1) Unidad, Richter, and Fetters [*Macro.* **48** 6638 (2015)] draw connections between the packing length, p, and certain rheological transitions they have found in polymer melts. Unidad describes three regimes seen in Figure 1 below: 1.) Rouse behavior for $M < M_c$; 2.) Reptation with constraint release and contour fluctuations between M_c and M_r; and 3.) Pure reptation behavior for high molecular weights $M > M_r$.

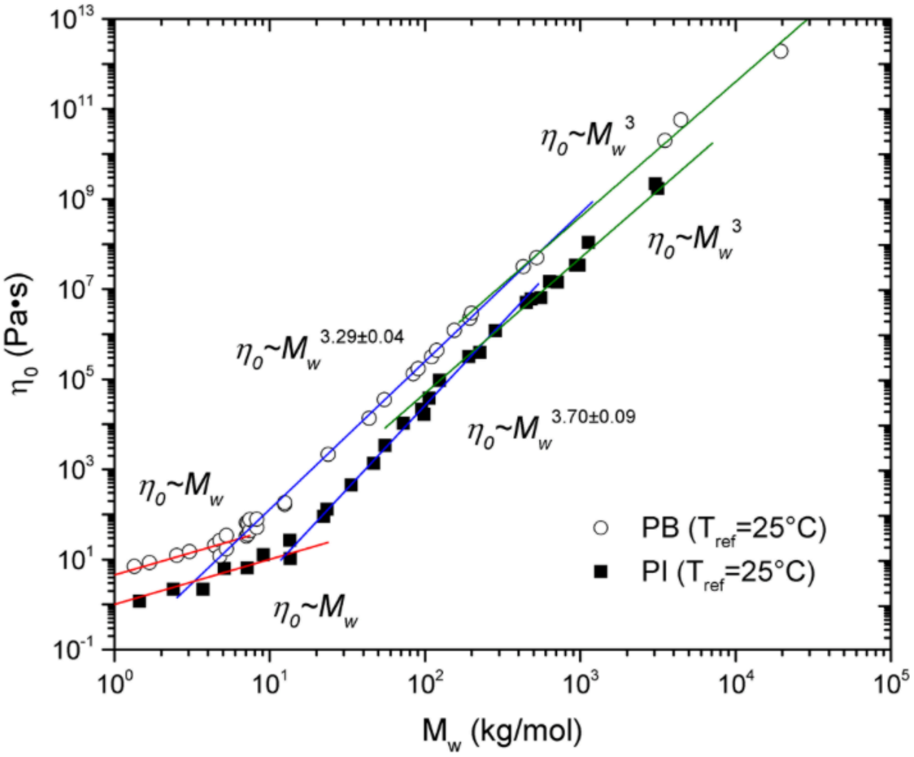

Figure 1. Experimental data for the zero-shear viscosity as a function of molecular weight of polybutadiene (PB) and polyisoprene (PI) melts. Data are obtained from various sources[9,11,12] and show the three scaling regimes. Lines show the different power law fits for each regime.

a) Give an equation that defines the packing length.

b) The entanglement molecular weight, M_e, is determined by the plateau modulus, $G_0 = \rho RT/M_e$. Derive this equation from the Gaussian probability function and explain why M_e is related to the plateau modulus.

c) Unidad relates M_c and M_r from Figure 1 with M_e using, $M_c = M_e[p^*/p]^{0.65}$ and $M_r = M_e[p^*/p]^{3.9}$, where p is the packing length, and p* is a constant of about 12 Å. What happens to the behavior seen in Figure 1 as p approaches p*? Can p be larger than p*? Explain.

d) Unidad describes the tube diameter, a, as "the end-to-end distance of an entanglement strand" citing Doi and Edwards. Explain this definition of the tube diameter. What happens to the tube at long times, $t > \tau_{entanglement}$. How is $\tau_{entanglement}$ affected by M_w?

e) Three parameters on the order of 1 nm are used to describe local polymer structure, the tube diameter, a, the packing length, p, and the Kuhn length, l_K. Explain what the Kuhn length is and how it relates to the persistence length, l_P.

2) The figure below by Wilding, Müller, and Binder shows a phase diagram for a polymer solution.

