Polymers in Soft Matter: From Structure to Emerging Applications

Part 2: Dynamics of Polymer Systems

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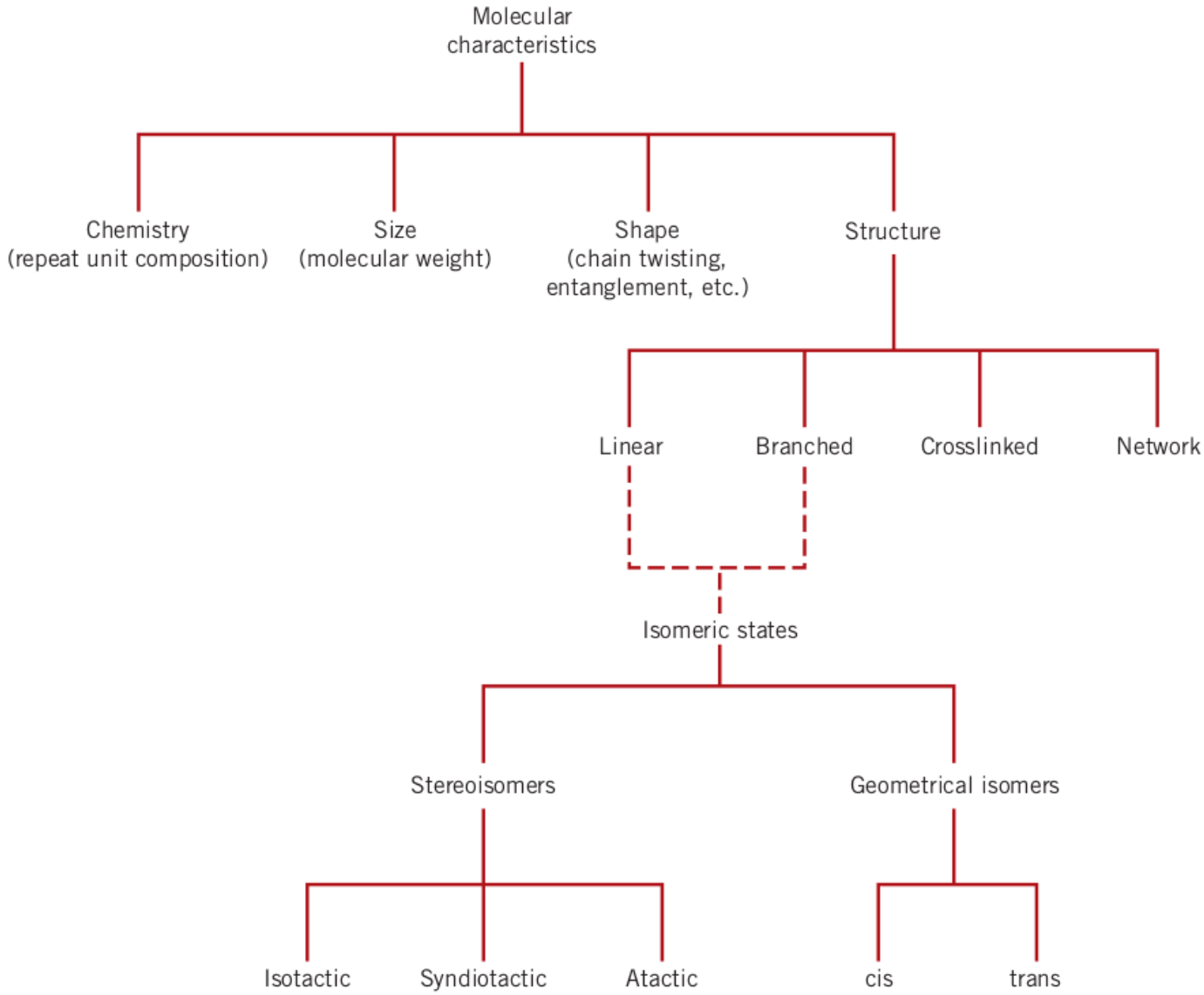
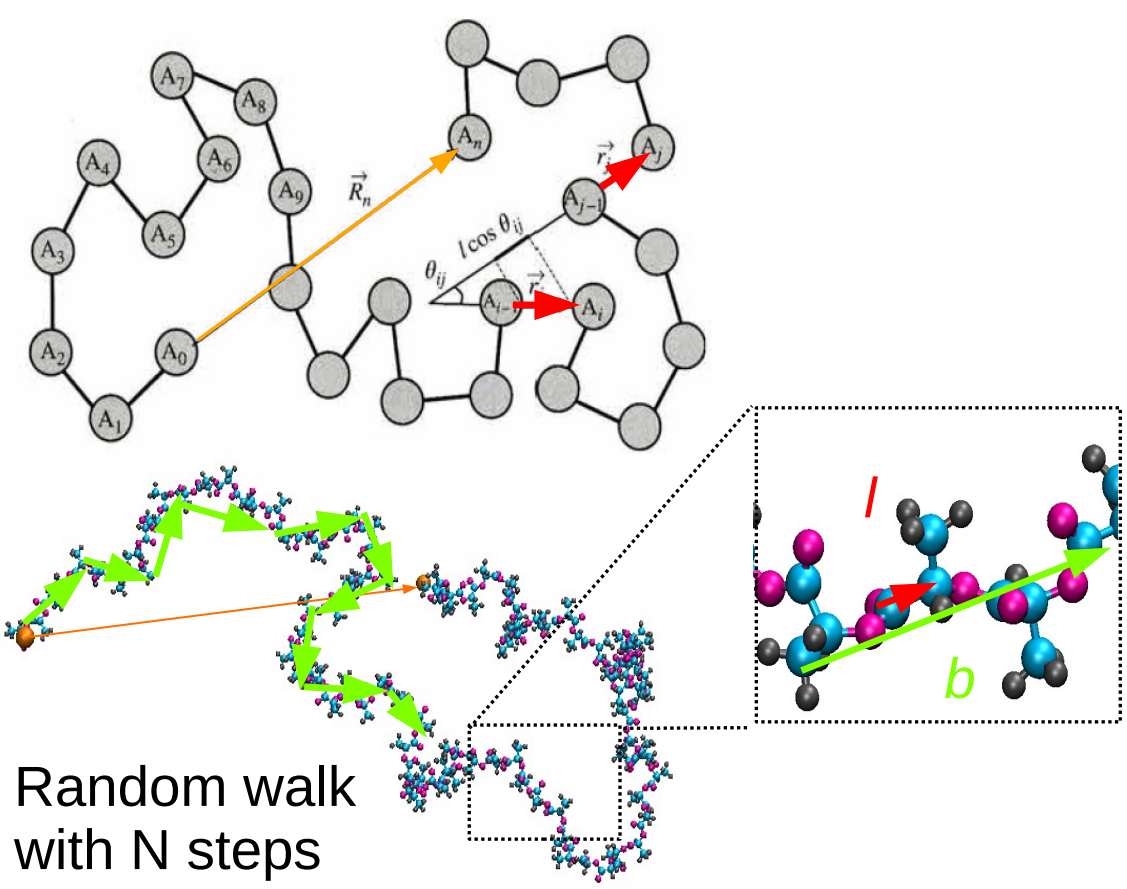


[1] Callister, W. D., Rethwisch, D. G. (2018). Materials Science and Engineering: An Introduction (10th ed.). Hoboken, NJ: Wiley

Conformation of an ideal chain



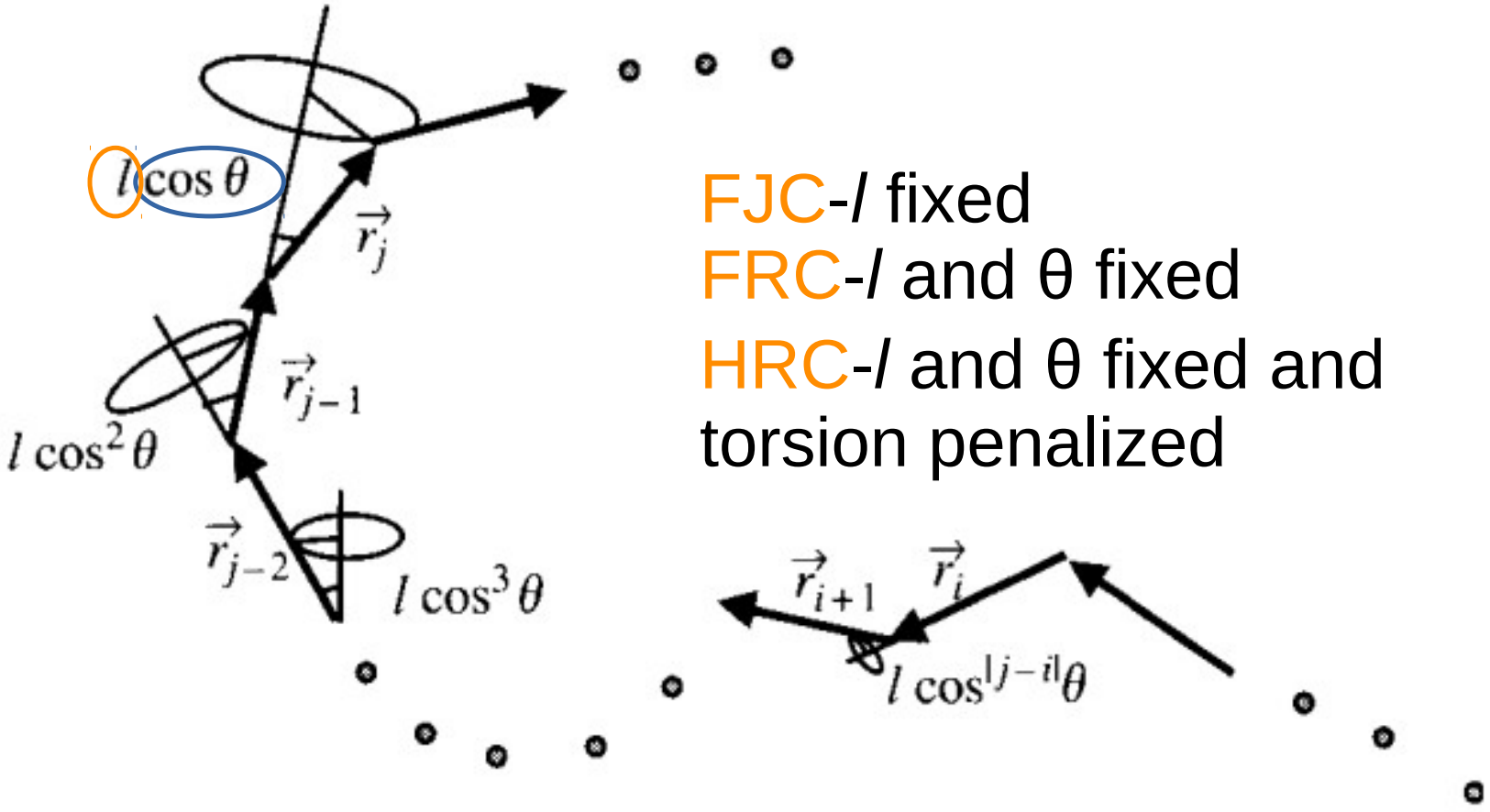
Random walk with N steps

- $R_g^2 = \frac{\sum_i^N m_i (R_i - R_{cm})^2}{\sum_i^N m_i}$
- $\langle R^2 \rangle = C_\infty n l^2 = N b^2$
- b Kuhn length
- ideal Gaussian behaviour

$$\langle R_g^2 \rangle = \frac{\langle R^2 \rangle}{6}$$

[1] Rubinstein, M.; Colby, R. H., Polymer physics. Oxford university press, 2003.

Ideal models



FJC-*l* fixed
FRC-*l* and θ fixed
HRC-*l* and θ fixed and torsion penalized

+ Worm-like chain model for semiflexible polymers

[1] Rubinstein, M.; Colby, R. H., Polymer physics. Oxford university press, 2003.

