Dynamics of Reversible Networks

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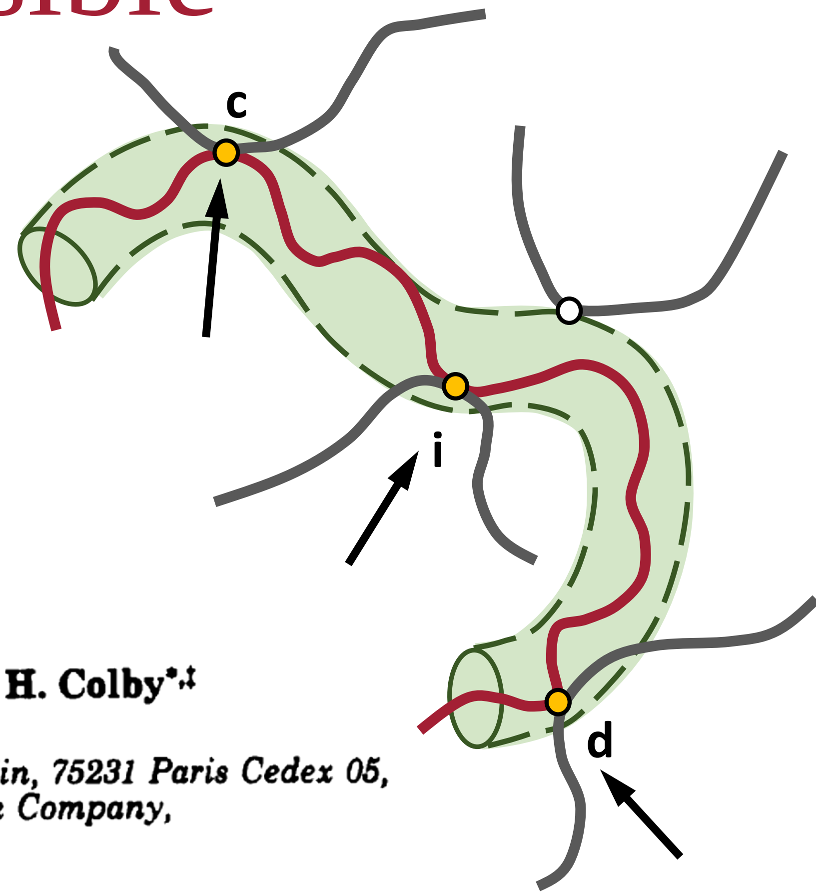

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Dynamics of Reversible Networks

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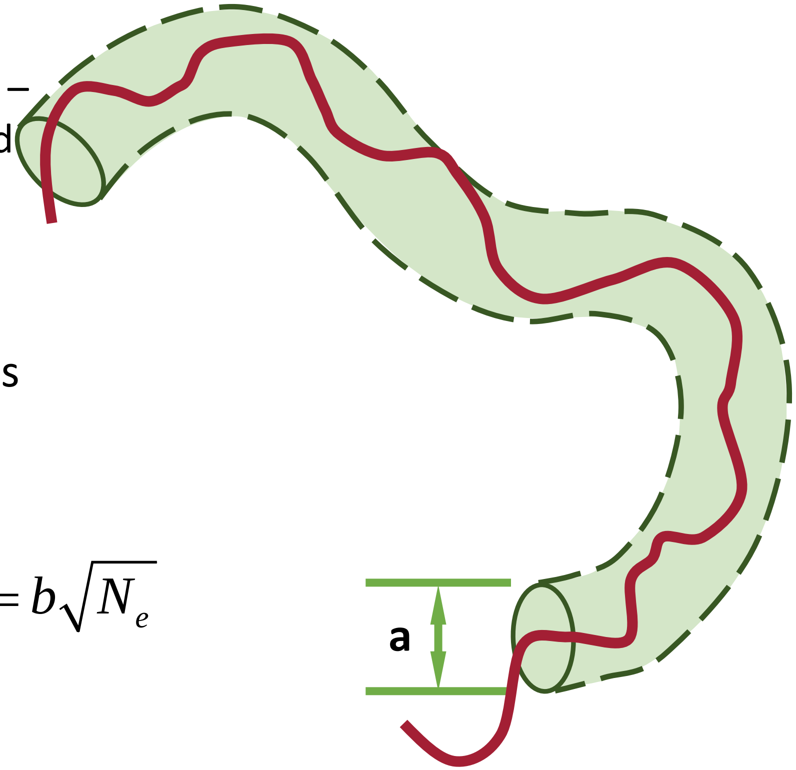
Recap of Simple Reptation Theory

Entangled polymer melt
Chains are all over the place in each others pervaded volume
Strands cannot tell which chain they belong to – excluded volume interactions are screened and ideal chain statistics are obeyed



Focus on one chain

Toplogical constraints due to other chains can be modeled as a confining tube.
Confining tube diameter = **a**

Strand with fluctuations of the order of **a** is an **entanglement strand**

$$a = b\sqrt{N_e}$$

Tube length $$L = \frac{N}{N_e} a$$

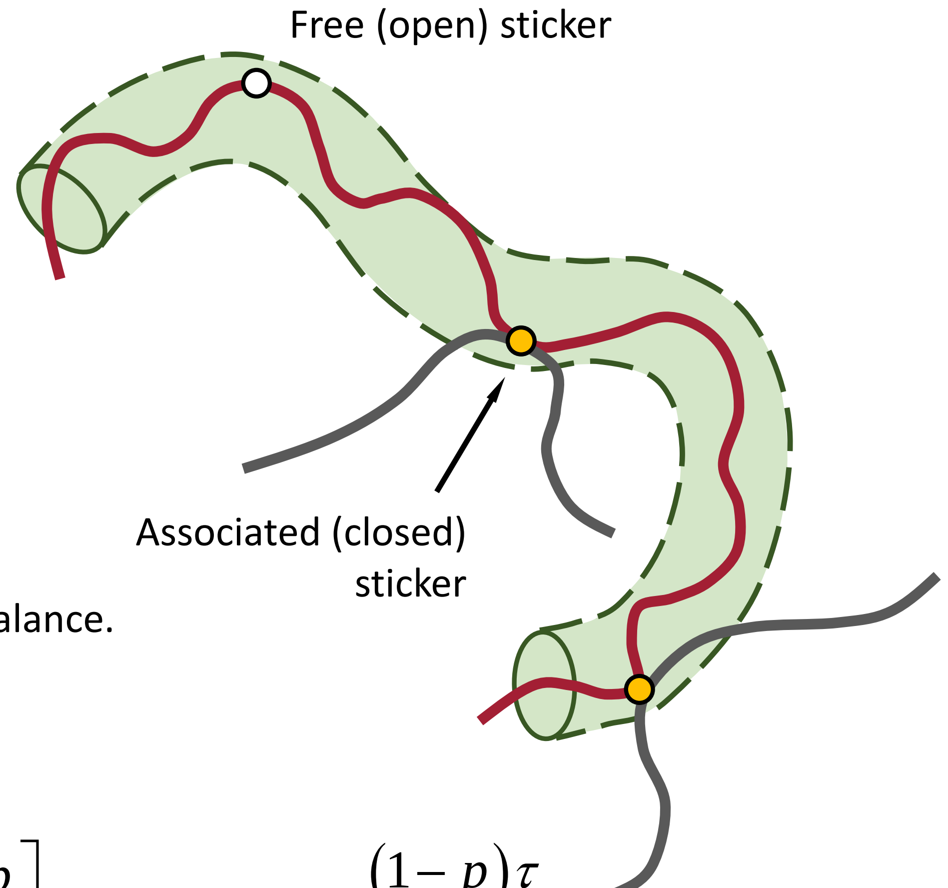
Chain diffuses along tube by Rouse motion $$D_c = \frac{kT}{N\zeta}$$

Reptation time $$T_d^0 = \frac{L^2}{D_c}$$

Sticky reptation

Each polymer chain has **N monomers**.

