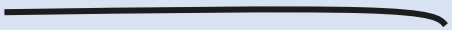
Polymers Dynamics by Dielectric Spectroscopy



What's a polymer bulk?

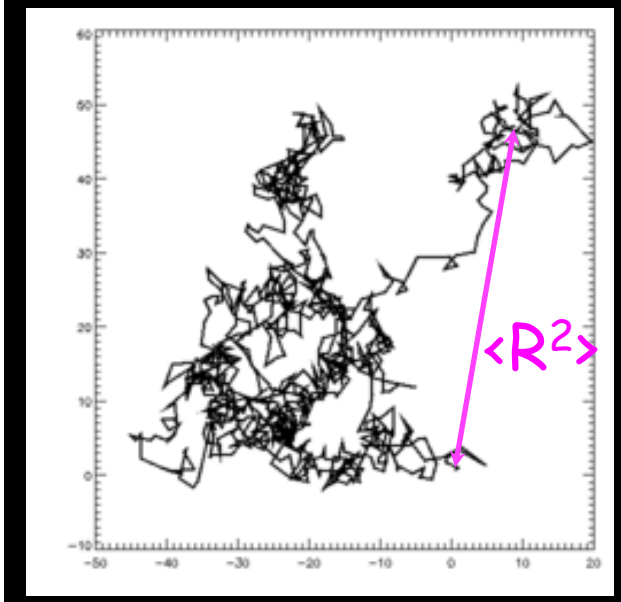
A condensed matter system where the structural units are macromolecules

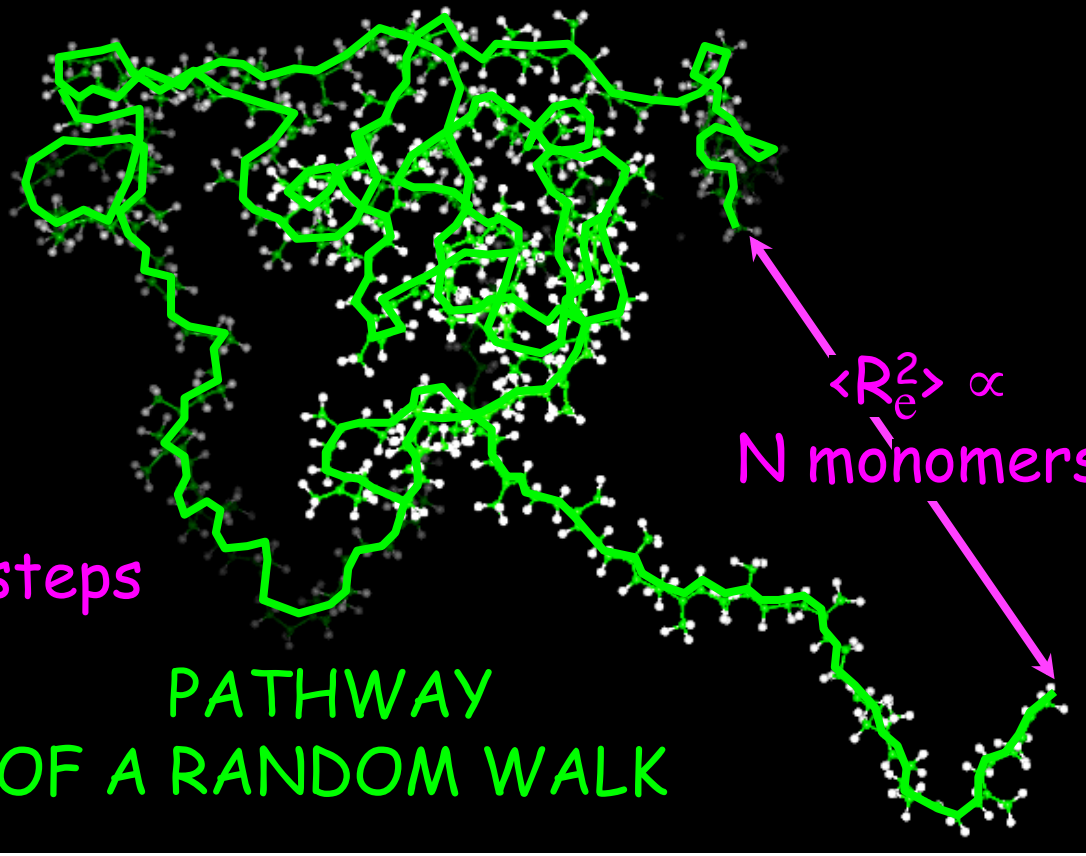
Shape of a Macromolecule in the Bulk

P. J. Flory
Nobel Prize 1974

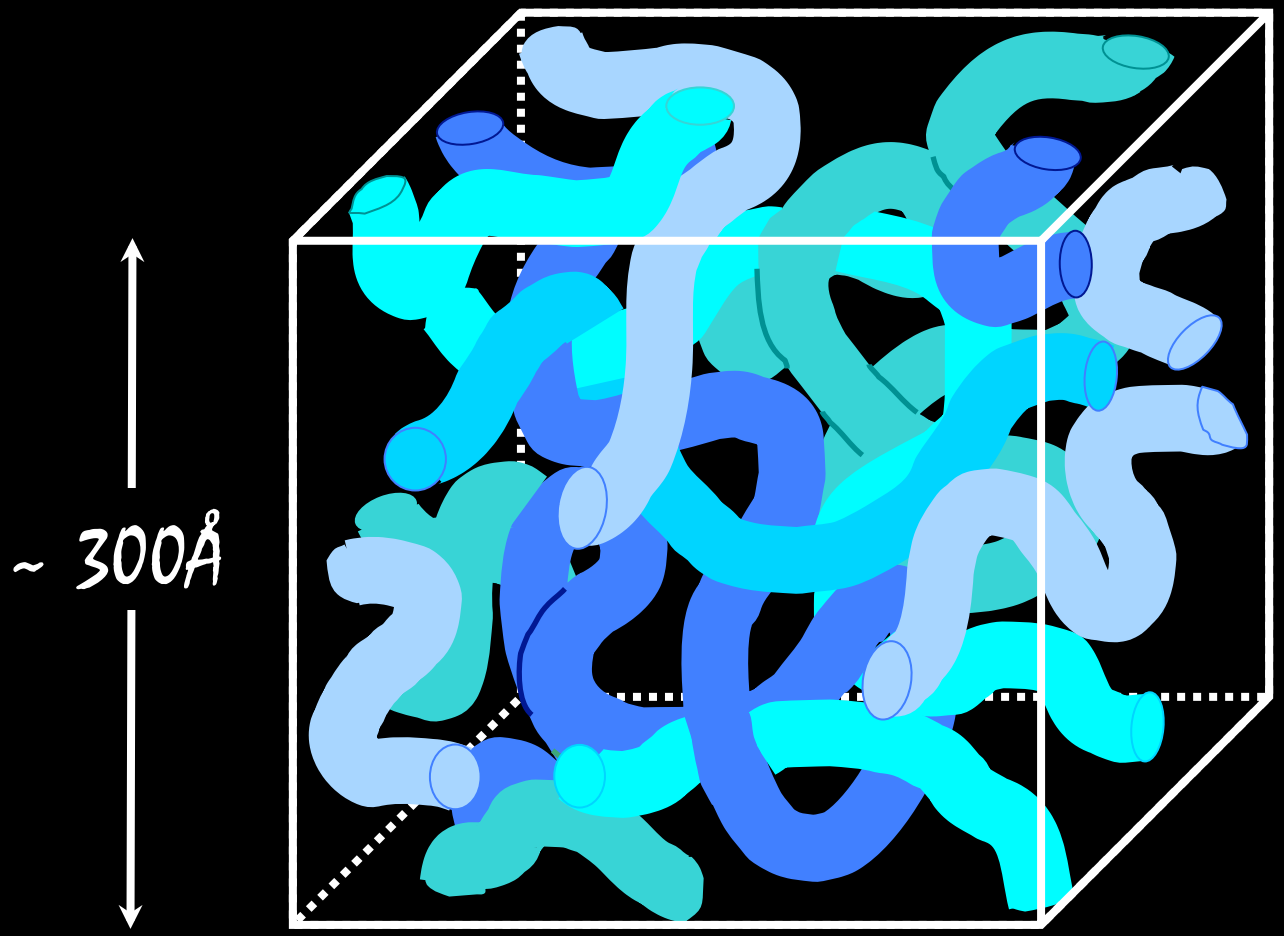
Flory's prediction in the 50's:

'RANDOM COIL'





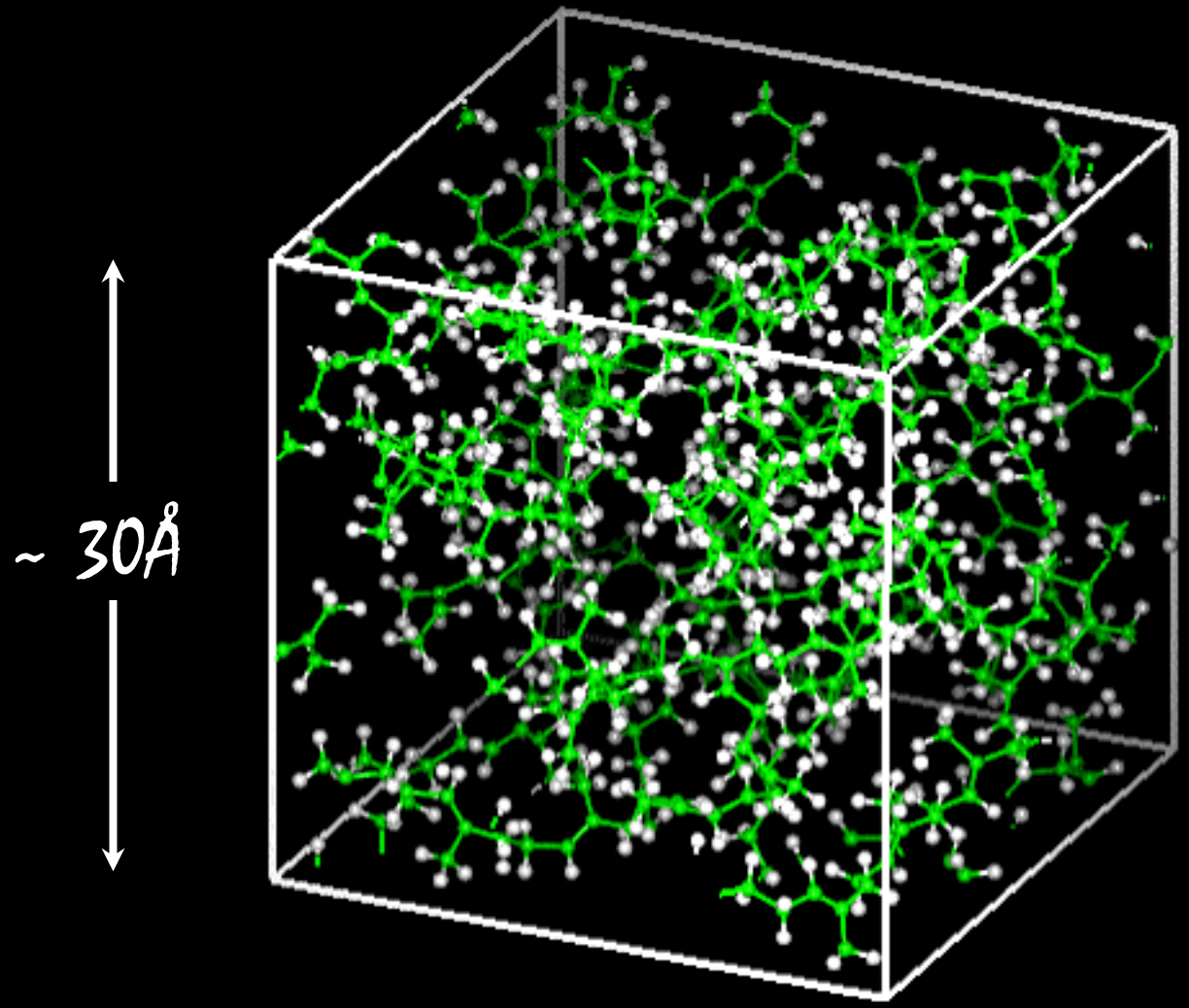
MACROMOLECULAR STRUCTURE



CHAIN: RANDOM COIL IN THE BULK

PACKING OF CHAINS: ‘LIQUID-LIKE’

ATOMIC STRUCTURE

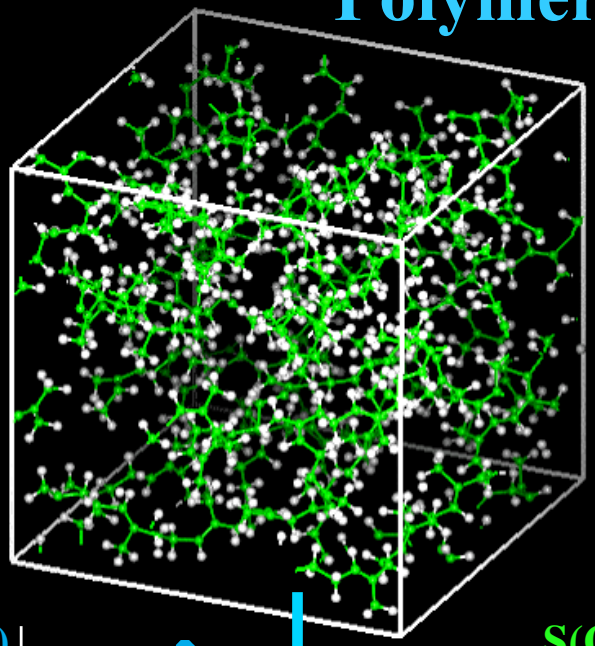


NO LONG-RANGE ORDER

ATOMIC STRUCTURE: LIQUID-LIKE!

