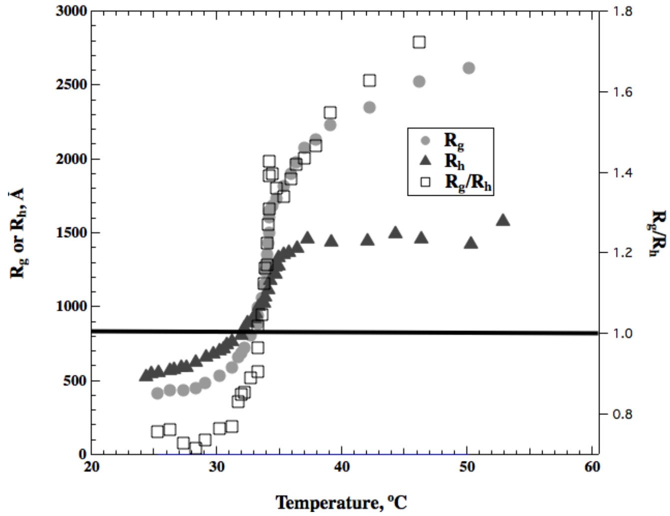
Quiz 11 Polymer Properties November 7, 2014

The following plot shows the behavior of R_g, R_h and R_g/R_h for polystyrene in cyclohexane.



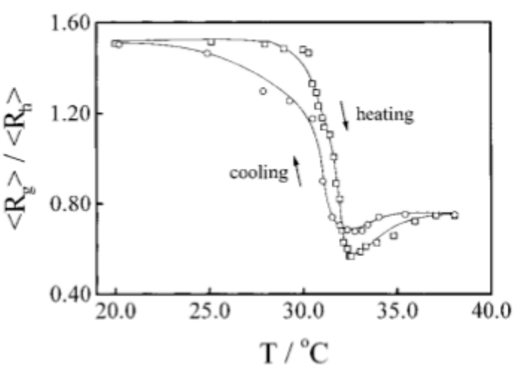


Figure 4. Temperature dependence of the ratio of radius of gyration to hydrodynamic radius ($\langle R_g \rangle / \langle R_h \rangle$) of the PNIPAM chains in the coil-to-globule (heating) and the globule-to-coil (cooling) transitions, respectively.

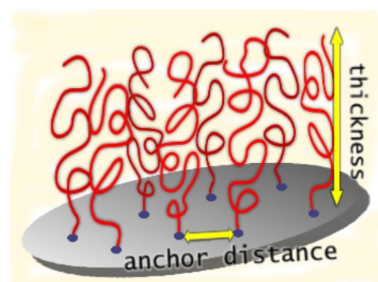


Figure for Part "e"

Wang X., Qiu X. , Wu C. Macro. 31 2972 (1998).
(http://www.eng.uc.edu/~gbeaucag/Classes/Properties/RgbyRhPNIPAAMma971873p.pdf)

a) How is R_h measured using DLS? Give and equation for $g_2(q,t)$, $g_1(q,t)$, and the Stokes-Einstein equation for D.
b) For a sphere we expect that R_h is the sphere radius. What is R_g/R_h for a sphere?
c) For an Gaussian coil R_h is calculated by the Kirkwood expression to be $R_h \sim (3/11)\, R_{eted}$, where R_{eted} is the mean end-to-end distance. What is R_g/R_h for a Gaussian coil? What value for R_g/R_h would you expect for an expanded coil chain?
d) Explain the behavior of R_g/R_h in the top plot above. (For the lower plot, explain the difference between the two curves and the minimum in the second plot above for extra credit if you have time.)
e) What is the estimated thickness of a layer of surface grafted Gaussian coils if the grafting density is one chain per $nl_k^2/16$ (Use the tensile blob model in your calculation and make some assumptions. Give your answer in terms of n and l_k.)

