Polymers Dynamics by Dielectric Spectroscopy
What’s a polymer bulk?

A condensed matter system where the structural units are macromolecules.
Flory's prediction in the 50's:

'RANDOM COIL'

\[ \langle R^2 \rangle \propto N \text{ monomers} \]

\[ \langle R^2 \rangle \propto n \text{ steps} \]

P. J. Flory
Nobel Prize 1974
MACROMOLECULAR STRUCTURE

CHAIN: RANDOM COIL IN THE BULK
PACKING OF CHAINS: ‘LIQUID-LIKE’

~ 300Å
ATOMIC STRUCTURE

~ 30Å

NO LONG-RANGE ORDER
ATOMIC STRUCTURE: LIQUID-LIKE!

Polymer

GLASSES

Molecular Glass

Metallic Glass

Fe

Ni

P

B

S(Q)

Q (Å⁻¹)

0

1

2

3

4

0

1.5

3

4.5

6

Q (Å⁻¹)

0

15

3

4.5

6

Q (Å⁻¹)

0

1

2

3

4

S(Q)
SMALL LENGTH SCALES  

ATOMIC STRUCTURE

≈ 30Å

GLASSY PROPERTIES

LARGE LENGTH SCALES

“RANDOM COIL” STRUCTURE

≈ 300Å

CHAIN PROPERTIES
Orthoterphenyl $[\text{C}_{18}\text{H}_{14}]$

**STRUCTURE FACTOR**

- Orthoterphenyl

**RELAXATION MAP**

- $\alpha$-relaxation
- $\beta$-relaxation
- $T_g$
Polyisoprene \([-\text{CH}_2-\text{CH}=\text{C(CH}_3)-\text{CH}_2-]\)_n

**STRUCTURE FACTOR**

**RELAXATION MAP**
POLYMER MELTS
CHAIN -“RANDOM COIL”- STRUCTURE

≈ 300Å
Polyisoprene [-CH$_2$-CH=C(CH$_3$)-CH$_2$-]$_n$

Coil diameter ≈ 100Å

RELAXATION MAP

End-to-end relaxation

α-relaxation

β-relaxation

T$_g$ (glass transition)

CH$_3$-rotation

Boson Peak

End-to-end vector

Coil diameter ≈ 100Å

End-to-end

Coil diameter ≈ 100Å

End-to-end vector

Coil diameter ≈ 100Å

End-to-end vector
Large Scale Dynamics
Large Scale Dynamics of Polymer Melts

Let Gaussian chains move!!

The Rouse Model

A Theory of the Linear Viscoelastic Properties of Dilute Solutions of Coiling Polymers

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Macromolecular chain with short-range interactions in a melt
Excluded volume interactions screened out

We define points \( (j) \) along the chain of coordinates \( \vec{r}_j \)
\[ \langle |\vec{r}_{j+1} - \vec{r}_j|^2 \rangle = b^2 \]
Sub-chain between \( j \) and \( j+1 \) large enough
End-to-End distribution Gaussian
Macromolecular chain with short-range interactions in a melt
Excluded volume interactions screened out

We define points \( j \) along the chain of coordinates \( \bar{r}_j \)
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Sub-chain between \( j \) and \( j+1 \) large enough
End-to-End distribution Gaussian

Entropic contribution to the free energy:
\[ \Delta F = \frac{3}{2} k_B T \frac{\langle \bar{r}_{j+1} - \bar{r}_j \rangle^2}{N' a^2} \]
Spring-like force:
\[ \bar{F} = \frac{3k_B T}{b^2} (\bar{r}_{j+1} - \bar{r}_j) \]

MAPPING ONTO A ‘BEAD-SPRING’-CHAIN!
Large Scale Dynamics of Polymer Melts

The Rouse Model

Rouse chain: target chain in a melt of similar chains

Intermolecular interactions: Mean-field approach

• Friction force: constant friction coefficient $\xi$
  \[
  \vec{F}_{\text{friction}} = -\xi \frac{d\vec{r}}{dt}
  \]

• Stochastic random force: $\vec{f}$

• Friction related to the random force (fluctuation-dissipation theorem)
  \[
  \left\langle \vec{f}_j(t) \vec{f}_i(t') \right\rangle = 6\xi k_B T \delta_{ji} \delta(t - t')
  \]