There are also **S stickers per chain**.
Stickers – potential sites for a reversible cross-link with other stickers



Microscopic parameters of a sticker

1. Fraction of stickers that are closed p
2. Lifetime of the closed state τ

Assume **thermal equilibrium**.
Open and closed stickers must obey detailed balance.

Fraction of open stickers = $(1-p)$

Lifetime of open stickers = τ_1

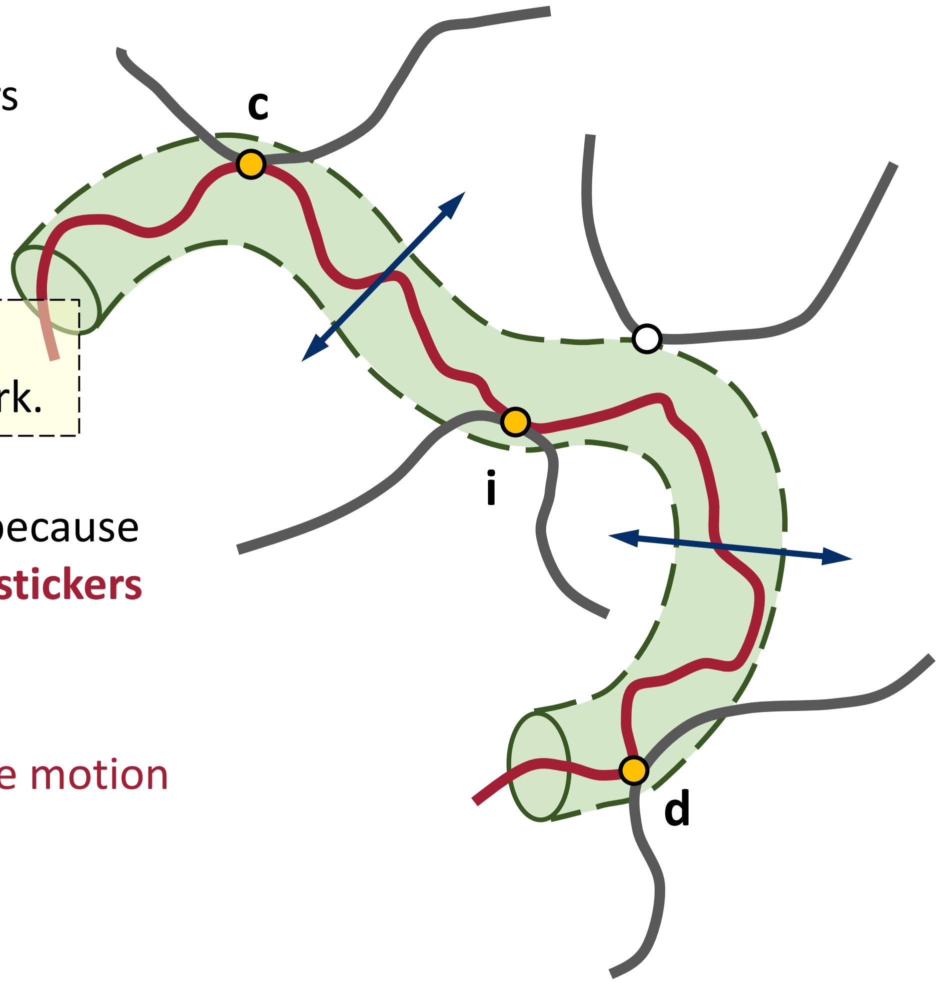
Rate of change of concentration of closed stickers $\frac{d}{dt}(cSp) = cS\left[\frac{1-p}{\tau_1} - \frac{p}{\tau}\right] = 0 \quad \Rightarrow \quad \tau_1 = \frac{(1-p)\tau}{p}$

Short time-scales $t < \tau$

Average length of strand between stickers

$$N_s = \frac{N}{S+1}$$

For times shorter than τ
the gel behaves like a permanent network.



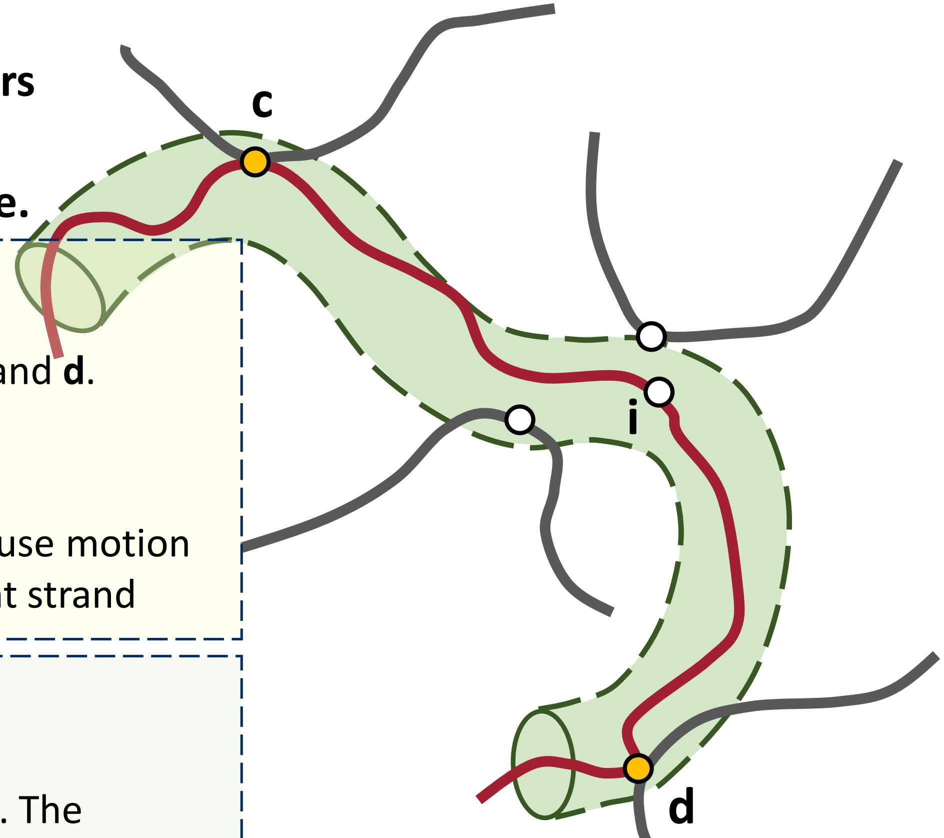
The chain cannot reptate along its tube because **stored loops cannot traverse the closed stickers c, i** and **d**

Segments **ci** and **id** simply undergo Rouse motion between fixed ends.

Sticker i opens $\quad t > \tau$

The **whole strand cd** with **$2N_s$ monomers** can now undergo Rouse motion.

Sticker i can now diffuse along the tube.



For $t < \tau_R(2N_s)$

Sticker **i** is "unaware" of the cross-links at **c** and **d**.

Curvilinear displacement along tube

$$l^2(t) = b^2 N_e \left(\frac{t}{\tau_e}\right)^{1/2}$$

Subdiffusive Rouse motion of entanglement strand

For $t > \tau_R(2N_s)$

Sticker **i** becomes "aware" of the constraints. The displacement freezes at that point.