Summary of the methods for real chains

- estimation of stiffness and size:
  - scattering techniques
  - viscometry
  - atomic force microscopy
  - simulations
  - Rotation Isomeric State (RIS) model
- molecular weight:
  - gel permeation chromatography
  - static light scattering (Zimm plot)
  - osmometry
  - nuclear magnetic resonance (functional-group analysis)

$\Rightarrow$ Real chains: solvent effects, temperature effects, deviations in architecture and composition, aggregation, model parameters for a given chemistry

Theoretical models for polymers

Parameters

- local stiffness
  - characteristic ratio
  - Kuhn length
  - persistence length
- size: radius of gyration, end-to-end distance
- characteristic times
- other characteristics: T_g, T_m, plateau modulus etc.

Length and time scales in polymers

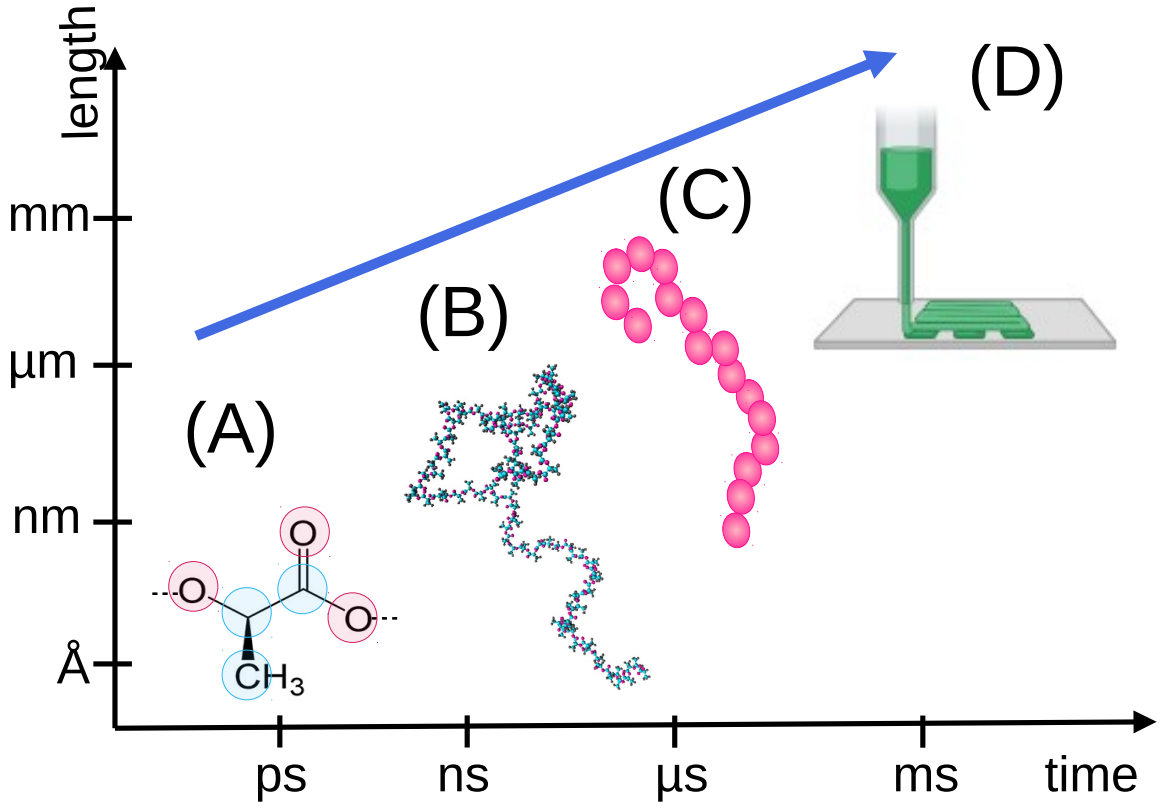
Scales:

(A) quantum

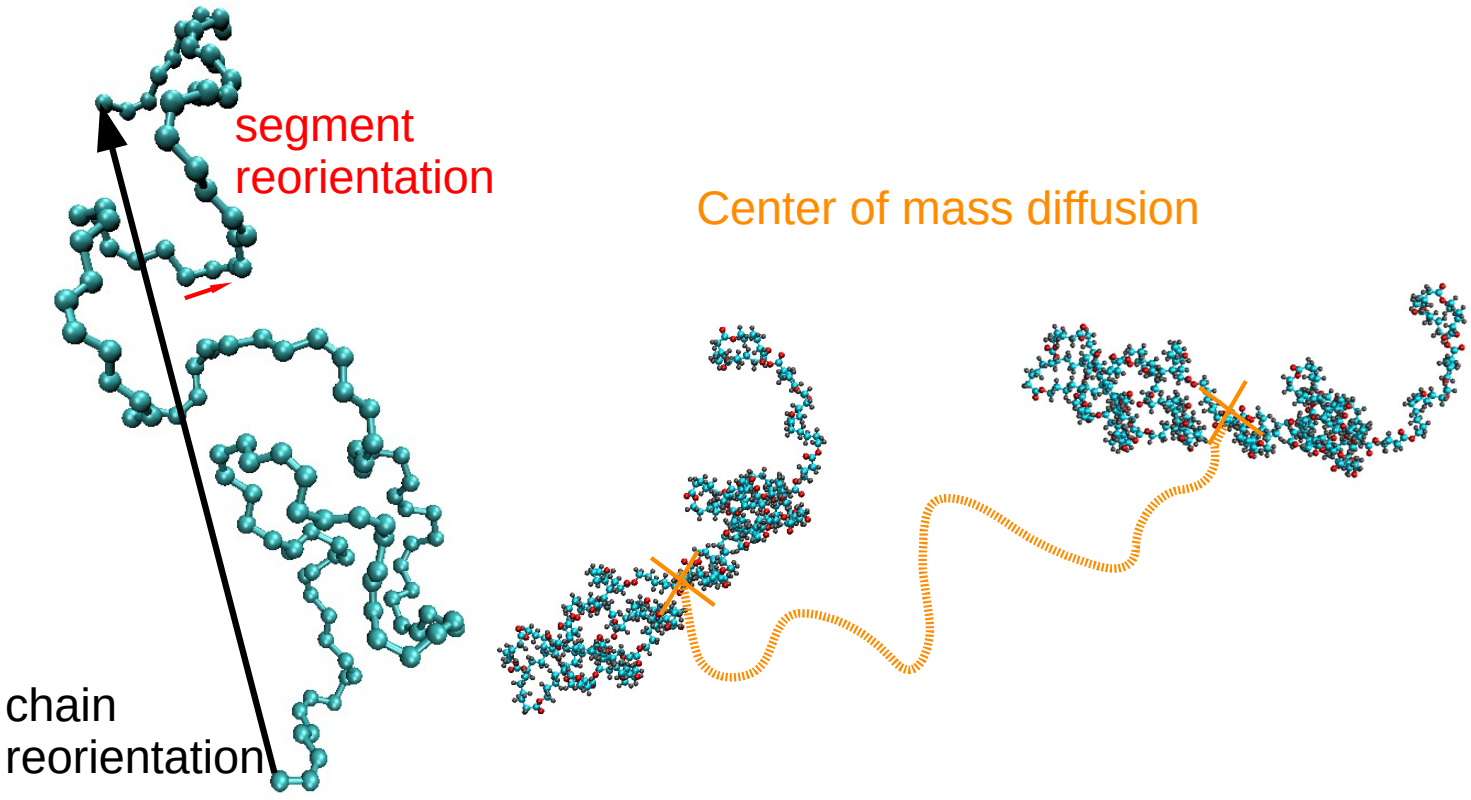
(B) atomistic and monomeric

(C) molecular

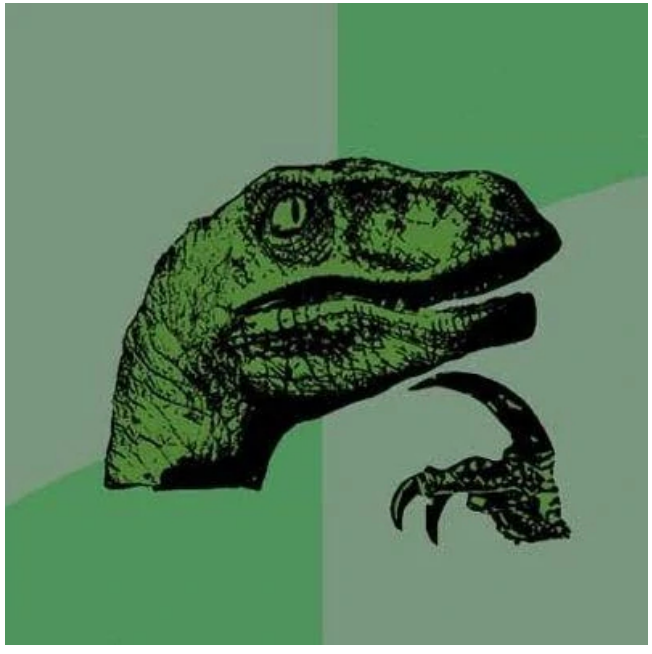
(D) continuum



Rotational and translational dynamics



- Rotational: reorientation of some parts or a whole chain
- Translational: diffusion of some parts or a whole chain



If a polymer chain fully reorients over its longest relaxation time, what is the typical distance its center of mass will have diffused during this reorientation process?

Theoretical models

Solution:

- Rouse: no hydrodynamics
- Zimm: with hydrodynamics

Melt:

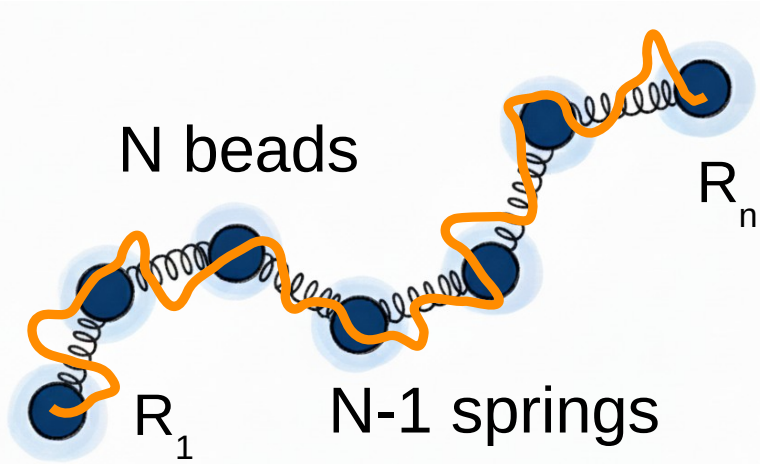
- Rouse: unentangled chains
- tube model: entangled dynamics

+ non-equilibrium dynamics (flow, turbulence, stretching)

- Finite Extensible Nonlinear Elastic (FENE) model
- tube-based constitutive models

Rouse model

- bead-spring representation
- beads with identical friction coefficient ζ
- no excluded volume
- no hydrodynamic interactions



Langevin equation:

$$\zeta \frac{d\mathbf{R}_n}{dt} = -k(-2\mathbf{R}_n - \mathbf{R}_{n+1} - \mathbf{R}_{n-1}) + \mathbf{f}_n(t), \qquad n = 2,3...N-1$$

