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Exercise 9 – Solution

1. As already mentioned in the previous exercise sheet, Rouse's model does not work well for diluted solutions because it does not take hydrodynamic effects into account (for this, we need the Zimm model). However, it works well for chains in a polymer melt as long as entanglement effects are not important (in this case, the other chains act as a very viscous solvent).

   i) Rouse-like behavior can therefore be expected if the molar mass, M, is less than a certain critical molar mass, $M_c = 2M_e$. What does M_e mean here? Explain, using the entanglement network model, how we can determine M_e from the shear modulus, which corresponds to the rubbery plateau.

   The entanglement molecular weight M_e represents the characteristic molar mass between entanglement points in a polymer. Entanglements occur when polymer chains become so intertwined that their motions are significantly restricted by neighboring chains.

   Let us recall the entanglement network model: in the rubbery plateau region, a polymer behaves like a crosslinked network. The shear modulus G in this region arises from entanglement interactions between chains, and can be related to the number of entanglements per unit volume N_e. For a polymer in the rubbery state, the shear modulus is given by $G = N_e kT$ (this is analogous to the shear modulus of an actual elastomer, where the shear modulus is $G = NkT$, with N representing the number of subchains per unit volume (which corresponds to the chain lengths between crosslinking points). The entanglement molar mass, M_e, can be expressed as the product of the number of segments between entanglement points per unit volume (N_a/N_e) and the density, ρ:

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

   Where N_a is Avogadro's number. Thus, we can relate the shear modulus to the molar mass between entanglement points by combining the two expressions:

$$M_e = \frac{N_a \rho}{N_e} = \frac{kTN_A \rho}{G} = \frac{RT\rho}{G}$$

ii) Rouse's model can also be used to describe fast relaxation modes (high p) even if $M >> 2M_e$, because these are associated with relatively localized movements that are not hindered by the entanglement. In contrast, slow relaxation modes that involve the whole chain are blocked by entanglement. If we admit (and this is a big simplification!), that the entanglement mainly affects τ_1, what can we say about τ_1 if the effects of the entanglement are permanent? What does N_m represent in this case?

Entanglement restricts the chain's motion and leads to a change in the relaxation behavior, particularly for the slow modes. If we consider the entanglement to have a permanent effect on τ_1, the slow relaxation mode (p = 1) becomes infinitely long. The polymer chain is effectively trapped in place, and prevented from fully relaxing or moving past the entanglement points. This is analogous to the situation in a chemically crosslinked network, where the polymer chain motion is restricted by the crosslinks.

In this case, N_m represents the entanglement density, which is the number of entanglement points per unit volume of the polymer (compare to Question 3v of the last sheet).

iii) We have seen, however, that the entanglement is not permanent and that we can model disentanglement using the tube model. This model implies that a chain can recover its random conformation and therefore relax all the stresses resulting from a deformation by diffusing outside a tube, which represents the topological constraint imposed by its neighbors, i.e. entanglement. We can assume that the diffusion coefficient of a chain along this tube is proportional to $1/M$. Where did this result come from?

The diffusion of a polymer chain inside the tube model is described by the process of reptation, i.e. the idea that the polymer chain diffuses along the tube created by entanglements. Over time the chain moves out of its confining tube, thereby relaxing the entanglement-induced stresses.

Rouse's model still governs the local motions of the chain segments within the tube. This means that the diffusion of chain segments within the tube is governed by the same dynamics as predicted by the Rouse model. According to Rouse, the diffusion coefficient is proportional to $1/M$ (Slide 280).

iv) Knowing that the length of the tube must be proportional to M, demonstrate that the disentanglement time, τ_d, is proportional to M^3.

We start with Fick's law which says that the distance diffused in time t is given by $x^2 = Dt$. The disentanglement time τ_d corresponds to the time it takes for the polymer chain to diffuse a distance equal to the length of the tube L and thus "escape" the entangled region. Using Fick's law, we can write:

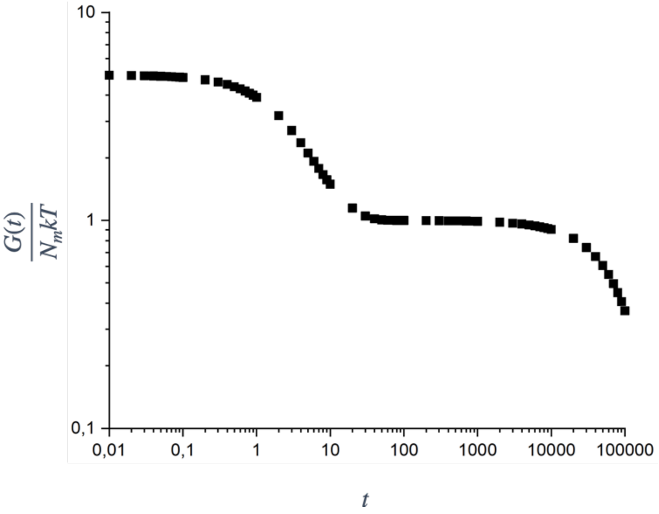
$$L^2 = D\tau_d$$

$$M^2 \propto \frac{1}{M}\tau_d \quad \Longrightarrow \quad \tau_d \propto M^3$$

v) If you have access to Excel, Origin, etc., plot in logarithmic scales

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

as a function of t between 0.01 and 100000 s, taking m = 5, τ_1 = 100000 s and $\tau_p = 40/p^2$. Here, we simulate the effect of entanglement by taking an arbitrarily large value for τ_1. Does this result remind you of anything?



Plot the result on a logarithmic scale! The result is supposed to remind you of the typical rheological curve for a polymer, which shows the evolution of the modulus over the logarithm of the time (or the temperature, in accordance to the time-temperature equivalence) as the polymer undergoes different relaxation processes.

- **At short times ($t < \tau_5$): the system behaves like a glassy state, where the modulus is high, due to the very slow relaxation of the polymer chains.**
- **At intermediate times (around τ_5 to τ_1): the first relaxation time τ_1 is arbitrarily large, simulating a strong entanglement effect, so that the system exhibits a rubbery plateau. The polymer has partially relaxed**

and shows a relatively constant value for the modulus in agreement with the static model of an entanglement network.

- **At long times ($t > \tau_1$): The system transitions to liquid-like behavior, where the modulus decreases as the polymer chains are fully relaxed and the material behaves more like a viscous fluid.**

Be careful with this interpretation, though! In a real polymer, the modulus in the glassy state is some three orders of magnitude higher than the rubbery plateau. Here, the value is rather small because by taking $m = 5$, our model is no longer valid for $t < \tau_5 = 40/25$, i.e. less than one second. 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 (we ignore for a moment, that small chain segments can still move below T_g).

2. We will now simulate the behavior of a freely jointed polymer that is slightly cross-linked.

   i) It is assumed that the crosslinking points are separated along the chains by n_x bonds such that $n >> n_x >> m$ and that the positions of the crosslinking points are fixed by the macroscopic deformation. In this case, relaxations involving chain segments longer than n_x are blocked, leading to infinite relaxation times for these modes:

$$\begin{cases} \tau_p \approx \dfrac{\xi_o n^2 l^2}{6\pi^2 p^2 kT}, & for \quad m \gg 1, p > p_x \\ \tau_p = \infty & for \quad p < p_x \end{cases} \tag{1}$$

Express p_x (the critical mode number where relaxations become blocked) and τ_x (the maximum relaxation time for modes that are not blocked) in terms n_x!

The number of segments involved in mode p is equal to n/p. The critical value of p, denoted as p_x , below which the movements are blocked corresponds to n_x:

$$p_x = \frac{n}{n_x}$$

For this critical mode, the relaxation time τ_x, which corresponds to the longest unblocked relaxation time is:

$$\tau_x = \frac{\xi_o n_x^2 l^2}{6\pi^2 kT}$$

ii) According to the phenomenological models (springs and dashpot) generalized for a linear viscoelastic material, the relaxation shear modulus is given by

$$G(t) = G_\infty + \sum_1^n G_i e^{-t/\tau_i}$$

Show that the effective value of G_∞ is $N_x kT$, where N_x is the number of crosslinking points per unit of volume. Have you seen this result before?

Let's use Rouse's expression for the time-dependent shear relaxation modulus, which for a polymer with crosslinks can be written as (in analogy to our last Exercise Sheet). In the present case, $\tau_p = \infty$ if $p < p_x$, i.e. if $p < n/n_x$.

$$G(t) = NkT \sum_{p=1}^{n/n_x} e^{-t/\infty} + NkT \sum_{p=n/n_x}^{m} e^{-t/\tau_p} \qquad \tau_p \approx \frac{\xi_o n^2 l^2}{6\pi^2 p^2 kT}, \text{for } p \geq n/n_x$$

where N is the number of polymer chains per unit volume (chain density). Here, the first sum corresponds to the modes $p \leq p_x = n/n_x$, where the relaxation times are infinite due to the crosslinking ($\tau_p = \infty$). The second sum corresponds to the modes p > p_x, where the relaxation times are finite.