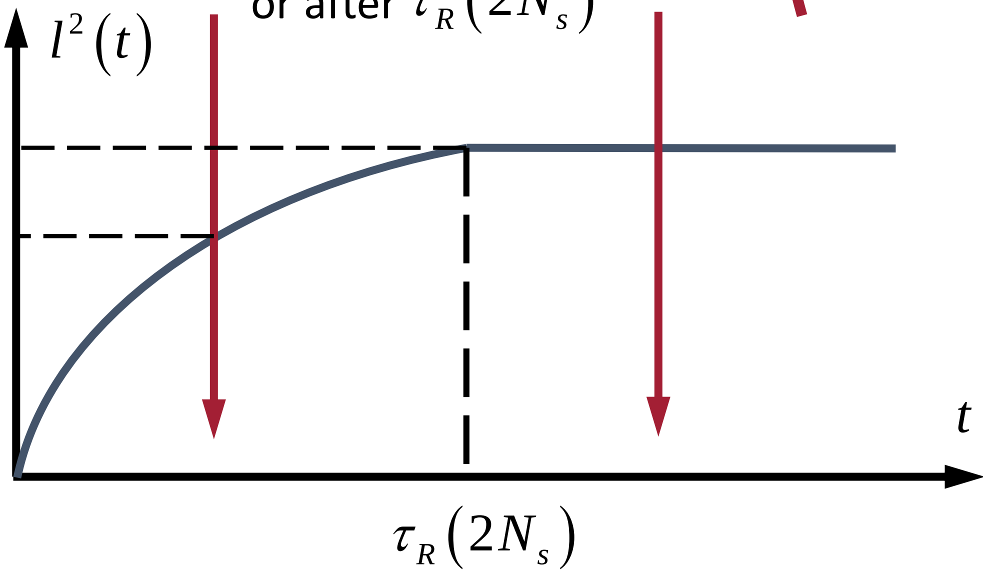
$$l^2(t) = l^2\left[\tau_R(2N_s)\right] = b^2(2N_s)$$

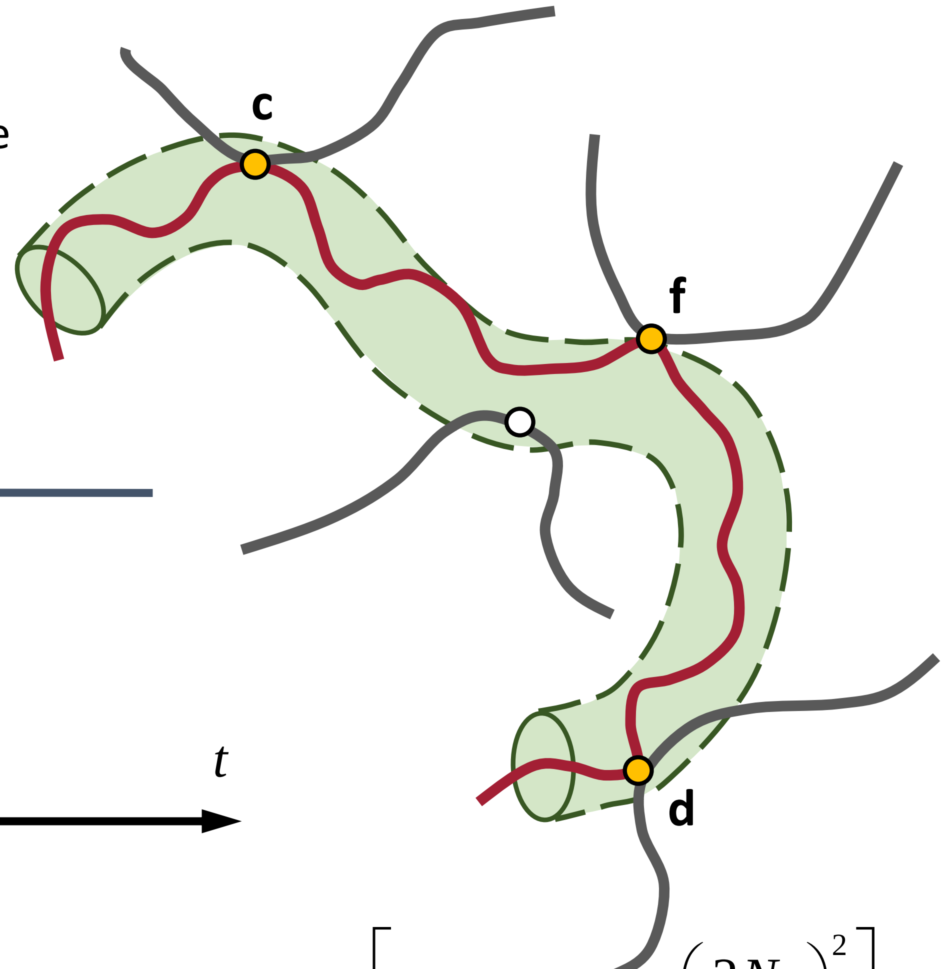
$$\left[\tau_R(2N_s) = \tau_e\left(\frac{2N_s}{N_e}\right)^2\right]$$

Sticker f forms $t \sim \tau_1$

Formation of new crosslink **f** freezes the displacement until that point.

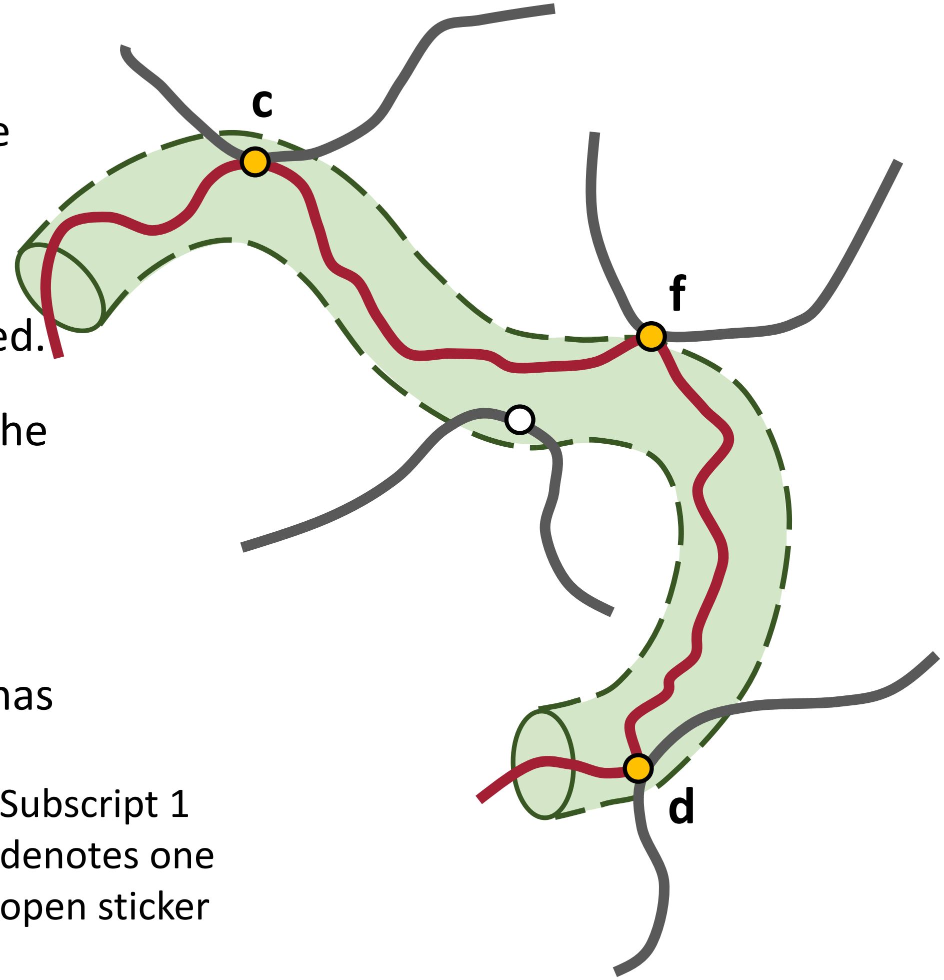
The new cross-link can form either before or after $\tau_R\left(2N_s\right)$





$$\left[\tau_R\left(2N_s\right) = \tau_e\left(\frac{2N_s}{N_e}\right)^2\right]$$

Sticker f forms $t \sim \tau_1$



Formation of new crosslink **f** freezes the displacement until that point.

Strands **cf** and **fd** now relax over a time $\tau_R(N_s)$ provided **c** and **d** remain closed.