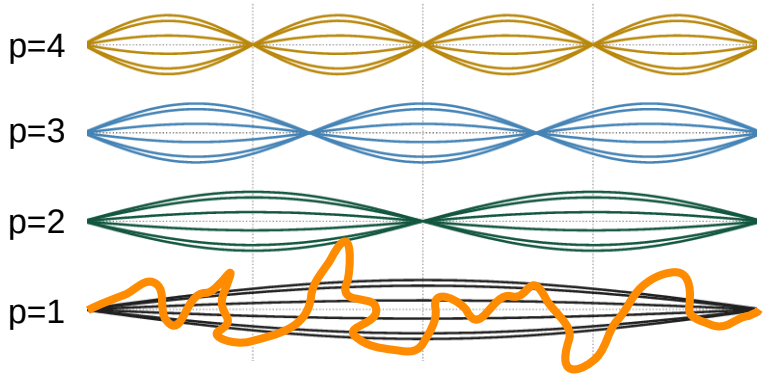
$$\zeta \frac{d\mathbf{R}_n}{dt} = -k(\mathbf{R}_1 - \mathbf{R}_2) + \mathbf{f}_n(t) \quad \zeta \frac{d\mathbf{R}_n}{dt} = -k(\mathbf{R}_N - \mathbf{R}_{N-1}) + \mathbf{f}_n(t)$$

k: spring constant, $\mathbf{f}_n(t)$: random thermal force (fluctuation–dissipation theorem)

Rouse normal modes

- normal coordinates

$$X_n = \frac{1}{N}\int_0^N dn \cos\left(\frac{p\pi n}{N}\right) R_n(t)$$



- relaxation of sections of N/p monomers, $t_p \approx t_0(\frac{N}{p})^2$
- coupled oscilators
- for p=0, CM motion

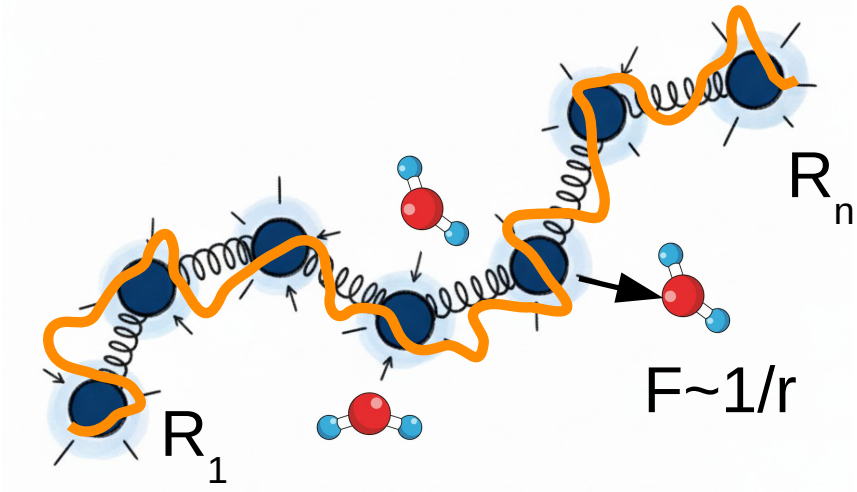
$$\tau_R = \frac{\zeta b^2}{6\pi^2 kT} N^2 \qquad D = \frac{kT}{N\zeta}$$

subdiffusive monomeric motion

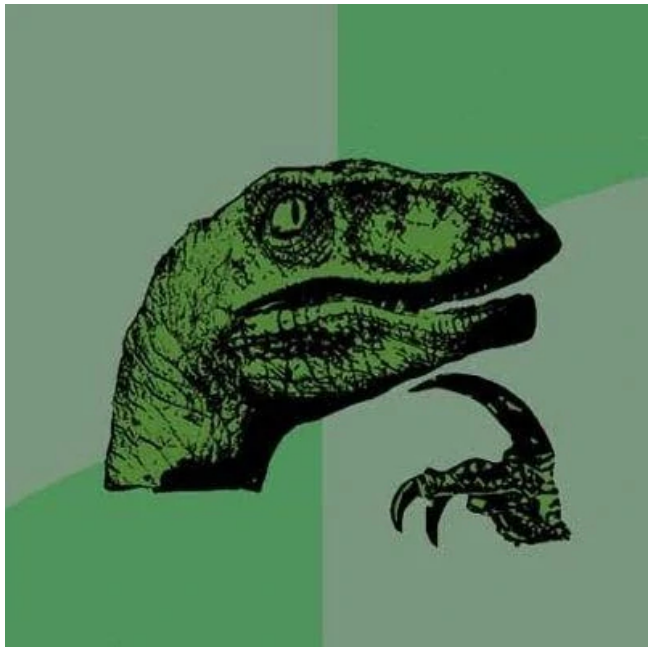
$$\langle (R_j - R_i)^2 \rangle \approx b^2 \left(\frac{t}{\tau_0}\right)^{1/2} \qquad \tau_0 < t < \tau_R$$

Zimm model

- hydrodynamic interactions included
- important in dilute solutions
- chain friction $\zeta_Z = \eta_s R$



- Zimm: $\tau_Z \propto N^{3\nu}$ ($\nu \approx 0{,}588$ in good solvent $\Longrightarrow N^{1{,}764}$)
- Rouse: $\tau_R \propto N^2$
- Zimm: $D_{cm} \propto N^{-\nu}$ (i.e., $N^{-0{,}588}$ in good solvent)
- Rouse: $D_{cm} \propto N^{-1}$

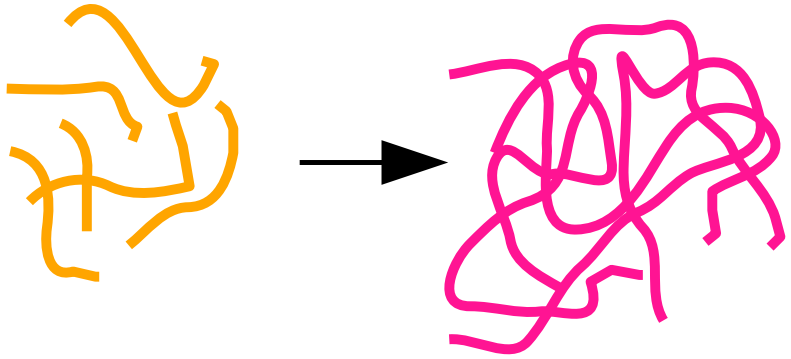


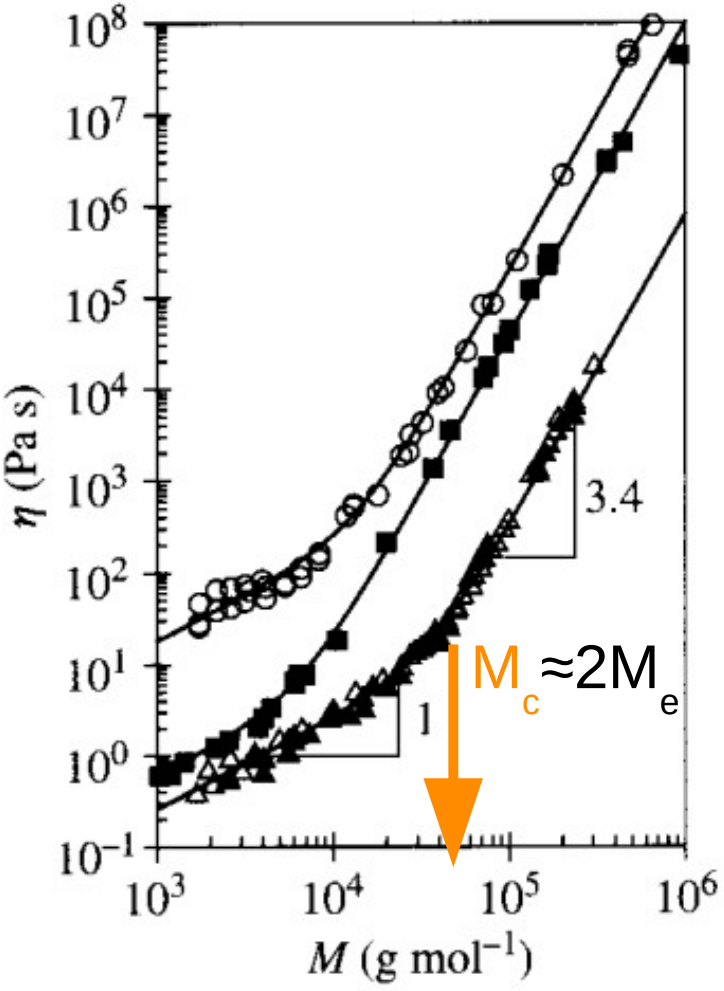
If a polymer chain fully reorients over its longest relaxation time, what is the typical distance its center of mass will have diffused during this reorientation process?Use the Einstein relation for free diffusion in 3D

