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A Simple Explanation of the Polymer Collapse Transition: The (6/5)ths and the (2/3)rds Laws[†]

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The polymer collapse transition has been the subject of continuing interest since the first work by Flory[1] in 1949. A useful recent review by Williams, Brochard, and Frisch[2] shows the status of the field. The present paper does not contribute new knowledge. What it does is derive the main features of polymer collapse with what I think is the simplest possible treatment. Hopefully, this paper will prove useful to (1) students, (2) others interested in understanding the basic physics with a minimum expenditure of time, and (3) those who cannot follow the more complicated treatments for whatever reason.

Theory

Since the treatment is so simple, we begin with the result.

$$W = [R^2 \exp(-b^2R^2)][\prod_{j=0}^{n-1}(1 - jl^3/R^3)]\left[\exp\left\{n\chi\left(1 - \frac{nl^3}{R^3}\right)\right\}\right] \tag{1}$$

W is the weighting factor (Boltzmann factor) associated with a single polymer molecule of size R, where R is taken to be the end-to-end length. The first term in square brackets is proportional to the total number of configurations of a chain of n segments ($b^2 = 3/2nl^2$, where l^2 is the mean square length of a segment along the contour length of the chain). If there were no interferences between segments, the first term would be all that is needed and $\langle R^2\rangle$ would be proportional to n. This can be verified either by using the definition of $\langle R^2\rangle$, for which case

$$\langle R^2\rangle = \int_0^\infty R^4 \exp(-b^2R^2)\,\mathrm{d}R \Big/ \int_0^\infty R^2 \exp(-b^2R^2)\,\mathrm{d}R = nl^2 \tag{2}$$

or by finding the value of R (R_m) that maximizes the first term

$$R_m^2 = {}^2\!/_3 nl^2 \tag{3}$$

The second term of eq 1 corrects for excluded volume. Let us generate one of the shapes enumerated by the first term by constructing the chain one segment at a time beginning at one end. The construction will be successful only if each of the n contiguous segments shows no overlap. We must therefore estimate the probability that n contiguous sites are all empty. We will use the approximation that the probability that a site is empty given that j segments have already been placed down is $1 - jl^3/R^3$. This "volume fraction of emptiness" term is obtained by assuming that the previously placed segments can occupy the given site with a probability proportional to their volume fraction. The joint probability that the n contiguous sites are all unoccupied is obviously given by the second term of eq 1.

The third factor is the usual energetic term that measures the heat of mixing n polymer segments viewed as being distributed at random with $(R/l)^3 - n$ solvent molecules. The volume fraction of solvent is $V_0 = 1 - nl^3/R^3$ and the χ parameter is $\chi = z(\epsilon^{21} - (\epsilon_{22} + \epsilon_{11})/2)$.

Equation 1 contains all the physics of both the expanded and collapsed states. It remains for us only to extract the information. This is strictly a mathematical question and introduces no new physics. The most straightforward approach would be evaluate various moments $\langle R^d\rangle$

$$\langle R^d\rangle = \int_0^\infty R^dW\,\mathrm{d}R \Big/ \int_0^\infty W\,\mathrm{d}R \tag{4}$$

as a function of the variables n, l, and χ. However, these integrals cannot be done in closed form. The other way is to evaluate the value of R that makes W a maximum (maximum term method). This method results in analytical formulas and has the advantage that it can be compared to previous treatments that also use the maximum term method, but as eq 2 and 3 show, there may be some slight inaccuracies introduced. The value of R that maximizes W is easily shown to be

$$\alpha^5 - {}^2\!/_3\alpha^3 = -n^{1/2}[n\alpha^6(\ln\,(1 - n^{-1/2}\alpha^{-3}) + n^{-1/2}\alpha^{-3}) + \chi] \tag{5}$$

where $\alpha = R/(nl)^{1/2}$. In obtaining (5) it was useful to replace the second term by

$$\prod_{j=0}^{n-1}\left(1 - \frac{jl^3}{R^3}\right) = \frac{[(R/l)^3]!}{[(R/l)^3 - n]![(R/l)^3]^n} \tag{6}$$

and to maximize the ln W.