No correlation between random forces!!
Large Scale Dynamics of Polymer Melts

The Rouse Model

The Rouse Equation of Motion

\[
\frac{d^2 \vec{r}_j}{dt^2} = \vec{F}_{\text{spring}} + \vec{F}_{\text{friction}} + \vec{f}_j
\]

\[
m \frac{d^2 \vec{r}_j}{dt^2} = \frac{3k_B T}{b^2} \left( \vec{r}_{j+1} + \vec{r}_{j-1} - 2 \vec{r}_j \right), \quad j \neq 1, N
\]

\[
\vec{F}_{\text{friction}} = -\xi \frac{d\vec{r}_j}{dt}
\]

Inertial term \( m \frac{d^2 \vec{r}_j}{dt^2} \approx 0 \) for \( t >> \frac{m}{\xi} \sim 10^{-13} - 10^{-12} \) s.

\[
\xi \frac{d\vec{r}_j}{dt} = \frac{3k_B T}{b^2} \left( \vec{r}_{j+1} + \vec{r}_{j-1} - 2 \vec{r}_j \right) + \vec{f}_j
\]

Brownian motion of coupled oscillators
Large Scale Dynamics of Polymer Melts

The Rouse Model

Transformation to ‘normal coordinates’ (Rouse modes) \( \vec{X}_p \Rightarrow \)

Independent equations of motion

\[
\vec{X}_p(t) = \frac{1}{N} \sum_{j=1}^{N} \vec{r}_j(t) \cos \left[ \frac{p \pi}{N} \left( j - \frac{1}{2} \right) \right], \quad p = 0, 1, \ldots, N - 1
\]

\[
\vec{r}_j(t) = \vec{X}_o(t) + 2 \sum_{p=1}^{N-1} \vec{X}_p(t) \cos \left[ \frac{\pi p}{N} \left( j - \frac{1}{2} \right) \right]
\]

\( \vec{X}_o(t) \) center of mass of the chain

\( \vec{X}_o(t) = \frac{1}{N} \sum_{j=1}^{N} \vec{r}_j(t) \)

\( \vec{X}_p(t) \) describes the motion of a subchain of ‘wavelength’ \( \sim \frac{N}{p} \) and length-scale \( \sim \left( \frac{Nb^2}{p} \right)^{1/2} \)
The Rouse Equation in normal coordinates

\[ \xi_p \frac{d\tilde{X}_p(t)}{dt} = -K_p \tilde{X}_p(t) + \tilde{g}_p \]

Independent equations!

\[ K_p = \frac{12k_B T\xi_p}{b^2 \xi} \sin^2 \left[ \frac{p\pi}{2N} \right] \]

\[ \xi_p = (2 - \delta_{op}) N \xi \]

\[ \tilde{g}_p = \frac{\xi_p}{N\xi} \sum_{j=1}^{N} \tilde{f}_j(t) \cos \left[ \frac{j\pi p}{N} \right] \]
The Rouse Model

Correlation function of the Rouse modes

\[
\langle \tilde{X}_p(t) \tilde{X}_q(0) \rangle = \frac{1}{\xi_p \xi_q} \int_0^t dt' e^{-\frac{(t-t')}{\tau_p}} \int_{-\infty}^{t''} dt'' e^{-\frac{t''}{\tau_q}} \langle \tilde{g}_p(t') \tilde{g}_q(t'') \rangle
\]

No correlation between random forces \( \Rightarrow \langle \tilde{g}_p(t') \tilde{g}_q(t'') \rangle \propto \delta_{pq} \delta(t'-t'') \)

Key results!!

- No spatial correlation
- No time correlation
- Orthogonality of Rouse modes

The most important magnitude!
Large Scale Dynamics of Polymer Melts

The Rouse Model

\[ \langle \ddot{X}_p(t) \ddot{X}_p(0) \rangle = \langle \ddot{X}_p^2(0) \rangle \exp \left[ -\frac{t}{\tau_p} \right] \]

\[ \langle \ddot{X}_p^2(0) \rangle = \frac{b^2}{8N \sin^2(p\pi/2N)} \]

Relaxation times

\[ \tau_p^{-1} = 4W \sin^2 \left( \frac{p\pi}{2N} \right) \]

\[ W = \frac{3k_B T}{\xi b^2} \]

Rouse rate

\[ \tau_p \approx \frac{1}{\pi^2 W \left( \frac{N}{p} \right)^2} \]

\[ N \propto M_w \Rightarrow \tau_p \propto M_w^2 \]

Large wave-length \( \left( \frac{N}{p} \right) \) \Rightarrow slower relaxation times

\[ \tau_1 \text{ (the slowest time)} = \text{the 'Rouse time'} \ \tau_R \]
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Large Scale Dynamics of Polymer Melts