After relaxation, the center of mass of the strand **cd** has moved by

$$\Delta_{cd} = \frac{l(\tau_1)}{2}$$

The center of mass of the whole chain has been displaced by

$$\Delta_1 = \frac{l(\tau_1)}{2}\frac{2}{S+1} = \frac{l(\tau_1)}{S+1}$$

Subscript 1 denotes one open sticker

Thus the chain has undergone an effective displacement along the tube although it cannot reptate as a whole in the normal fashion – this is **sticky reptation.**

The General Case – The k-step

A **k-strand** "dies" when one of its k open stickers close.

$$\tau_k = \frac{\tau_1}{k}$$

Longer strands live for shorter durations but have larger Rouse times.

Mean square curvilinear displacement is therefore

$$l_k^2 = \begin{cases} b^2 (k+1) N_s & \tau_k > \tau_R \\ b^2 N_e \left(\tau_k / \tau_e \right)^{1/2} & \tau_k < \tau_R \end{cases}$$

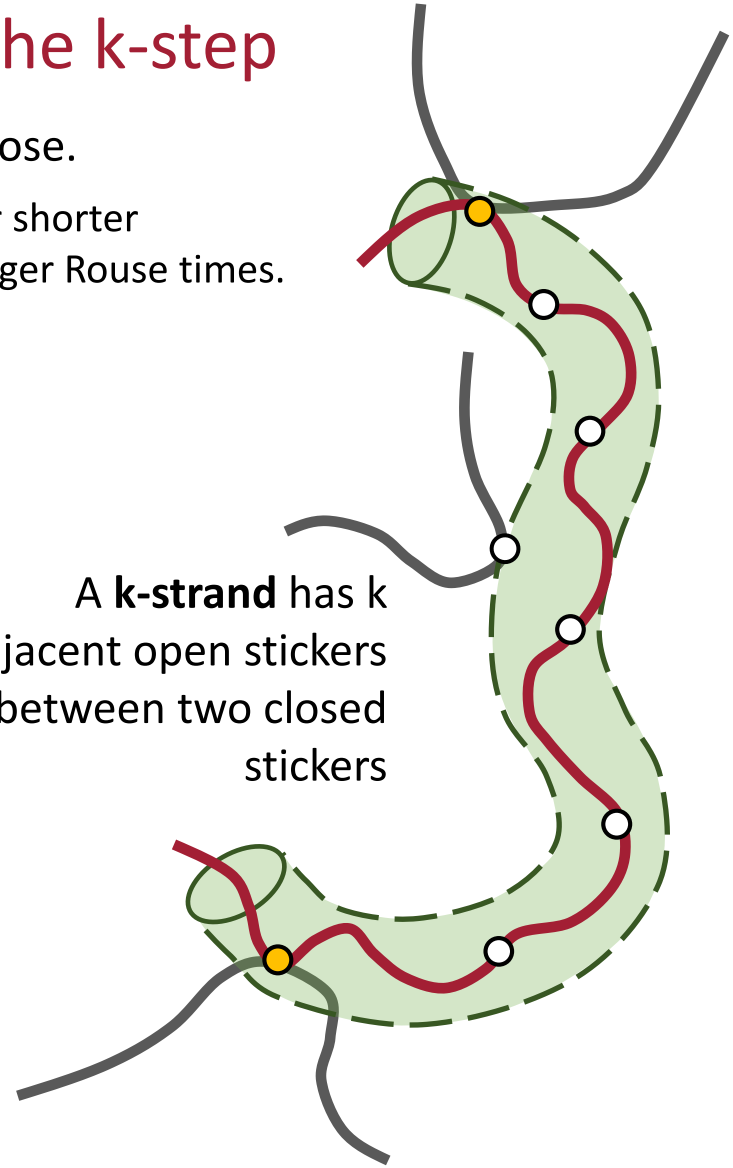
At what k does a strand live long enough to just relax fully?

$$\frac{\tau_1}{k_{\max}} = \tau_R \left[(k_{\max} + 1) N_s \right]$$

$\tau_k > \tau_R$ is equivalent to $k < k_{\max}$

Longer strands than k(max) die partly relaxed.
Shorter strands than k(max) die fully relaxed.

A **k-strand** has k adjacent open stickers between two closed stickers



The General Case – The k-step

Finding the effective displacement of the whole chain

$$\Delta_k = \frac{1}{2} l_k \begin{cases} \dfrac{k+1}{S+1} & \tau_k > \tau_R \text{ or } k < k_{\max} \\ \dfrac{k_{\max}+1}{S+1} & \tau_k < \tau_R \text{ or } k > k_{\max} \end{cases}$$

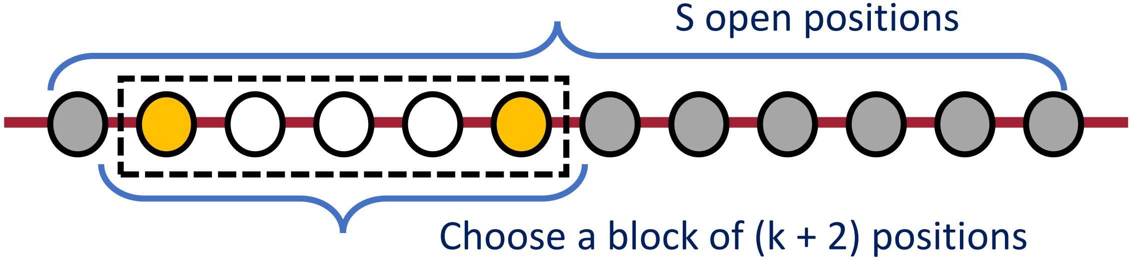
All stickers participate.

Only k(max) stickers participate.

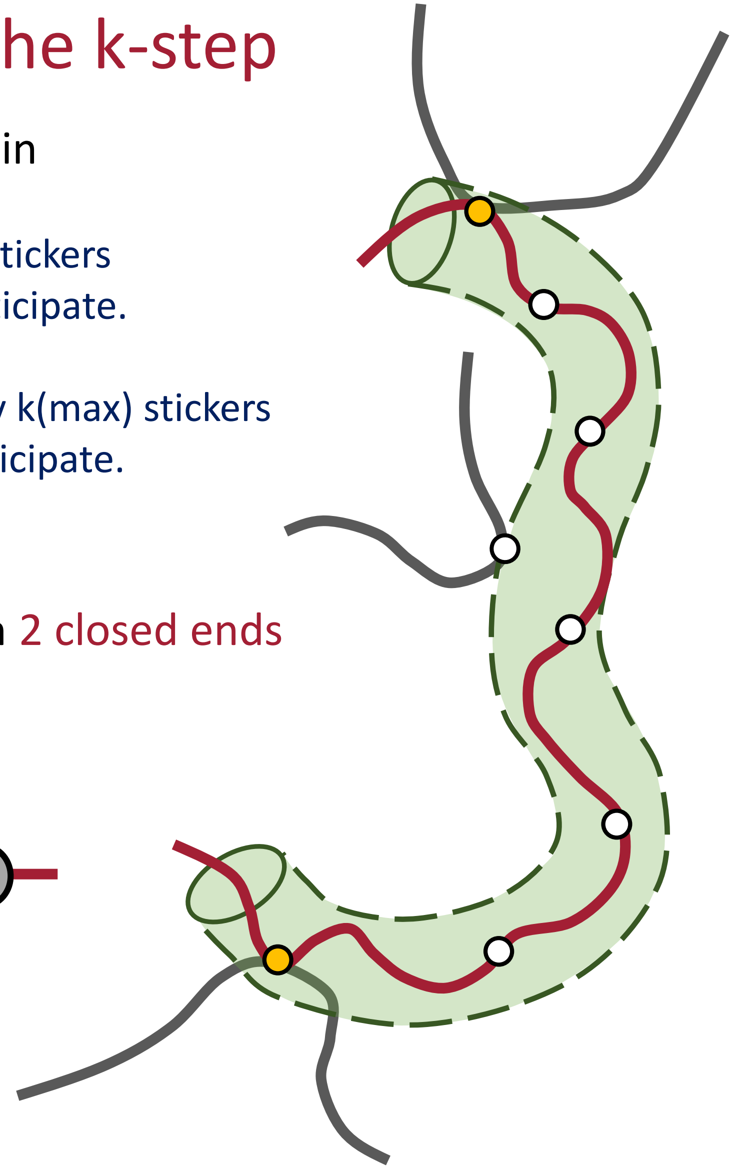
½ because ends are fixed.

