Quiz 13 Polymer Physics April 24, 2020

Diblock copolymers can form an ordered state (lamellar domains of the two blocks for instance), usually at elevated temperatures or a disordered state at low temperatures (a more or less normal polymer melt). Even in the disordered state the two blocks tend to segregate leading to concentration fluctuations that can be observed by dynamic light scattering or a similar technique using synchrotron X-rays (small-angle X-ray PCS). In these techniques the time dependent structure factor S(q,t) is measured which is expected to follow an exponential decay in time. S(q,t) as a function of q shows a peak associated with fluctuations associated with the size of the blocky fluctuations. The relaxation time associated with the exponential decay of intensity with time at various q's also shows a peak indicating that relaxations near the size scale of the fluctuations are slow, while smaller or larger scale fluctuations are faster.

T. Ghasimakbari and D. C. Morse *Dynamics and Viscoelasticity of Disordered Melts of Symmetric Diblock Copolymers* Macromolecules **52** 7762–7778 (2019) discuss the dynamics of diblock copolymers in the disordered state. They performed coarse grain simulations of deblock copolymers and obtained S(q,t) and the stress relaxation modulus G(t).



a) The graphical abstract above shows the behavior of G(t) as a function of t/τ_0 where τ_0 is the Rouse relaxation time. This is a log-log plot so an exponential decay looks like a knee. At low χN the system is miscible and disordered and approaches microphase separation at higher χN , above about 10.5. Give the Rouse prediction for G(t), compare that with Ghasimakbari's plot and comment on what happens at large χN .

b) Figure 2 shows the behavior of the block copolymer diffusion coefficient, *D*, divided by the homopolymer diffusion coefficient, D_0 . Both diffusion coefficients follow $D = \frac{k_B T}{N\zeta}$, which is not shown in the plot. Derive this expression and explain the behavior seen in Figure 2 for χN above about 10.5.

c) Ghasimakbari is able to obtain the time correlation function for the end-to-end vector for the block copolymers from his coarse grain simulations, $E(t) = \langle \mathbf{R}_{e}(t) \cdot \mathbf{R}_{e}(0) \rangle$, which is expected to follow an exponential decay in time following the Rouse theory,

$$E(t) = \frac{8b^2N}{\pi^2} \sum_{p=1,3,\dots}^{\infty} \frac{1}{p^2} \exp\left(-\frac{t}{\tau_p}\right).$$
 Define *p* and τ_p in this equation with at least two sentences for

each term.

d) Ghasimakbari plots the Rouse relaxation times from the diffusion coefficient and from the end-to-end vector versus χN in Figure 5. In the caption he mentions that $D = k_B T/N\zeta$. Comment on the behavior seen in Figure 5.



Figure 5. Evolution of the end-to-end autocorrelation terminal relaxation time τ_e and the diffusion time τ_d with $\chi_e N$. Both relaxation times are normalized by the value of τ_e in a homopolymer melt, denoted by τ_{e0} . The diffusion time τ_d is defined to be the terminal internal relaxation time τ_1 predicted by the Rouse model by using a friction coefficient ζ obtained from the tracer diffusivity, by setting $D = k_{\rm B} T/N\zeta$.



Figure 18. Normalized stress relaxation modulus, $NG(t)/ck_BT$ for disordered melts of chains of length N = 16 over a wide range of values of $\chi_e N$. The value at the ODT is $(\chi_e N)_{\text{ODT}} = 21.72$.

e) Ghasimakbari mentions that "*The Rouse model predicts a power-law decay* $G(t) \sim t^{1/2}$ *at times* $t << \tau_R$ followed by exponential decay at times $t > \tau_R$." Explain why this transition occurs. A power-law of -1/2 on a log-log plot can be estimated by drawing by hand a line spanning two decades in x and minus one decade in y. Sketch such a line in figure 18 to verify that the transition mentioned by Ghasimakbari occurs in these results.