The Rouse Model: Experimental evidences

Dynamics of End-to-End vector

\[ \vec{R}_N(t) = \vec{r}_N(t) - \vec{r}_1(t) \]

\[
\vec{R}_N(t) = -4 \sum_{p: \text{odd}}^{N-1} \tilde{X}_p(t) \cos \left( \frac{p\pi}{2N} \right)
\]

Correlation of \( \vec{R}_N(t) \)

\[
\langle \vec{R}_N(t)\vec{R}_N(0) \rangle \approx \frac{8b^2N}{\pi^2} \sum_{p: \text{odd}} \frac{1}{p^2} \exp \left( -\frac{t}{\tau_p} \right) \quad \text{for } p \ll N
\]

\[
\tau_p = \frac{\tau_1}{p^2}; \quad \tau_1 \equiv \tau_R \quad (\text{Rouse time})
\]

\[
\langle \vec{R}_N(t)\vec{R}_N(0) \rangle \approx \frac{8b^2N}{\pi^2} \sum_{p: \text{odd}} \frac{1}{p^2} \exp \left( -\frac{tp^2}{\tau_R} \right)
\]

Dominated by \( \tau_R \)!
Large Scale Dynamics of Polymer Melts

The Rouse Model: Experimental evidences

Following $\langle \vec{R}_N(t)\vec{R}_N(0) \rangle$ by dielectric spectroscopy

Molecular (electrical) dipoles of macromolecules

Most polymers: $\vec{\mu}_{\parallel}$ randomly oriented

$\Rightarrow \sum \vec{\mu}_{\parallel} = 0$

Type A' polymers: $\vec{\mu}_{\parallel}$ always same direction

$\Rightarrow \vec{P} \propto \vec{R}_N$

$\langle \vec{P}(t)\vec{P}(0) \rangle \propto \langle \vec{R}_N(t)\vec{R}_N(0) \rangle$ can be followed by dielectric experiments!

$\tau_R$ experimentally determined $\Rightarrow \tau_R \propto M_w^2$ can be checked!
The Rouse Model: Experimental evidences

Following $\langle R_N(t)R_N(0) \rangle$ by dielectric spectroscopy

Type A' polymers: $\bar{\mu}_\parallel$ always same direction

$\Rightarrow \bar{P} \propto R_N$

- Polyisoprene PI
- Poly(propylene glycol) PPG
- Poly(propylene oxide) PPO
- Poly(alkylene oxide) PAO's
Large Scale Dynamics of Polymer Melts

The Rouse Model: Experimental evidences

Following $\langle \tilde{R}_N(t)\tilde{R}_N(0) \rangle$ by DS

$$\varphi(t) = \frac{\langle \tilde{R}_N(t)\tilde{R}_N(0) \rangle}{\langle \tilde{R}_N^2(0) \rangle} = \frac{8}{\pi^2} \sum_{p: \text{odd}} \frac{1}{p^2} \exp \left( -\frac{t}{\tau_p} \right)$$

$$\tau_p = \frac{\tau_1}{p^2}; \quad \tau_1 \equiv \tau_R$$

Frequency domain:

$$\Phi''(\omega) = \frac{\varepsilon''}{\varepsilon_o - \varepsilon_\infty} = \frac{8}{\pi^2} \sum_{p: \text{odd}} \frac{1}{p^2} \frac{\omega \tau_p}{1 + \omega^2 \tau_p^2}$$
Large Scale Dynamics of Polymer Melts

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$$\omega_{\text{max}} \tau_R = 1$$

$$\frac{8}{\pi^2} \sum_{p: \text{odd}} \frac{1}{p^2} \frac{\omega \tau_p}{1 + \omega^2 \tau_p^2}$$
Large Scale Dynamics of Polymer Melts

The Rouse Model: Experimental evidences

Following $\langle \vec{R}_N(t)\vec{R}_N(0) \rangle$ by DS

polyisoprene

$\text{C}_\text{H}_3$

$-[\text{CH}_2-\text{CH}=\text{C-CH}_2]_n$.