Probability of finding a series of k open stickers with 2 closed ends

$$p_k = (S - k - 1)\, p^2 (1 - p)^k$$



Frequency of a k-step $\nu_k = p_k / \tau_k$



Sum over all possible k's

Total curvilinear displacement of the chain over a time T

$$\Delta^2 = \sum_{k=1}^{S-2} \nu_k \Delta_k^2 T + E + F$$

End strands　　Fully free chains

End strands

Suppose the **x**-th sticker closed from the end.
This creates *one fixed side* and *one free side*.

Instead of the $\frac{1}{2} l_k$ before, we would have:

$$\frac{l_k x + \frac{1}{2} l_k (k+1-x)}{k+1} = \frac{x+k+1}{2(k+1)} l_k$$

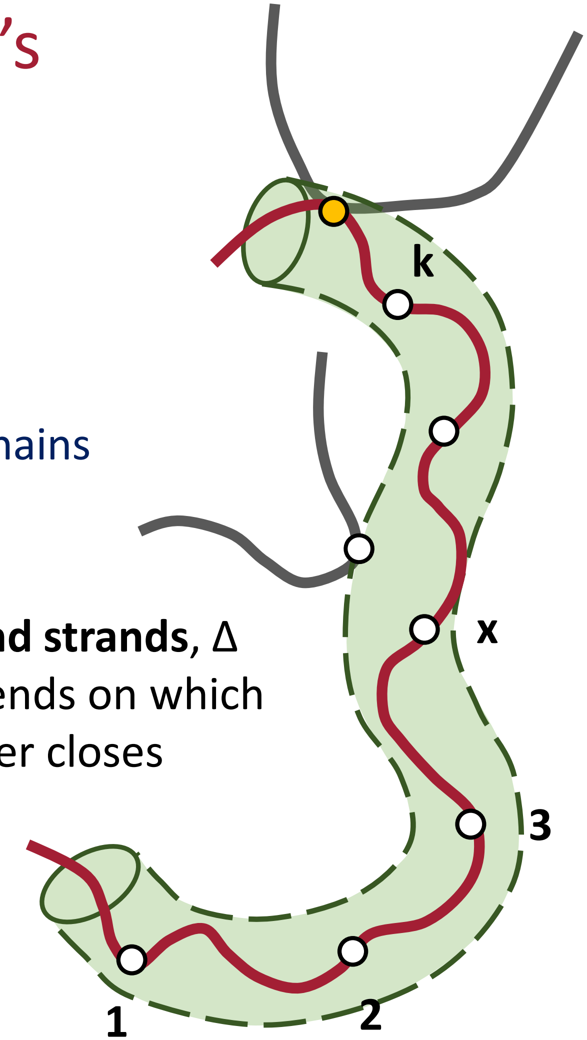
Averaging

$$\frac{1}{k} \sum_{x=1}^{k} \frac{x+k+1}{2(k+1)} l_k = \frac{3}{4} l_k$$

All 1 ≤ x ≤ k are equally probable

For **fully free chains**, we simply have $1 l_k$

In **end strands**, Δ depends on which sticker closes



Sum over all possible k's

Total curvilinear displacement of the chain over a time T

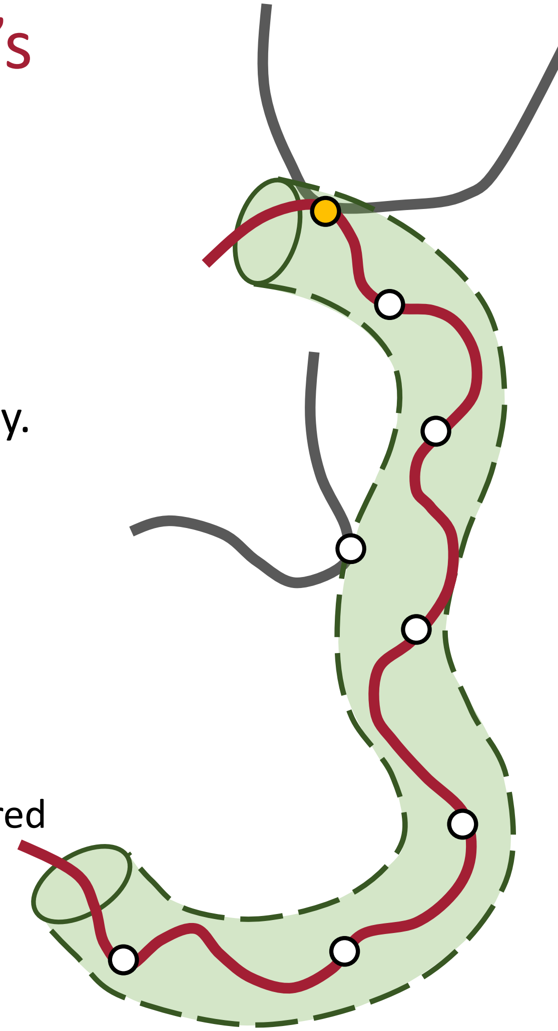
$$\Delta^2 = \sum_{k=1}^{S-2} \nu_k \Delta_k^2 T + \sum_{k=1}^{S-1} \nu_k^{\mathrm{end}} \left(\Delta_k^{\mathrm{end}}\right)^2 T + \nu_S \Delta_S^2 T$$

Further computations are similar to simple reptation theory.

Compute curvilinear and 3D self diffusion coefficients:

$$D_c = \frac{\Delta^2}{T} \qquad D_{\mathrm{self}} = \frac{R^2}{T_d} \qquad R^2 = Nb^2$$

$$T_d = \frac{1}{D_c}\underbrace{\left(a\frac{N}{N_e}\right)^2}_{\text{Tube length squared}}$$