We can compare this to the original Flory result by expaning the ln term.

$$\alpha^5 - {}^2\!/_3\alpha^3 = n^{1/2}[{}^1\!/_2 - \chi] + n^{3/2}\alpha^6(\sum_{k=3}^{\infty}(n^{-k/2}\alpha^{-3k}/k)) \tag{7}$$

The right-hand side descends in powers of $n^{1/2}$ so that for $\alpha > 1$ we have for n large

$$\alpha^5 - {}^2\!/_3\alpha^3 = n^{1/2}[{}^1\!/_2 - \chi] \tag{8}$$

which is the Flory result except for the unimportant coefficient of ${}^2/_3$ multiplying α^3. There is a simple way to get rid of this coefficient. If we were to have maximized RW rather than W, then eq 3 would read $R_m^2 = nl^2$, which is identical with eq 2. This suggests that we maximize RW in the more general problem. The only effect is to change the left-hand side of eq 5, 7, and 8 from $\alpha^5 - {}^2/_3\alpha^3$ to $\alpha^5 - \alpha^3$.

When ${}^1/_2 - \chi > 0$ we have

$$\alpha = [{}^1\!/_2 - \chi]^{1/5}n^{1/10}$$

$$R^2 = [{}^1\!/_2 - \chi]^{2/5}n^{6/5}l^2 \qquad \text{expanded polymer} \tag{9}$$

which means that R^2 varies as $n^{6/5}$.

As χ becomes greater than ${}^1/_2$, eq 8 gives a nonsensical result, the only real solution for α being negative. To understand the collapse transition one must resort to eq 5. The fact that the bracketed part of the right-hand side is a function of $n^{1/2}\alpha^3$ suggests that we use $\alpha = an^{-1/6}$ as a trial solution. Then we obtain

$$A^5n^{-5/6} - {}^2\!/_3A^3n^{-3/6} = -n^{1/2}[A^6(\ln\,(1 - A^{-3}) + A^{-3}) + \chi] \tag{10}$$

[†] Stockmayer's abilities and efforts as a teacher should be acknowledged in this honorary issue, not only his publications. This paper constitutes a very simple way to derive the properties of expanded and collapsed states in isolated polymers and it should prove useful for the instruction of students.

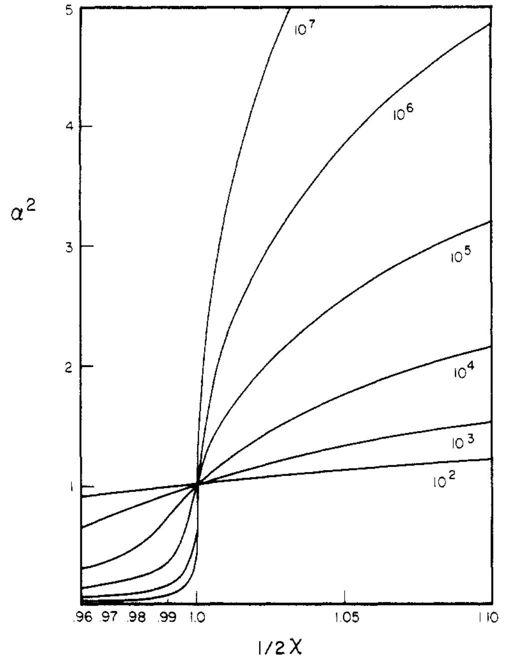

Figure 1. Expansion factor α^2 vs. normalized temperature for various values of molecular weight.

For large n the left-hand side is zero, and A can be chosen to make the right-hand side zero. We therefore have

$$\alpha = An^{-1/6}$$

$$R^2 = A^2n^{2/3}l^2 \qquad \text{collapsed polymer} \qquad (11)$$

The value of A is calculated by equating the right-hand side to zero. Retaining the first three terms in the expansion of ln $(1 - A^{-3})$, we obtain

$$A = [3(\chi - \tfrac{1}{2})]^{-1/3} \qquad (12)$$

Figure 1 displays the collapse transition α^2 vs. $(2\chi)^{-1}$ for various values of molecular weight. As the molecular weight becomes larger, the transition becomes sharper and sharper. One might be tempted to conclude that the transition is first order, but as we now show, this is not the case.

To determine the order of the transition we write the energy in reduced units ($F = -\kappa T \ln W$, $S = -\partial F/\partial T$, $U = F - TS$).

$$E = \frac{U}{\kappa T\chi n} = 1 - n^{-1/2}\alpha^{-3} \qquad (13)$$

In Figure 2 we display E vs. $(2\chi)^{-1}$ curves for various n. These curves were obtained from eq 13 and 5. It is "evident" that in the limit of infinite molecular weight we obtain a second-order transition in the Ehrenfest sense. It is a curiosity that in polymer science second-order transitions in the Ehrenfest sense have appeared in four different problems: (1) the helix–random coil transition in DNA,[3] (2) the isolated polymer adsorbed to a plane surface,[4] (3) the glass transition,[5] and (4) the collapse transition. The first two cases are exact treatments of models while the second two cases are approximate treatments of models. In all of the rest of physics and chemistry there are not this many second-order transitions. However, because we should be working with

$$F = -\kappa T \ln \left(\int W \, \mathrm{d}R \right) \qquad (14)$$

rather than with $F = -\kappa T \ln W$ the above arguments for the order of the collapse transition are not conclusive.