Frequency domain:

$$\Phi''(\omega) = \frac{\varepsilon''}{\varepsilon_o - \varepsilon_\infty} = \frac{8}{\pi^2} \sum_{p: \text{odd}} \frac{1}{p^2} \frac{\omega \tau_p}{1 + \omega^2 \tau_p^2}$$

Figure 7. Rouse model prediction without taking sample polydispersity into account (dashed line) compared to BDS data points. The dotted line represents the modeled contribution of the $\alpha$-relaxation (see text).
Large Scale Dynamics of Polymer Melts

The Rouse Model: Experimental evidences

Following $\langle \mathbf{R}_N(t)\mathbf{R}_N(0) \rangle$ by DS

polyisoprene

$\begin{array}{c}
\text{CH}_3 \\
-[\text{CH}_2\text{CH}=\text{C-CH}_2]_n
\end{array}$

Frequency domain:

Including polydispersity

$$
\varepsilon_N^*(\omega) = \frac{\Delta \varepsilon}{M_n} \int_0^\infty M \frac{2b^2}{N} \sum_{p:odd} \cot^2 \left( \frac{p \pi}{2M} \right) \frac{\omega \tau_p}{1 + \omega^2 \tau_p(M)^2} g(M) dM
$$

Figure 8. Resolved normal mode relaxation of PI-29 sample (see text). The lines represent the behavior predicted by the Rouse model including for the actual sample polydispersity (solid line) and without it (dotted line). Triangles correspond to the difference between the experimental
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Large Scale Dynamics of Polymer Melts

The Rouse Model: Experimental evidences

Following $\langle \vec{R}_N(t)\vec{R}_N(0) \rangle$ by DS

polyisoprene

$\text{CH}_3$

$-[\text{CH}_2-\text{CH}=&\text{C-CH}_2]-_n$

Revisiting the molecular weight effects on dielectric relaxations of linear cis-polyisoprene 1,4

Riedel Clement$^{1,2,*}$, Alegría Angel$^1$, Tordjeman Philippe$^2$, Colmenero Juan$^1$

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The Rouse model fails for very high molecular weights!
Large Scale Dynamics of Polymer Melts

Entanglements: Experimental evidences

Dynamic structure factor

\[ M_w = 2000 \text{g/mol (} n \sim 70) \]

\[ M_w = 14200 \text{g/mol (} n \sim 500) \]

polyethylene -[CH\textsubscript{2}-CH\textsubscript{2}]-\textsubscript{n}
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Large Scale Dynamics of Polymer Melts

The Rouse Model: Experimental evidences

SUMMARY

Rouse fails at $M > M_c$

Rouse approximations do not properly describe the many-body interactions of a melt of long macromolecules.

Random forces acting on beads are likely spatial- and time-correlated!
Generalized Langevin Equation (GLE)

Models based on GLE: Renormalized Rouse Models (RRM)

\[ m \frac{d^2 \vec{r}_j}{dt^2} = - \frac{\partial}{\partial \vec{r}_j} W(\{\vec{r}_i\}) - \sum_n^t \int_0^t d\tau \Gamma_{jn}^{\alpha\beta}(\tau; t - \tau) v_n^\beta(t - \tau) \vec{e}_\alpha + \vec{F}_j(t) \]

Problems:

How to construct a Memory function from first principles

Until now only phenomenological approaches
The ‘tube’ concept

Let’s assume:
- tagged chain mobile
- rest of the chains (matrix) fixed

Chain motion restricted to a tube-like region

Tube diameter \( d \approx 2d_{\text{max}} \)

\[
d_{\text{max}} = \frac{2\pi}{Q_{\text{max}}} \quad \text{Inter-macro-molecular distances}
\]
Large Scale Dynamics of Polymer Melts

Entanglements: tube/reptation model

The ‘tube’ concept

Let’s assume:
• tagged chain mobile
• rest of the chains fixed

Chain motion restricted to a tube-like region

Tube diameter

\[ d \approx 6 \text{ Å} \]

\[ d = 2d_{\text{max}} \]

\[ d_{\text{max}} = \frac{2\pi}{Q_{\text{max}}} \]

\[ Q_{\text{max}} \approx 1 \text{ Å}^{-1} \]

Inter-macro-molecular distances

Inter/intra

270 K
160 K
4 K
Large Scale Dynamics of Polymer Melts

Entanglements: tube/reptation model

Edwards & deGennes

Real situation: all chains move!

Intermolecular interactions, uncrossability and chain connectivity

$\approx 50-70\text{Å}$

FICTITIOUS TUBE along the contour length of a tagged chain
Entanglements: tube/reptation model

Edwards & de Gennes

Real situation: all chains move!