ANSWERS: **Quiz 11 Polymer Properties November 7, 2014**

1) a)

In order to be able to use the *fluctuation* of the intensity around the average value, we need to find a way to represent the fluctuations in a convenient manner. In Section 5.3b in our discussion of Rayleigh scattering applied to solutions, we came across the concept of fluctuations of polarizabilities and concentration of scatterers and the role they play in light scattering experiments. In the present section, what we are interested in is the *time dependence* of such fluctuations. In general, it is not convenient to deal with detailed records of the fluctuations of a measured quantity as a function of time. Instead, one reduces the details of the fluctuations to what is known as the *autocorrelation function* $C(s,t_d)$, as defined below:

$$C(s,t_d) = \lim_{t_n \to \infty} \frac{1}{t_n} \int_0^{t_n} i(s,t)i(s,t+t_d)dt = \overline{i(s,0)i(s,t_d)}$$
$$\approx \lim_{n \to \infty} \frac{1}{n} \sum_{k=0}^{n} i(s,k\Delta t)i(s,(k+j)\Delta t) \quad (103)$$

where $t_d = j\Delta t$. The last part of the equation shows how the autocorrelation function is calculated experimentally when the intensity is measured in discrete time steps as illustrated in Figure 5.16a. The time t_d is known as the *delay time* since it represents the delay in time between the two signals $i(s,k\Delta t)$ and $i(s,(k+j)\Delta t)$ and is equal to $j\Delta t$ (see Figure 5.16a). The

$$\frac{C(s,t_d)}{[\bar{i}(s)]^2} = g_2(s,t_d) = 1 + \xi |g_1(s,t_d)|^2$$

$$g_1(s,t_d) = \exp(-s^2 D t_d)$$

$$D = \frac{k_B T}{6\pi\eta R_H}$$

b) R_g for a sphere is $(3/5)^{1/2}$ R and if R_h = R then R_g/R_h = 0.775 or about 0.8.
c) For a Gaussian chain $R_g = R_{eted}/\sqrt{6}$ so $R_g/R_h = 11/(3\sqrt{6}) = 1.50$. For an expanded coil chain we would expect a larger value than 1.5.
d) At high temperature the coil displays the expected value for an expanded coil, $R_g/R_h > 1.5$. The theta transition seems to occur near R_g/R_h = 1 not at 1.5. This is not expected. Below the theta temperature the chain collapses to a value similar to that of a sphere. The collapsed coil displays a R_g/R_h smaller than 0.8 which is unexpected. The behavior is roughly what is calculated but seems to be a little off in the experimental data.

The second plot shows the behavior of a synthetic polymer that mimics protein folding. First, the process is different on folding and on unfolding since the structure takes different pathways for folding and unfolding. Second, collapse occurs on heating since this is an LCST system. Third, the dip at high temperature is due to rearrangement of the structure after it collapses. This is similar to a molten globule to native transition in proteins.

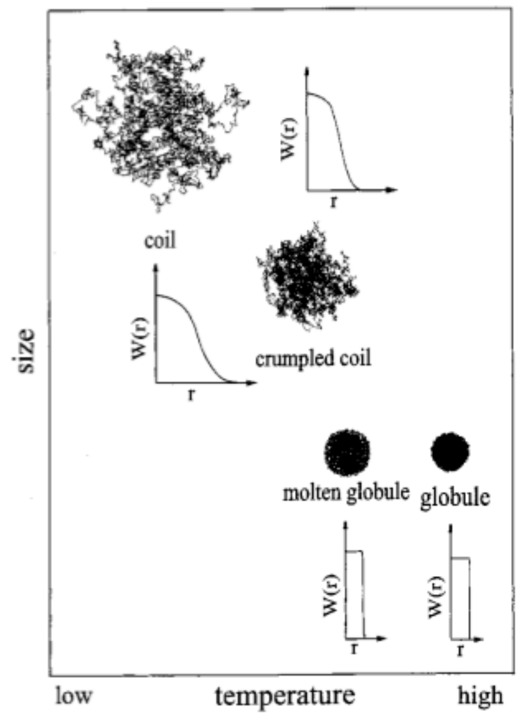


Figure 7. Schematic of four thermodynamically stable states and their corresponding chain density distributions ($W(r)$) along the radius in the coil-to-globule and the globule-to-coil transitions.

1.5 = Random Coil
~0.56 = Globule
Globule to Coil => Smooth Transition
Coil to Globule => Intermediate State
Less than $(3/5)^{1/2}$ = 0.77 (sphere)

e) The layer thickness would be about 4 times the free coil end-to-end distance.

$$R_{eted} = n^{1/2} l$$

$$\xi = \left(\frac{n^{1/2} l}{4}\right)$$

blobs $R = N_\xi \xi^1$

$$n_\xi^{1/2} l = \xi = \frac{n^{1/2} l}{4}$$

$$n_\xi = \frac{n}{16}$$

$$N_\xi = \frac{n}{n_\xi} = 16$$

$$R = 16\xi = 4 n^{1/2} l_k = 4 R_{eted}$$