GLASSES

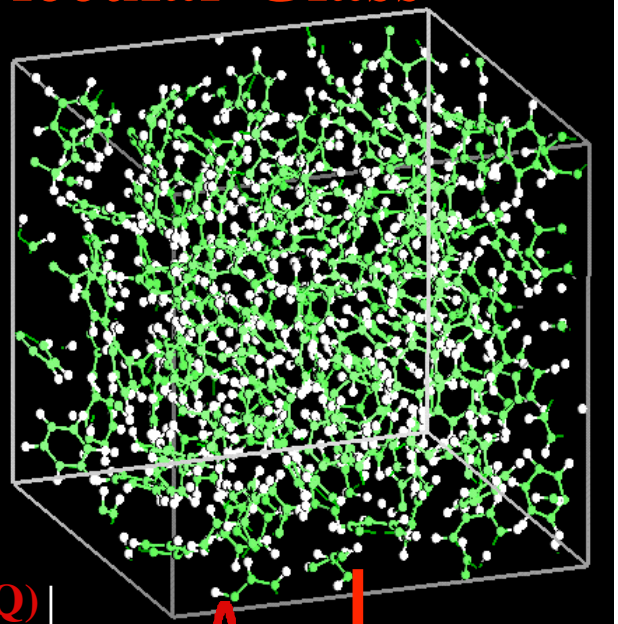
Polymer

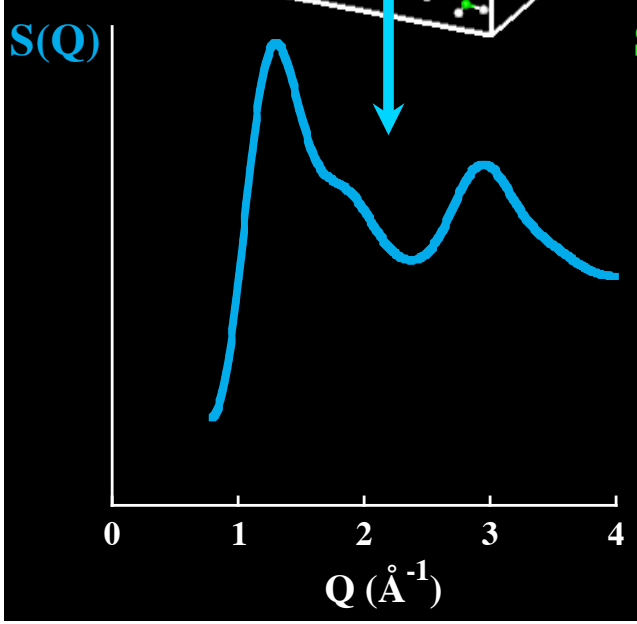


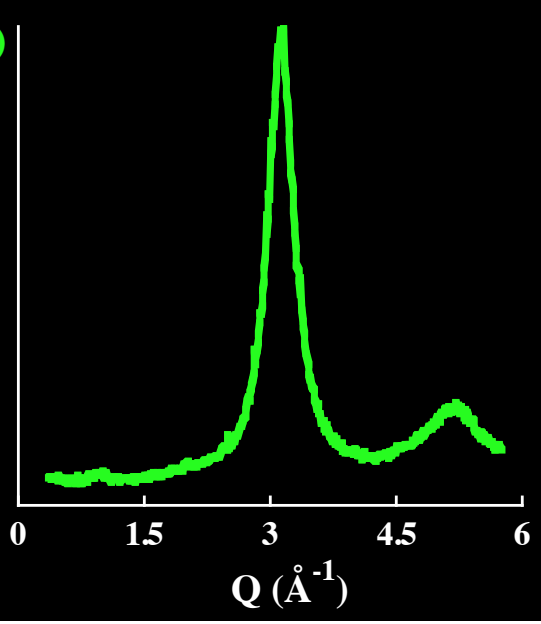
Metallic Glass

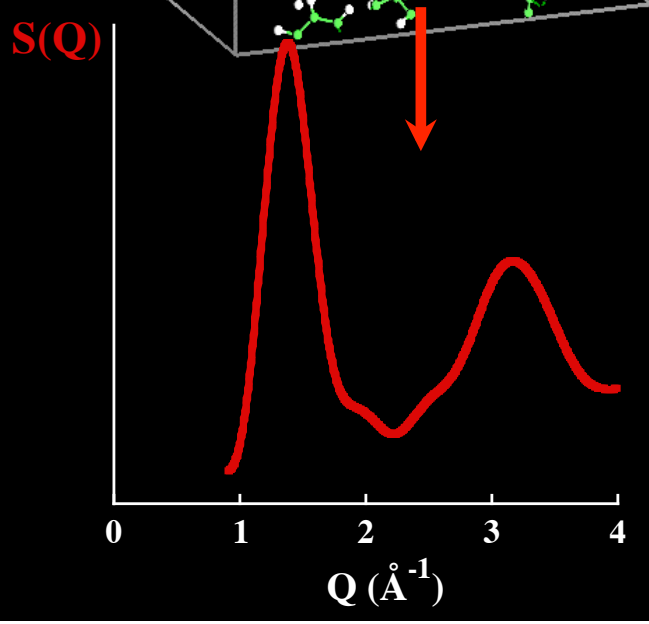
$Fe_{40}Ni_{40}P_{14}B_6$

Molecular Glass





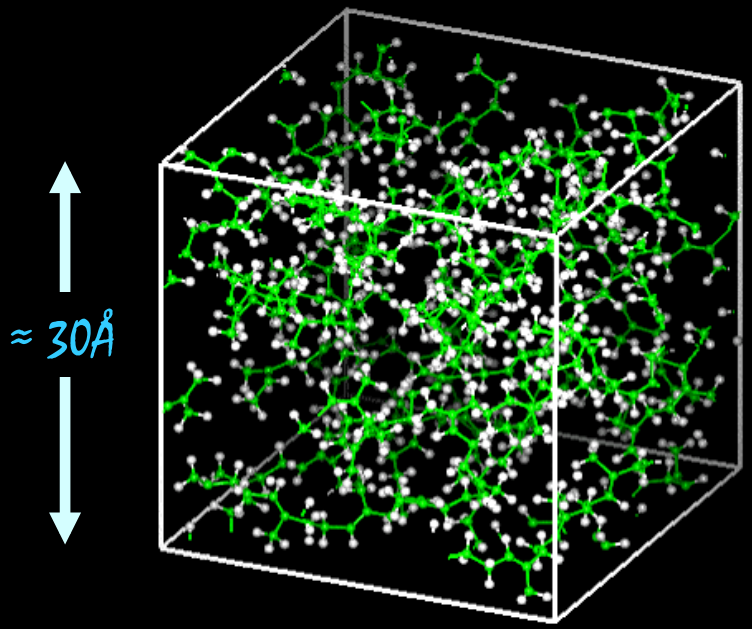




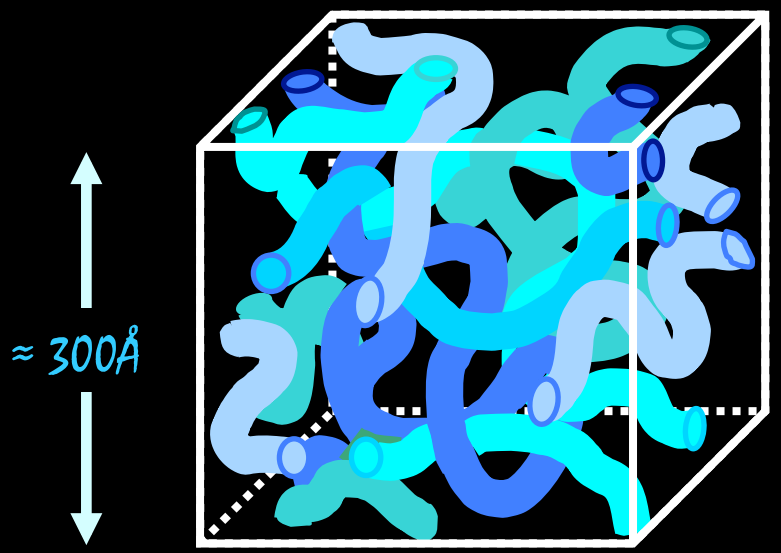
SMALL LENGTH SCALES

LARGE LENGTH SCALES

ATOMIC STRUCTURE



"RANDOM COIL" STRUCTURE

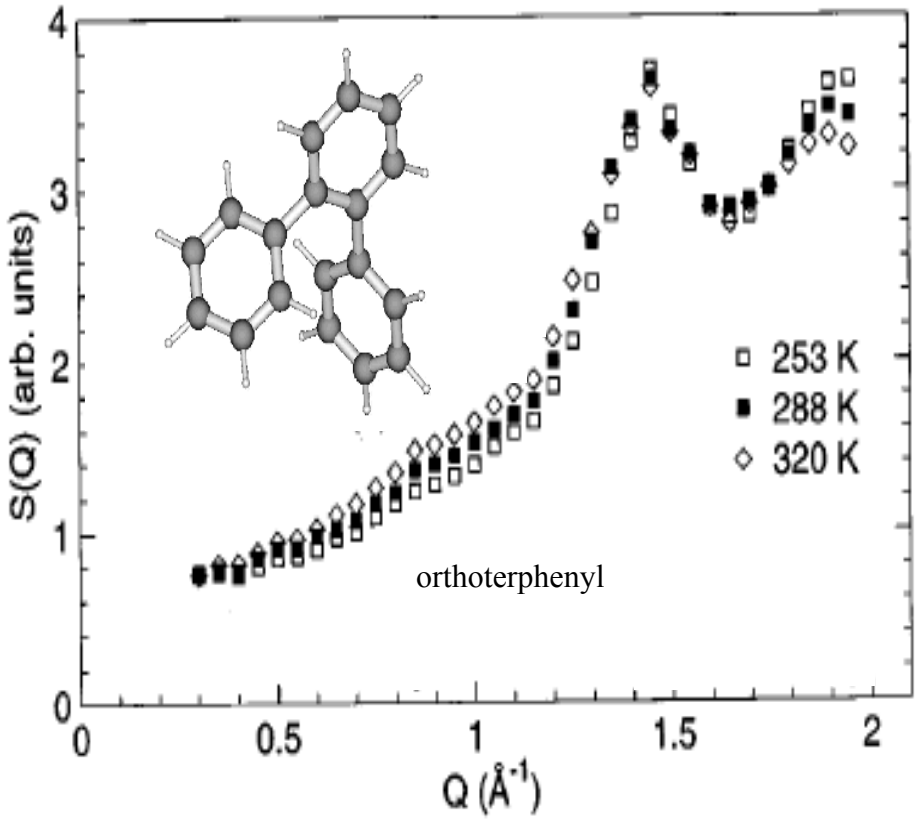


GLASSY PROPERTIES

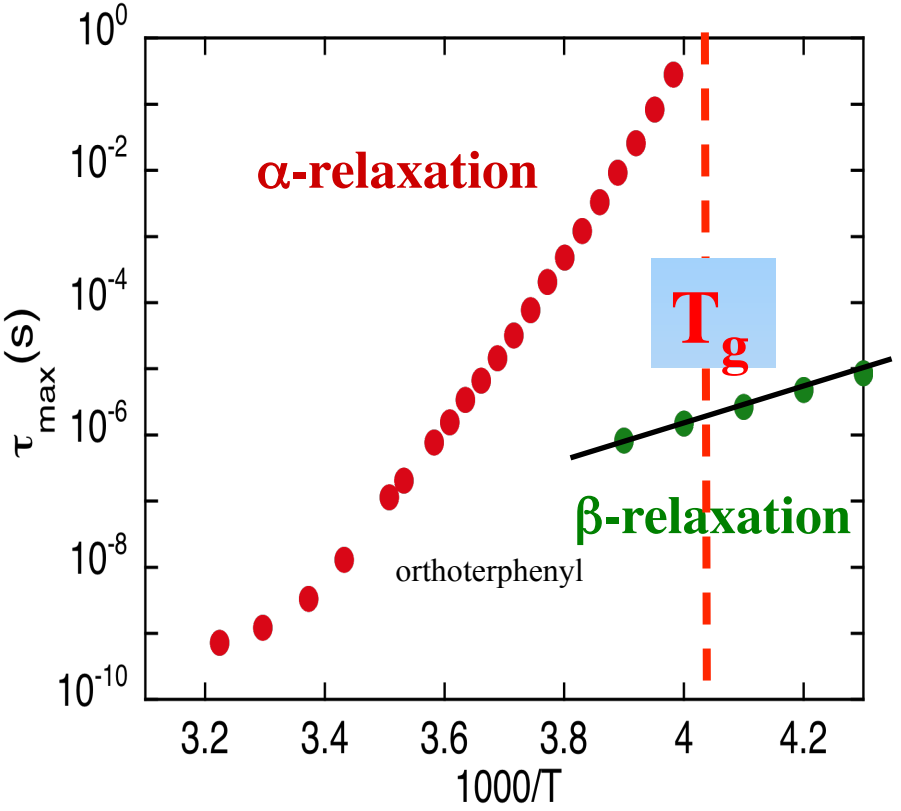
CHAIN PROPERTIES

Orthoterphenyl [$C_{18}H_{14}$]

