

POLYMER COLLAPSE

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INTRODUCTION

“The better the solvent the greater the ‘swelling’ of the molecule. Conversely, the poorer the solvent the smaller the molecule” (1). By this laconic sentence, Flory described in 1953 the evolution of the average coil dimensions of a polymer chain in solution as the pair interaction between monomers varies. In a *good solvent* the monomer pair interaction is repulsive and tends to swell the coil; its radius R is determined by a balance between this repulsive energy and an elastic (entropic) energy prohibiting large deformations. It is then found (1, 24) that $R \sim N^{3/5}$, where N is the number of monomers in the chain. In a *poor solvent* the monomer-monomer interaction is attractive and the complete collapse of the chain is hindered only by the steric repulsion between segments; the internal concentration $c_i(T)$ is controlled only by these interactions and is independent of N . The volume of the polymer globule is linear in N and in this collapsed regime $R \sim N^{1/3}$. (Phase separation sets a lower limit to the quality of the solvent; when it occurs there is coexistence of a solvent-rich phase with a few contracted chains and a second polymer-rich phase.) In a Θ -*solvent*, when attractive and repulsive forces compensate the chains are quasi-ideal and $R \sim N^{1/2}$.

The transition from an expanded coil to a collapsed globule state effected by changing the quality of the solvent has been the focus of interests of many experimentalists and theoreticians for the last 15 years. It can be induced by a change in temperature, a change in pressure, or by mixing two or more solvents of different qualities. The experimental ob-

servations are tricky and the theoretical descriptions a source of dispute. Both aspects are discussed in this paper.

SOME EXPERIMENTAL OBSERVATIONS

The first experimental evidence for a *globule-coil transition* was probably the denaturation of proteins on heating. The tertiary structure of proteins is compact (globule) and corresponds to the biologically active state. When the protein is heated, the chain unfolds into a looser spatial conformation (coil) and its biochemical activity stops. Although this observation stimulated the theoretical work of the Russian school [see a recent review article by I. M. Lifschitz et al (2)], we do not consider this important problem of protein conformation any further here since the interaction effects are somewhat more complex than for homopolymers and a comparison with a tractable theory is difficult. Its relationship to what follows should nonetheless be kept in mind.

The aim of the experiments with homopolymers is to measure the radius of gyration of a coil in dilute solution as the quality of the solvent is decreased. The temperature is the usual parameter varied; as the observations reported are near the upper critical solution temperature, the temperature is decreased from the good solvent to the poor solvent regime of the phase diagram (see Figure 1).

The region of interest where contraction of the coil can be seen is sandwiched between the θ -region and the coexistence curve where phase separation will take place. Thus, one has to use extremely *dilute solutions* to measure the variation of the radius of gyration of a single coil in a sufficiently large temperature range. Furthermore, for finite concentrations, single chain contraction and interpenetration of different chains will be competitive mechanisms before phase separation sets in by coalescence

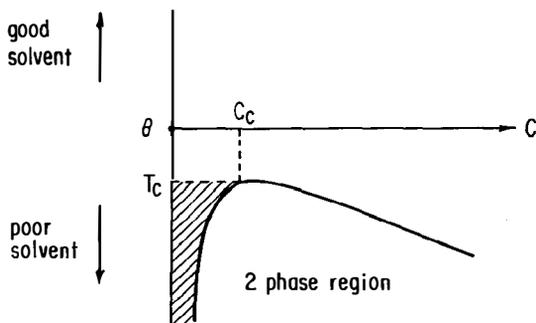


Figure 1 Phase diagram for a flexible polymer in a solvent, showing the coexistence curve (full line) and the poor solvent region (hatched) of dilute collapsed coils.

of either collapsed coils or aggregates. Interchain aggregation is reduced as the concentration is lowered. For highly dilute solutions the signal is weak and the technique used has to be very sensitive to provide results with a reasonable signal-to-noise ratio.

Also the position of the coexistence curve is a function of N ($c_c \sim N^{-1/2}$, $T_c \sim N^{+1/2}$); the shorter the chain, the further away is the coexistence curve from its asymptotes. Longer chains will precipitate first and the experimental observations could be perturbed by fractionation effects. Polymers with a *narrow polydispersity* should be used.

As for the value of N , a compromise has to be found: a small N allows a larger temperature range for a given concentration before phase separation occurs. However, the different theoretical predictions discussed below usually hold in the limit of infinite chains. Also, there is some dispute among theoreticians about whether the transition between the extended and collapsed state is smooth and continuous or discrete. For a finite chain the transition is broadened as the value of N decreases. It would be more easily detected if N were large. These requirements—very dilute solutions of long chains, low polydispersity—explain the experimental difficulties for obtaining reliable results in a bad solvent.

