School of Engineering
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Polymer Science 2025/26

Exercise 9 – Solutions

1. In a relaxation test, a constant shear strain γ_0 is applied and we monitor the stress $\sigma(t) = \mathrm{G}(t)\gamma_0$ as a function of time. The relaxation modulus according to the generalized Maxwell model is

$$\mathrm{G}(t) = \mathrm{G}_\infty + \sum_{i=1}^{n} G_i e^{-t/\tau_i} \quad ,$$

where the parameters G_∞ and G_i are adjustable (within the limit of an infinite number of elements, the G_i can be replaced by a continuous function, the relaxation time spectrum, and the sum by an integral).

In the Rouse model for a dilute solution of N_m chains per unit volume, each chain contains n bonds, the expression for $\mathrm{G}(t)$ is

$$\mathrm{G}(t) = N_m \mathrm{k}T \sum_{p=1}^{m} e^{-t/\tau_p} \qquad \tau_p \approx \frac{\xi m^2 R_s^2}{6\pi^2 p^2 \mathrm{k}T} \quad , \qquad p = 1,2, \ldots$$

Assume $m \gg p$ and $m \gg 1$.

i) Explain the meaning of m, p, ξ and R_s^2. Why is $\mathrm{G}_\infty = 0$ here?

In the Rouse model, a polymer chain of n bonds (each of length a) is represented as a series of m beads connected by $m-1$ harmonic springs. The beads experience friction with the surrounding medium, so that the viscous drag force on the i^{th} bead is

$$\boldsymbol{f_i = \xi \frac{\mathrm{d}\vec{r}_i}{\mathrm{d}t}}$$

where ξ is the friction coefficient per bead.

Each spring between adjacent beads represents an entropic freely jointed subchain consisting of $n/(m-1)$ bonds, with an average mean-square end-to-end distance

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$$R_s^2 = \frac{n}{m-1}a^2 \approx \frac{n}{m}a^2 \qquad \text{for } m \gg 1$$

The index p labels the Rouse relaxation modes, which correspond to collective motions of wavelength comprising n/p bonds:

- **$p = 1$: motion of the entire chain**
- **$p = 2$: motion involving half the chain length**
- **$p = 3$: motion involving one-third of the chain, and so on.**

Each mode relaxes exponentially with a characteristic time $\tau_p \propto 1/p^2$. In the long-time limit ($t \to \infty$), all modes have relaxed, the system can no longer sustain stress, and the relaxatino modulus tends to zero, so that the residual or equilibrium modulus $G_\infty = 0$.

This reflects the fact that an uncrosslinked Rouse chain has no permanent network connectivity and therefore behaves as a viscous liquid at long times.

ii) If the monomeric friction coefficient is $\xi_o = \xi m/n$, show that

$$\tau_p \approx \frac{\xi_o n^2 a^2}{6\pi^2 p^2 \mathrm{k}T}, \qquad for \quad m \gg 1, p$$

and therefore, that the longest Rouse time τ_1 scales as M^2.

In the Rouse model, friction is additive: the total friction of a bead is the friction of all monomers that it contains. If each monomer has a friction coefficient ξ_o, then a bead (comprising n/m bonds) has $\xi = \xi_o n/m$. Using the expression for the mean-square end-to-end distance from above, we obtain:

$$\tau_p \approx \frac{\xi m^2 R_s^2}{6\pi^2 p^2 \mathrm{k}T} = \frac{\xi_o \frac{n}{m} m^2}{6\pi^2 p^2 \mathrm{k}T} \frac{n}{m} a^2 = \frac{\xi_o n^2 a^2}{6\pi^2 p^2 \mathrm{k}T}$$

As the chain molar mass M is proportional to the number of bonds (monomers) n:

$$\tau_p \propto n^2 \propto M^2$$

This also shows that the longest Rouse time τ_p scales as M^2.