STRUCTURE FACTOR

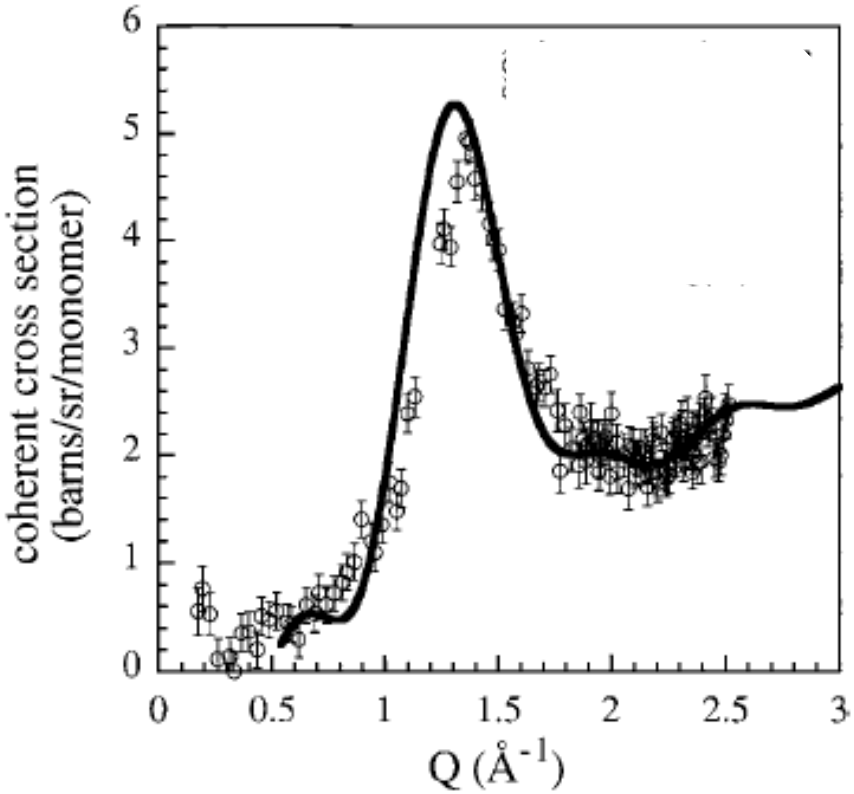


RELAXATION MAP



Polyisoprene $[-CH_2-CH=C(CH_3)-CH_2-]_n$

STRUCTURE FACTOR



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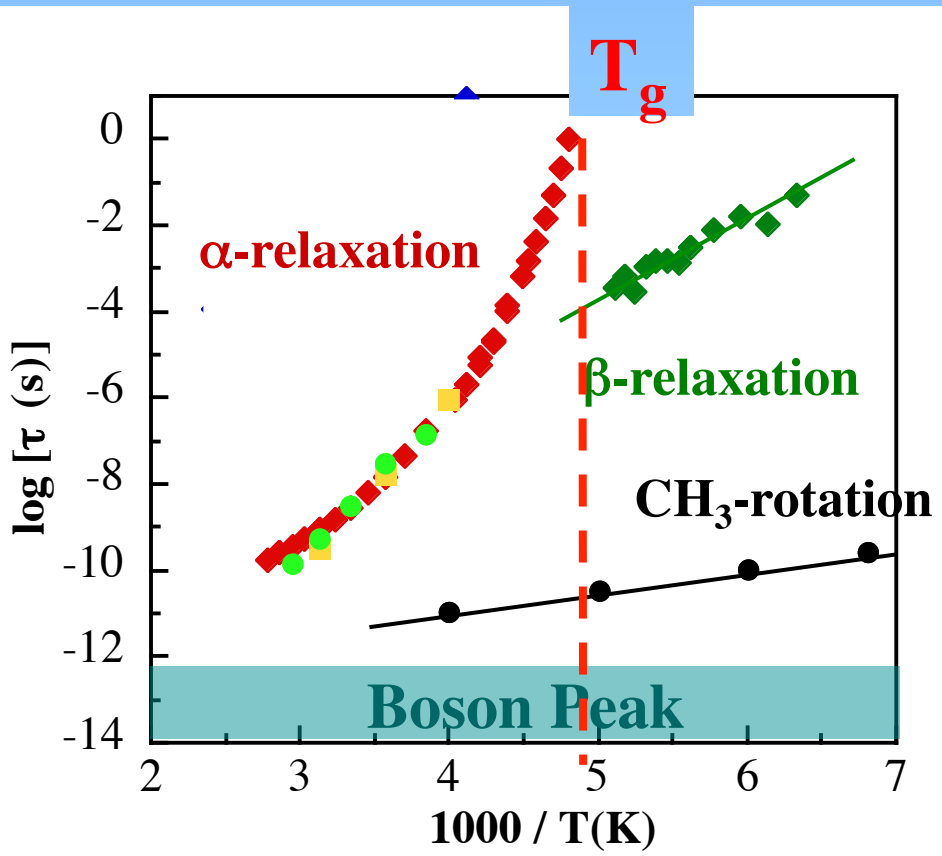
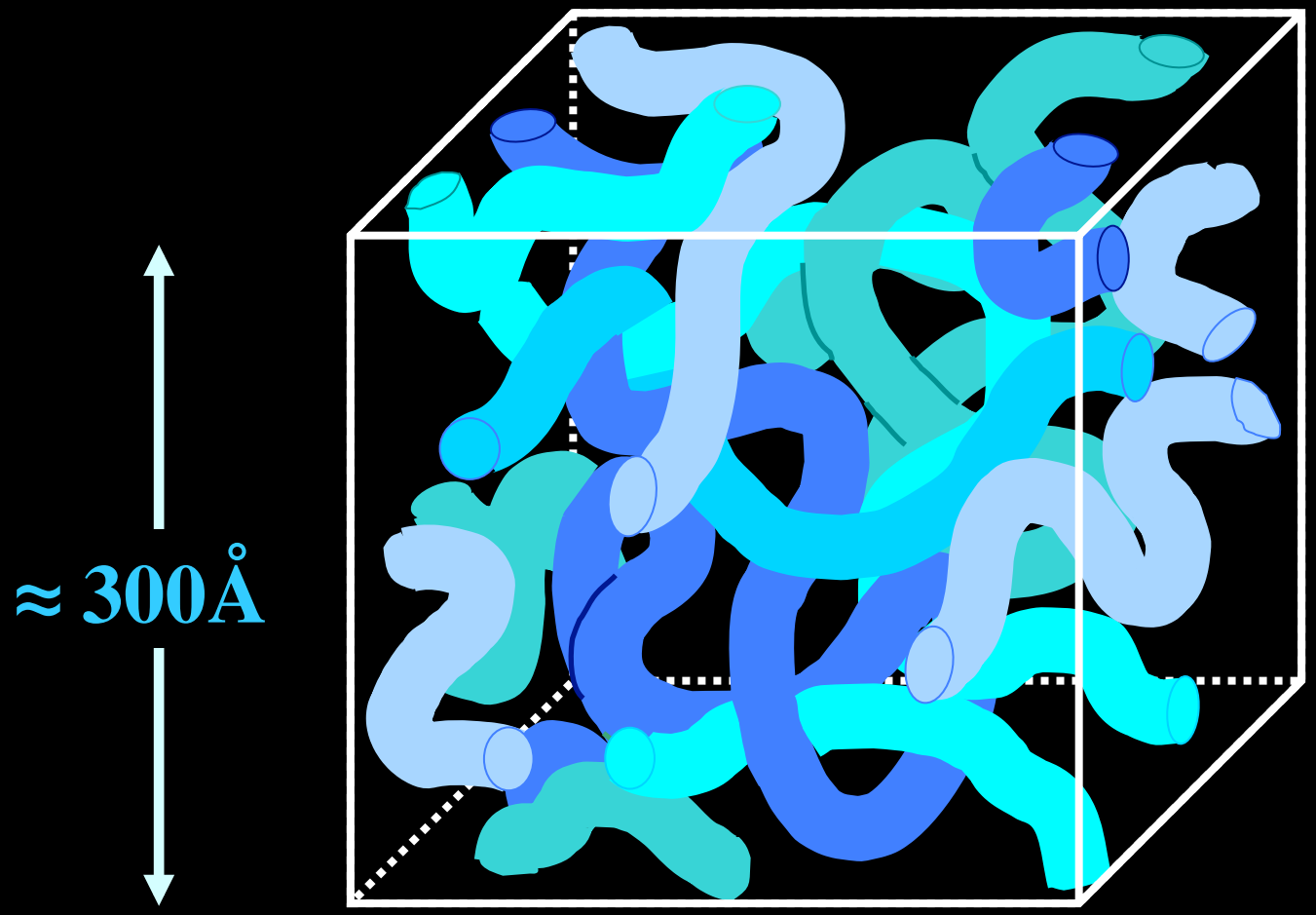
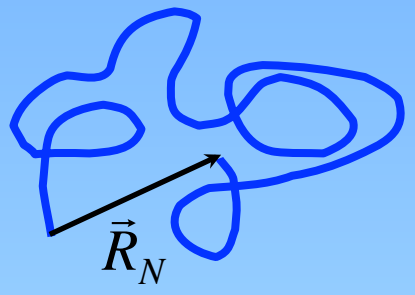


POLYMER MELTS
CHAIN -"RANDOM COIL"- STRUCTURE



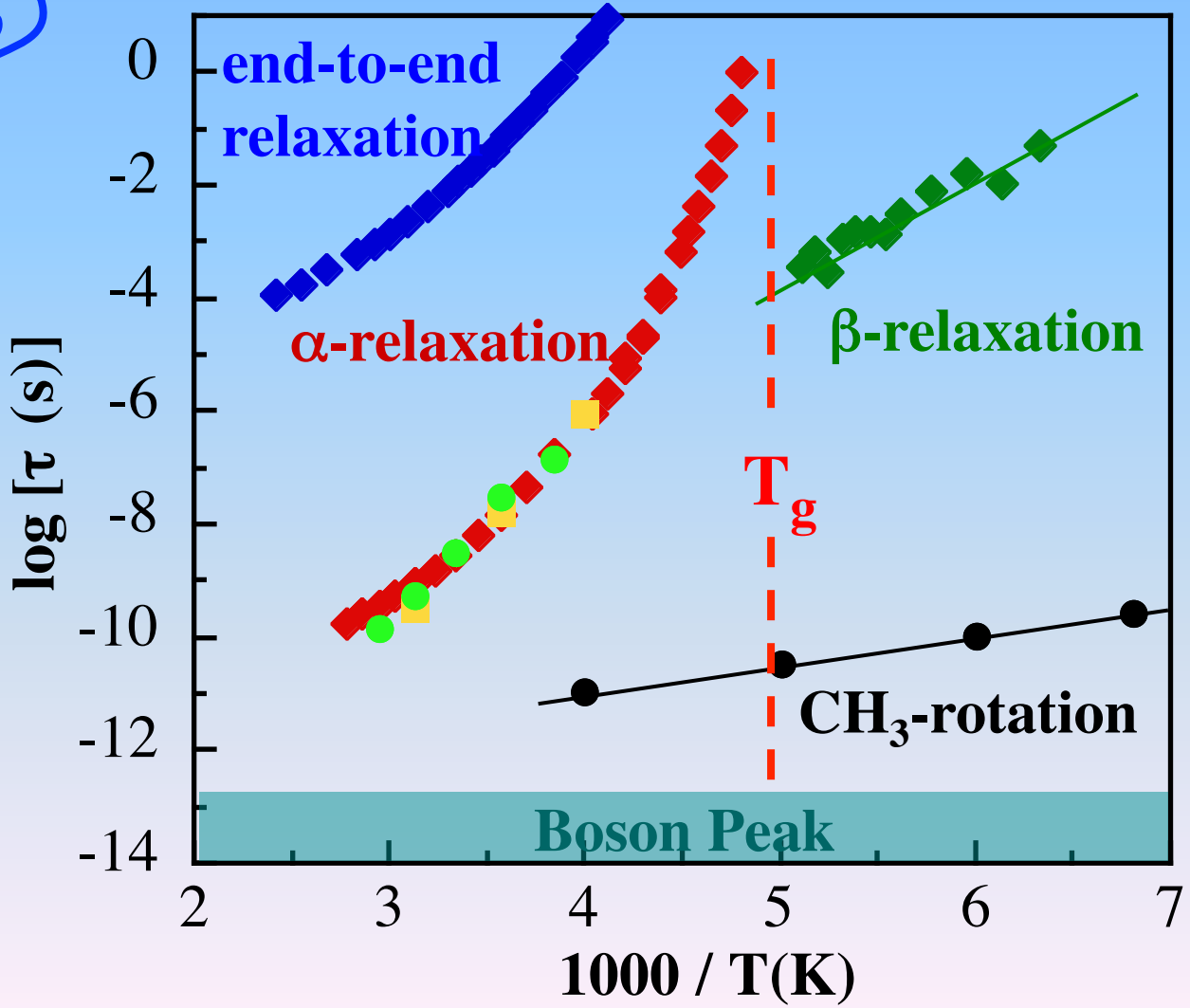
Polyisoprene $[-CH_2-CH=C(CH_3)-CH_2-]_n$

Coil diameter ≈100Å



End-to-end vector

RELAXATION MAP



Large Scale Dynamics

Let Gaussian chains move!!

The Rouse Model

P. Rouse, J. Chem. Phys. 21 (1953) 1272

Large Scale Dynamics of Polymer Melts

The Rouse Model

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 21, NUMBER 7 JULY, 1953

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

PRINCE E. ROUSE, JR.
The Franklin Institute, Laboratories for Research and Development, Philadelphia, Pennsylvania

(Received January 27, 1953)

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The action of a velocity gradient disturbs the distribution of configurations of the polymer molecules away from its equilibrium form, storing free energy in the system. The coordinated thermal motions of the segments cause the configurations to drift toward their equilibrium distribution. The coordination is taken into account by the mathematical requirement that motions of the atom which joins two submolecules change the configurations of both submolecules. By means of an orthogonal transformation of coordinates, the coordination of all the motions of the parts of a molecule is resolved into a series of modes. Each mode has a characteristic relaxation time. The theory produces equations by means of which the relaxation times, the components of the complex viscosity, and the components of the complex rigidity can be calculated from the steady flow viscosities of the solution and the solvent, the molecular weight and concentration of the polymer, and the absolute temperature.

