Quiz 14 Polymer Properties December 1, 2014

Kalathi, Kumar, Rubinstein, and Grest (*Macromolecules* **47** 6925 (2014)) simulated polymer chains of variable flexibility and molar mass to observe the transition from Rouse to entangled dynamics. The figure below shows the behavior of the correlation function for chain position as a function of time for a completely flexible chain of 500 Rouse units of variable Rouse mode, p. The dashed lines are fits to an exponential decay function.

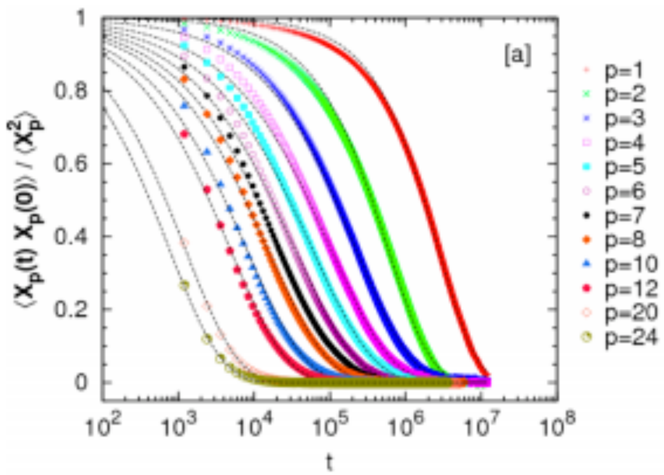


Figure a

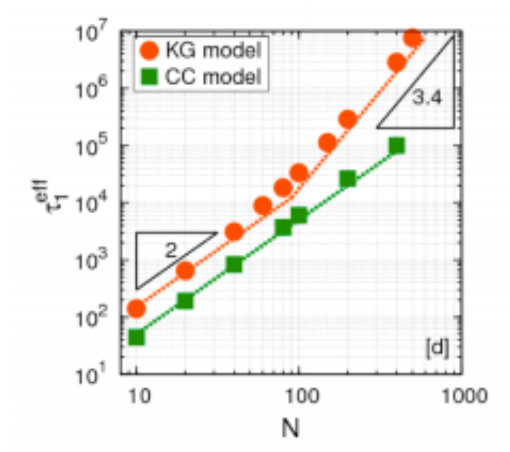


Figure b

(Both Figures from Kalathi, Kumar, Rubinstein, and Grest, *Macromolecules* **47** 6925 (2014))

a) Draw a cartoon of the Rouse model and give equations describing the spring constant and friction factor for the Rouse units.

b) Give a force balance (equation of motion, or Langevin equation) for a Rouse unit, and a proposed function that can be used as a solution for this series of differential equations.

c) Kalathi et al. find the results shown in Figure a from their simulation. What function would be used to obtain the relaxation time from this figure? How do you expect the relaxation time to change as a function of p? How would the magnitude of the Rouse vibration, $\langle X_p^2 \rangle$, change with p?

d) Figure b shows τ_1 as a function of N. Explain the behavior of the top curve.

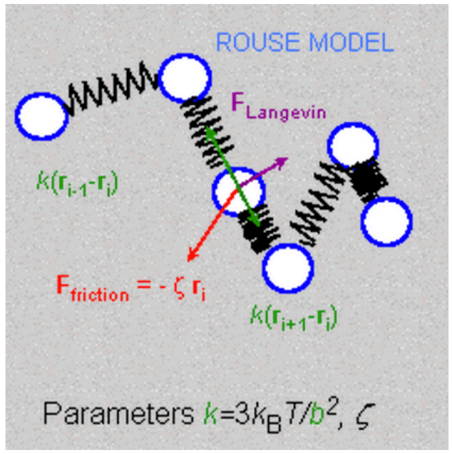
e) The longest relaxation time (except for p = 0) for the Rouse model is given by

$$\tau_R = \frac{1}{3\pi^2}\frac{\left(\frac{\zeta_R}{a_R^2}\right)}{kT}R_0^4$$

. What is the main assumption of the Rouse model that is inherent to this equation? Does this equation agree with the figures from Kalathi et al.?

ANSWERS: **Quiz 14 Polymer Properties December 1, 2014**

a) $k_{spr} = \dfrac{3kT}{2n_R l^2}$; $\zeta_R = 6\pi a_R \eta_0$; $\tau_R = \dfrac{\zeta_R}{k_{spr}}$



b)

$$\varsigma_R \frac{dz_l}{dt} = b_R(z_{l+1} - z_l) + b_R(z_{l-1} - z_l) \qquad z_l \sim \exp\left(-\frac{t}{\tau}\right)\exp(il\delta)$$

c) $\dfrac{\langle X_p(t)X_p(0)\rangle}{\langle X_p^2\rangle} = \exp\left(\dfrac{-t}{\tau_p}\right)$

The relaxation time is longest for the smallest p.

$$\tau^{-1} = \frac{b_R}{\zeta_R}(2 - 2\cos\delta) = \frac{4b_R}{\zeta_R}\sin^2\frac{\delta}{2} \qquad \delta_p = \frac{\pi}{(N_R - 1)}p$$

The magnitude is largest for the smallest p.

$$\langle X_p^2\rangle = \frac{2}{3\pi^2}\frac{R_0^2}{p^2} = \frac{2}{3\pi^2}\frac{Nl^2}{p^2}$$

d) At low N we expect Rouse behavior, at high N we expect to observe reptation. The Rouse model predicts

$$\tau_R = \frac{1}{3\pi^2}\frac{\left(\frac{\zeta_R}{a_R^2}\right)}{kT}R_0^4 \qquad \tau_R \sim \frac{N^2}{kT}$$

The reptation model predicts that $\tau \sim N^3$. Experimentally in reptation it is observed that $\tau \sim N^{3.4}$.

e) The main assumption is that the ratio (ζ_R/a_R^2) is constant, where the Rouse relaxation time is associated with the first mode of vibrations. Figure b supports this assumption for small N since $R_0^4 \sim N^2$.