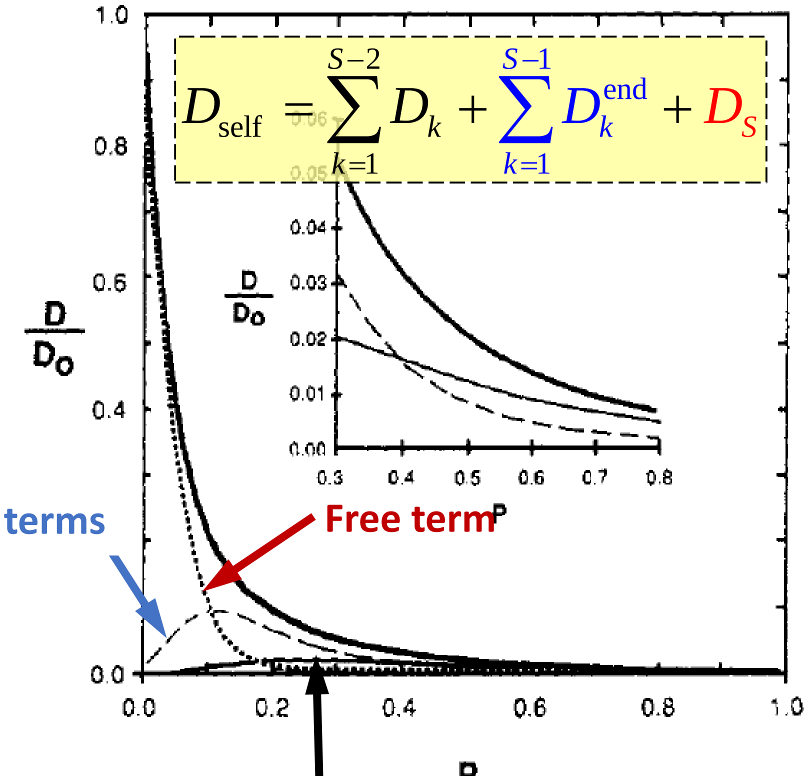


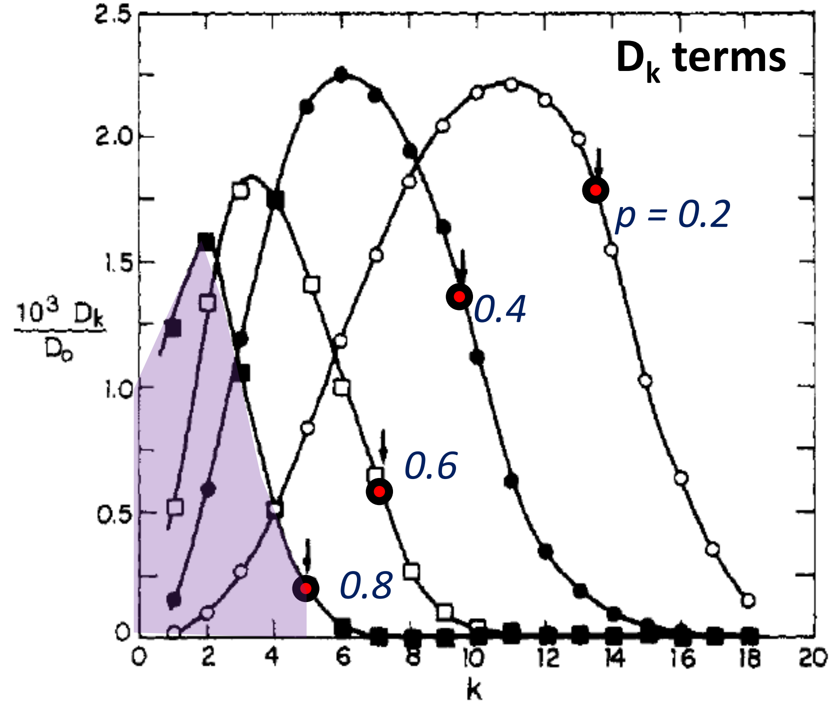
Three contributions to the self diffusion coefficient

$$D_{\mathrm{self}} = \sum_{k=1}^{S-2} D_k + \sum_{k=1}^{S-1} D_k^{\mathrm{end}} + D_S$$

Relative contributions of the three terms

$$D_{\text{self}} = \sum_{k=1}^{S-2} D_k + \sum_{k=1}^{S-1} D_k^{\text{end}} + D_S$$





For large p, **k < k(max)** terms dominate in the sum

$$D_{\text{self}} \approx \frac{a^2}{2\tau S^2}\left(1 - \frac{9}{p} + \frac{12}{p^2}\right)$$

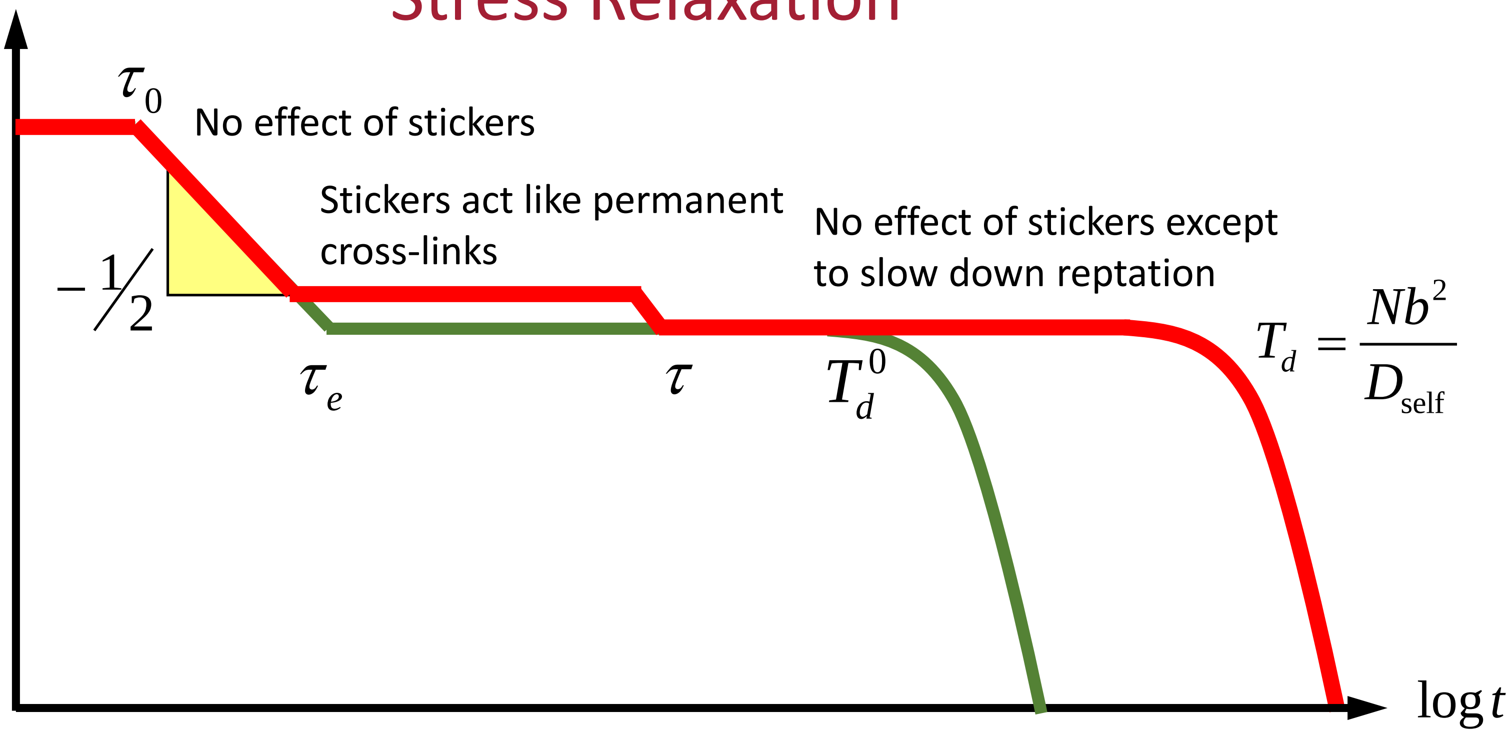
D_k terms dominate when p is large.

D_k terms dominate when N and S are large.

What happens if p = 1?