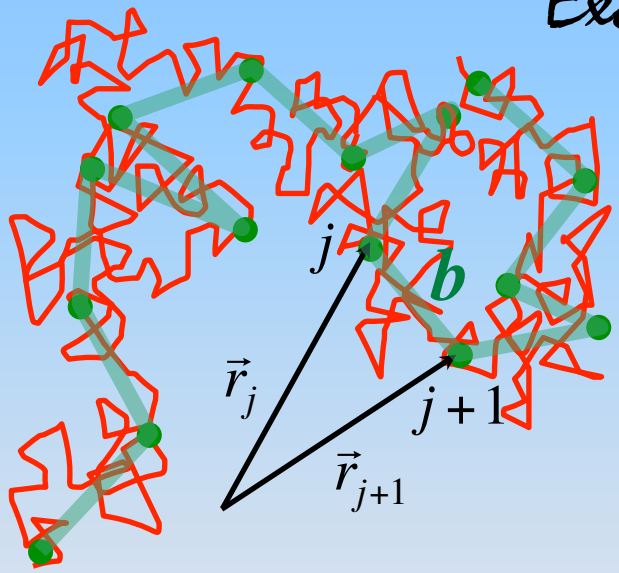
Limitations of the theory may arise from the exclusion from consideration of (1) very rapid relaxation processes involving segments shorter than the submolecule and (2) the obstruction of the motion of a segment by other segments with which it happens to be in contact. Another possible cause of disagreement between the theory and experimental data is the polydispersity of any actual polymer; this factor is important because the calculated relaxation times increase rapidly with increasing molecular weight.

Large Scale Dynamics of Polymer Melts

The Rouse Model

Macromolecular chain with short-range interactions in a melt

Excluded volume interactions screened out



We define points (j) along the chain of coordinates $\vec{r}_j$ $\left\langle \left| \vec{r}_{j+1} - \vec{r}_j \right|^2 \right\rangle = b^2$

Sub-chain between j and $j+1$ large enough

↓

End-to-End distribution Gaussian

Large Scale Dynamics of Polymer Melts

The Rouse Model

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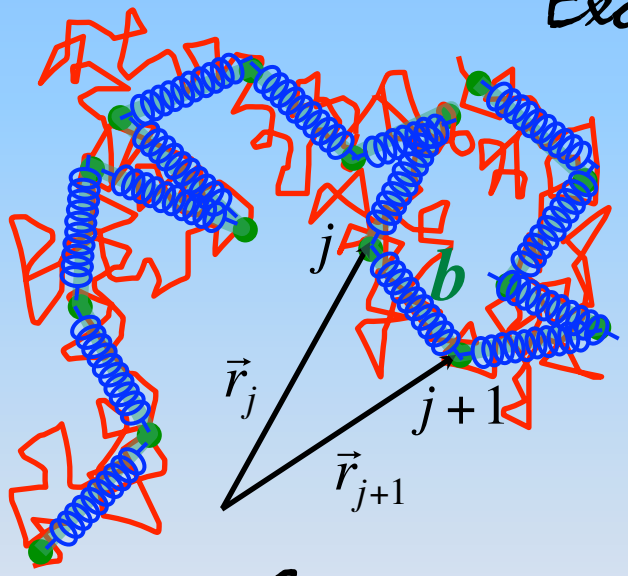

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Sub-chain between j and $j+1$ large enough

↓

End-to-End distribution Gaussian

Entropic contribution to the free energy: $\Delta F = \frac{3}{2} k_B T \frac{\left(\vec{r}_{j+1} - \vec{r}_j \right)^2}{N' a^2}$

Spring-like force: $\vec{F} = \frac{3 k_B T}{b^2} \left(\vec{r}_{j+1} - \vec{r}_j \right)$

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 ξ

$$\vec{F}^{\,friction} = -\xi \frac{d\vec{r}}{dt}$$

- Stochastic random force: $\vec{f}$
- Friction related to the random force (fluctuation-dissipation theorem)

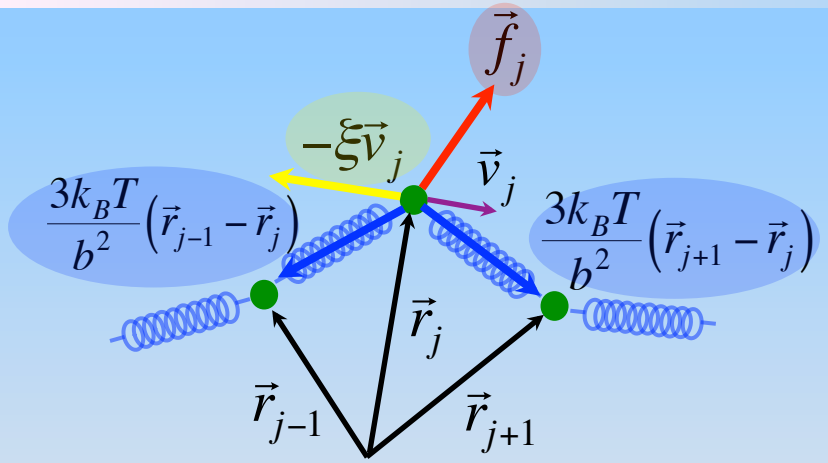
$$\left\langle \vec{f}_j(t)\vec{f}_i(t') \right\rangle = 6\xi k_B T \delta_{ji}\delta(t-t')$$

No correlation between random forces!!

Large Scale Dynamics of Polymer Melts

The Rouse Model

The Rouse Equation of Motion



$$m\frac{d^2\vec{r}_j}{dt^2} = \vec{F}_j^{spring} + \vec{F}_j^{friction} + \vec{f}_j$$

$$\vec{F}_j^{spring} = \frac{3k_BT}{b^2}\left(\vec{r}_{j+1} + \vec{r}_{j-1} - 2\vec{r}_j\right), \quad j \neq 1, N$$

$$\vec{F}_j^{friction} = -\xi\frac{d\vec{r}_j}{dt}$$

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

$$\boxed{\xi\frac{d\vec{r}_j}{dt} = \frac{3k_BT}{b^2}\left(\vec{r}_{j+1} + \vec{r}_{j-1} - 2\vec{r}_j\right) + \vec{f}_j}$$

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 $\sim \left(\frac{Nb^2}{p}\right)^{1/2}$

Large Scale Dynamics of Polymer Melts

The Rouse Model

The Rouse Equation in normal coordinates

$$\xi_p \frac{d\vec{X}_p(t)}{dt} = -K_p \vec{X}_p(t) + \vec{g}_p$$

Independent equations!

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

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

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

Large Scale Dynamics of Polymer Melts

The Rouse Model

Correlation function of the Rouse modes

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

The most important magnitude!

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

No spatial correlation → orthogonality of Rouse modes

No time correlation → $\left\langle \vec{X}_p(t)\vec{X}_p(0)\right\rangle \propto exp\left[-\frac{t}{\tau_p}\right]$

Key results!!

Large Scale Dynamics of Polymer Melts

The Rouse Model

$$\left\langle \vec{X}_p(t)\vec{X}_p(0)\right\rangle = \left\langle \vec{X}_p^2(0)\right\rangle \exp\left[-\frac{t}{\tau_p}\right] \qquad \boxed{\left\langle \vec{X}_p^2(0)\right\rangle = \frac{b^2}{8N\sin^2\left(p\pi/2N\right)}}$$

Relaxation times $\boxed{\tau_p^{-1} = 4W\sin^2\left[\frac{p\pi}{2N}\right]}$ $W = \frac{3k_BT}{\xi b^2}$ Rouse rate

for $p << N$ $\boxed{\tau_p \approx \frac{1}{\pi^2 W}\left(\frac{N}{p}\right)^2}$ $N \propto M_w \Rightarrow \underline{\tau_p \propto M_w^2}$

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

τ_1 (the slowest time) = the 'Rouse time' τ_R

Large Scale Dynamics of Polymer Melts

The Rouse Model

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Large Scale Dynamics of Polymer Melts

The Rouse Model: Experimental evidences

Dynamics of End-to-End vector $\vec{R}_N(t) = \vec{r}_N(t) - \vec{r}_1(t)$

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

Correlation of $\vec{R}_N(t)$ $\left\langle \vec{R}_N(t)\vec{R}_N(0)\right\rangle \cong \frac{8b^2N}{\pi^2} \sum_{p:odd} \frac{1}{p^2} exp\left(-\frac{t}{\tau_p}\right)$ for $p << N$

$\tau_p = \frac{\tau_1}{p^2}$; $\tau_1 \equiv \tau_R$ (Rouse time)

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

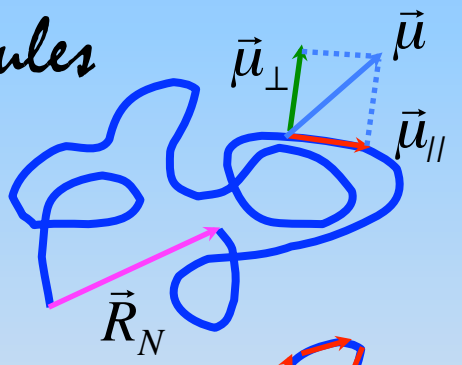
Dominated by τ_R!

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

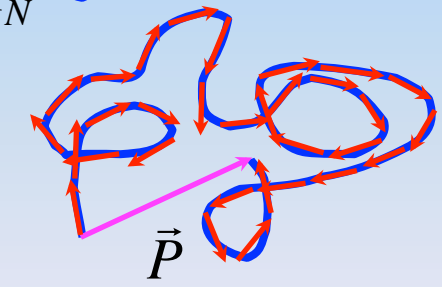


Most polymers: $\vec{\mu}_{//}$ randomly oriented

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

Type A' polymers: $\vec{\mu}_{//}$ 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!

τ_R experimentally determined $\Rightarrow$ $\tau_R \propto M_w^2$ can be checked!

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

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

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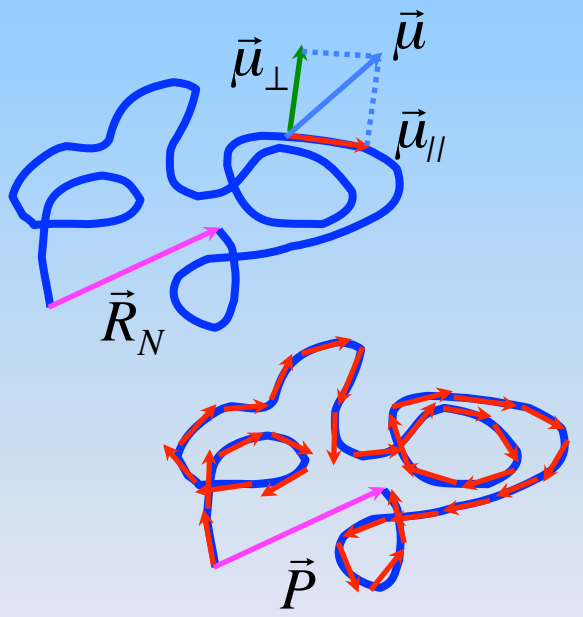

- Polyisoprene PI
- Poly(propilene glycol) PPG
- Poly(propilene oxide) PPO
- Poly(alkylene oxide) PAO's

Large Scale Dynamics of Polymer Melts

The Rouse Model: Experimental evidences

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

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

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

Frequency domain:

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

Large Scale Dynamics of Polymer Melts

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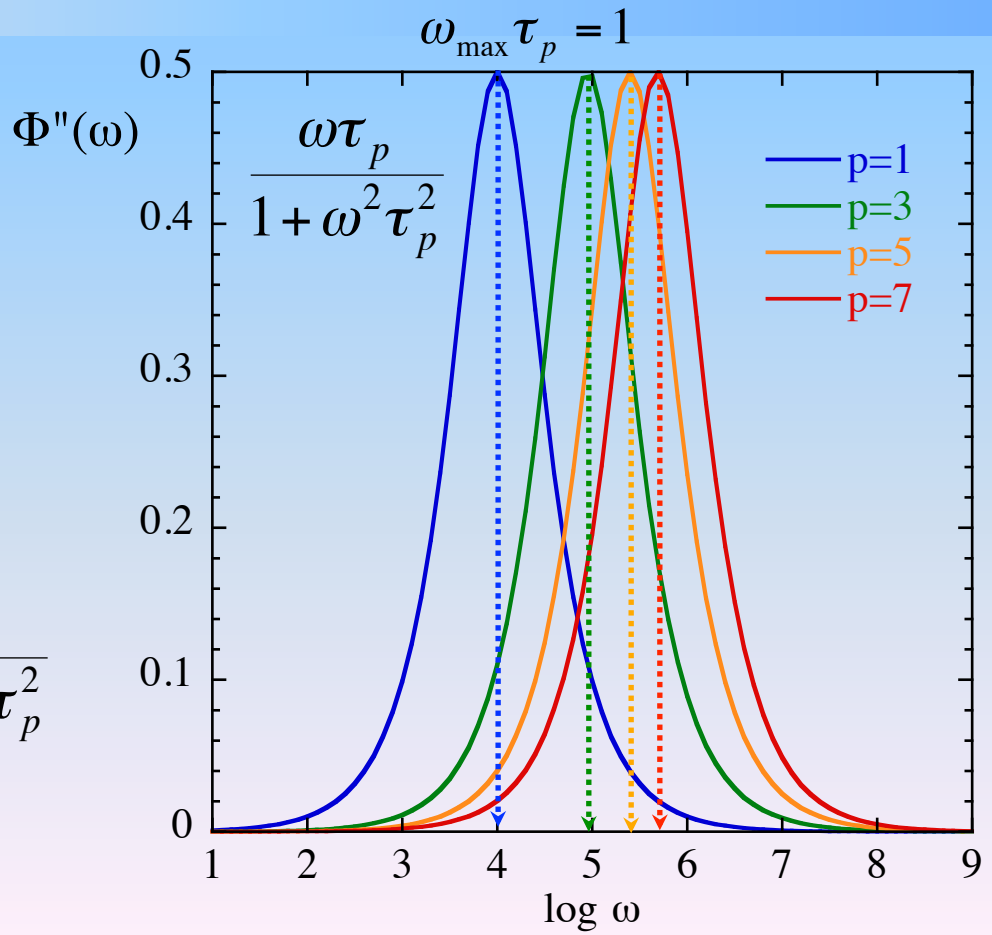