Different techniques have been used:

1. Viscosity measurements give a hydrodynamic radius of the coil R'_H (3a–c, 4).
2. Conventional light scattering measures the radius of gyration R_G (4, 5) down to $\sim 100 \text{ \AA}$.
3. Elastic neutron scattering also gives R_G (6) down to a few 10 \AA ; X-ray scattering can also be used (7).
4. Inelastic light scattering (photon correlation) (8, 9) measures a Brownian diffusion coefficient from which one extracts another hydrodynamic radius R_H (2). This technique is more appropriate to highly dilute solutions than elastic light scattering since it can differentiate directly the signal given by the polymer from the signal due to the solvent without any signal subtraction [(polymer + solvent) – solvent] as in all elastic scattering techniques: Swislow et al (8) measured R_H for a concentration as low as 10^{-7} g/ml , whereas the lower limit for elastic light scattering is of the order of 10^{-5} g/ml .⁴
5. Sun et al (10) have found that they could use the same technique to deduce the geometrical size from the angular dependence of the intensity of the auto-correlation function of light scattered by the solution, with a greater sensitivity than with elastic light scattering.
6. Ultracentrifugation also provides a measurement of the hydrodynamic radius (11, 48).

Polymer collapse has been studied experimentally in two-component systems such as the simple polystyrene-cyclohexane system, which we describe more fully below, and also in potentially biologically interesting but complex four-component DNA polyelectrolyte (11–16) systems. Lerman's ψ condensation (11) of viral DNA (e.g. molecular weight 30×10^6) in aqueous salt solutions (e.g. NaCl, MgCl₂) can be induced by addition of relatively low molecular weight, water soluble polymers such as poly(ethylene oxide) (PEO, e.g. of molecular weight 7000). At DNA volume fractions of about 10^{-7} one finds sharp increases in the sedimentation coefficient of radioactively labeled DNA for critical PEO volume fractions of about 0.1 for salt concentrations in the range of 0.01–2 *M*. Further hydrodynamic and spectroscopic studies on more concentrated DNA solutions and X-ray studies on the aggregates formed from these solutions appear to be consistent with a reversible phase transformation of DNA into a nonfibrous, compact state (11), which has recently been suggested to be a globule produced by negative excluded volume collapse of the original DNA coil (17). Similar DNA condensation phenomena can be induced by addition of polyamines and cations, etc (13–16). Aqueous salt DNA solutions of much lower molecular weight show a well-defined order-disorder transition (18), but the relationship of ordered collapse states and this phenomenon is not understood.

We now discuss in some detail the observations on the binary system polystyrene/cyclohexane. This extensively studied system best represents the universal behavior of a flexible chain in a bad solvent. Polystyrene prepared by anionic polymerization has a reasonably low polydispersity ($1.06 \leq M_w/M_n \leq 1.3$). The temperature where the interaction between monomers changes sign, the Θ -temperature, is about 35.4°C for this system; furthermore, its static and dynamic properties in a good solvent and in a Θ -solvent are now well known.

Slagowski, Tsai & McIntyre (5) reported the first measurements of R_G as a function of temperature on a polymer of 4.4×10^7 mol wt at concentrations down to 2.10^{-5} g/ml. They observed a dramatic change of R_G as the temperature was lowered from slightly above to under the Θ -temperature. For $T - \Theta = -1.4^\circ\text{C}$, the lowest temperature they could reach before phase separation, the molecular expansion factor $\alpha = [R_G(T)]/[R_G(\Theta)]$ became 0.58, still a long way from the totally collapsed state of densely packed segments ($\alpha_{\text{collapse}} \sim 0.1$).

A low molecular weight ($M_w = 29000$) was chosen by Nierlich, Cotton & Farnoux (6). At a concentration of 3.4×10^{-3} g/ml they could reach a temperature such that $T - \Theta = -26.8^\circ\text{C}$ before precipitation; this T corresponds to $\alpha = 0.87$ while $\alpha_{\text{collapse}} \sim 0.33$ for a compact sphere. They

found two domains of variations of R_G as a function of $\tau = [(T - \Theta)/\Theta]$: one where R_G decreases very slowly (Θ -region) followed by a faster contraction where $R_G \sim |\tau|^{-0.32 \pm 0.05}$ in accordance with the prediction of de Gennes (see theory section below).