$$\langle R^2(t)\rangle = 6Dt$$

Non-entangled vs. entangled polymer melts

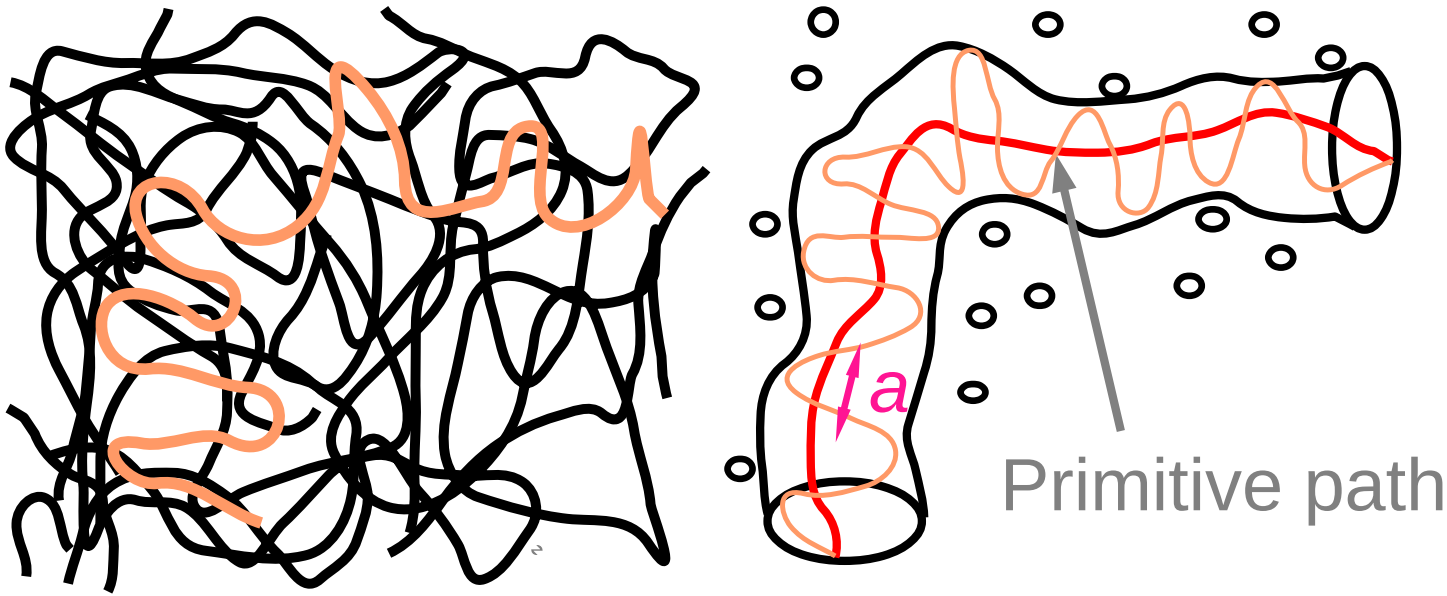
- critical molecular weight M_c





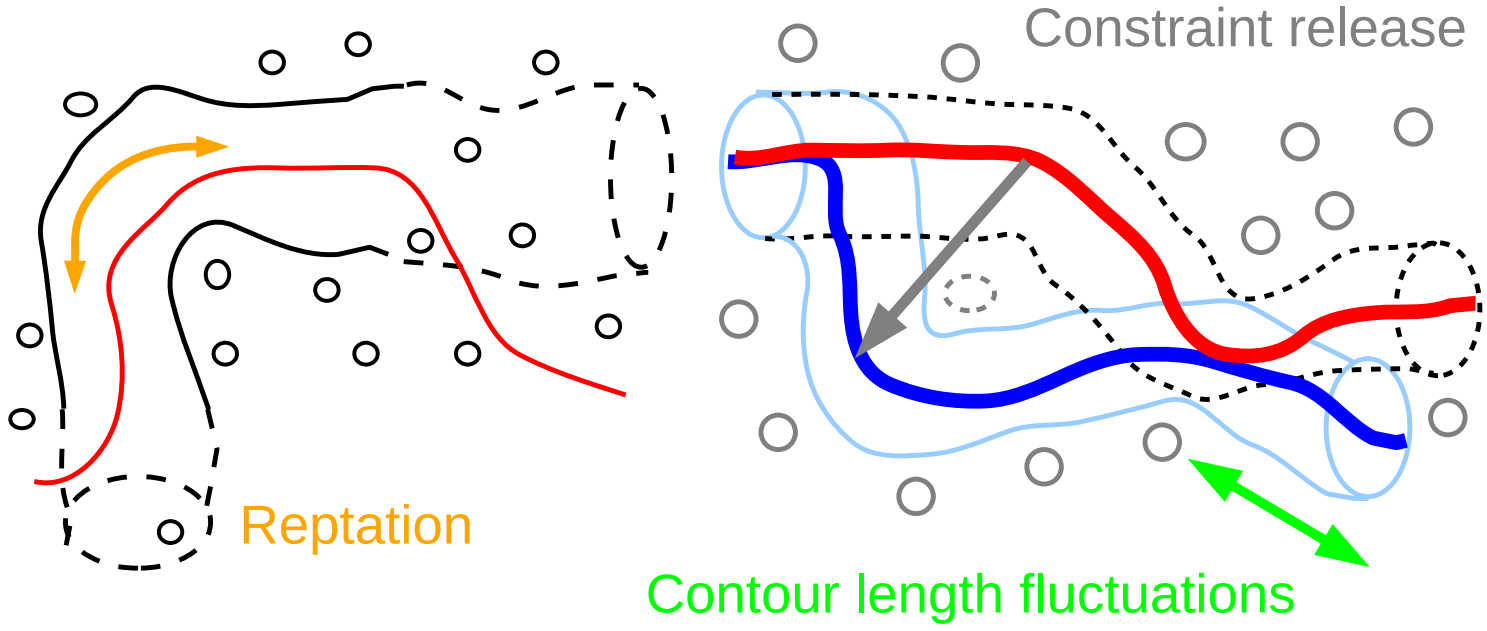
Tube model

- entanglements: topological constraints caused by the surrounding chains
- tube: mean field picture of fixed obstacles
- primitive path: N/N_e strands of a length a
- tube diameter: a, basic length scale



Relaxation in entangled systems

- reptation: main relaxation mechanism
- contour length fluctuations: correction for the fixed length of the primitive path, important in short chains
- constraint release: correction for the motion of the surrounding chains



Predictions of the tube model

- longest relaxation time (reptation time, τ_{rep}, τ_d):

$$\tau_{rep} \propto N^3$$

- center-of-mass diffusion coefficient (D):

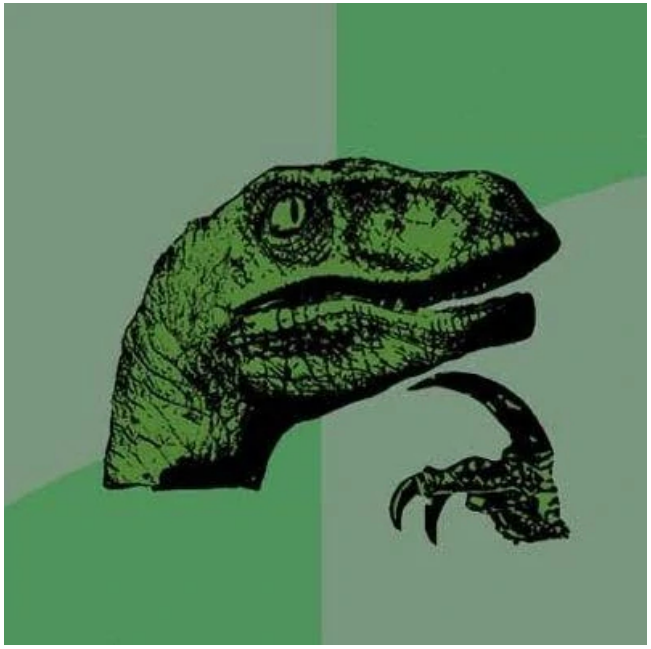
$$\text{theoretical} \quad D \propto N^{-2}$$

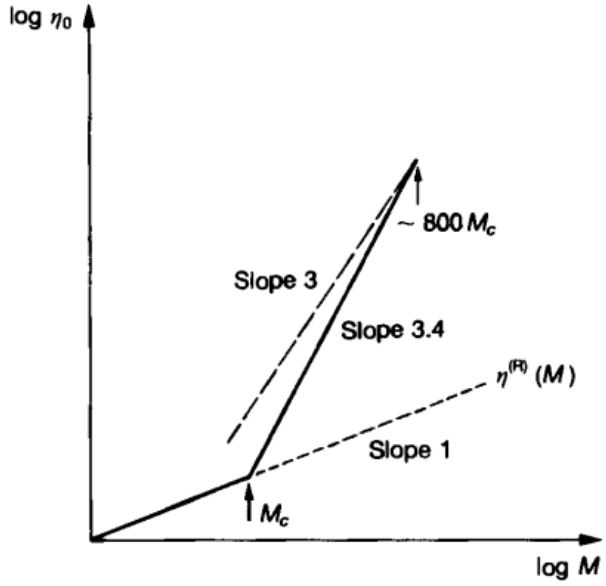
$$\text{experimental} \quad D \propto N^{-2,3}$$

- zero-shear viscosity (η_0):

$$\text{theoretical} \quad \eta_0 \propto N^3$$

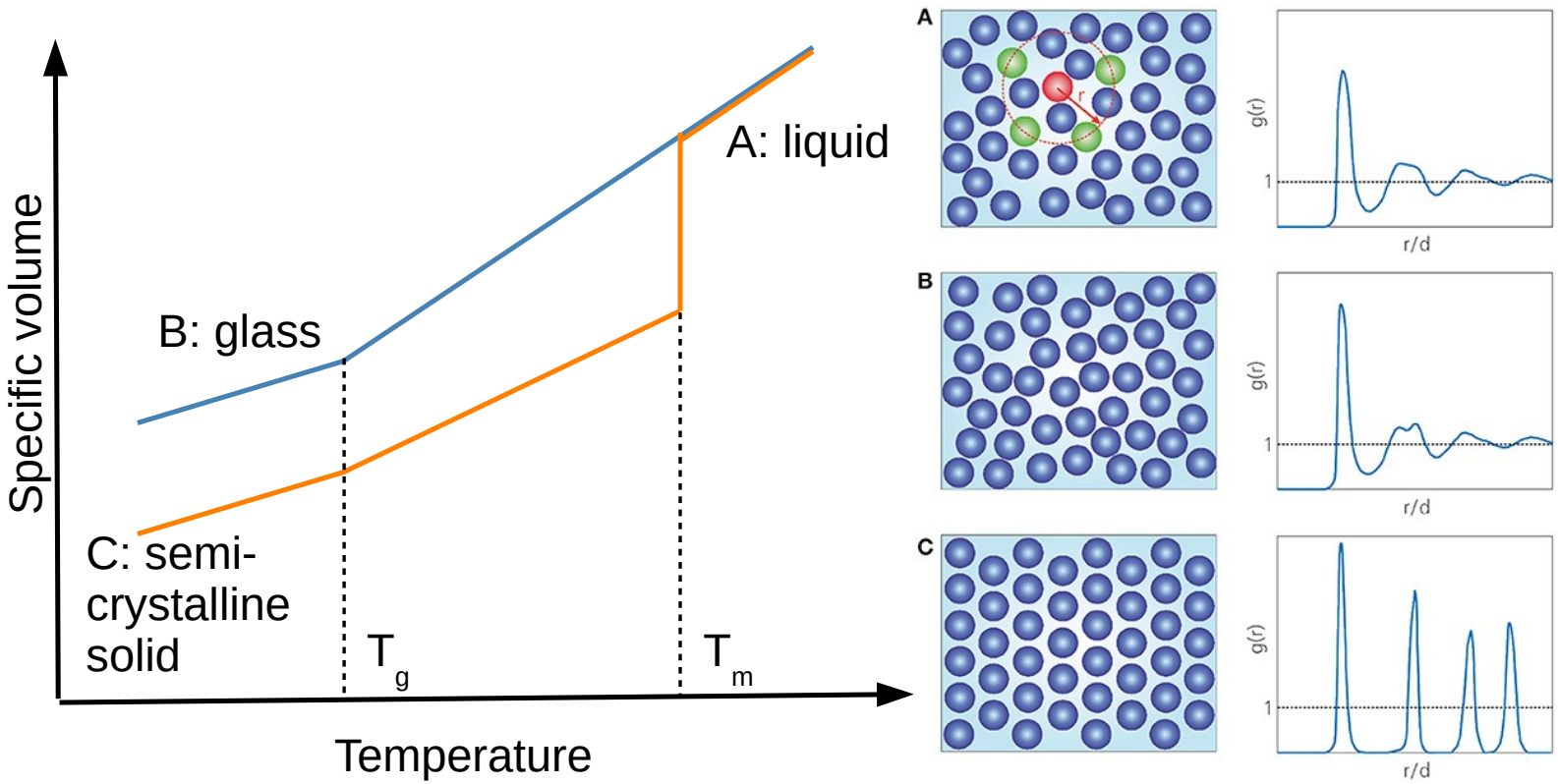
$$\text{experimental} \quad \eta_0 \propto N^{3,4}$$





Viscosity measured experimentally scales as $N^{3,4}$. The discrepancy is related to the additional relaxation mechanisms. Explain the change of the slope.