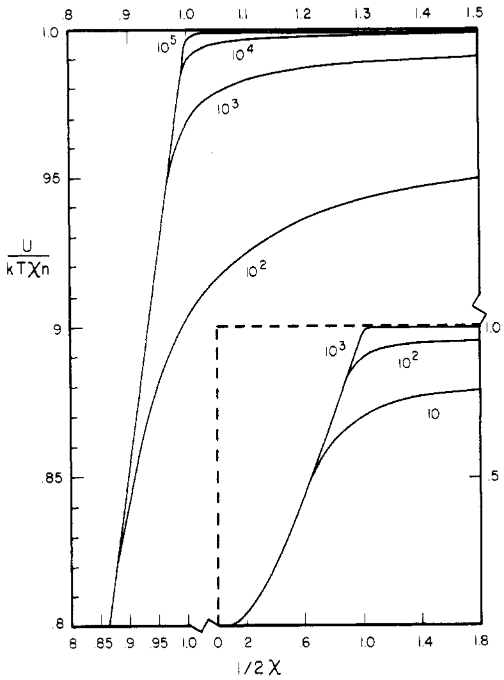

Figure 2. Normalized energy vs. the normalized temperature for various molecular weights.

One should also point out that the order and nature of the transition have been the source of much discussion, some claiming that it is sensitive to the exact nature of the segment–segment interaction.[6]

The functional form of the limiting curves ($n = \infty$) can be obtained from eq 13 provided we are not too close to $\chi = {}^1/_2$. Above the critical temperature, substituting eq 9 into eq 13 we obtain

$$E = 1, \qquad \chi < \tfrac{1}{2} \qquad (15)$$

Now in the $\chi > {}^1/_2$ region we can relate χ to E by solving eq 13 for $n^{1/2}\alpha^3$ and placing it into the right-hand side of eq 5, which we equate to zero.

$$\chi = -\frac{(1 - E + \ln E)}{(1 - E)^2} \quad \chi > \tfrac{1}{2} \qquad (16)$$

Discussion

This treatment is very much like the 30-year-old treatment of Flory,[7] with two minor differences: (1) Our intuition is addressed to probabilities in the partition function W (eq 1) while Flory worked more with free energies, which are logs of probabilities. It is more fundamental as well as simpler to deal with the partition function since thermodynamic quantities are derived from W and not inversely. One needs more intuition to deal with the derivative quantities directly. (2) Our treatment gives the actual $(n^{2/3})$rds law as well as the (6/5)ths law.

The method is easily generalized to d dimensions. In eq 1 we replace $(l/R)^3$ by $(l/R)^d$ and the first R^2 term by R^{d-1} since it represents the surface area of a d-dimensional sphere and use $b^2 = d/2nl^2$. The result is

$$\alpha^{d+2} - \frac{d-1}{d}\alpha^d = -\frac{dn^{d/2}\alpha^{2d}}{3}[\ln (1 - \alpha^{-d}N^{(-d+2)/2}) + N^{(-d+2)/2}\alpha^{-d}] + \frac{d\chi}{3n^{d/2-2}} \qquad (17)$$

Were we to maximize RW rather than W, then the coefficient $(d - 1)/d$ on the left-hand side would be 1. This formula gives reasonable results even for $d = 1$! By expanding the ln term and considering terms to second order we obtain

$$R_{\mathrm{m}}^2 \propto N^{6/(d+2)}, \qquad 1 \le d \le 4$$

$$R_{\mathrm{m}}^2 \propto N, \qquad 4 \le d \qquad \text{expanded state} \tag{18}$$

which gives the correct results for all d greater than or equal to 1. For the collapsed state we use $\alpha^{-d}N^{(-d+2)/2} = A$ as a trial solution

$$R_{\mathrm{m}}^2 \propto N^{2/d} \qquad \text{collapsed state} \tag{19}$$

which again is the correct result for all d.

Modification of our treatment places us in contact with existing work. Were we to use the radius of gyration S rather than R as our measure of polymer size and were we to take better account of the energetics, then the result would be very much like the Sanchez development.[8]

Our treatment should prove useful when attempting to solve a larger polymer problem in which excluded volume is only one factor. Common sense then suggests that the "simplest possible treatment" for the excluded volume problem would be most easily incorporated into the solution of the larger problem.

Acknowledgment. I thank I. C. Sanchez for several helpful suggestions.

