Quiz 3
Polymer Physics
February 7, 2019

Blaber, Mahmoudi, Spencer and Matsen J. Chem. Phys. **150** 014904 (2019) *Effect of chain stiffness on the entropic segregation of chain ends to the surface of a polymer melt* discuss the possible segregation of chain ends to the surface of polymer melts. They use the following equation to model the change in surface tension, γ, (energy per area) with molecular weight, N,

$$\frac{\gamma_{en}}{a\rho_0 k_B T} \approx \Gamma_\infty - \frac{2A}{N}, \qquad (3)$$

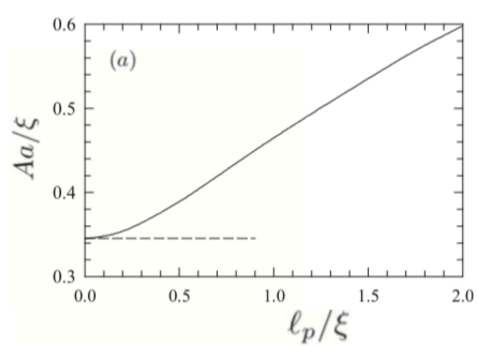
where A is a constant associated with the distribution of chain ends, $\delta\phi_e(z)$, within one R_{eted} from the surface.

$$\delta\phi_e(z) \approx \frac{A}{N^{1/2}} B\left(\frac{z}{aN^{1/2}}\right), \qquad (1)$$

$B()$ is a complicated function.

a) The experimentally verified Equation (3) is similar to the Flory-Fox equation, $T_g = T_{g,\infty} - \frac{K}{M_n}$. Explain the origin of equation (3) and the reason for the factor "2". What does the first term after the equal sign correspond to?

b) Blaber et al. assume that the chain persistence length is proportional to a chain bending modulus κ, $\ell_p = b\kappa$. Blaber et al. propose that changes in chain stiffness can lead to greater segregation (larger "A") since folding of a chain at the interface is inhibited by chain stiffness and this encourages "entropic" segregation of chain ends to the surface. The following plots show the dependence of surface tension on chain persistence (eqn. 3) from Blaber et al.'s calculations based on "self-consistent field theory". The dashed lines are for freely jointed Gaussian chains. ξ is the breadth of the surface concentration profile for end-group segregation (see plot at end of this quiz). Does the entropy proposition make sense to you? Explain. Do you believe the result for the first plot where A is linear in persistence? Why does Γ_∞ increases to a plateau with chain stiffness? Why is Γ_∞ 0 at 0 persistence?



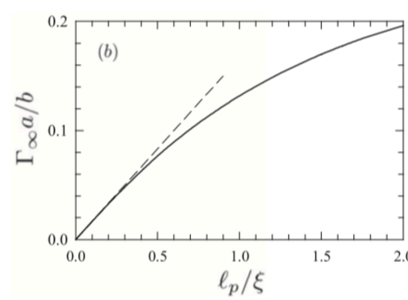


FIG. 2. (a) Dimensionless surface excess of chain ends, A, and (b) dimensionless surface tension, Γ_∞, as a function of persistence length, ℓ_p, calculated in the long-chain limit. The dashed lines denote the Gaussian-chain predictions in Eqs. (22) and (23).

c) In class we discussed the dependence of chain persistence length with molecular weight in the context of C_n and C_∞. What are C_n and C_∞? How does C_n change with molecular weight. How does it change with chain index?

d) Consider Blaber's results in the context of a changing persistence length with molecular weight. How does this impact his entropic model?

e) Blaber indicates that the "entropic" segregation drives low molecular weight species in a polydisperse sample to the surface. There is some experimental support for this proposition. Is this consistent with the dependence of persistence on molecular weight in part c?

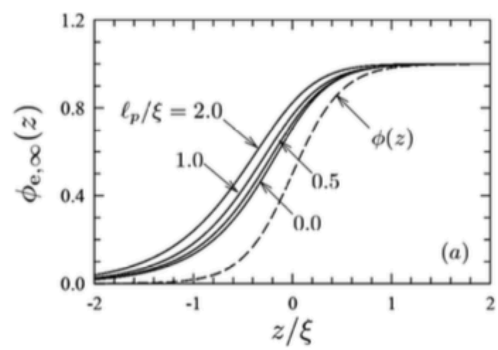


FIG. 1. (a) Concentration of chain ends, $\phi_{e,\infty}(z)$, and (b) self-consistent field, $w_{\infty}(z)$, calculated in the long-chain limit (i.e., $\ell_c \to \infty$) for different persistence lengths, ℓ_p. The $\ell_p = 0$ curves are given by Eqs. (19) and (20). The dashed curve in (a) denotes the total polymer concentration, $\phi(z)$.

This plot shows the profile of chain ends as a function of distance from the surface "z". ξ is the breadth of the surface concentration profile for end-group segregation.

Quiz 3

a) The concentration of end-groups is proportional to

$$\phi_e \sim \frac{2}{M}$$

The first term Γ_∞ corresponds to the $M \to \infty$ limit.

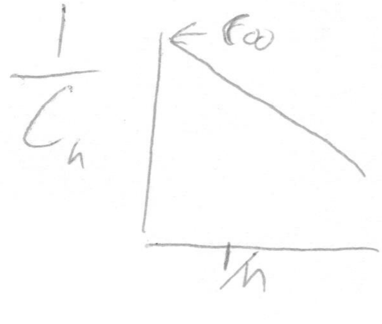
The surface tension in the absence of chain ends.

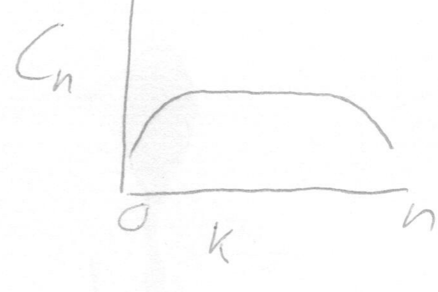
b) The entropy proposition seems convoluted. I have no idea why chain stiffness would impact end group segregation and entropy doesn't help.

I suppose in the limit of rods, only one end could be at the surface so $\phi_{e_{rods}} \sim \frac{\phi_{e_{coils}}}{2}$ and there could be a gradient from flexible to rods. ~~that a should probably be $\frac{1}{l_p}$ not l_p in the x axis.~~

c) $$C_n = \frac{\langle R_n^2 \rangle}{\langle R^2_{ideal} \rangle} = \frac{\langle R_n^2 \rangle}{n_k l_k^2} = \frac{L\, l_{ep}}{L\, l_k} = \frac{l_{ep}}{l_k}$$

when $n \Rightarrow \infty$ C_∞





d) He predicts a new dependence of the chain persistence impact on the molecular weight dependence of surface tension

$$\gamma \sim kT\left(\Gamma_\infty - \frac{2A}{N}\right)$$

So $A(l_p)$. but if $\frac{1}{l_p} \sim \frac{K_1}{N} + K_2$

this becomes some function of N co

he doesn't have an inverse relationship then.

anyway eqn (3) is wrong

Actually a ness he set a chain stiffness but never really measures l_p for his result.

(e)

low MW → low lp

for low lp you get more end group repulsion

so it is consistent with his proposition

and with experiment.