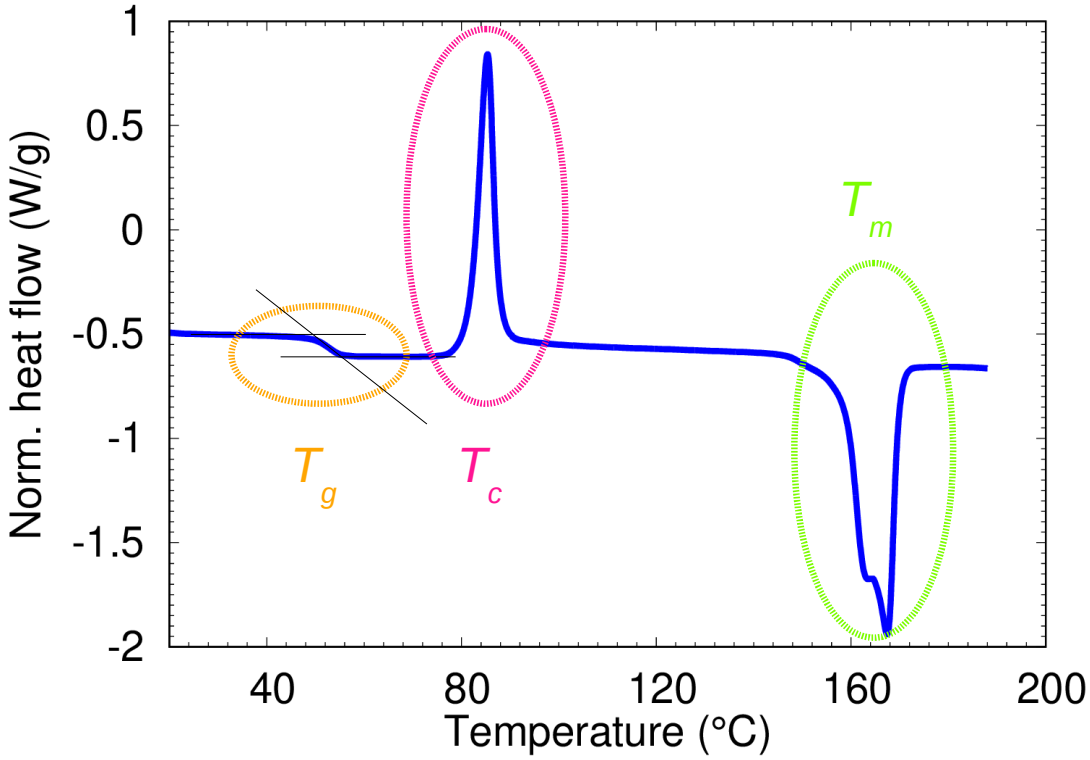
Glass transition temperature



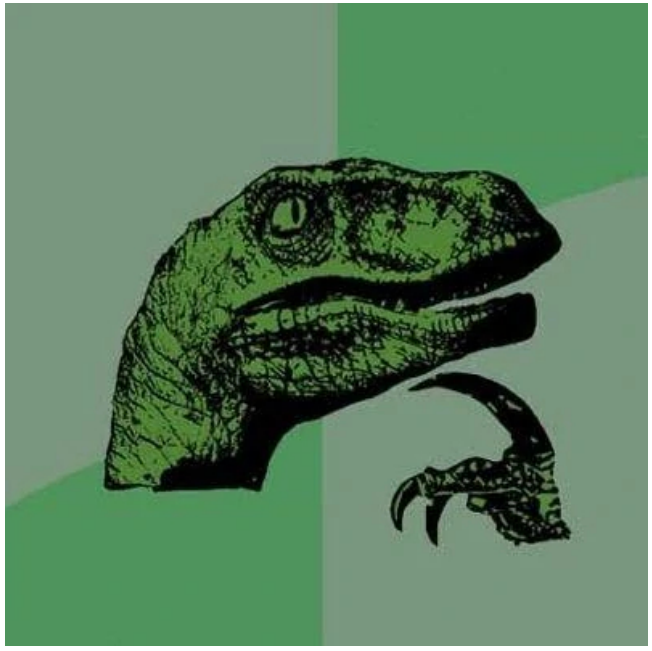
- calorimetric T_g: differential scanning calorimetry
- dynamic T_g: dielectric spectroscopy

[1] Janssen Liesbeth M. C., Mode-Coupling Theory of the Glass Transition: A Primer, Frontiers in Physics, 2018

Calorimetric glass transition temperature



- dependence on the heating rate and the sample preparation (memory)
- broad T_g related to polydispersity, structural heterogeneity, processing conditions etc.
- integrals under peaks can be related to the degree of crystallinity



Explain the quantitative effect of the heating rate.

Segmental relaxation

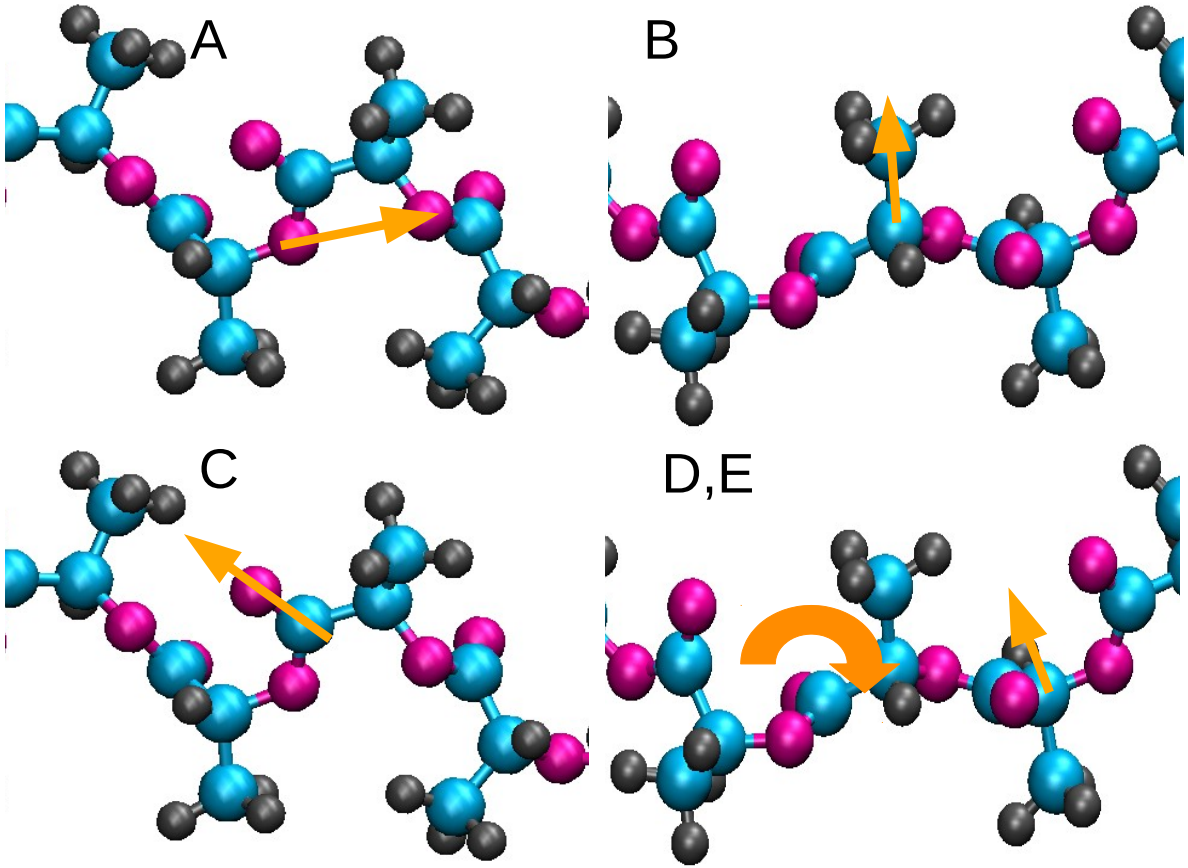
(A) backbone

(B) side groups

(C) dipole moment

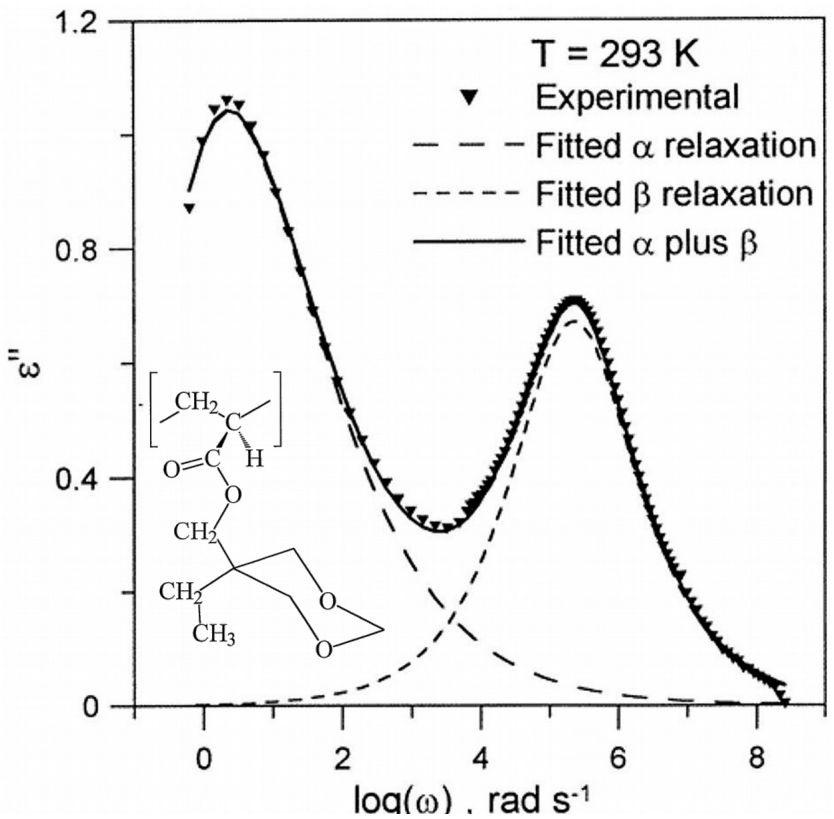
(D) torsional rotation

(E) C-H bond vector



Dielectric spectroscopy

- movement of dipoles in the presence of an electric field

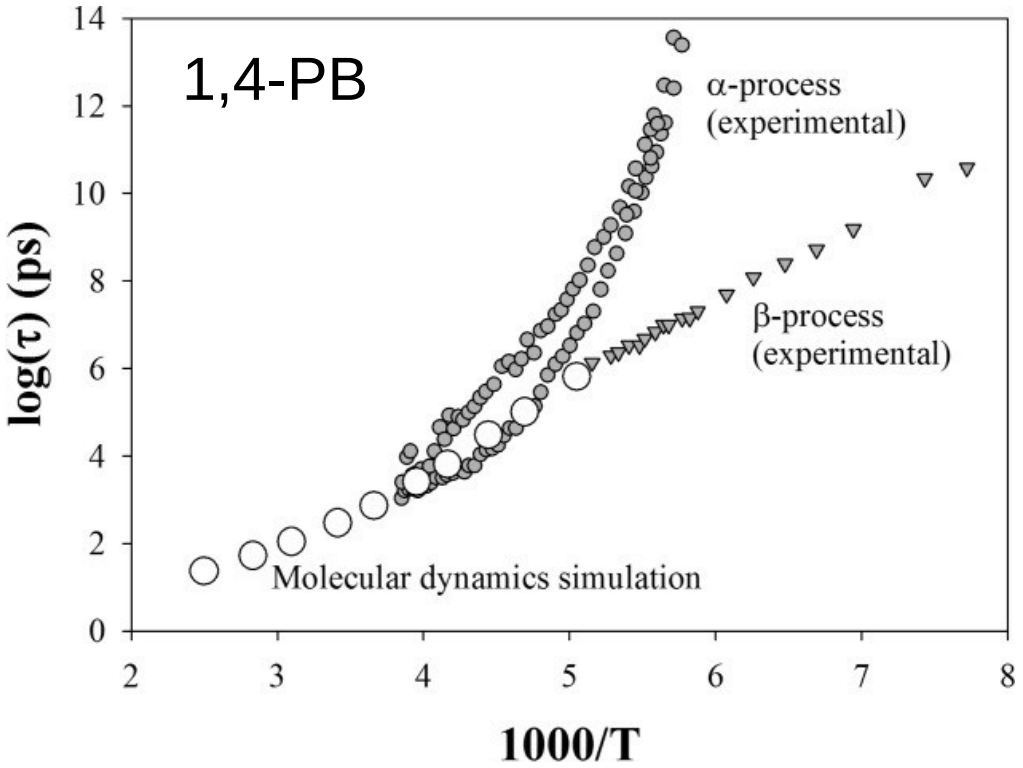


- permitivity
  $\epsilon^*(\omega) = \epsilon'(\omega) - j\epsilon''(\omega)$
- α relaxation: associated with the glass transition
- β relaxation: rotation of side groups or motion of a few main-chain atoms
- stretched exponential function

$$\Phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right]$$

[1] Huang Y. Saiz E. Ezquerra T. A. Guzmán J. Riande E., Macromolecules, 2002, 35, 5, 1785-1790