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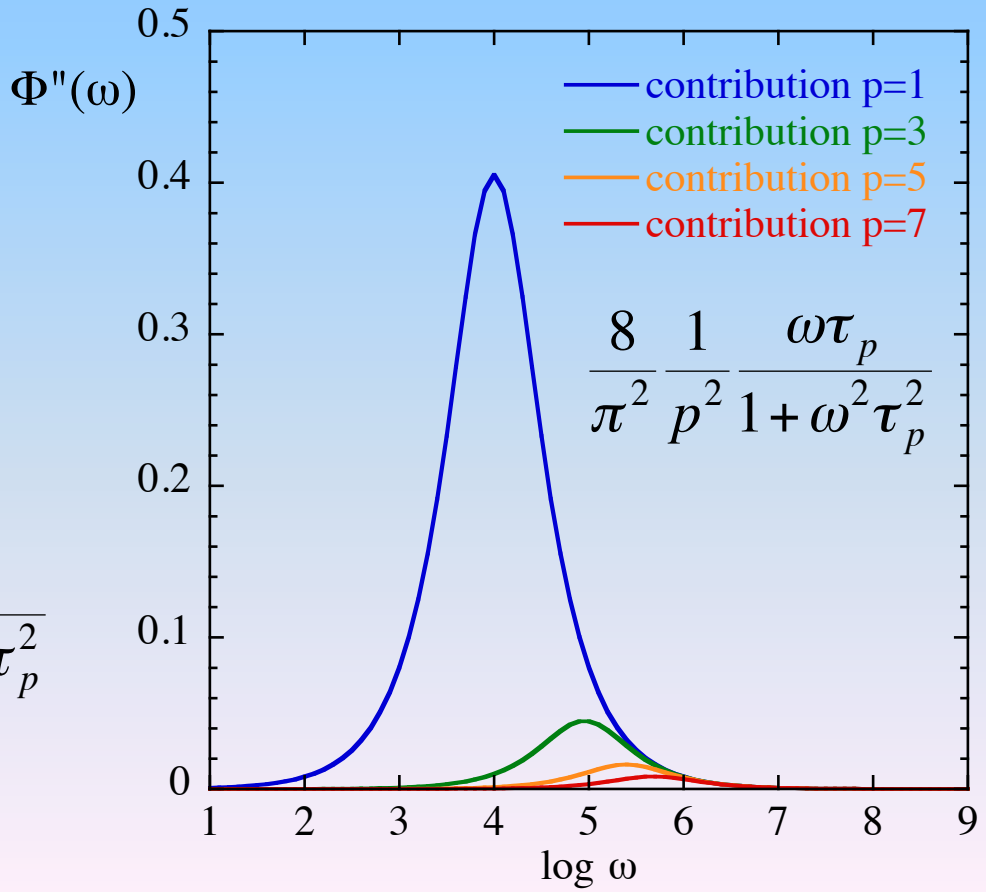

Large Scale Dynamics of Polymer Melts

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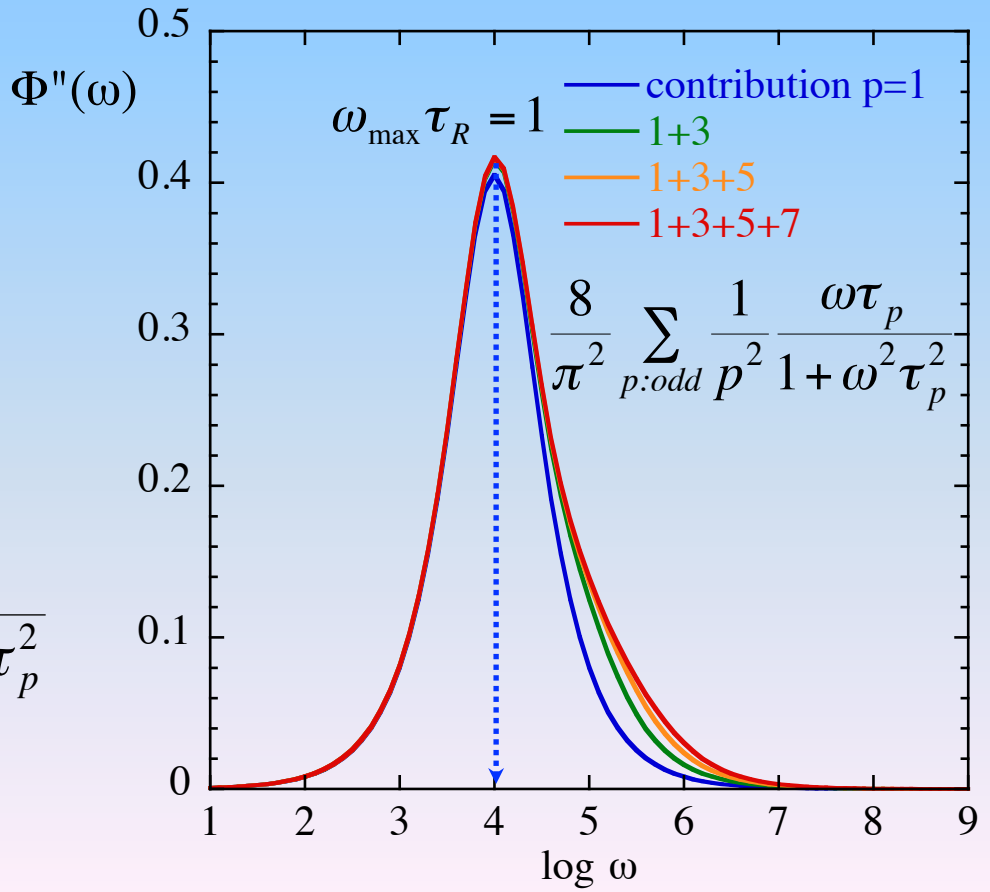
Frequency domain:

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

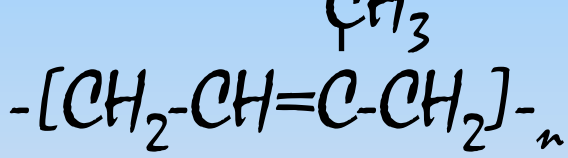


Large Scale Dynamics of Polymer Melts

The Rouse Model: Experimental evidences

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

polyisoprene



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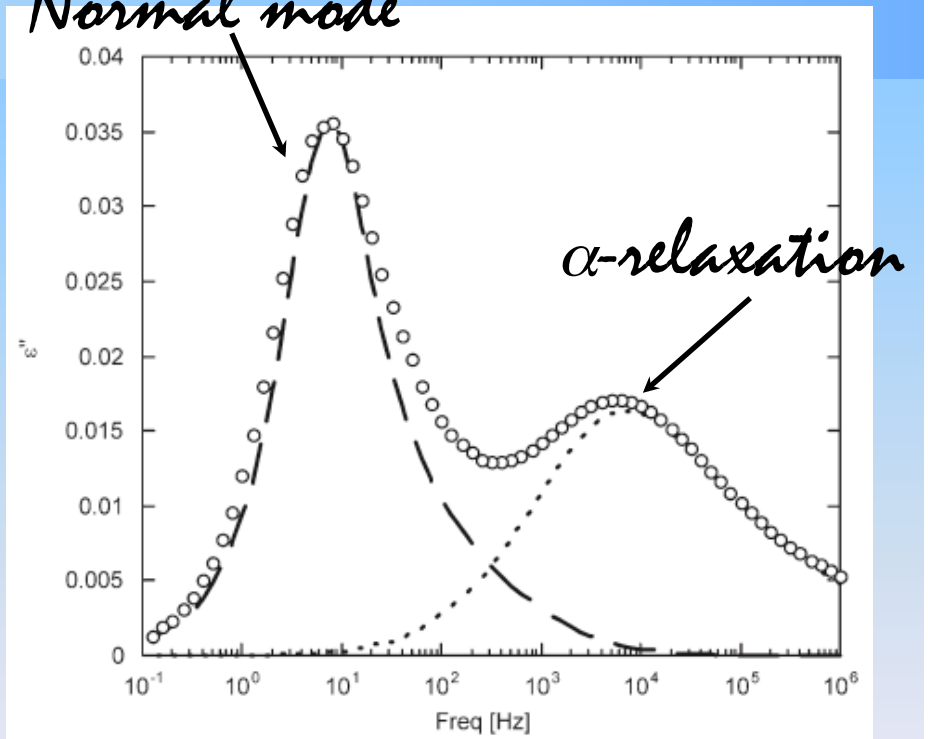


Figure 7. Rouse model prediction without taking sample polydispersity into account (dashed line) compared to BDS data points. The dotted line represents the modeled contribution of the α-relaxation (see text).

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

$$-[CH_2\text{-}CH{=}C(CH_3)\text{-}CH_2]-_n$$

Frequency domain:

Including polydispersity

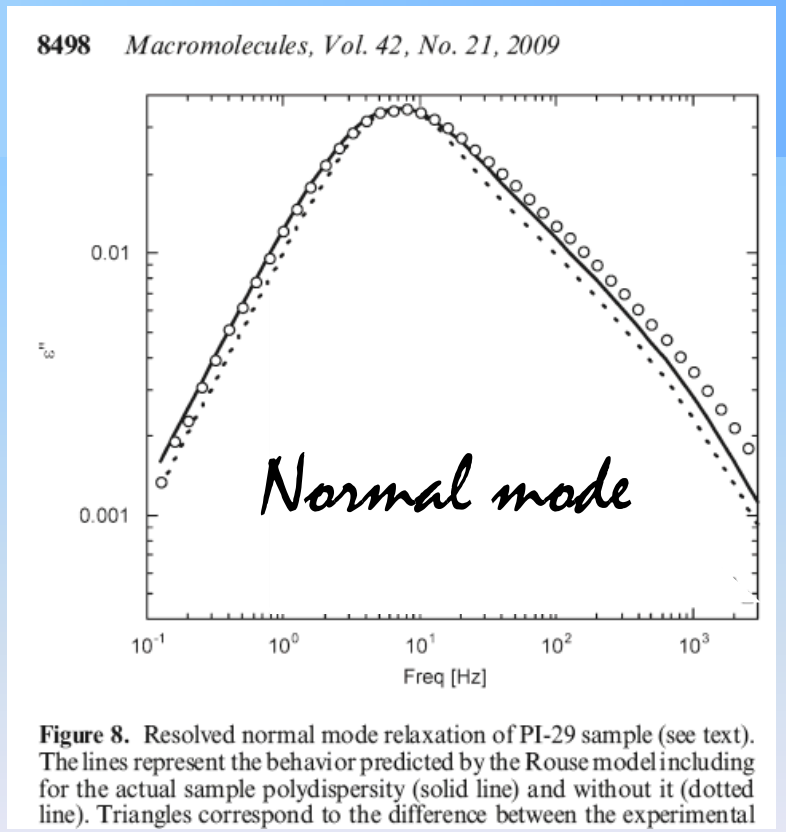


Figure 8. Resolved normal mode relaxation of PI-29 sample (see text). The lines represent the behavior predicted by the Rouse model including for the actual sample polydispersity (solid line) and without it (dotted line). Triangles correspond to the difference between the experimental

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

Large Scale Dynamics of Polymer Melts

The Rouse Model

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 21, NUMBER 7 JULY, 1953

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

PRINCE E. ROUSE, JR.
The Franklin Institute, Laboratories for Research and Development, Philadelphia, Pennsylvania

(Received January 27, 1953)

The necessary coordination of the motions of different parts of a polymer molecule is made the basis of a theory of the linear viscoelastic properties of dilute solutions of coiling polymers. This is accomplished by use of the concept of the submolecule, a portion of polymer chain long enough for the separation of its ends to approximate a Gaussian probability distribution. The configuration of a submolecule is specified in terms of the vector which corresponds to its end-to-end separation. The configuration of a molecule which contains N submolecules is described by the corresponding set of N vectors.

The action of a velocity gradient disturbs the distribution of configurations of the polymer molecules away from its equilibrium form, storing free energy in the system. The coordinated thermal motions of the segments cause the configurations to drift toward their equilibrium distribution. The coordination is taken into account by the mathematical requirement that motions of the atom which joins two submolecules change the configurations of both submolecules. By means of an orthogonal transformation of coordinates, the coordination of all the motions of the parts of a molecule is resolved into a series of modes. Each mode has a characteristic relaxation time. The theory produces equations by means of which the relaxation times, the components of the complex viscosity, and the components of the complex rigidity can be calculated from the steady flow viscosities of the solution and the solvent, the molecular weight and concentration of the polymer, and the absolute temperature.

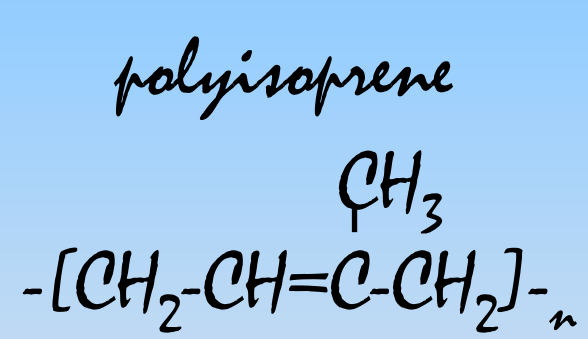
Limitations of the theory may arise from the exclusion from consideration of (1) very rapid relaxation processes involving segments shorter than the submolecule and (2) the obstruction of the motion of a segment by other segments with which it happens to be in contact. Another possible cause of disagreement between the theory and experimental data is the polydispersity of any actual polymer; this factor is important because the calculated relaxation times increase rapidly with increasing molecular weight.