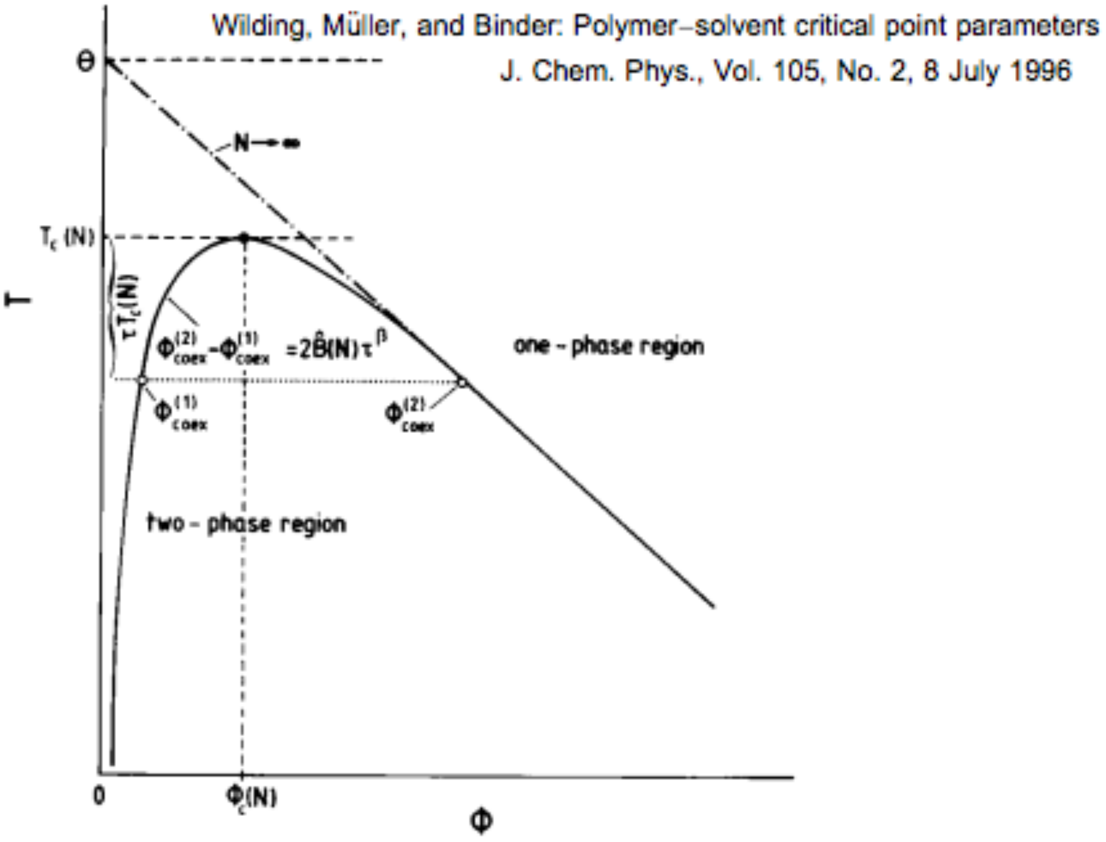
Wilding, Müller, and Binder: Polymer–solvent critical point parameters
J. Chem. Phys., Vol. 105, No. 2, 8 July 1996

FIG. 1. Schematic phase diagram of a polymer solution in the space of the temperature T and the volume fraction ϕ. The coexistence curve separates a dilute solution of collapsed chains [at $\phi^{(1)}_{\text{coex}}$] from a semidilute solution of overlapping chains [at $\phi^{(2)}_{\text{coex}}$]. These two branches of the coexistence curve merge at a critical point $T_c(N)$, $\phi_c(N)$. For $N\rightarrow\infty$ the critical point merges with the Θ point of a dilute polymer solution [$T_c(N\rightarrow\infty)\rightarrow\Theta$, $\phi_c(N\rightarrow\infty)\rightarrow 0$] and the unmixing transition has a tricritical character. At $T=\Theta$, the chain configurations are ideal Gaussian coils, while their structure at $T_c(N)$ is nontrivial.

a) Give an equation that describes the behavior of Figure 1.
b) How are the critical temperature and critical composition determined from the equation of part a?
c) Give an equation for the overlap concentration, ϕ^*. How would ϕ^* impact the phase diagram shown in Figure 1?
d) Explain what the caption means when it mentions that the chain in the collapsed state is Gaussian while in solution it is an expanded coil. Why is the structure "non-trivial" at the critical point?
e) Is it possible to have a thermodynamically stable ***dilute*** polymer solution below the theta temperature? Why does the theta temperature "have a tricritical character"?