Recently, different groups have started more systematic studies, using inelastic light scattering. Bauer & Ullman (9) have determined the change in hydrodynamic radius R_H with temperature at and below Θ for polystyrene molecules varying in molecular weight by three orders of magnitude: from 5×10^4 to 4.4×10^7 . The concentrations, ranging from 1.5×10^{-3} g/ml for the lowest M_w to 10^{-5} g/ml for the highest one, were similar to the ones used in the previous R_G measurements. They observed a smooth decrease in molecular size with decreasing temperature, but the effect was not large and they never reached the collapsed state. Plotting $\alpha_H = [R_H(T)]/[R_H(\Theta)]$ as a function of $M(\Theta\tau)^2$, they found that all the experimental points fell on a single curve, $R_H \sim M^{0.446} |\tau|^{-0.108}$, as we shall see, a result different from the theoretical prediction and interpreted by the authors as related to the fact that the asymptotic limit of large N is not yet reached for R_H .

The region of high M (2.6×10^7 , $M_w/M_n \sim 1.3$) and very dilute solution ($c \sim 10^{-7}$ g/ml) has been investigated by Nishio et al (41), who reported for the first time the observation of the coil-globule transition in the polystyrene/cyclohexane system. The collapse occurs at 32°C , the transition region has a width of about 5°C and corresponds to $\alpha_H \sim 0.4$. $\{\alpha_H = [R_H(T)]/[R_H(\Theta)]$ may be different from $\alpha = [R_G(T)]/[R_G(\Theta)]$ if the asymptotic limit of large N is reached faster for R_G than for R_H . This point is discussed extensively in Ref. (9). Furthermore, the macromolecule in its compact state behaves more like a solid sphere and the ratio of R_H to R_G is different from what it would be in the expanded coil state.} At higher concentrations, the temperature dependence of R_H is approximately the same, but complete collapse is not reached before the onset of intermolecular aggregation (Figure 2); so their results are consistent with those reported previously at moderate concentration. The same group also showed (10) that for the same molecular weight and lowest concentration R_G had a very similar behavior to R_H , with α_{collapse} smaller (~ 0.2). They interpreted their results in terms of a mean field theory and showed

$$R_G \sim |\tau|^{-0.34 \pm 0.04}$$

$$R_H \sim |\tau|^{-0.36 \pm 0.04}$$

in the collapsed state. (See Table 1.)

It should also be noted that Pritchard & Caroline (19), measuring R'_H

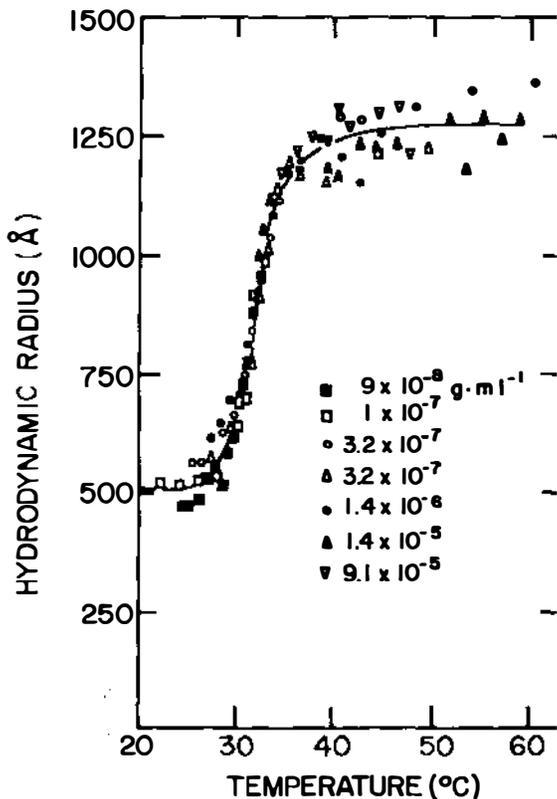


Figure 2 Variation of R_h with temperature for polystyrene ($M_w = 2.7 \times 10^7$) in cyclohexane [from Ref. (8)].

in conditions similar to those of Nierlich et al (6) ($M_w = 37000$, $c \sim 2.6 \times 10^{-3}$ g/ml) observed a smooth decrease of the hydrodynamical radius with temperature, with no indication of a θ -region ($R_G \approx \text{constant}$) or a collapse region. The same conclusion was reached by Delsanti (20) by viscosity measurements on a polymer of $M_w = 4.11 \times 10^5$, ($M_w/M_n < 1.1$) and by Cuniberti & Bianchi (4) ($M_w = 4.23 \times 10^5$).