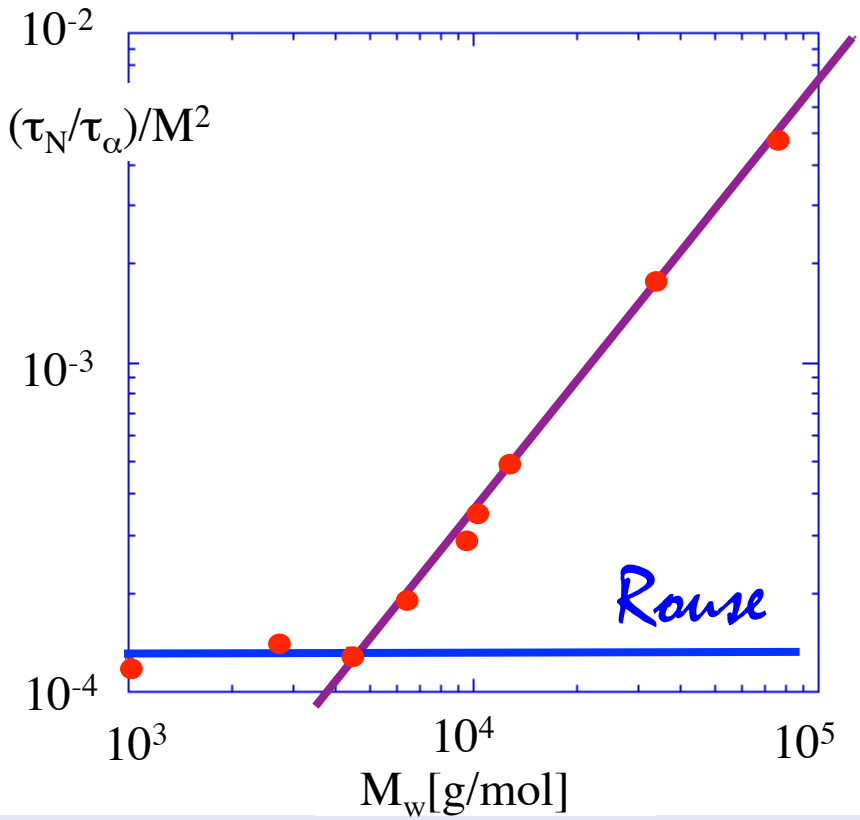
Large Scale Dynamics of Polymer Melts

The Rouse Model: Experimental evidences

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

polyisoprene





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

Riedel Clement[1,2,*], Alegria Angel[1], Tordjeman Philippe[2], Colmenero Juan[1]

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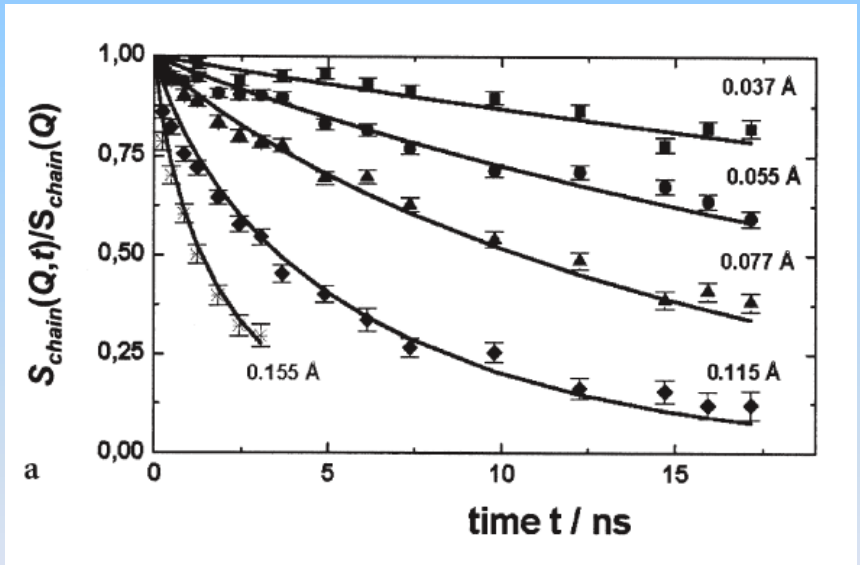
* Correspondant author: riedel@ies.univ-montp2.fr

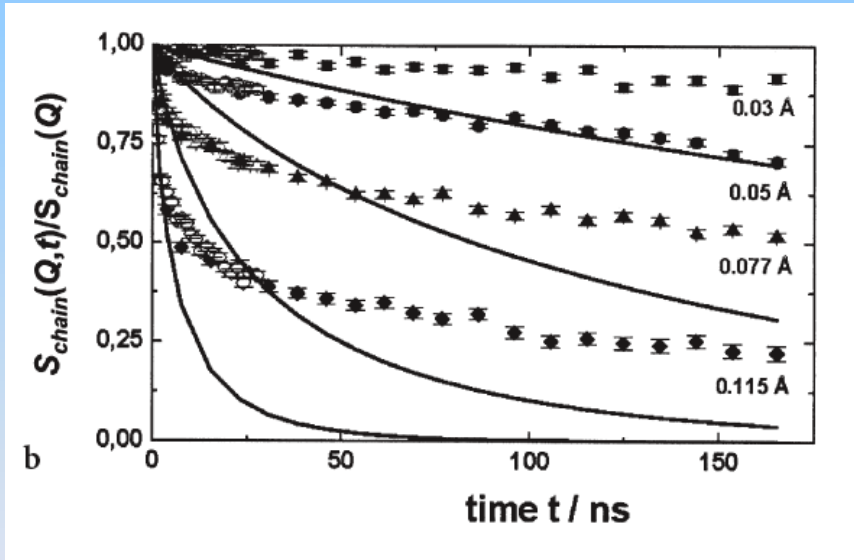
The Rouse model fails for very high molecular weights!

Large Scale Dynamics of Polymer Melts

Entanglements: Experimental evidences

Dynamic structure factor





M_w=2000g/mol (n~70)

M_w=14200g/mol (n~500)

polyethylene $-[CH_2-CH_2]-_n$

Large Scale Dynamics of Polymer Melts

The Rouse Model

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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!

Large Scale Dynamics of Polymer Melts

Generalized Langevin Equation (GLE)

Models based on GLE: Renormalized Rouse Models (RRM)

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

Problems:

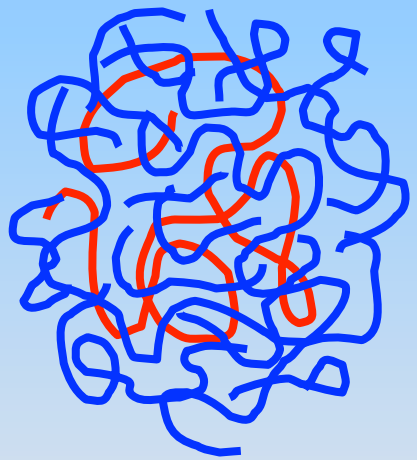
How to construct a **Memory function** from first principles

Until now only phenomenological approaches

Large Scale Dynamics of Polymer Melts

Entanglements: tube/reptation model

The 'tube' concept

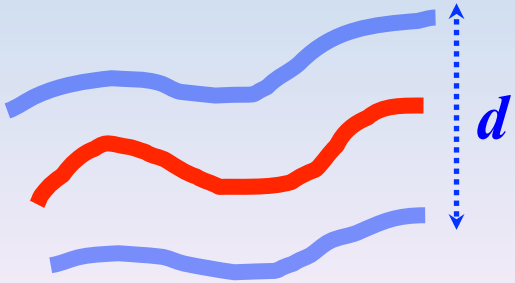


Let's assume:

- tagged chain mobile
- rest of the chains (matrix) fixed

↓

Chain motion restricted to a tube-like region



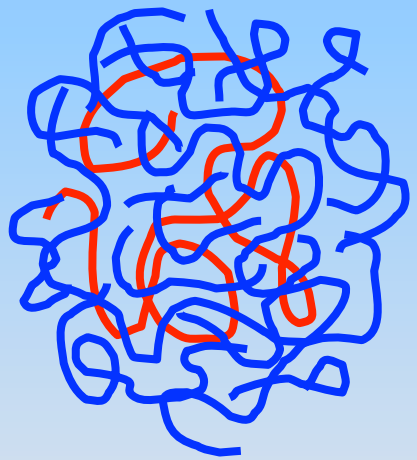
Tube diameter $d \sim 2d_{max}$

$$d_{max} = \frac{2\pi}{Q_{max}}$$ Inter-macro-molecular distances

Large Scale Dynamics of Polymer Melts

Entanglements: tube/reptation model

The 'tube' concept

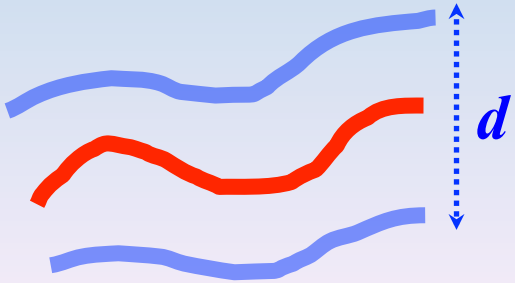


Let's assume:

- tagged chain mobi
- rest of the chains

↓

Chain motion restri



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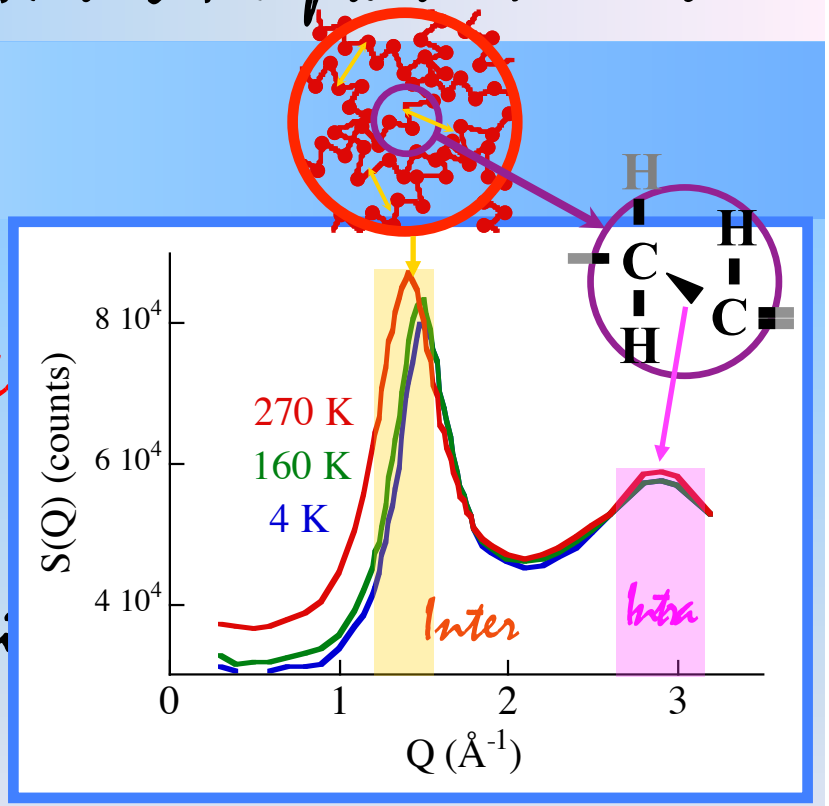


$Q_{max} \approx 1 Å^{-1}$

↓

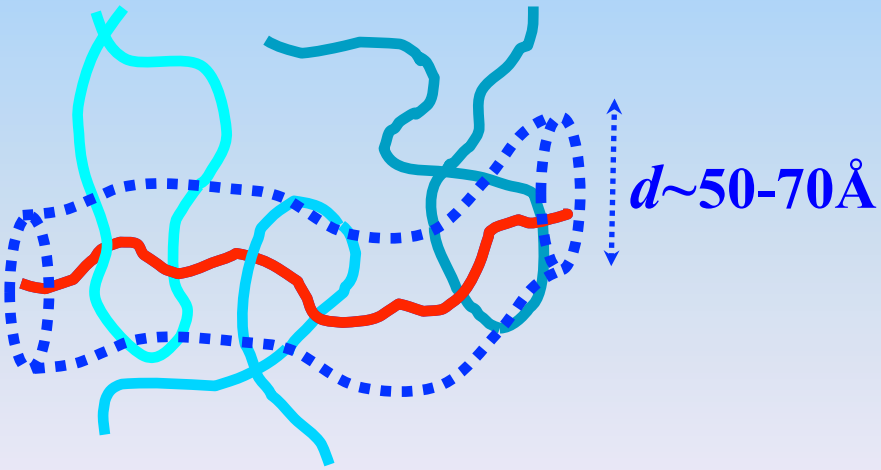
$d \approx 6 Å$

Large Scale Dynamics of Polymer Melts

Entanglements: tube/reptation model

Edwards & deGennes

Real situation:
all chains move!



Intermolecular interactions,
uncrossability
and chain connectivity

↓

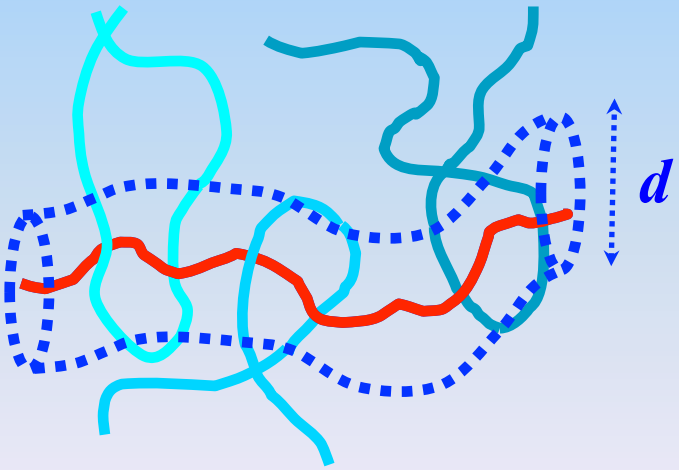
FICTITIOUS TUBE along the
contour length of a tagged chain

Large Scale Dynamics of Polymer Melts

Entanglements: tube/reptation model

Edwards & deGennes

Real situation:
all chains move!



