

Quiz 9 Polymer Physics 11/29/00

The Rouse model is used to construct more complicated models for polymer dynamics that deal with chain entanglements such as the tube (reptation) model. In the tube model the polymer chain retains Rouse dynamics within the confines of a **rigid** tube of cross-sectional area $\langle a_R^2 \rangle$, the root-mean-square (RMS) size of a Rouse unit. The tube follows a random walk in 3-D space.

- a) If the tube length is $L_p = N_R a_R$, the number of Rouse units in a chain times the square root of the RMS Rouse size, and if the chain in the axial direction of the tube follows Rouse dynamics, with a friction factor of ζ_R for each Rouse unit,
- What** is the total chain friction factor **along the tube axis** for the chain in the tube, ζ_p ?
 - How does** this compare with the Rouse chain friction factor in 3D space?
- b) The Einstein relationship tells us that the diffusion coefficient should follow $D = kT/\zeta$.
- What is** the diffusion coefficient for the entire chain for motions along the length of the tube (along the tube axis)?
 - What is** the predicted molecular weight dependence of this diffusion coefficient?
 - How** does this compare with the Rouse diffusion coefficient?
- c) For Brownian motion, such as motion of the chain in the tube, the distance traveled, d , in time, t , is given by $d = \sqrt{Dt}$.
- What is the average** time for the chain to move the length of the tube (this is called the reptation time, τ_d)?
 - How** does τ_d scale with molecular weight?
 - How** does this compare with the scaling of the lowest order Rouse time, τ_R , with molecular weight?
 - How** does this compare with the observed relaxation time for entangled systems (same as the scaling behavior of τ_0 with molecular weight)?
- d) The diffusion coefficient for center of mass motion of a chain in a tube in 3D-space is determined by considering the size of the random walk tube in 3-d space, $R_0 = N_R^{1/2} a_R$, and the time required to move the length of the tube. ($D = (\text{distance})^2/\text{time}$)
- What is** the molecular weight dependence of the diffusion coefficient for chain motion in 3D-space for a chain confined to a tube?
 - How** does this compare with the Rouse diffusion coefficient you gave above?
- e) In general terms, **why** is the Rouse model used as the basis for more complicated polymer dynamics such as systems with hydrodynamic interactions or entanglements? (i.e. **What experimental data supports the Rouse model?**)

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a) If the chain follows Rouse dynamics in the tube axial direction, called the *primitive path* of the chain, the total chain friction factor is the same as the Rouse chain friction factor, $\zeta_p = N_R \zeta_R$.

b) The diffusion coefficient along the primitive path is the Rouse diffusion coefficient, $D = kT/N_R \zeta_R$. The diffusion coefficient along the primitive path scales with the inverse of the molecular weight just as the Rouse diffusion coefficient scales.

c) $\tau_d = (L_p)^2/D_p$, where p indicates along the primitive path. Then, $\tau_d = (N_R a_R)^2 / (kT/N_R \zeta_R) = a_R^2 N_R^3 / kT$. The *reptation* relaxation time scales with the cube of the molecular weight. The Rouse relaxation time scales with the square of the molecular weight, $\tau_R = N^2 (a_R^2 / (3kT \zeta_R))$. For entangled systems $\tau_0 \propto (\text{molecular weight})^{3.4}$, so the reptation solution doesn't completely explain the observed behavior.

d) $D_{\text{center of mass}} = N_R a_R^2 / \zeta_d = N_R a_R^2 / (a_R^2 N_R^3 / kT) = kT / (N_R \zeta_R)$. The center of mass diffusion coefficient scales with N^{-2} . The Rouse chain 3D diffusion coefficient scales with $1/N$.

e) The Rouse Model explains the behavior of a number of experimentally observed dynamic features in terms of molecular weight and thermal dependence. These include:

- Prediction of a Debye relaxation behavior for $\tau_{nm}(\omega)$ and N^2 dependence for τ_{nm} .
- Linear dependence on molecular weight for τ_0 in unentangled systems.
- Dependence of storage modulus on $\omega^{-1/2}$.
- Dependence of time dependent modulus on $t^{-1/2}$.
- Observed behavior of the relaxation time on the square of the molecular weight.