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Communications to the Editor

Concentration-Dependent Relaxation Times of Linear Polymers in Dilute Solutions

The relaxation of a distorted polymer chain in dilute solutions to its equilibrium configuration has been of considerable experimental and theoretical investigation over the past several decades.[1] Extensive studies[1–5] of the oscillatory flow birefringence and linear viscoelastic properties of polymer solutions have provided much insight into this relaxation process. Experimental work has shown that the intermolecular interactions (both hydrodynamic and excluded volume) occurring in dilute solutions affect the relaxation times of the various "Rouse–Zimm modes" significantly. The measurements of the flow birefringence and the viscoelastic properties of linear chains by Schrag and co-workers[2–5] show that the longest relaxation time is affected the most by the presence of other chains. Recently, the initial concentration dependence of the relaxation time (τ_p) of the pth mode of the bead–spring model has been derived by Muthukumar and Freed[6] to be

$$\tau_p/\tau_p{}^0 = 1 + cAp^{-\kappa} + \ldots \tag{1}$$

where $\tau_p{}^0$ is the value of τ_p at infinite dilution, c is the polymer concentration, A is a constant in units of inverse concentration and κ is a positive constant. Both A and κ depend on the strength of the excluded volume interaction. κ is 0.5 in Θ solvents and 0.65–0.80 in good solvents. The experimental data of Schrag and co-workers[3–5] and Dill[7] on a variety of polymers show that the mode dependence of τ_p given by eq 1 is an adequate description at low concentrations of $c[\eta] < 1$, where $[\eta]$ is the intrinsic viscosity. The oscillatory flow birefringence data on the linear 390 000 MW PS and the 400 000 MW PMS for $1 \le c[\eta] \lesssim 5$ show that $\tau_p(c[\eta])$ can be empirically fitted[3,4] by

$$\tau_p = \tau_p{}^0 \exp(Acp^{-\kappa}) \tag{2}$$

For $c[\eta] \gtrsim 5$, the experimental data deviate from eq 2. Here we present a simple derivation to obtain the nonlinear dependence of τ_p on c.

By considering the interplay of the equilibrium screening length (due to the excluded volume effect) and the dynamic screening length (arising from the hydrodynamic interaction), Muthukumar and Edwards[8–10] have recently derived the following coupled equations for the shear viscosity (η) of the polymer solution as a function of polymer monomer density ρ and the chain contour length L (see eq 20–22 of ref 8)

$$(\eta - \eta_0)/\eta_0 = \lim_{k \to 0} k^{-2}\xi_{\mathrm{H}}{}^{-2}(k) \tag{3}$$

$$\xi_{\mathrm{H}}{}^{-2}(k) = \frac{\rho l}{\pi \eta_0} \int_{2\pi/L}^{\infty} \mathrm{d}q \, \frac{(k^2 l_1/3)J(q)}{\left(\dfrac{k^2 l_1}{6}\right)^2 + q^2} \tag{4}$$

$$J^{-1}(q) = \frac{1}{3\pi^2 \eta_0} \int_0^{\infty} \mathrm{d}j \, \frac{j^2}{j^2 + \xi_{\mathrm{H}}{}^{-2}(j)} \, \frac{j^2 l_1/3}{\left(\dfrac{j^2 l_1}{6}\right)^2 + q^2} \tag{5}$$

Here, η_0 is the shear viscosity of the solvent and l is the Kuhn step length. The variables k and j are wavevectors which are Fourier conjugate variables to the spatial position. The q variable is a wavenumber conjugate to the arc length position of a monomer along the chain configuration. This mode variable q is related to the pth "Rouse–Zimm mode" through $q = 2\pi p/L$. These equations are the generalization of the original equations of Freed and Edwards[11] for Θ solutions to non-Θ conditions. l_1 is the renormalized Kuhn step length due to the excluded volume effect and is dependent on both q and the static screening length, ξ_{s}, through (see eq 4.9 and 6.1 of ref 9)

$$l_1{}^3\left(\frac{1}{l} - \frac{1}{l_1}\right) = \frac{12w\xi_{\mathrm{s}}}{\pi} \, \frac{1 + \xi_{\mathrm{s}}\left(\dfrac{3q}{l_1}\right)^{1/2}\left(\dfrac{6q\xi_{\mathrm{s}}{}^2}{l_1} - 1\right)}{1 + \dfrac{36q^2\xi_{\mathrm{s}}{}^4}{l_1{}^2}} \tag{6}$$

where

$$\xi_{\mathrm{s}}{}^{-2} = \frac{6w\rho/l_1}{1 + \dfrac{27}{8\pi}\,\dfrac{w\xi_{\mathrm{s}}}{l_1{}^2}} \tag{7}$$

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