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a) The graphical abstract above shows the behavior of G(t) as a function of t/τ_0 where τ_0 is the Rouse relaxation time. This is a log-log plot so an exponential decay looks like a knee. At low γN the system is miscible and disordered and approaches microphase separation at higher γN . above about 10.5. Give the Rouse prediction for G(t), compare that with Ghasimakbari's plot and comment on what happens at large γN .

The Rouse prediction is from Colby Rubenstein:

$$G(t) \approx \frac{kT}{b^3} \phi \left(\frac{t}{\tau_0}\right)^{-1/2} \exp(-t/\tau_{\rm R}) \quad \text{for } t > \tau_0.$$
(8.48)

The exponential decay in time follows Ghasimakbari's plot at low χN . At high χN micro-phase separation occurs and a modulus enhancement occurs at long times associated with micro-phase separation. The material is behaving like a solid, so this is something like the formation of a gel network based on the microphase separated phases.

b) Figure 2 shows the behavior of the block copolymer diffusion coefficient, D, divided by the homopolymer diffusion coefficient, D_0 . Both diffusion coefficients follow $D = \frac{k_B T}{N\zeta}$, which is not shown in the plot. Derive this expression and explain the behavior seen in Figure 2 for γN above about 10.5.

The Einstein-Stokes equation predicts that the diffusion coefficient will follow $D \sim kT/\zeta =$ kT/($6\pi\eta R_{\rm H}$). For the Rouse theory $\zeta = N \zeta_b$ and RH is the radius of a Rouse unit, b, so D ~ kT//(N6 π nb), where 6π nb = ζ_b the friction factor for a single Rouse unit. Above $\gamma N = 10.5$ diffusion slows due to microphase separation that forms a gel network in the sample.

c) Ghasimakbari is able to obtain the time correlation function for the end-to-end vector for the block copolymers from his coarse grain simulations, $E(t) = \langle \mathbf{R}_{e}(t) \cdot \mathbf{R}_{e}(0) \rangle$, which is expected to follow an exponential decay in time following the Rouse theory, Define \mathbf{n} and \mathbf{r} in this sector for the sector \mathbf{r}_{p} .

Define p and τ_p in this equation with two sentences for each term.

p is the Rouse mode. In analogy to a guitar string, the first mode is vibration of the entire string as a unit, second mode is two half strings independently vibrating, third is three. etc. Each mode is treated as a simple relaxer so a single exponential decay in time with the time constant τ_p . τ_p can be determined from

$$\tau_p \approx \tau_0 \left(\frac{N}{p}\right)^2$$
 for $p = 1, 2, \dots, N$. (8.44)

From Colby and Rubenstein.

d) Ghasimakbari plots the Rouse relaxation times from the diffusion coefficient and from the end-to-end vector time decay versus χN in Figure 5. In the caption he mentions that $D = k_B T/N \zeta$. Comment on the behavior seen in Figure 5.

The relaxation time increases above $\chi N = 10.5$ due to the formation of a microphase separated network.

e) Ghasimakbari mentions that "The Rouse model predicts a power-law decay $G(t) \sim t^{-1/2}$ at times $t << \tau_R$ followed by exponential decay at times $t > \tau_R$." Explain why this transition occurs. A power-law of -1/2 on a log-log plot can be estimated by drawing by hand a line spanning two decades in x and minus one decade in y. Sketch such a line in figure 18 to verify that the transition mentioned by Ghasimakbari occurs in these results.

Below the Rouse time, 10^0 on the x-axis of the plot, the material behaves as a simple fluid. Above this point the Rouse relaxations internal to the chain dominated by the Rouse relaxation time for the lowest order mode control the time dependent modulus. This is characterized by an exponential decay in the Rouse relaxation time.



Figure 18. Normalized stress relaxation modulus, $NG(t)/ck_BT$ for disordered melts of chains of length N = 16 over a wide range of values of $\chi_e N$. The value at the ODT is $(\chi_e N)_{ODT} = 21.72$.