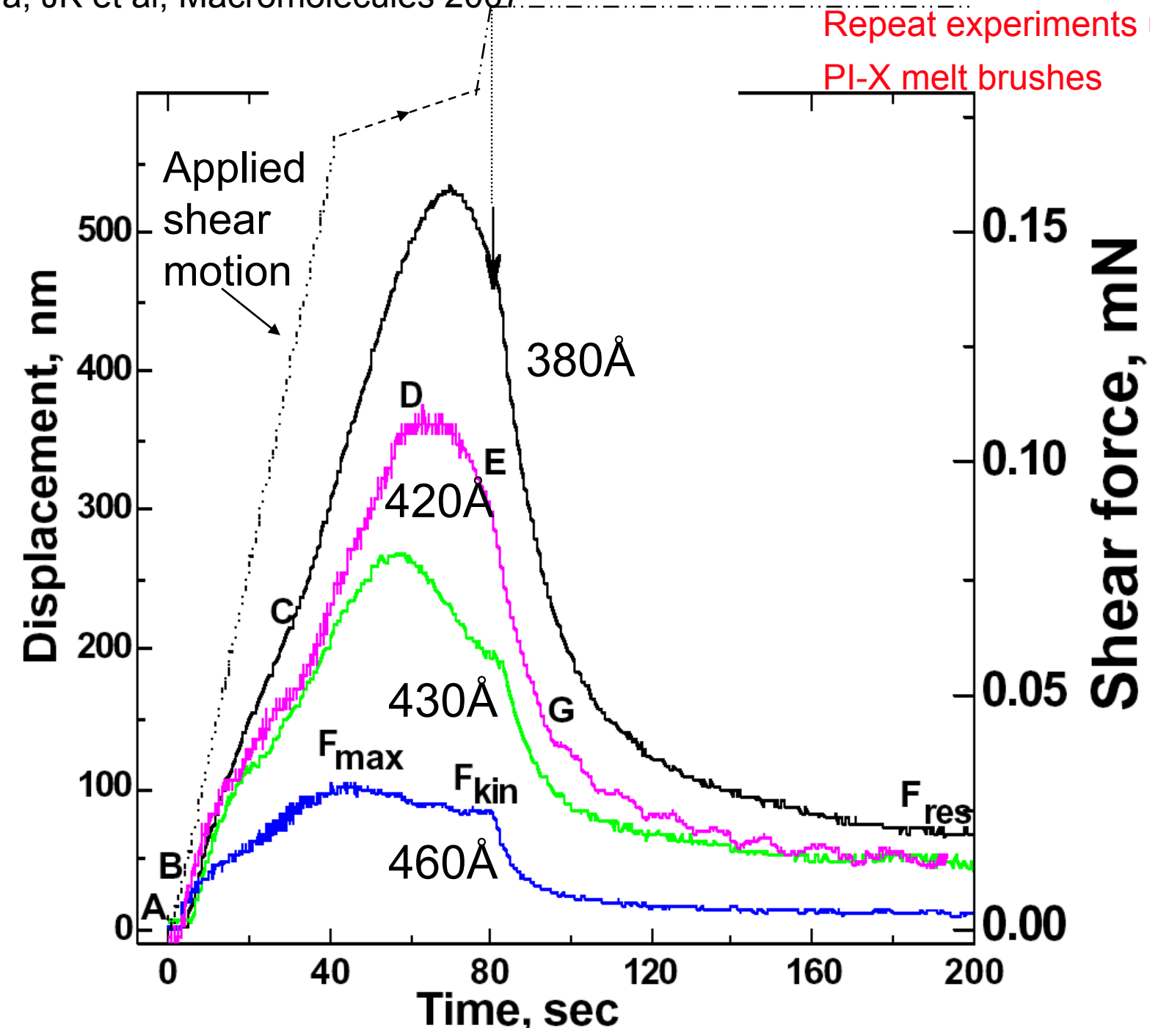
Variation of shear force following cessation of applied lateral motion (predicted slope for PEP-X brushes in toluene (at D = 7nm) ≈ 0.04)

Move to melt-brushes



Tsrakova, JK et al, Macromolecules 2007

Repeat experiments using PI-X melt brushes



A similar analysis applies to the PI-X melt brush relaxation, but with a predicted logarithmic argument an order of magnitude larger than for PEP-X!