Before discussing the theoretical models and the interpretation of the experimental results in terms of those models, it is possible to draw the following conclusions:

1. A rapid collapse of a single polymer coil, in a narrow range of temperatures, can occur before interchain aggregation takes place.
2. The region of collapse can be observed only for highly dilute solutions. Inelastic light scattering is a very suitable method of observation from

Table 1 Experimental values of the exponents describing the variation of R_G and R_H with the degree of polymerization N and the reduced temperature $\tau = [(T - \Theta)/\Theta]^2$

Experiment	R_G	R_H
Nierlich et al (6)	$ \tau ^{-0.32 \pm 0.05}$..
Bauer & Ullman (9)	$(N^{0.398} \tau ^{-0.204})$	$N^{0.446} \tau ^{-0.108}$
Sun et al (10)	$ \tau ^{-0.34 \pm 0.04}$	$ \tau ^{-0.36 \pm 0.04}$

*The value in brackets corresponds to a fit of the results of (5) and (6) by the authors cited.

that point of view, although it provides a less direct measurement of the size of the molecule (R_H).

However, many more experiments are clearly needed both in the high- M region, where the broader molecular weight distribution could easily perturb the observation of the transition, and in the lower M region, where a sharp transition has not been observed and discrepancies exist between the experiments reported so far.

Computer simulation studies on short chains using either Monte-Carlo methods (21a,b) or exact enumeration techniques (22, 23a-c) have also been reported: they show a gradual collapse of the chain, which tends to be steeper as the length of the chain increases.

THEORETICAL MODELS

There has been much controversy over many years among theoreticians about the existence of the coil-globule transition and its type: first-order or second-order. The transition region has been extensively described in the mean-field approximation, which seems adequate enough to yield predictions in agreement with most of the experimental results. Using the analogy between the excluded-volume problems and critical phenomena, de Gennes has remarked that the Θ -point is a tricritical point and mean-field theory can be employed except for some logarithmic corrections. The critical dimensionality below which mean field breaks down is $d_c = 3$ instead of $d_c = 4$, as for a chain in a good solvent.

Mean Field Theory (Flory-Huggins)

Using a lattice model in which solvent molecules and monomers occupy equivalent sites, Flory (1) derived an expression for the free-energy of mixing, F_m , of a polymer with a solvent, which can be written for a single chain (24)

$$\left(\frac{F_m}{kT}\right)_{\text{site}} = (1 - \phi)\ln(1 - \phi) + \chi\phi(1 - \phi) \quad 1.$$

where ϕ is the volume fraction of sites occupied by a monomer segment, and N the number of monomers in the chain. The first term describes the change in entropy of mixing energy between solvent molecules and monomer segments in terms of a dimensionless parameter χ , the Flory interaction parameter. Equation 1 can be expanded for small ϕ as:

$$\left(\frac{F_m}{kT}\right)_{\text{site}} \approx \frac{1}{2}\phi^2(1 - 2\chi) + \frac{1}{6}\phi^3 + \dots \quad 2.$$

An alternative form, independent of a lattice, for low concentrations of monomer segments per cm^3 , c , is

$$\left(\frac{F_m}{kT}\right)_{\text{cm}^3} \approx c + \frac{1}{2}vc^2 + \frac{1}{6}wc^3 + \dots \quad 3.$$

where v, w, \dots are successive virial coefficients of the monomer-monomer segment interaction. As $\phi = ca^3$ (a = monomer size), the correspondence between these equations shows that

$$v = a^3(1 - 2\chi). \quad 4.$$

v is the excluded volume parameter. v changes sign at the Θ -temperature, as it is positive in a good solvent and negative in a bad solvent, and can be written as

$$v = v_0 \frac{T - \Theta}{\Theta} = v_0\tau, \text{ for } T \text{ near } \Theta. \quad 5.$$

The third virial coefficient w is dominated by steric effects and is essentially positive and constant ($w = a^6$) for a flexible polymer (for a chain with a persistence length $b, v \sim b^2a\tau$ and $w \sim a^3b^3$).

At $T = \Theta$ the second term in c^2 , which represents the two-body interaction between monomers, disappears; the three-body interaction (c^3 term) still exists and has to be included in the Θ -region. Calculations that retain only the second-order term can describe the expanded state in good solvent; at least third-order terms have to be included to describe properly the Θ -region and the collapsed state in a bad solvent.