FICTITIOUS TUBE along the contour length of a tagged chain

↓

The 'tube' becomes effective at $t \geq \tau_e$

$$\left\langle r^2(\tau_e) \right\rangle \approx d^2 \qquad \left\langle r^2(t) \right\rangle \propto t^{1/2} \quad \text{(Rouse)}$$

$$\Downarrow$$

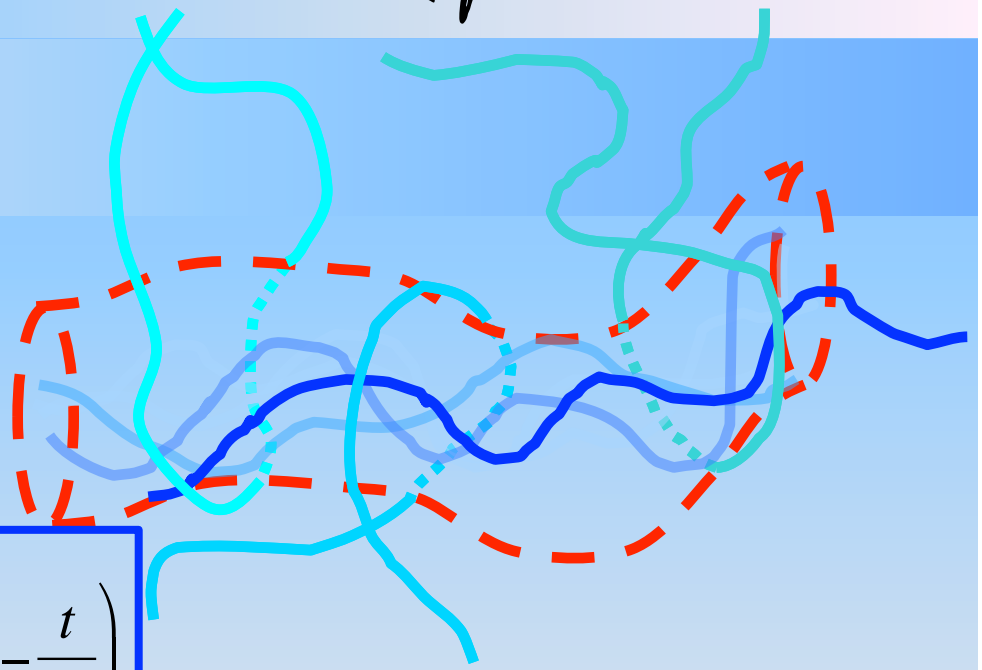
$\tau_e \propto d^4$ Independent of N!!

Large Scale Dynamics of Polymer Melts

Reptation Model

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

'Survival probability of unrelaxed chain segments within the tube'



$$\mu_D(t) = \frac{\langle \vec{R}_N(t)\vec{R}_N(0)\rangle}{\langle \vec{R}_N^2(0)\rangle} = \frac{8}{\pi^2}\sum_{p:odd}\frac{1}{p^2}\exp\left(-\frac{t}{\tau_d}\right)$$

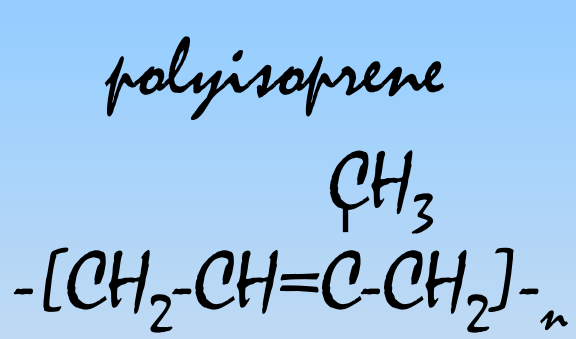
Formally equal to the Rouse expression but with $\tau_d \propto N^3$

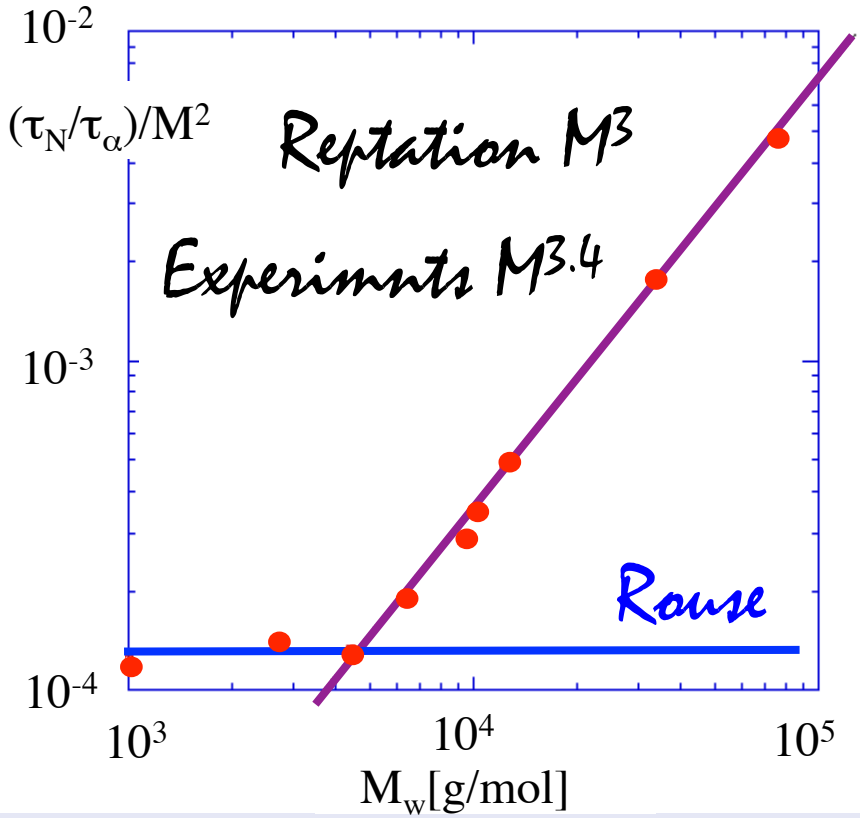
Large Scale Dynamics of Polymer Melts

Crossover from Rouse to Reptation

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

polyisoprene





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

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* Correspondant author: riedel@ies.univ-montp2.fr

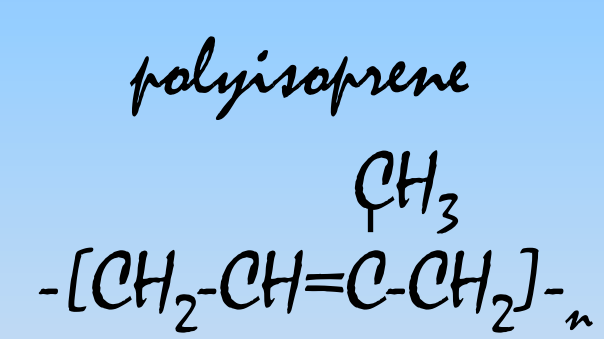
The Rouse model fails for very high molecular weights!

Large Scale Dynamics of Polymer Melts

High molecular weight crossover: Pure Reptation ?

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

polyisoprene



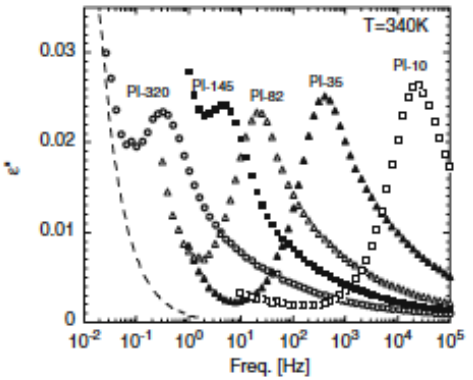
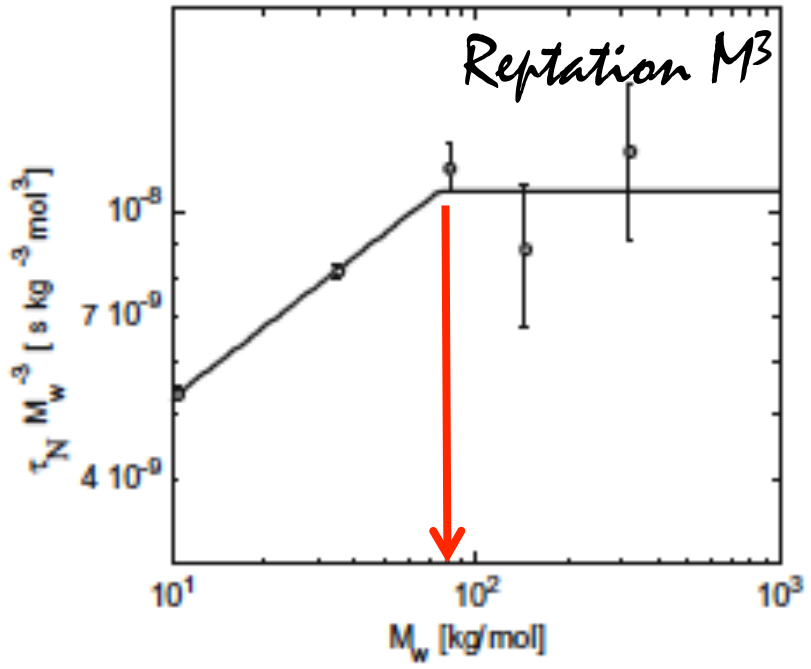


Fig. 3 Normal mode of the high molecular weight PI samples. *Dashed line* represents the calculated conductivity contribution to the dielectric losses for the PI-320 sample

Rheol Acta (2010) 49:507–512



Rheol Acta (2010) 49:507–512
DOI 10.1007/s00397-010-0433-1

ORIGINAL CONTRIBUTION

High and low molecular weight crossovers in the longest relaxation time dependence of linear cis-1,4 polyisoprene by dielectric relaxations

Clément Riedel · Angel Alegría · Philippe Tordjeman · Juan Colmenero

Large Scale Dynamics of Polymer Melts

Entanglements: tube/reptation model

Summary

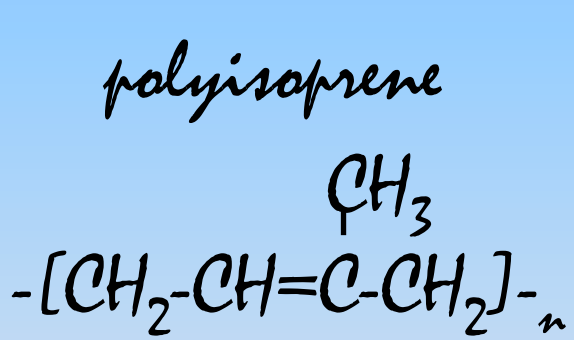
- Tube/reptation models capture the main entanglement effects
- Corrections are usually needed to describe experimental data:
  - Contour length fluctuations
  - Constraint release
  - ...
- However, whether the tube picture is indeed correct still remains a matter for debate

Large Scale Dynamics of Polymer Melts

Temperature dependence

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

polyisoprene



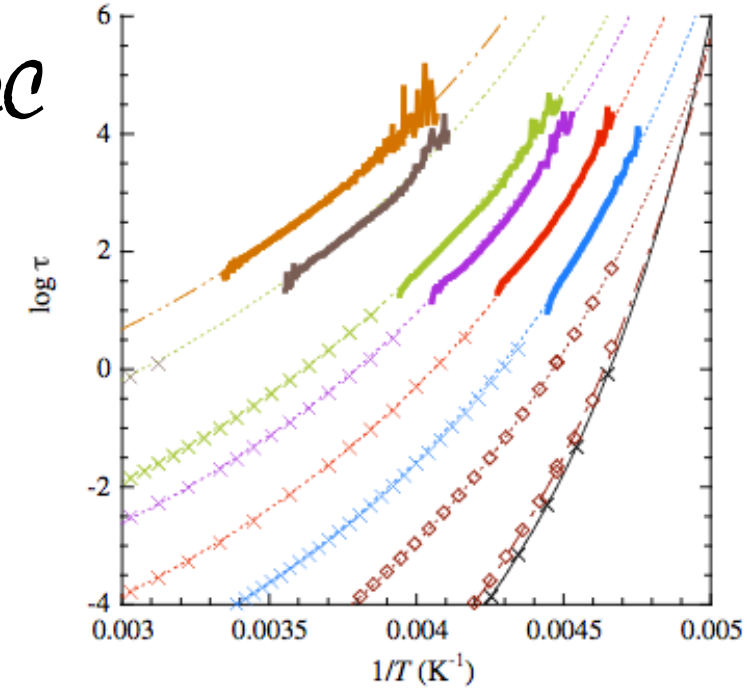


FIG. 2 (color online). From left to right: Times for chain relaxation of PI400 ($M_w = 400$ kDa), PI320 ($M_w = 320.2$ kDa), PI82 ($M_w = 82$ kDa), PI53 ($M_w = 53$ kDa), PI19 ($M_w = 19$ kDa), PI10 ($M_w = 10.5$ kDa), PI1 ($M_w = 1.2$ kDa), and α relaxation of PI1 and PI82. Data for PI1 were shifted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

PRL 113, 078302 (2014) PHYSICAL REVIEW LETTERS week ending 15 AUGUST 2014

Polymer Chain Dynamics: Evidence of Nonexponential Mode Relaxation Using Thermally Stimulated Depolarization Current Techniques