For the long-time limit, the second sum tends to zero because $t \gg \tau_p$, while the modes with p < p_x do not relax and contribute a constant value to the shear modulus, leading to:

$$G_\infty = NkT \sum_{p=1}^{n/n_x} e^{-t/\infty} = NkT \sum_{p=1}^{n/n_x} 1 = \frac{nNkT}{n_x} = N_x kT$$

where N_x is the number of crosslinks per unit volume. So, if $t >> \tau_x$, we find the behavior of an ideal elastomer with a shear modulus that is proportional to the crosslinking density.

Note that the model is only valid for times in the range $\tau_p < t < \infty$, where $p << n$. If p becomes too large, the segments between the beads have too few bonds to be considered Gaussian chains, and the model breaks down.

iii) Why is Equation 1 no longer valid when p approaches n? In what time interval can we therefore apply this model?

The model assumes that the polymer segments behave like Gaussian chains. For Rouse's model to be valid, the number of bonds per segment (related to p) should be large enough such that the chain segments can be treated as statistically independent and have a Gaussian distribution of their conformations. However, as p gets closer to n, the segments become increasingly short, and the Gaussian approximation no longer holds.

Therefore, the model is only valid when $p << n$, meaning the segments are long enough to maintain the Gaussian chain behavior. In terms of the relaxation time τ_p, this condition translates to the model being applicable for times τ_p that satisfy:

$$\tau_p < t < \infty \quad \text{with} \quad p \ll n$$

3. In the case of an entangled but not crosslinked polymer, the behavior can be simulated very simply by posing $\tau_p = \tau_d$ if $p < p_e$.

i) What do τ_p and τ_d mean?

τ_d is the relaxation time of a given mode, τ_d is the disentanglement time (how long it takes for the chain to escape the entanglement constraints), and p_e is the critical mode number below which relaxation is blocked by the entanglement.

ii) In the tube model, the tube diameter, d_e, is given by

$$d_e = \sqrt{n_e}\,l = \sqrt{\frac{M_e}{M_b}}\,l$$

What do M_e and M_b mean?

M_e: entanglement molecular weight, which represents the molar mass of the polymer chain between two entanglement points.

M_b: this is the average molar mass per bond, which corresponds to the molar mass of a single chemical bond in the polymer chain (i.e. the molar mass of half a monomer unit in case of polyethylene)

iii) Show also that the length of the tube L can be expressed as:

$$L = \frac{M}{M_e}\sqrt{\frac{M_e}{M_b}}\,l$$

The total polymer chain consists of M/M_e subchain segments separated by entanglement points. Each segment has a length d_e.

iv) According to Rouse's model, the diffusion coefficient of a chain inside the tube is

$$D_R = \frac{kTM_b}{\xi_o M}$$

Schow that

$$\tau_e = \frac{\xi_o l^2}{6\pi^2 kT}\left(\frac{M_e}{M_b}\right)^2 \qquad \text{and} \qquad \tau_d = 6\pi^2\left(\frac{M}{M_e}\right)^3 \tau_e$$

Tip: to find the relationship between τ_d and τ_e, start by using Fick's law to express τ_d, and then multiply and divide by τ_e.

We have already shown that

$$\tau_e \approx \frac{\xi_o {n_x}^2 l^2}{6\pi^2 kT}$$

In analogy, we can now write using the expression from *ii*) with n_e being the number of bonds between entanglement points:

$$\tau_e \approx \frac{\xi_o {n_e}^2 l^2}{6\pi^2 kT} = \frac{\xi_o l^2}{6\pi^2 kT}\left(\frac{M_e}{M_b}\right)^2$$

For τ_d, we use Fick's law, the expression of the diffusion coefficient according to Rouse (see Slides), the expression for L from *iii*). For finding a relation to τ_e, let us then just multiply and divide by τ_e using the expression from above:

$$\tau_d = \frac{L^2}{D_R} = \frac{\xi_o M}{kTM_b}\left(\frac{M}{M_e}\sqrt{\frac{M_e}{M_b}}\,l\right)^2 = \frac{\xi_o M}{kTM_b}\left(\frac{M}{M_e}\sqrt{\frac{M_e}{M_b}}\,l\right)^2 \frac{6\pi^2 kT\tau_e}{\xi_o {n_e}^2 l^2} = 6\pi^2\left(\frac{M}{M_e}\right)^3 \tau_e$$

v) Show schematically the behavior of an entangled chain by indicating τ_e and τ_d on a plot of shear modulus $G(t)$ versus time t.

We must use the usual diagram of the elastic behavior of an amorphous polymer in the linear domain, i.e. G (or E) vs. log t, with the glassy regime, the glass transition, the rubbery plateau and the terminal zone, plus the right orders of magnitude. τ_e marks the beginning of the rubbery plateau, where entanglement effects start to dominate the polymer's mechanical response. τ_d marks the end of the rubbery plateau, where the chain has fully disentangled and begins to exhibit a liquid-like response (see Slide 290).