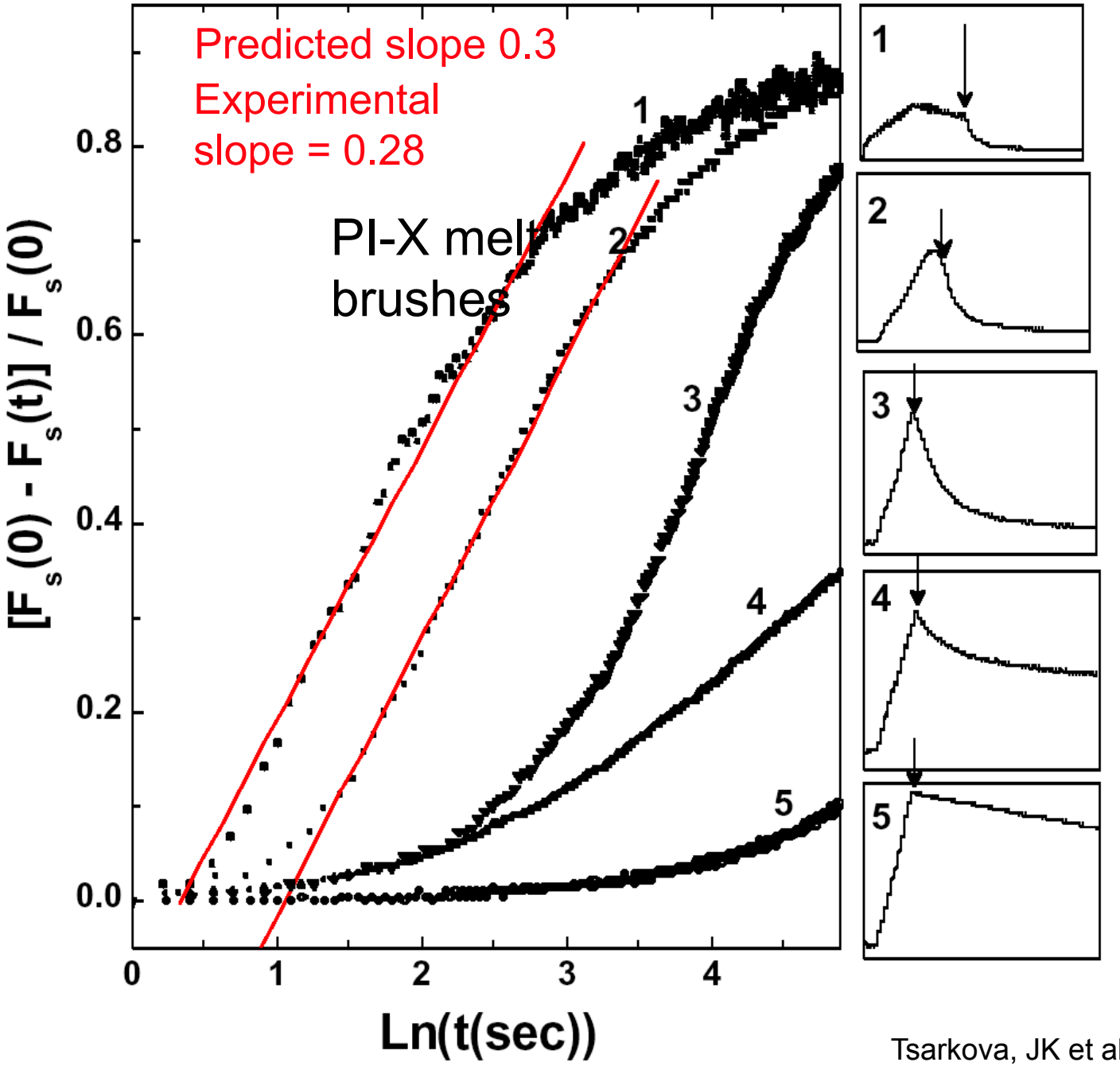
$$\frac{F_S(0)-F_S(t)}{F_S(0)} \cong \frac{l_r(t)}{L_0} = \frac{l_e}{\alpha L_0}\ln\left(\frac{t}{\tau_1}\right)$$

Earlier PEP-X brushes in toluene, predicted slope $\frac{l_e}{\alpha L_0}$ ≈ 0.04
(for ϕ corresponding to D = 7nm)
measured slope = 0.038

Expt. 0.038

For PI-X melt brushes, predicted slope $\frac{l_e}{\alpha L_0}$ ≈ 0.3
(independent of ϕ)

(nearly order of magnitude difference due to larger l_e, smaller L_0



Experiments show close quantitative agreement with new predicted logarithmic argument of stress relaxation, confirming the brush interdiffusion and relaxation picture

Tsarkova, JK et al., *Macromolecules* 2007

So using simple tools of reptation under constraint and arm-retraction, can account for new forms of interdiffusion, disentanglement and relaxation - for surface-attached polymers - not envisaged at time these tools were formulated.

Open questions include interdiffusion of charged polymers - crucial for understanding biological lubrication, and dominated by effects very different to neutral chains such as counterions and salt concentration, as well as hydration effects.

Interdiffusion in nanometrically confined systems - competition of different length scales

Summary

The reptation model and the 1980 PG paper set the field for molecular understanding of interdiffusion processes (both χ and mobility-dominated), and introduced the tools to treat more complex cases

Extension to interdiffusion of entangled chains - chemically identical but of different lengths (with Brochard) - reconciled with experiments showing fast-mode interdiffusion

With auxilliary tools (e.g. arm-retraction) can understand interdiffusion/relaxation processes in new and unanticipated configurations