S. Arrese-Igor,[1] A. Alegría,[1,2] and J. Colmenero[1,2,3]
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[2]*Departamento de Física de Materiales UPV/EHU, Apartado 1072, 20080 San Sebastián, Spain*
[3]*Donostia International Physics Center, Paseo Manuel Lardizabal 4, 20018 San Sebastián, Spain*
(Received 28 March 2014; published 14 August 2014)

Large Scale Dynamics of Polymer Melts

ACS Macro Letters
Letter
pubs.acs.org/macroletters

Chain Dynamics on Crossing the Glass Transition: Nonequilibrium Effects and Recovery of the Temperature Dependence of the Structural Relaxation

S. Arrese-Igor,*[†] A. Alegría,[†,‡] and J. Colmenero[†,‡,§]

Temperature dependence

Following $\langle \vec{R}_N(t)\vec{R}_N(0)\rangle$ and α-relaxation by DS and TSDC

polyisoprene

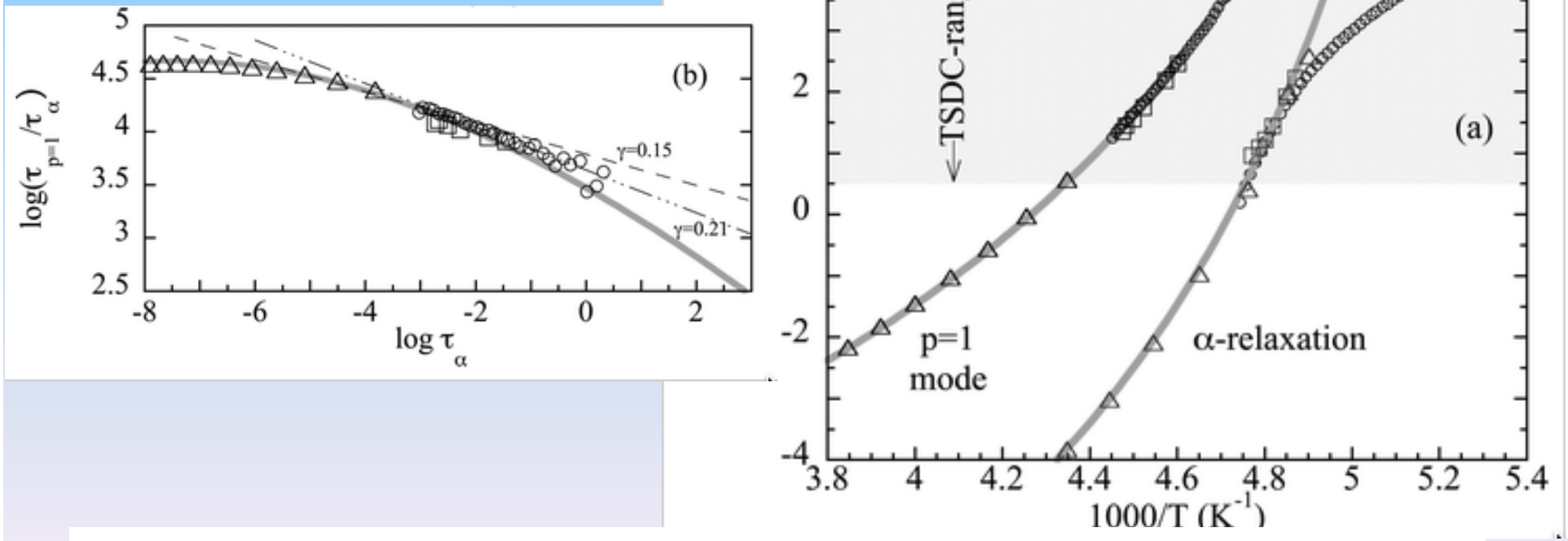


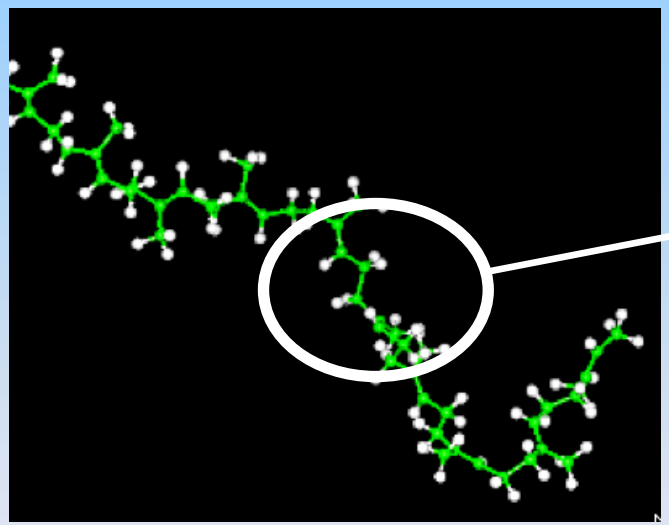
Figure 2. Panel (a) τ(*T*) for the *p* = 1 chain mode and α-relaxation of PI10 and (b) the ratio $\tau_{p=1}/\tau_\alpha$. (Δ) isothermal measurements; (□) variable rate global TSDC; (○) PP-TSDC. The lines in (a) are WLF and VFT law fits of the isothermal measurements and their ratio in (b). Dashed and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

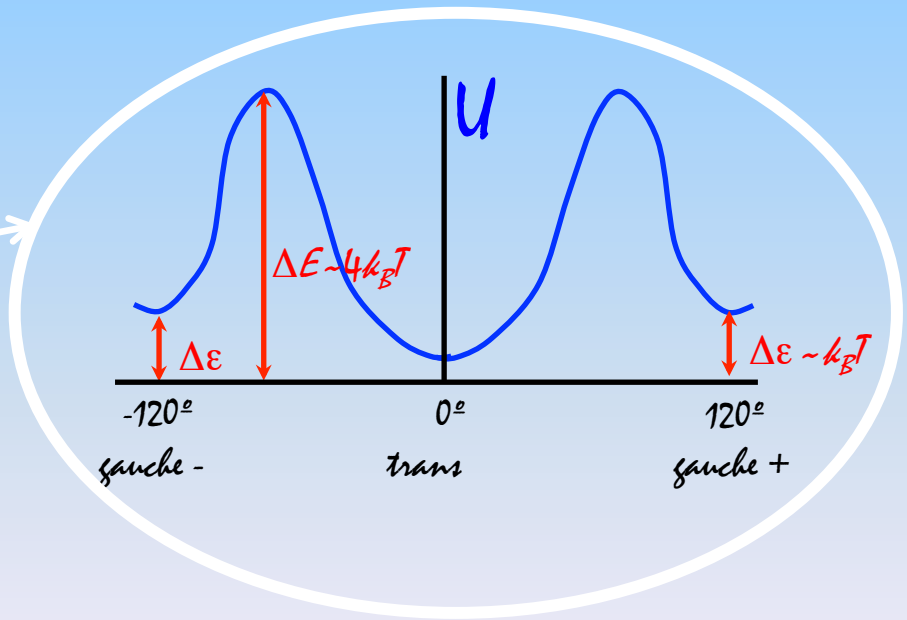
Chain dynamics: Determination of monomeric friction

Molecular Dynamics Simulations

Rouse Model fails at high-Q (short distances)

Local potentials and chain stiffness enter the game!!



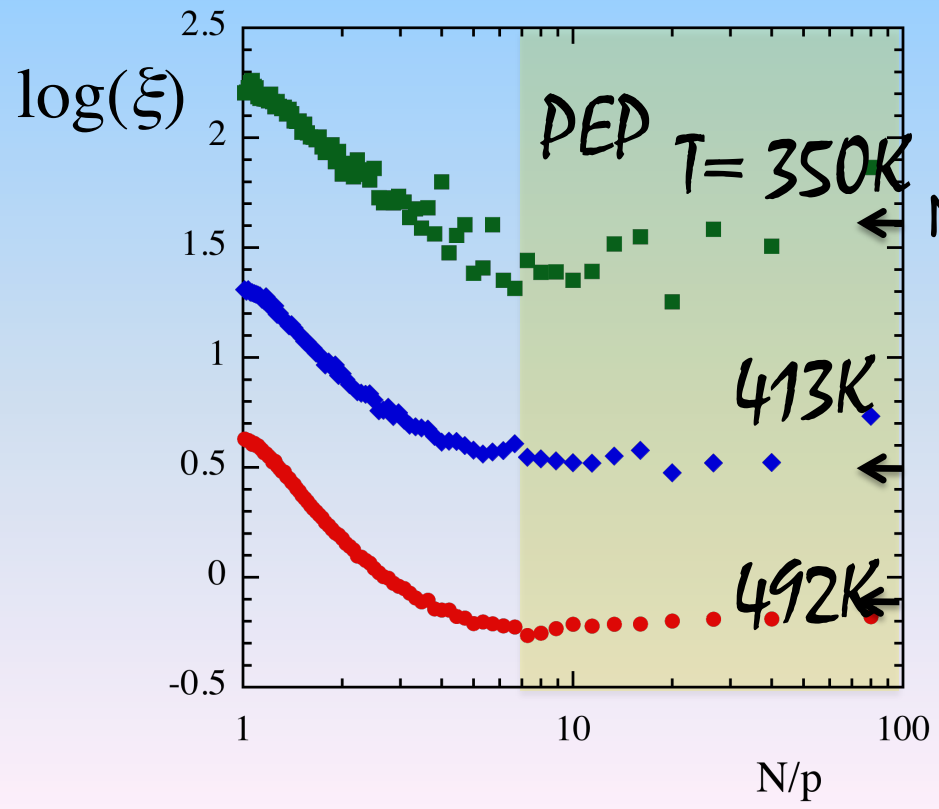


Chain dynamics: Determination of monomeric friction

Molecular Dynamics Simulations

Rouse Model fails at high-Q (short distances)

Friction depends on the wavelength of chain modes



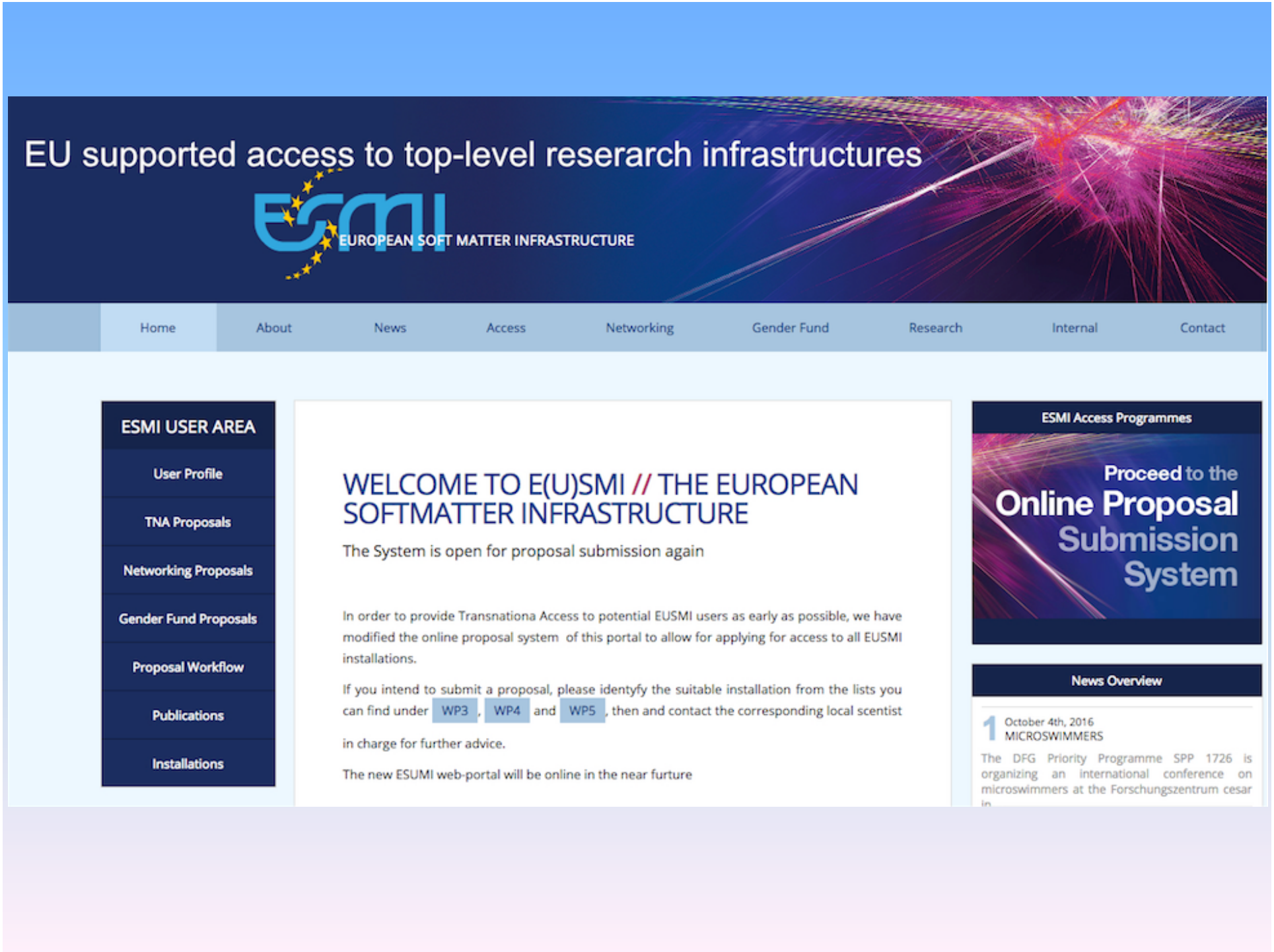
← Neutron scattering values

Large Scale Dynamics of Polymer Melts

Advanced Topics

Following $\left\langle \vec{R}_N(t)\vec{R}_N(0)\right\rangle$ and α-relaxation by DS and TSDC

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