Glass transition temperature



- Vogel–Fulcher–Tammann

$$\tau(T) = \tau_0 \exp\left(\frac{B}{T - T_0}\right)$$

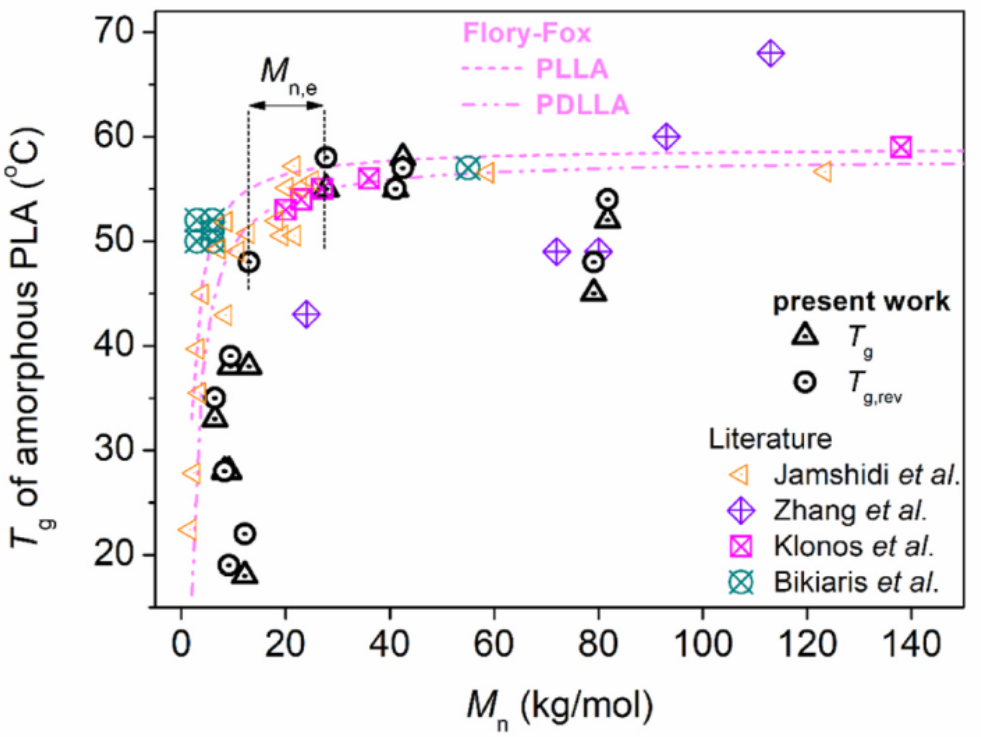
- Arrhenius

$$\tau(T) = \tau_0 \exp\left(\frac{E_a}{k_B T}\right)$$

- VFT: temperature dependent activation energy, cooperative mechanism, α relaxation
- Arrhenius: constant activation energy, small-scale motions below T_g, β relaxation

[1] Smith, G.D. and Bedrov, D., J. Polym. Sci. B Polym. Phys., 2007, 45, 627-643.

Glass transition temperature: other effects



- Flory-Fox

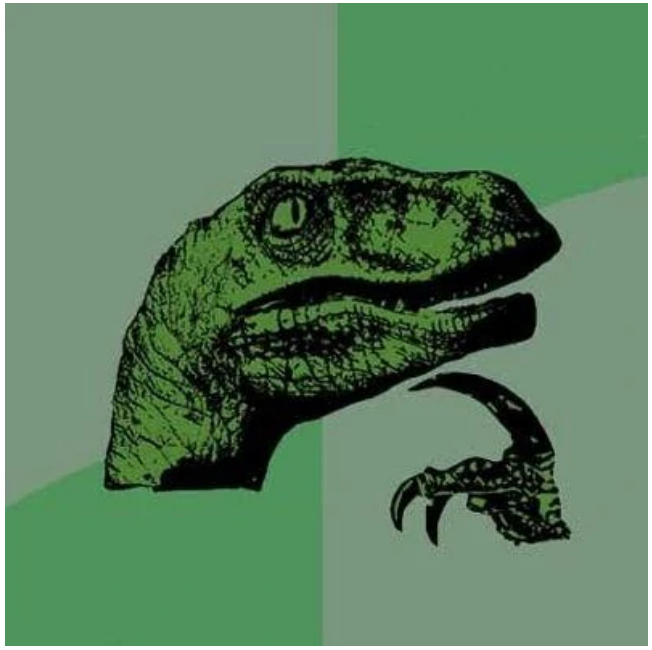
$$T_g = T_{g,\infty} - \frac{K}{M_n}$$

- empirical
- K-material dependent

Other effects:

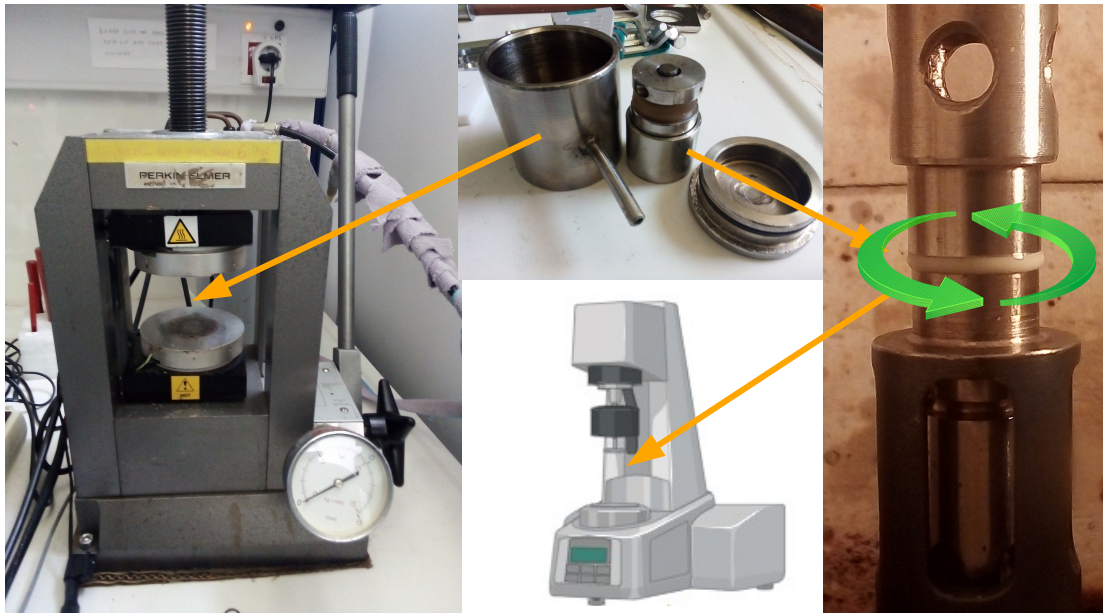
- chain rigidity ↑, crosslinking ↑
- plasticizers ↓, nanofillers ↕

[1] A. Klonos, N. D. Bikiaris, P. Barmpalexis, A. Kyritsis, Polymer, vol. 305, p. 127177, 2024.



Explain why chains with low molecular weight have lower T_g.

Linear rheology

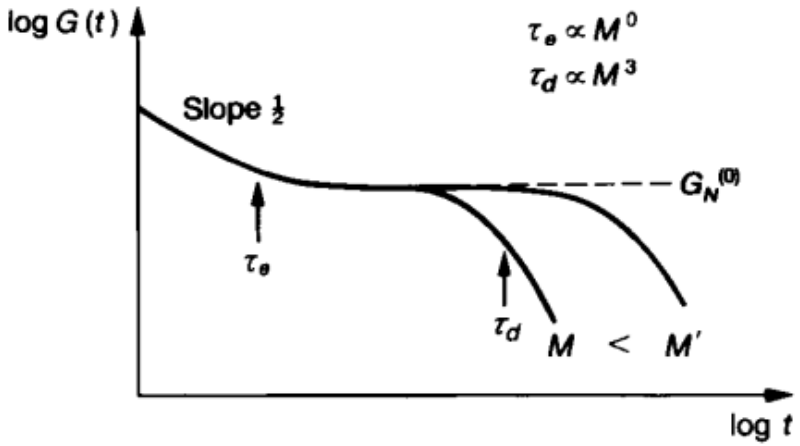


- power technique to detect basic characteristics (molecular weight distribution, degree of branching, degree of entanglement)
- small deformation limit: modulus is constant in the given strain range
- Small Amplitude Oscillatory Shear (SAOS): measurement of complex modulus

Relaxation modulus

$$G^*(\omega) = i\omega \int_0^\infty G(t) e^{-i\omega t} dt$$

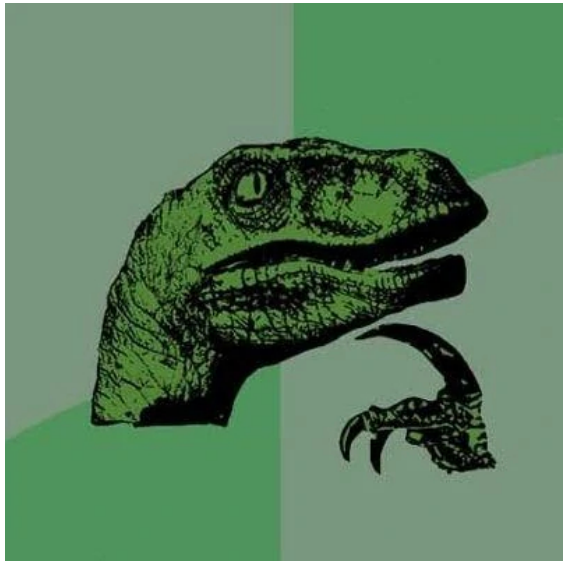
$$G^*(\omega) = G'(\omega) + iG''(\omega)$$

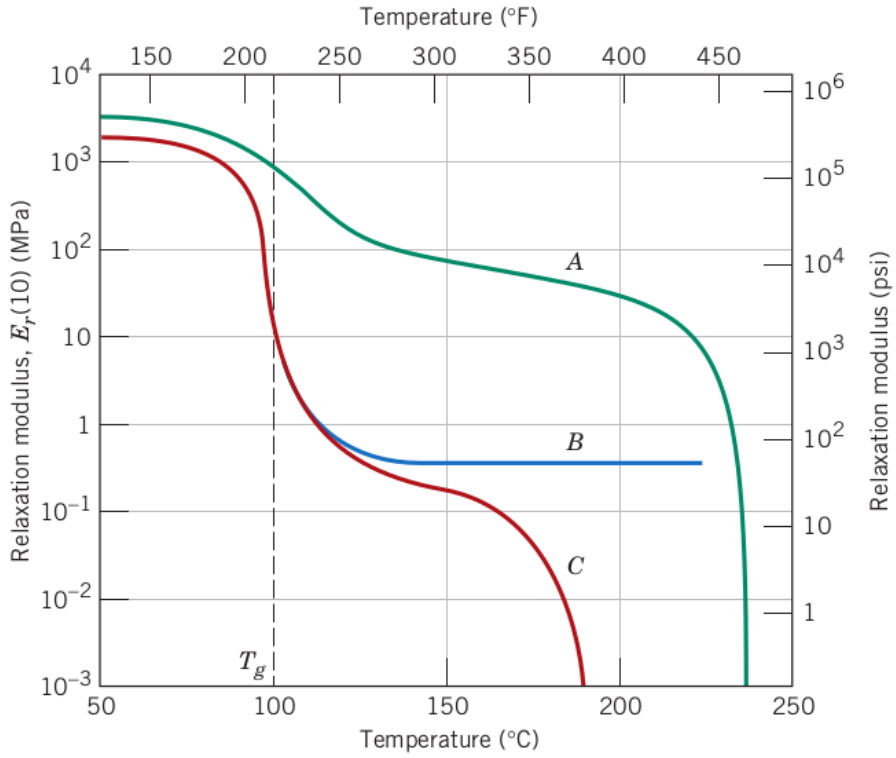


- Storage modulus
  $G'(\omega) = \omega \int_0^\infty G(t) \sin(\omega t) dt$
- Loss modulus
  $G''(\omega) = \omega \int_0^\infty G(t) \cos(\omega t) dt$

- τ_e entanglement time: local relaxation of an M_e segment, independent of total M, chemistry specific
- τ_d disentanglement time: terminal relaxation, tube escape

[1] M. Doi and S. F. Edwards, The Theory of Polymer Dynamics. Oxford University Press, USA, Nov. 1986.