FICTITIOUS TUBE along the contour length of a tagged chain

The ‘tube’ becomes effective at \( t \geq \tau_e \)

\[
\langle r^2(\tau_e) \rangle \approx d^2 \quad \langle r^2(t) \rangle \propto t^{1/2} \quad \text{(Rouse)}
\]

\[
\tau_e \propto d^4 \quad \text{Independent of } N!!
\]
Following $\langle \tilde{R}_N(t)\tilde{R}_N(0) \rangle$ by DS

‘Survival probability of unrelaxed chain segments within the tube’

Formally equal to the Rouse expression but with $\tau_d \propto N^3$

$$\mu_D(t) = \frac{\langle \tilde{R}_N(t)\tilde{R}_N(0) \rangle}{\langle \tilde{R}^2_N(0) \rangle} = \frac{8}{\pi^2} \sum_{p: \text{odd}} \frac{1}{p^2} \exp\left(-\frac{t}{\tau_d}\right)$$
Large Scale Dynamics of Polymer Melts

Crossover from Rouse to Reptation

Following $\langle \vec{R}_N(t)\vec{R}_N(0) \rangle$ by DS

polyisoprene

CH$_3$

-$[\text{CH}_2-\text{CH}=\text{C}-\text{CH}_2]_n$

The Rouse model fails for very high molecular weights!

$\tau_N \propto \frac{M^2}{\tau_\alpha}$

$M_w [\text{g/mol}]$

$10^{-4}$

$10^{-3}$

$10^{-2}$

$10^3$ $10^4$ $10^5$

Reptation $M^3$

Experiments $M^{3.4}$

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Large Scale Dynamics of Polymer Melts

High molecular weight crossover: Pure Reptation?

Following $\langle \mathbf{R}_N(t) \mathbf{R}_N(0) \rangle$ by DS

polyisoprene

$\quad \text{CH}_3$

$\quad -[\text{CH}_2-\text{CH}=\text{C-CH}_2]_n$
Entanglements: tube/reptation model

Summary

• Tube/reptation models capture the main entanglement effects.
• Corrections are usually needed to describe experimental data:
  Contour length fluctuations
  Constraint release
  ...
• However, whether the tube picture is indeed correct still remains a matter for debate.
Large Scale Dynamics of Polymer Melts

Temperature dependence

Following $\langle \tilde{R}_N(t) \tilde{R}_N(0) \rangle$ by DS and TSDC

Polyisoprene

$$\begin{align*}
\text{CH}_3 \\
-[\text{CH}_2-\text{CH}=&\text{C}-\text{CH}_2]-_n
\end{align*}$$

FIG. 2 (color online). From left to right: Times for chain relaxation of PI400 ($M_w = 400$ kDa), PI320 ($M_w = 320.2$ kDa), PI82 ($M_w = 82$ kDa), PI53 ($M_w = 53$ kDa), PI19 ($M_w = 19$ kDa), PI10 ($M_w = 10.5$ kDa), PI1 ($M_w = 1.2$ kDa), and a relaxation of PI1 and PI82. Data for PI1 were shifted $-0.0004$ in the x axis. Thick lines: times by TSDC curve analysis. Crosses $\times$ ($\circ$ for PI1): times by BDS. Thin lines: fits of BDS times to a WLF (chain) or Vogel-Fulcher-Tammann equation [21] ($\alpha$ relaxation; dashed line for PI1 and solid line for PI82).
Large Scale Dynamics of Polymer Melts

Temperature dependence

Following \( \langle \bar{R}_N(t)\bar{R}_N(0) \rangle \) and \( \alpha \)-relaxation by DS and TSDC

polyisoprene

Figure 2. Panel (a) \( \tau(T) \) for the \( p = 1 \) chain mode and \( \alpha \)-relaxation of PI10 and (b) the ratio \( \tau_{p=1}/\tau_{\alpha} \). (Δ) isothermal measurements; (○) variable rate global TSDC; (○) PP-TSDC. The lines in (a) are WLF and VFT law fits of the isothermal measurements and their ratio in (b). Dashed and dotted dashed lines in (b) show the power law description valid in limited ranges.
Chain dynamics: Determination of monomeric friction

Molecular Dynamics Simulations

Rouse Model fails at high-Q (short distances)

Local potentials and chain stiffness enter the game!!

\[ \Delta \varepsilon \sim k_B T \]
Rouse Model fails at high-Q (short distances)

Friction depends on the wavelength of chain modes

$log(\xi)$

Neutron scattering values

$T = 350K$

$413K$

$492K$
Following $\langle \tilde{R}_N(t)\tilde{R}_N(0) \rangle$ and $\alpha$-relaxation by DS and TSDC

- Normal Mode under confinement
- Normal Mode in nanocomposites
- Type A polymers with non-linear architectures
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