Stress Relaxation

$$G(t) = \frac{\sigma(t)}{\gamma}$$



$$G_1 = cRT\left(\frac{1}{N_e} + \frac{p}{N_s}\right)$$

Entanglements   Stickers

$$G_2 = cRT\left(\frac{1}{N_e}\right)$$

Only entanglements

$$T_d = \left(\frac{N}{N_e}\right)\frac{2S^2\tau}{1 - 9/p + 12/p^2}$$

To correct for **tube length fluctuations** and **constraint release**

$$T_d = \left(\frac{N}{N_e}\right)^{1.5}\frac{2S^2\tau}{1 - 9/p + 12/p^2}$$

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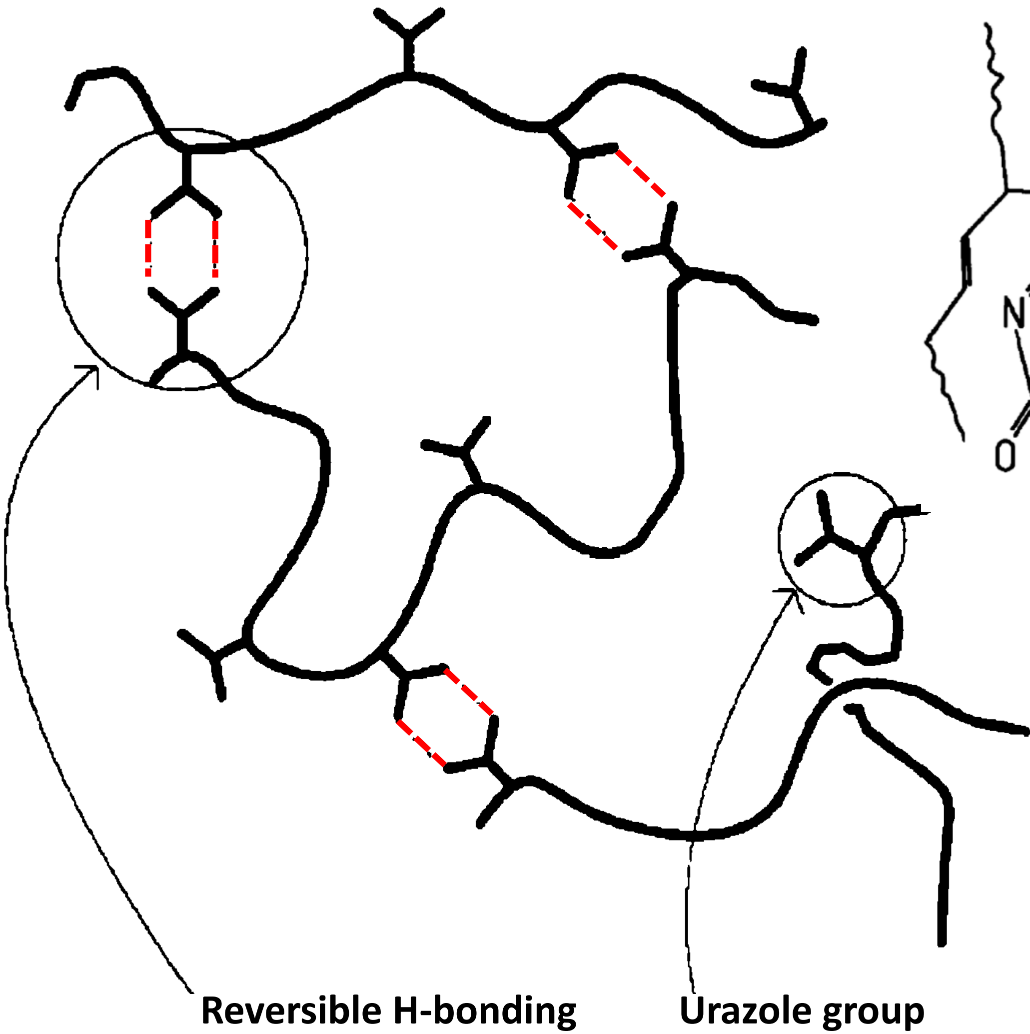
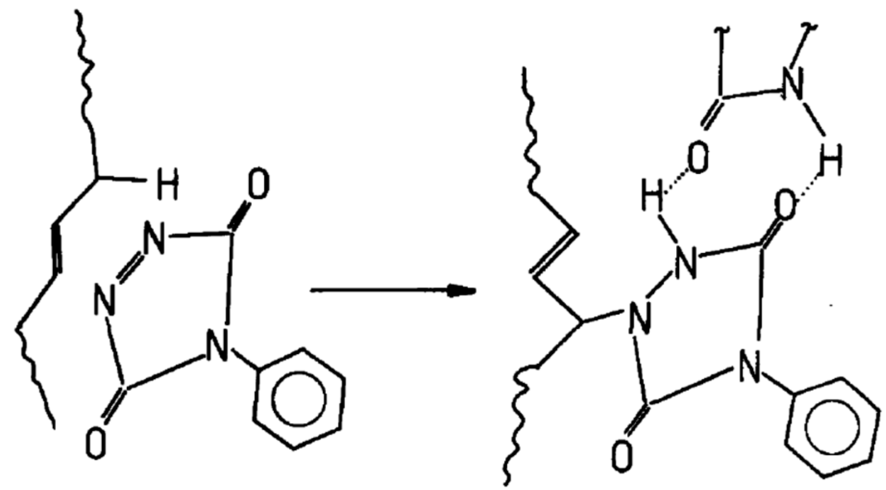
Urazole-modified polybutadiene





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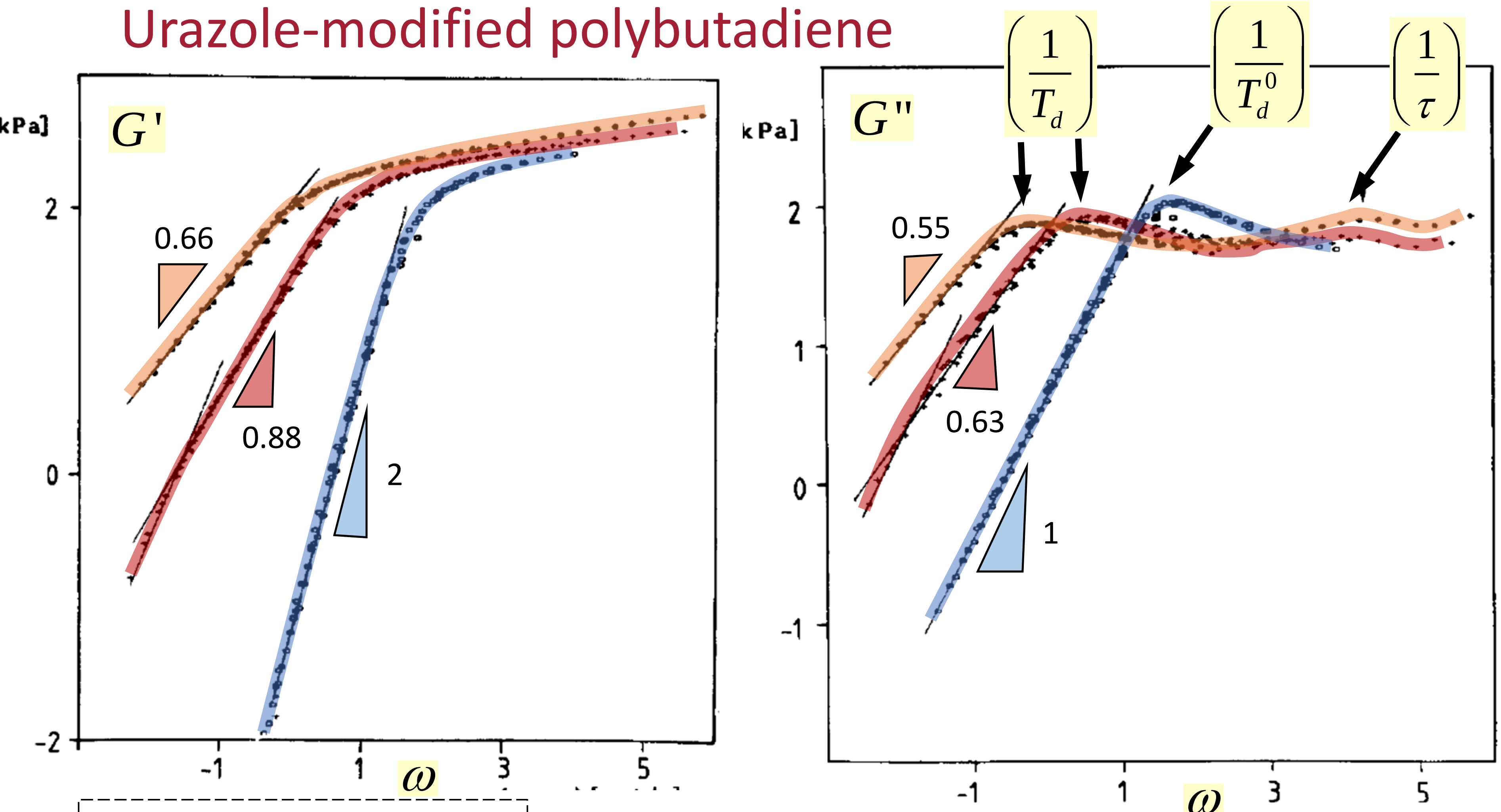
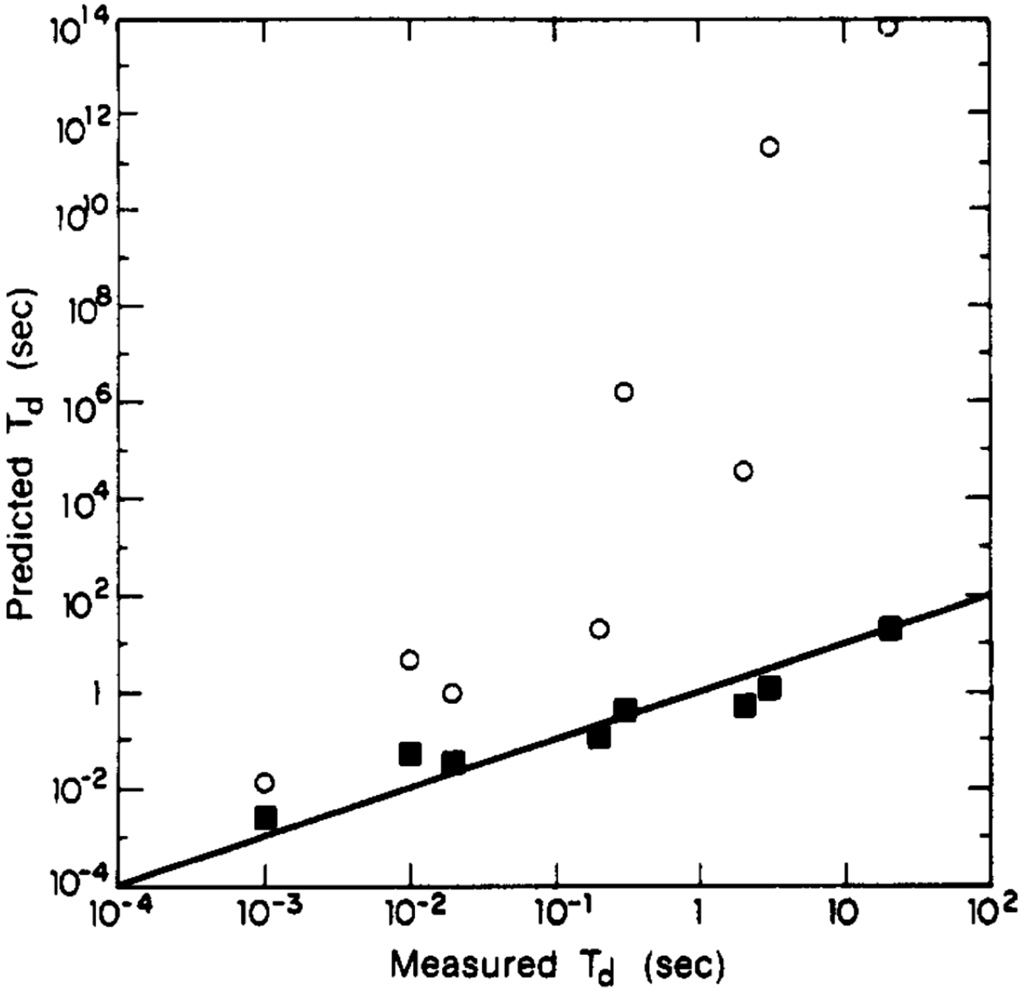
Urazole-modified polybutadiene