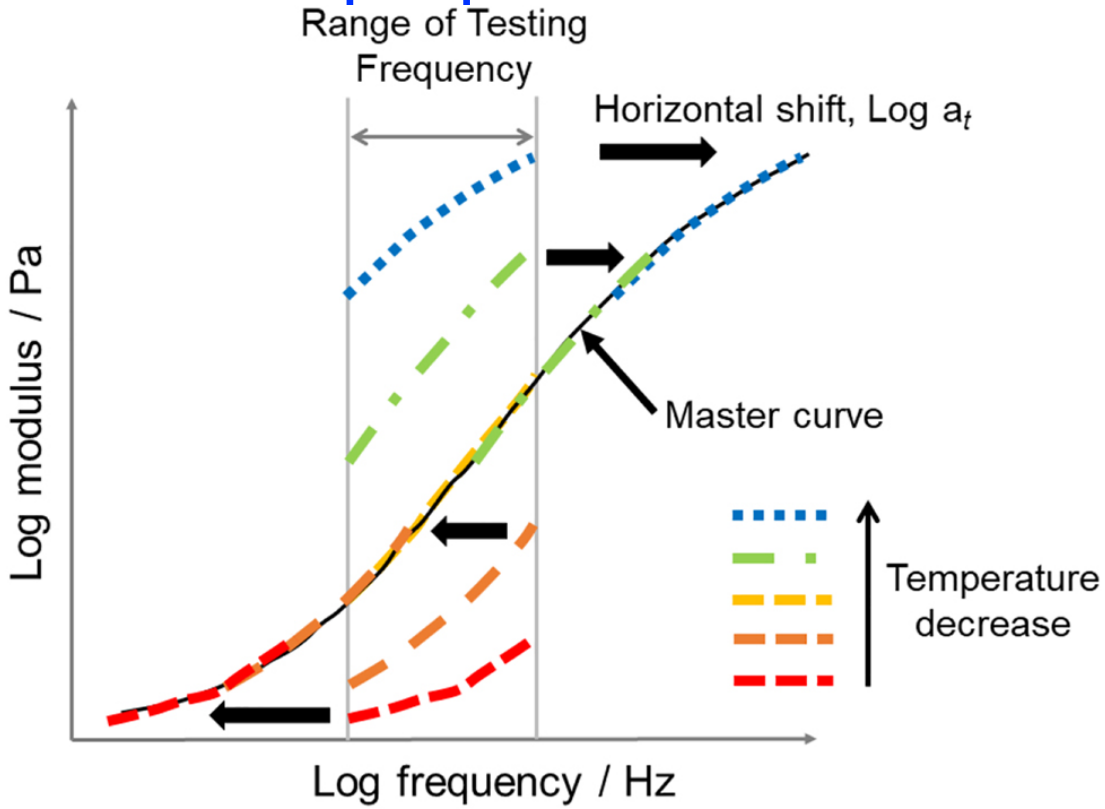




Assign the following materials to the curve: amorphous polystyrene, crystalline isotactic polystyrene, lightly crosslinked atactic polystyrene.

[1] Callister, W. D., Rethwisch, D. G. (2018). Materials Science and Engineering: An Introduction (10th ed.). Hoboken, NJ: Wiley

Time-temperature superposition

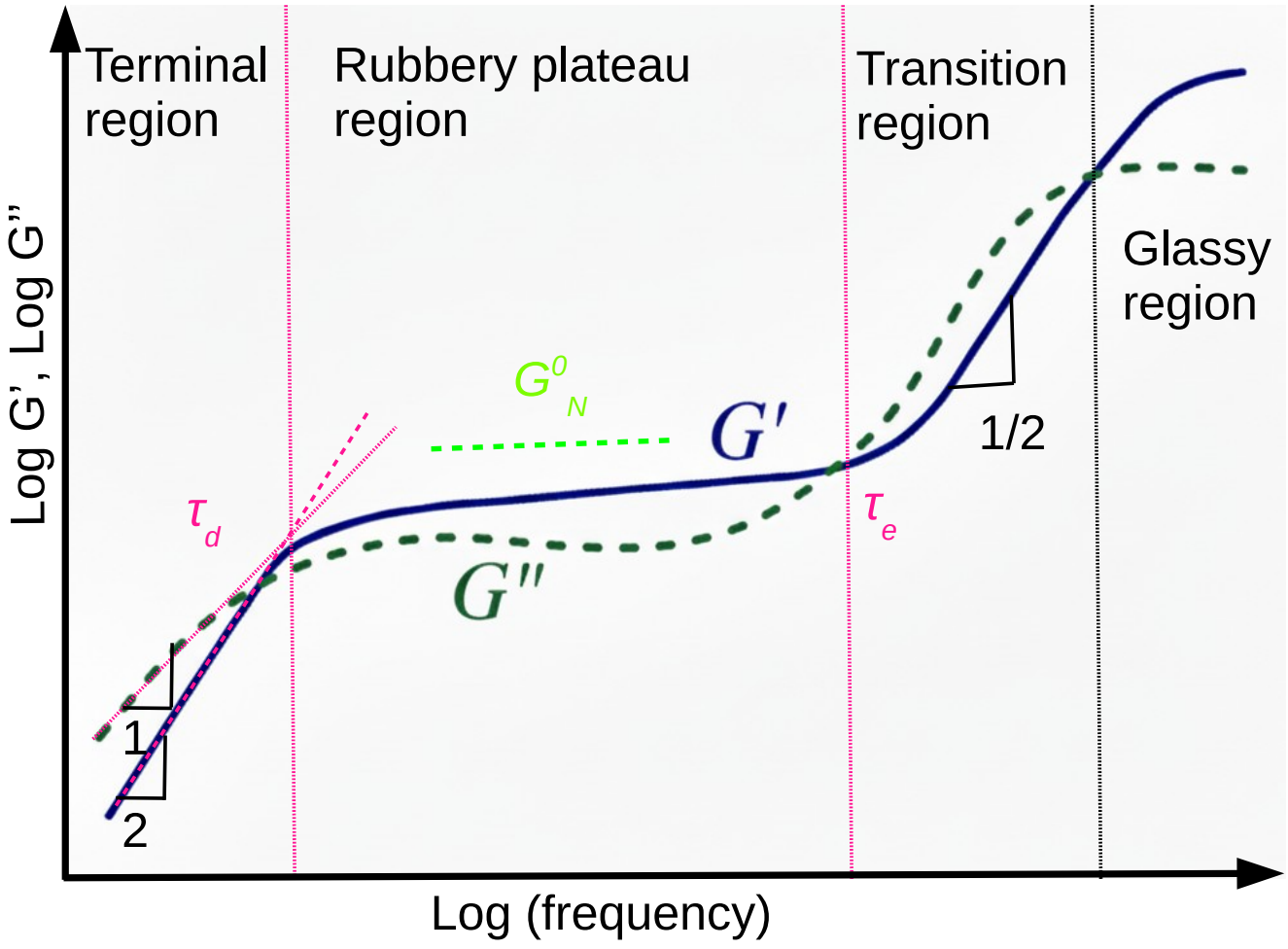


- all molecular relaxation times (τ_i) for a given temperature (T) change by the same factor when the temperature is shifted to a reference temperature (T_0)

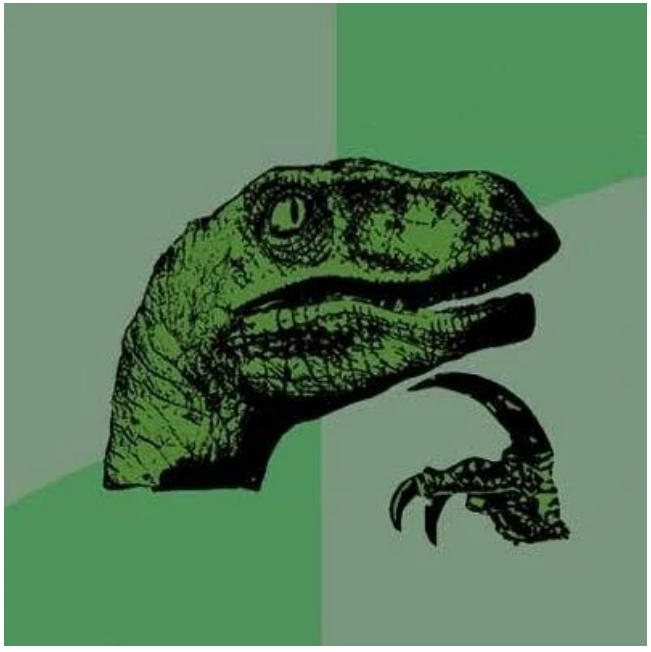
$$G(t,T) = b_T G\left(\frac{1}{a_T}, T_0\right)$$

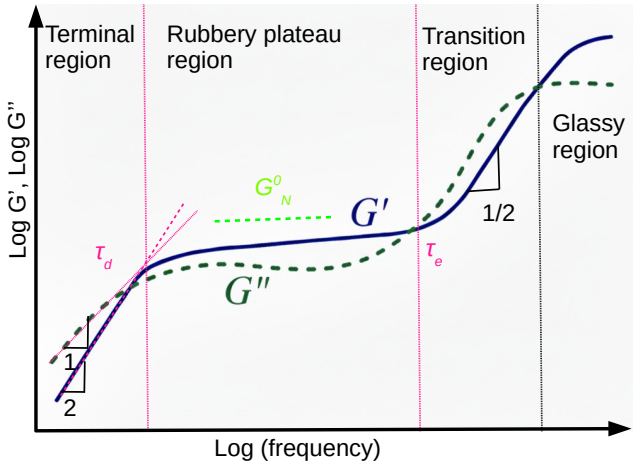
[1] Ramli, H., Zainal, N., Hess, M., Chan, C. (2022). Chemistry Teacher International, 4(4), 307-326

Viscoelastic spectra: theoretical predictions



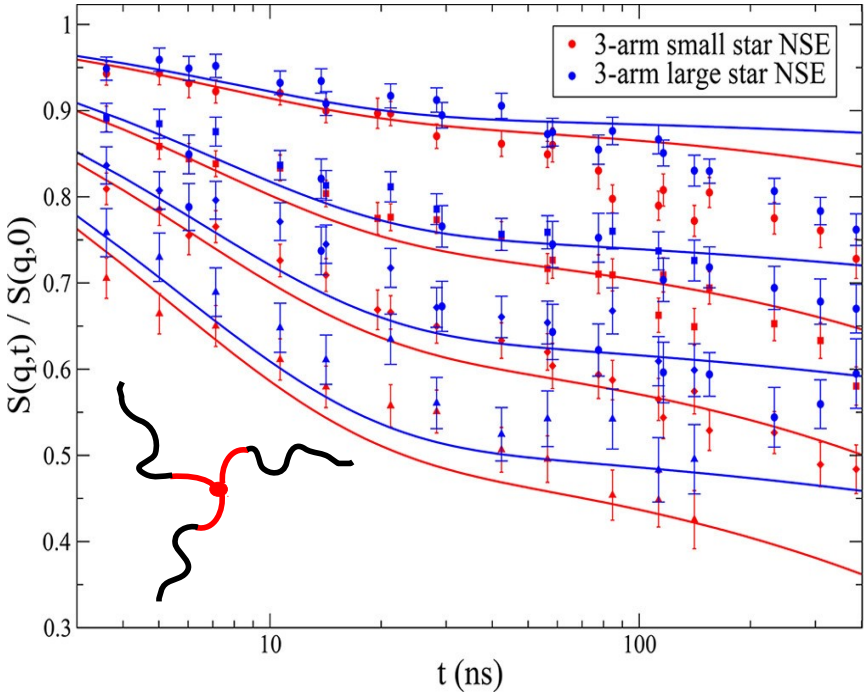
- G_N^0 chemistry-specific $G_N^0 \approx \frac{\rho RT}{M_e}$
- t_d dependent on molecular weight $\tau_d \propto M^{3,4}$





Identify the region of the linear viscoelastic spectrum (Log G', Log G'' vs. Log ω) that is most sensitive to the effects such as polymer architecture.