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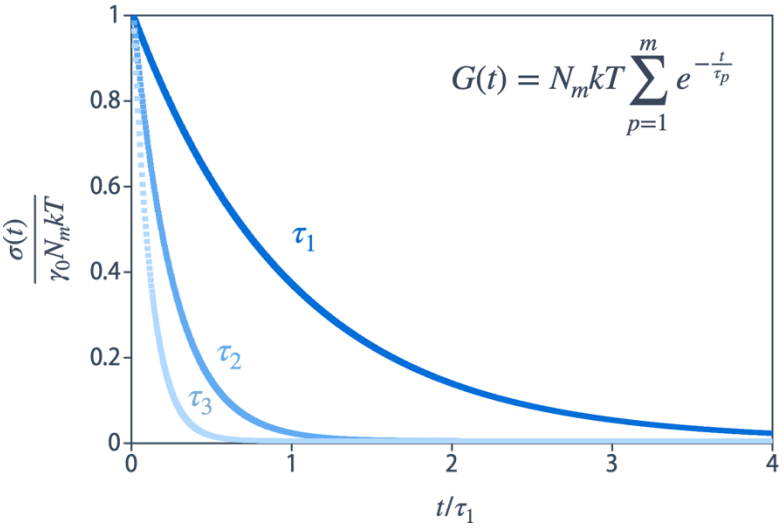
iii) Draw schematically the evolution of $\sigma/N_m kT$ as a function of t/τ_1 for the contributions coming from p = 1, and add the decays for p = 2 and p = 3. Discuss the contribution of the fast modes for $t \geq \tau_1$?

Let $x \equiv t/\tau_1$. According to Rouse, $\tau_p = \tau_1/p^2$. Hence:

$$\frac{G(t)}{N_m kT} = \sum_{p=1}^{m} e^{-t/\tau_p} = \sum_{p=1}^{m} e^{-p^2 x}$$

The three contributions required are therefore

$$\text{for } p = 1: \quad e^{-x}, \qquad p = 2: \quad e^{-4x}, \qquad p = 3: \quad e^{-9x}$$



So, at $t = \tau_1$, the $p = 2$ term is about of the $\approx 5\%$ of the $p = 1$ contribution, and the $p = 3$ term is negligible ($\approx 0.03\%$ of $p = 1$).

For $t \geq \tau_1$, the fast modes (large p) have essentially decayed away and contribute negligibly to the stress. The stress is therefore dominated by the slowest mode $p = 1$. Hence, the longest Rouse time controls the long-time decay and the approach to viscous behavior.

iv) The choice of m (number of beads/modes) is arbitrary. Is the Rouse model still reasonable when $m \to n$ (i.e., when beads correspond to single bonds)?

The Rouse model assumes that each bead represents a segment long enough for its conformations to be described by Gaussian chain statistics and entropic elasticity. Increasing m means dividing the chain into more but smaller segments.

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For long times $t \gg \tau_p$, the fast modes (large p) have already relaxed and can be neglected. But to describe very short times, one must include modes with sufficiently high p. If m (and thus the maximum p) becomes too large, each segment corresponds to only a few bonds, or in the limit $m \to n$, to a single bond. In that case, the basic assumptions of the Rouse model break down: the springs no longer represent entropic elasticity but enthalpic bond stretching.

Therefore, the Rouse model is not reasonable when $m \to n$. It only applies to timescales much longer than those of local bond vibrations, where the chain can be viewed as a sequence of coarse-grained, freely jointed chain segments.

v) Suppose $\tau_1 = \infty$ and $\tau_p = 0$ for $p > 1$. Write the resulting expression for $G(t)$. Interpret your result.

Setting $\tau_1 = \infty$ and $\tau_p = 0$ for $p > 1$:

$$G(t) = N_m kT\, e^{-t/\infty} + N_m kT \sum_{p=2}^{m} e^{-t/\tau_p} = N_m kT + N_m kT \sum_{p=2}^{m} 0 = N_m kT$$

Thus, the relaxation modulus is constant in time. All higher modes ($p > 1$) relax instantaneously and do not contribute at $t > 0$. The lowest mode ($p = 1$) never relaxes, corresponding to a frozen overall chain conformation. The system therefore behaves as an elastic solid with modulus $G = N_m kT$.

