Dynamics of Reversible Networks

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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

Topological 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 $$T_d^0 = \frac{L^2}{D_c}$$
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 \( \tau \)

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

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

Lifetime of open stickers = \( \tau_1 \)

Rate of change of concentration of closed stickers

\[
\frac{d}{dt} (cSp) = cS \left[ \frac{1 - p}{\tau_1} - \frac{p}{\tau} \right] = 0 \Rightarrow \tau_1 = \frac{(1 - p)\tau}{p}
\]
Short time-scales \( t < \tau \)

Average length of strand between stickers

\[
N_s = \frac{N}{S + 1}
\]

For times shorter than \( \tau \) 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 \( t > \tau \)

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.

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

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

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

\( \ell^2(t) \)

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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 \( \tau_R \left( N_s \right) \) 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

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

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

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

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

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

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

½ because ends are fixed.

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

\[
p_k = (S - k - 1) p^2 (1 - p)^k
\]

Choose a block of (k + 2) positions

**Frequency** of a k-step

\[
\nu_k = \frac{p_k}{\tau_k}
\]
**Sum over all possible k’s**

**Total curvilinear displacement of the chain** over a time $T$

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

**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:

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

Averaging

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

All $1 \leq x \leq k$ are equally probable.

For **fully free chains**, we simply have $1 l_k$.
Sum over all possible k’s

**Total curvilinear displacement of the chain** over a time $T$

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

Further computations are similar to simple reptation theory.

Compute curvilinear and 3D self diffusion coefficients:

$$D_c = \frac{\Delta^2}{T} \quad D^\text{self} = \frac{R^2}{T_d}$$

$$R^2 = Nb^2$$

$$T_d = \frac{1}{D_c} \left( \frac{a}{N/N_e} \right)^2$$

**Three contributions** to the self diffusion coefficient

$$D^\text{self} = \sum_{k=1}^{S-2} D_k + \sum_{k=1}^{S-1} D^\text{end}_k + D_S$$
Relative contributions of the three terms

For large $p$, $k < k(\text{max})$ terms dominate in the sum

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

What happens if $p = 1$?

- $D_k$ terms dominate when $p$ is large.
- $D_k$ terms dominate when $N$ and $S$ are large.
**Stress Relaxation**

\[ G(t) = \frac{\sigma(t)}{\gamma} \]

\[ G(t) = cRT \left( \frac{1}{N_e} + \frac{p}{N_s} \right) \]

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

\[ T_d = \frac{Nb^2}{D_{self}} \]

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

- No effect of stickers
- Stickers act like permanent cross-links
- No effect of stickers except to slow down reptation

\[ \tau_0 \]

\[ \frac{1}{2} \]

\[ \tau_e \]

\[ \tau \]

\[ T_d^0 \]

\[ \log G(t) \]

\[ \log t \]

\[ \log (\sigma(t)) \]

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Urazole-modified polybutadiene
Urazole-modified polybutadiene

\[ G' \]

\[ G'' \]

\[ \frac{1}{T_d} \]

\[ \frac{1}{T_d^0} \]

\[ \frac{1}{\tau} \]

\[ M_n = 48500 \]

\[ \frac{M_w}{M_n} = 1.06 \]

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

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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

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

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

For $Sp << 1$ both models agree

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

$$T^L_{d} = \frac{Nb^2}{D_s} = \tau_e \left( \frac{N}{N_e} \right)^{3.5} \frac{1}{(1 - p)^S}$$

as both expressions Taylor expand to

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