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Exercise 9

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.

   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?

   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?

   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.

   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?

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!

   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?

   iii) Why is Equation 1 no longer valid when p approaches n? In what time interval can we therefore apply this model?

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?

   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?

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

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

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

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

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

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.

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.