This limiting case mimics a permanently crosslinked rubber network, where the global motion of chains (translation or reptation) is prevented. The constant shear modulus $G = NkT$ is identical in form to the entropic elasticity of elastomers, where N is the density of active network chains. In essence, this simplified Rouse model represents a melt in which all chains are effectively crosslinked at their ends, leading to purely elastic behavior.

2. The Rouse model does not describe dilute polymer solutions accurately because it neglects hydrodynamics interactions between beads (these are accounted for in the Zimm model). However, the Rouse model works well for chains in a polymer melt as long as entanglement effects are negligible (in this case, the other chains act as a highly viscous solvent).

   i) Rouse-like behavior can therefore be expected if the molar mass M is smaller than a certain critical molar value, $M_c = 2M_e$. What does M_e represent here? Using the

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concept of the entanglement network, explain how M_e can be determined experimentally from the rubbery plateau shear modulus.

The entanglement molecular weight M_e represents the characteristic molar mass of a polymer segment between two entanglement points. Entanglements occur when polymer chains are so interpenetrated that their motion is topologically constrained by neighboring chains.
In the entanglement network model, the melt in the rubbery plateau behaves like a transiently crosslinked network. The shear modulus G in this region arises from these temporary entanglement junctions and is analogous to the modulus of an elastomer:

$$G = N_e kT$$

where N_e is the number density of entanglement strands. For an elastomer, this expression has the same form as $G = NkT$, where N is the crosslink density.

The number of entanglement strands per unit volume N_e can be expressed in terms of the density ρ and the entanglement molar mass M_e:

$$N_e = \frac{\rho N_A}{M_e}$$

Combining the two relations gives:

$$G = \frac{\rho k N_A T}{M_e} = \frac{\rho R T}{M_e} \quad \rightarrow \quad M_e = \frac{\rho R T}{G}$$

ii) The Rouse model can still describe fast relaxation modes (large p) even when $M >> 2M_e$, because these correspond to localized segmental motions that are not hindered by entanglements.

In contrast, slow modes involving the entire chain are blocked by entanglements. Assuming (as a simplification) that entanglements mainly affect the slowest relaxation mode τ_1, what can we say about τ_1, if the entanglements were permanent? What would represent in this limiting case?

Entanglements restrict chain motion and strongly affect the slow relaxation modes. If entanglements were permanent, the slowest relaxation mode (p = 1) would no longer relax: its relaxation time τ_1 would become effectively infinite.

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The polymer chain would thus remain trapped within its constraints and unable to fully relax the stress, just as in a chemically crosslinked network, where crosslinks permanently fix the chain ends.

In this limiting case, N_m represents the entanglement density, i.e. the number of elastically active strands (segments between entanglement points) per unit volume. This corresponds directly to the network density in an elastomer, and the material would behave as a permanently elastic solid.

iii) In reality, entanglements are not permanent. The tube model describes the disentanglement process, in which a chain gradually escapes from its confining tube by reptation. This model implies that the chain can eventually recover its random coil conformation and relax all stresses.

Assuming that the diffusion coefficient along the tube scales as $D \propto 1/M$, explain where this scaling originates from.

In the tube model, the motion of the polymer is restricted to reptation, which is a diffusion-like motion of the chain along its confining tube formed by entanglements.

The local segmental motions inside the tube still follow Rouse dynamics. According to the Rouse model, the diffusion coefficient is inversely proportional to molar mass: $D \propto M^{-1}$. This relationship arises because the total friction coefficient of the chain scales linearly with its molar mass M, as it is the sum of the friction coefficients of all monomers, and diffusion is inversely proportional to friction.

Thus, the $D \propto 1/M$ scaling in the tube model originates directly from the Rouse description of segmental dynamics and the additive nature of friction along the chain.

iv) Knowing that the tube contour length (i.e. the total length the chain must diffuse to fully disentangle) is proportional to M, demonstrate that the disentanglement time τ_d scales as M^3.