In Eq. 3, c is the average monomer concentration inside the coil.

$$c = \frac{N}{R^3} \quad 6.$$

In the mean field approximation all correlations between monomer segments are ignored and the average of c^p ($p = 2, 3, \dots$) is replaced by the p th power of the average

$$\langle c^p \rangle \rightarrow \langle c \rangle^p. \quad 7.$$

The total free energy also includes an "elastic" term expressing the entropic contribution due to swelling or contraction of a polymer coil of

radius R . Assuming a Gaussian distribution of monomer segment units in the polymer coil,

$$\frac{Fel}{kT} \simeq a^2 + a^{-2} \quad 8.$$

where α is the molecular expansion factor, which equals R/R_0 where $R_0 = N^{1/2}a$ is the rms radius for a random walk.

Integrating Eq. 3 over a volume R^3 , replacing c by its value given by Eq. 6, and minimizing the total free energy

$$F_{\text{tot}} = F_m + F_{el} \quad 9.$$

with respect to α , one finds an expression for α :

$$\alpha^5 - \alpha^3 - \frac{y}{\alpha^3} \simeq N^{1/2} \frac{v}{a^3} = x \quad 10.$$

where y is a dimensionless parameter $y \simeq (w/a^6)$, related to the flexibility of the chain, and x depends on the molecular weight of the polymer and on its interaction energy with the solvent. In the poor solvent region where $x \ll 0$, it is found that the radius of a flexible chain varies as

$$R \sim N^{1/3} |\tau|^{-1/3}. \quad 11.$$

We follow here the presentation of de Gennes (25), but all calculations based on an extension of Flory's theory (2, 25, 30, 32a,b) are fundamentally similar in their approach, even if they differ in detailed treatment such as, for instance, inclusion of a gradient term ($\nabla\phi$) to take care of any spatial variation of the segment density in the free energy.

In the case of the ψ condensation of a single DNA coil in salt solution, Frisch & Fesciyan (26) developed a mean field Flory-Krigbaum dilute polymer solution theory. Polyelectrolyte effects were included at the level of a Donnan-type equilibrium in the DNA polyelectrolyte coil. This description suffices at sufficiently high salt concentration at the onset of the ψ transition. Specific adsorption of the added PEO in the DNA was neglected. The resulting theory leads to a collapsed radius R , which is given by Eq. 11, obtained from Eq. 10, with v as in Eq. 5 a function of an effective Θ temperature. Θ_{eff} now depends linearly on the volume fraction of added PEO and varies with the ionic strength of the solution. The theoretical location of the ψ transition as a function of salt and PEO concentration is in good numerical agreement with available experimental data. Shortly afterwards and independently, Post & Zimm (27) developed a Flory lattice model that is fundamentally similar to the above.

A thorough discussion of the behavior of the size of the polymer chain as a function of the parameters x and y has been presented by de Gennes (25), Frisch & Fesciyan (26) and by Post & Zimm (27). The influence of the flexibility of the chain has also been discussed by Ptitsyn et al (28).

For flexible chains there is a continuous contraction of the chain when the temperature is lowered from $T > \Theta$ to $T < \Theta$. However, there is a critical value of ν (i.e. flexibility) where for some value of x (i.e. solvent quality and chain size) the free energy has two stable points. This would imply an abrupt transition to the collapsed state and suggests the feasibility of a first-order phase transition. However, as pointed out by de Gennes (25): "Since we are dealing with a *finite* system the sharp transition may be an artefact of the self-consistent field method." In the limit $N \rightarrow \infty$, the two minima merge into one, whatever the flexibility may be. The sharp transition probably indicates a fast change in the polymer size from the open, extended configuration to a small, compact form with a high density of segments. Estimating the value of ν for different polymers, Post & Zimm (27) predict that DNA should experience an abrupt "transition" while polystyrene should show a gradual collapse.

The type of phase-transition experienced by a single chain has been much discussed. As stated above, the appearance of a discontinuity in the radius of gyration for *finite* chains of sufficient rigidity hinted at a first-order transition; this was also suggested by Domb (22) in a review of the numerical analyses of self-avoiding walk with nearest-neighbor attractive forces.

In a recent paper, using the self-consistent field approach of Edwards (32), Moore (31) concluded that in the infinite N limit the chain undergoes a Landau-type second-order transition at the Θ -temperature. For finite chains, the transition is pseudo-second-order and takes place at a temperature less than Θ . The same conclusion was also reached by Sanchez (29) in a mean-field calculation that accounted (with some approximations) for all higher order terms in the virial expansion of the inter-segment interaction energy.