Unmodified	PB50-0
1% modified	PB50-1
2% modified	PB50-2

$$M_n = 48500 \qquad \frac{M_w}{M_n} = 1.06$$

Urazole-modified polybutadiene



Gonzalez model

All stickers must open for reptation to occur

$$T_d = \tau_e \left(\frac{N}{N_e} \right)^{3.5} \exp(Sp)$$

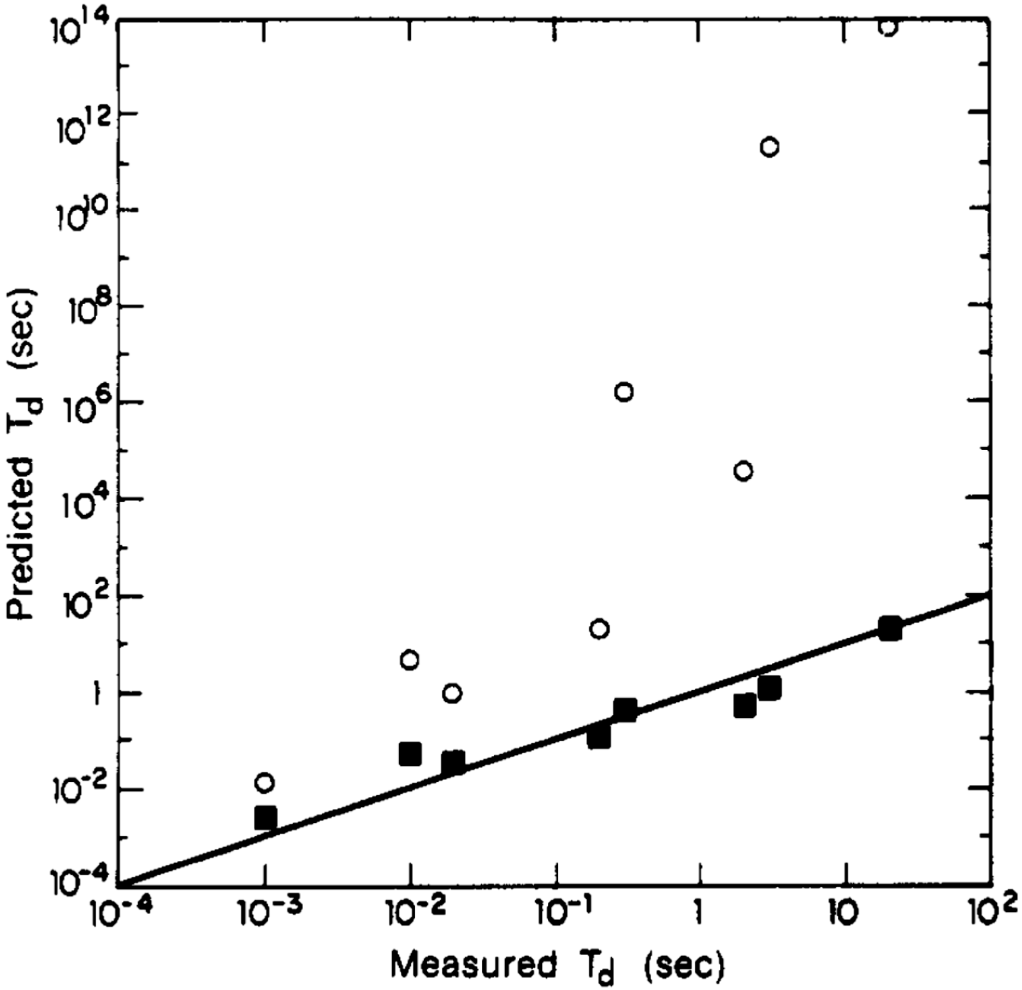
Sticky reptation

Parts of the chain can relax if a few consecutive stickers open

$$T_d = \left(\frac{N}{N_e} \right)^{1.5} \frac{2S^2\tau}{1 - 9/p + 12/p^2}$$

$$\approx \tau \left(\frac{N}{N_s} \right)^{3.5} \left(\frac{N_s}{N_e} \right)^{1.5} \frac{15p - 11}{8}$$

Urazole-modified polybutadiene



For Sp << 1 both models agree

$$T_d^{\mathrm{Gonzalez}} = \tau_e \left(\frac{N}{N_e}\right)^{3.5} \exp(Sp)$$

$$T_d^{\mathrm{LRC}} = \frac{Nb^2}{D_S} = \tau_e \left(\frac{N}{N_e}\right)^{3.5} \frac{1}{(1-p)^S}$$

as both expressions Taylor expand to

$$\tau_e \left(\frac{N}{N_e}\right)^{3.5} \left(1 + Sp + O(Sp)^2\right)$$