Neutron spin echo



$$S_{\text{total}}(\vec{q},\omega) = S_{\text{coh}}(\vec{q},\omega) + S_{\text{inc}}(\vec{q},\omega)$$

$$S_{\text{coh}}(\vec{q},t) = \left\langle \sum_{m=1}^{N}\sum_{n=1}^{N} e^{i\vec{q}(\vec{R}_n(t)-\vec{R}_m(0))} \right\rangle$$

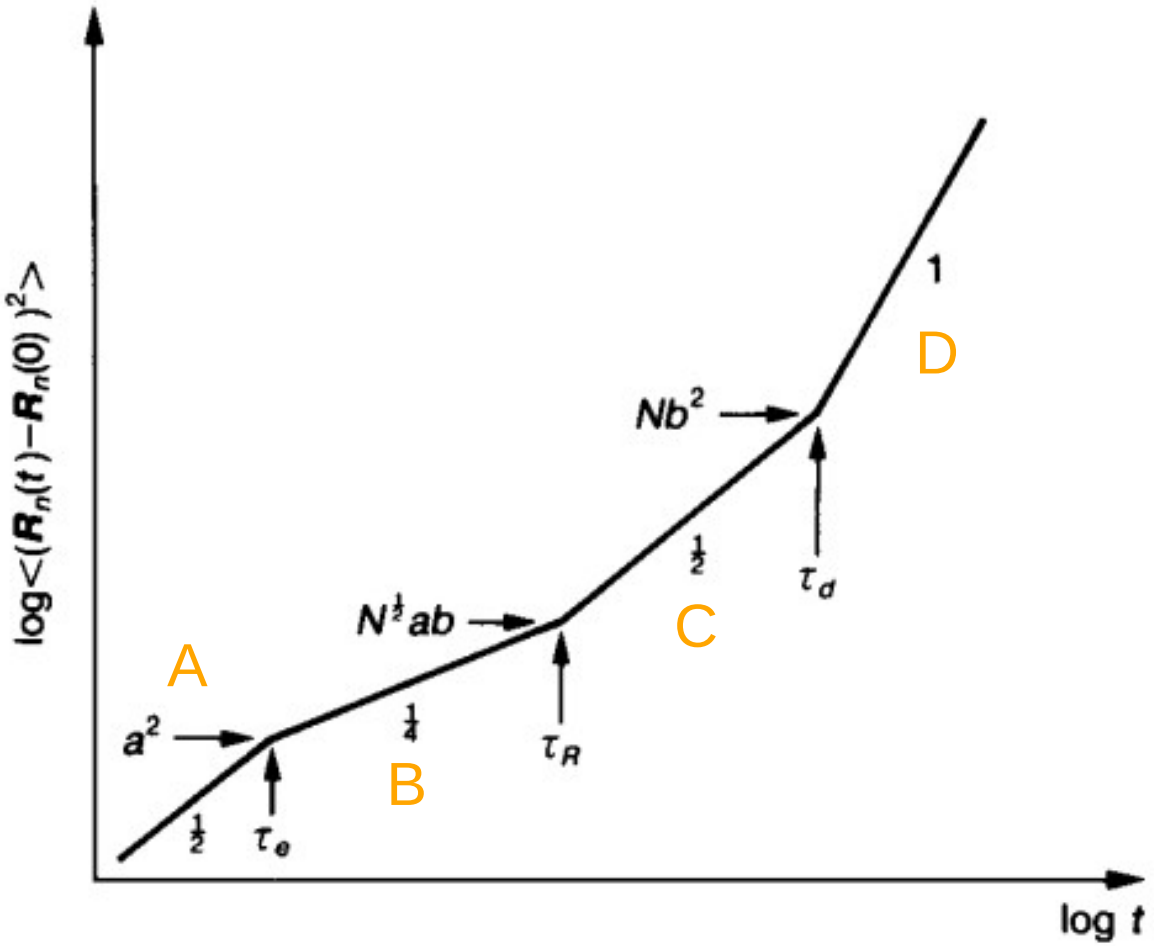
- deuterated background, labelling through protonation
- intermediate time scales, local, sub-Rouse chain dynamics
- application of the theoretical models to obtain τ_e, a
- Gaussian aproximation:

$$\frac{S(q,t)}{S(q)} \approx \exp\left(-\frac{1}{6}q^2\langle\Delta R^2(t)\rangle\right)$$

[1] Stefan Holler, Angel J. Moreno, Michaela Zamponi, Petra Bačová, Lutz Willner, Hermis Iatrou, Peter Falus, and Dieter Richter, Macromolecules 2018 51 (1), 242-253

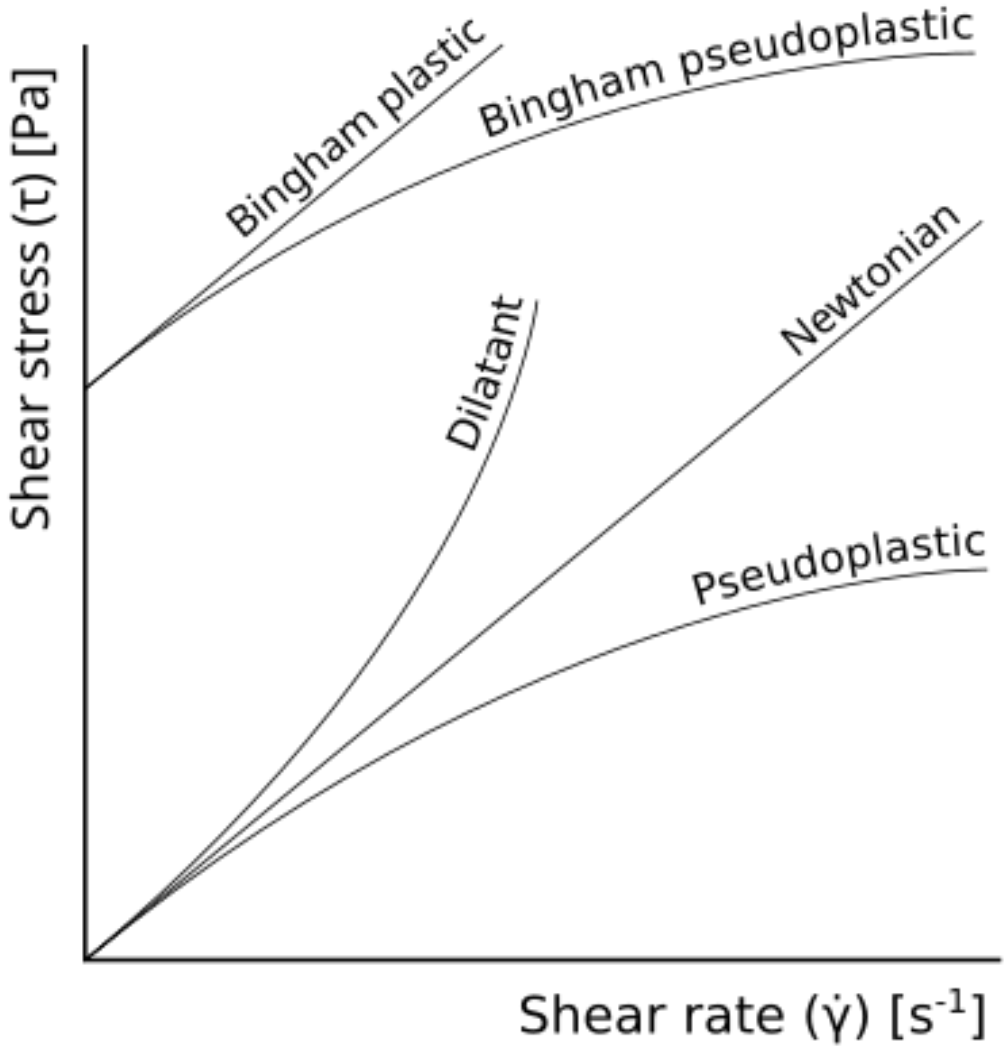
MSD: theoretical prediction

(A) Rouse
(B) Rouse in tube
(C) reptation
(D) free diffusion



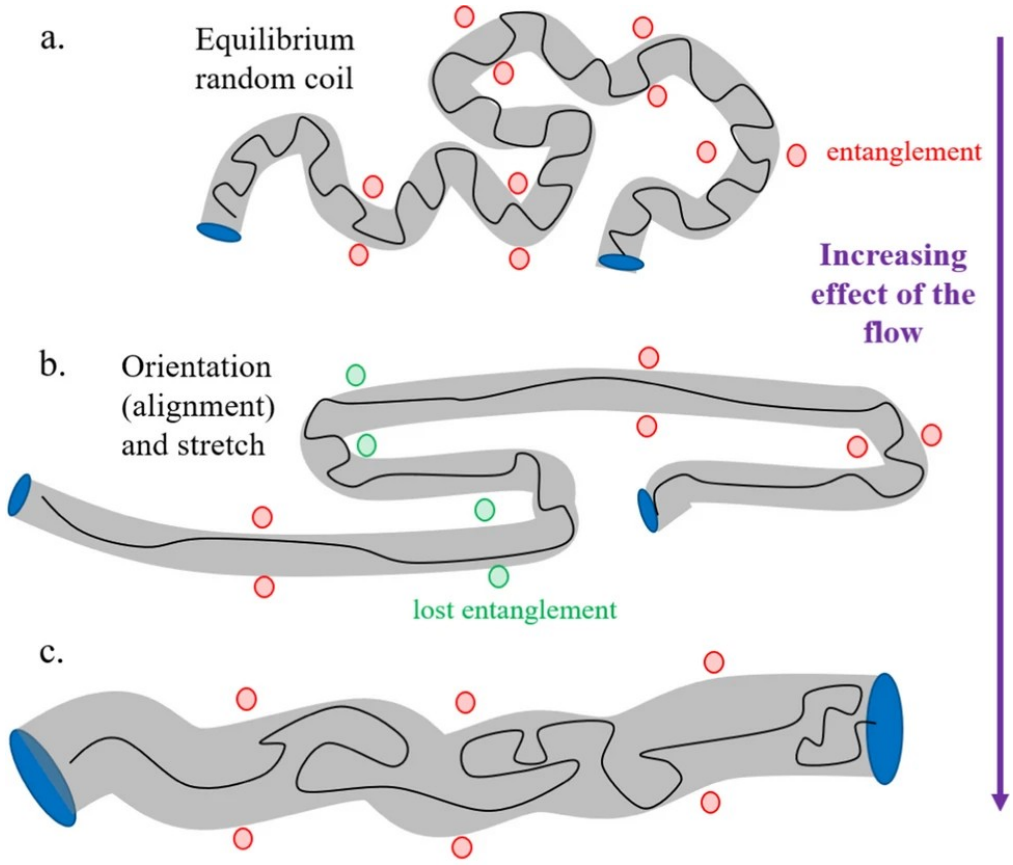
+ microrheology
+ molecular dynamics simulations

Non-equilibrium behaviour



[1] https://en.wikipedia.org/wiki/Shear_thinning

Non-equilibrium relaxation



Entanglement loss, merging of tube segments, and tube diameter increase

+ tumbling of rings
+ hierarchical relaxation in complex structures

[1] Pyromali, C., Taghipour, H., Hawke, L.G.D.
Rheol Acta 63, 541–572 (2024).

Keep calm and stay tuned!

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- ☞ https://polysim.eu/

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