The polymer chain is confined to a tube whose contour length L scales linearly with the chain molar mass M. The tube can be viewed as a primitive path composed of M/M_e entanglement strands, each of a constant length d_e:

$$L = \frac{M}{M_e} d_e \propto M$$

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The chain escapes its confining tube by reptation, i.e. by diffusion along the tube contour. The disentanglement (reptation) time τ_d corresponds to the time required to diffuse a distance of L.

$$L^2 = D\tau_d$$

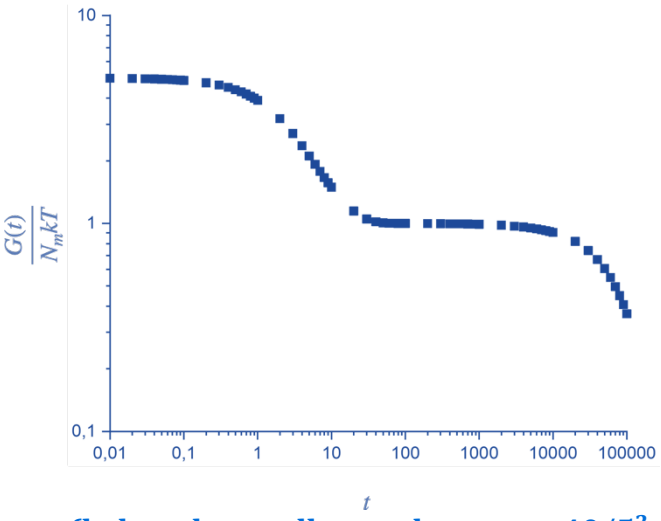
The diffusion coefficient for motion of the chain along the tube follows Rouse-like behavior, thus scaling inversely with molar mass: $D \propto M^{-1}$. For τ_d it therefore follows:

$$\tau_d = \frac{L^2}{D} \propto \frac{M^2}{M^{-1}} = M^3$$

v) Using Excel, Origin, or another plotting tool, plot on logarithmic axes:

$$\mathrm{G}(t) = N_m \mathrm{k}T \sum_{p=1}^{m} e^{-t/\tau_p}$$

for t ranging from 0.01 and 10^5 s, taking m = 5, $\tau_1 = 10^5$ s, and $\tau_p = 40/p^2$. Here, we simulate the effect of entanglements by assigning an arbitrarily large value to τ_1. What feature of the resulting curve does this remind you of?



- **very short times (below the smallest τ_p: here $\tau_5 = 40/5^2 = 1.6$ s): the sum is dominated by all modes that are still unrelaxed, so the modulus is high.**

  Note: the Rouse sum with m = 5 is not intended to represent the true glassy state. Only 5 modes are included, which limits the short-time behavior. In reality, the modulus in the glassy state is orders of magnitude higher than in the rubbery plateau and requires many more (and faster) modes to be described properly.

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In any case, this type of model is anyways not valid in the glassy state because the viscosity as well as the relaxation times effectively become infinite below T_g. For $T < T_g$, the modulus is dominated by van der Waals forces and not by conformational changes.

- **intermediate times (roughly from the largest short-mode, τ_5, up to the very large τ_1): the slowest mode $p = 1$ remains essentially unrelaxed because τ_1 is arbitrarily long. When the fast modes $p = 2 \ldots 5$ have relaxed, the result is a nearly constant level of $G(t)$, resembling the rubbery plateau.**
- **long times ($t > \tau_1$): the slowest mode finally decays, and $G(t)$ falls to zero (terminal flow/complete stress relaxation).**

Thus, the plot reproduces the typical viscoelastic relaxation curve of polymers: high modulus at short times → fast Rouse relaxations inside the tube → rubbery plateau at intermediate times → terminal decay at long times as the chain escapes the tube.

Reading suggestion:

- Reader on the Rouse Model.

(You can download this document from the Moodle-folder 'Reading Recommendation'.)

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