Recent Theory of Excluded Volume

The analogy between the statistics of long, flexible polymer chains and phase transition problems has led to a new description of the excluded volume problem in which simple scaling properties appear (33, 34). A complete concentration temperature phase diagram has emerged (35) in which the conformation of a polymer as a function of $\tau = [(T - \Theta)/\Theta]$ and c can be described by two characteristic lengths, the radius of gyration of the macromolecule R and a screening length ξ ($\xi < R$). We refer the reader to Ref. (24) for a clear and accessible introduction to the subject.

We focus here on the conformation of a single coil as a function of temperature. The width of the transition region between good solvent ($T > \Theta$; swollen chain) and poor solvent behavior ($T < \Theta$; collapsed

chain) can be roughly deduced from Eq. 3 for the free-energy, by estimating the relative importance of the second virial terms (in what follows we ignore systematically numerical coefficients and focus on exponents):

$$\left(\frac{F_2}{kT}\right)_{cm^3} \simeq \frac{1}{2} \nu c^2 \text{ with } c \simeq N/R^3. \quad 12.$$

Integrated over a volume V of the order of R^3 , this gives an energy (neglecting all numerical factors)

$$\frac{F_2'}{kT} \simeq \frac{N^2}{R^3} \nu. \quad 13.$$

For temperatures close to Θ , ν is small and the coil has an almost random configuration where $R \sim N^{1/2}a$; for a flexible chain, $\nu \sim a^3(T - \Theta/\Theta) = a^3(\Delta T/\Theta)$, so that

$$\frac{F_2'}{kT} \simeq N^{1/2} \frac{\Delta T}{\Theta}. \quad 14.$$

The F_2 term will be a weak perturbation as long as $F_2/kT < 1$; i.e. $\Delta T < \Theta N^{-1/2} = \Delta T^*$. The width of the transition ($\Theta \pm \Delta T^*$) is of the order of $\Theta N^{-1/2}$; it becomes smaller as N increases. This width is of the same order as $T_c - \Theta$, where T_c is the critical temperature for demixing of chains.

In the collapsed region, the average concentration inside the coil is controlled only by the interactions and is independent of N . The radius of the coil is such that

$$\frac{c}{a^3} \frac{4\pi}{3} R^3 = N. \quad 15.$$

Thus

$$R \sim N^{1/3}a. \quad 16.$$

This result holds for three dimensions ($d = 3$). For $d = 2$, using the results of Stephen (38), one expects $R \sim N^{1/2}\tau^{0.1}$.

For a long chain in the collapse region ($|\Delta T| > \Delta T^*$) a physical picture of the correlations in the chain can be understood as follows (36): let us compute an energy $F_2(n)$, not for the whole chain, but for some (variable) number n of monomers. As in Eq. 14,

$$\frac{F_2(n)}{kT} \simeq n^{1/2} \frac{|\Delta T|}{\Theta}. \quad 17.$$

Varying n ($n \leq N$), we find that there exist a critical number of monomers n_c such that $F_2(n_c) \simeq kT$.

$$n_c \simeq \left(\frac{\Theta}{|\Delta T|}\right)^2 \quad 18.$$

For $n < n_c$, $F_2(n)$ is a weak perturbation compared with kT and the chain is ideal. The ideal chain dimension corresponding to n_c is

$$r_c = n_c^{1/2} a \simeq a \frac{\Theta}{|\Delta T|}. \quad 19.$$

For $n > n_c$, $F_2(n)$ is larger than kT and cannot be treated as a perturbation. The polymer can be viewed as a chain of renormalized beads ("blobs") of dimension r_c ; the number of such beads is N/n_c , which leads to a collapsed chain radius

$$R \sim \left(\frac{N}{n_c}\right)^{1/3} \quad r_c \sim N^{1/3} |\tau|^{-1/3}. \quad 20.$$

Note that if $n_c \rightarrow N$ the chain is ideal, $T = \Theta$; if $n_c \rightarrow a$ the chain is collapsed at all scales. The same physical picture is obtained when $T > \Theta$: for correlations over length scales $r < r_c$, the chain appears ideal, while for $r > r_c$, the correlations are those of a swollen chain ($R \sim N^{3/5} r^{1/5}$).

In a poor solvent the scaling arguments give the same exponents as the mean field theory, at least in three dimensions, which is the only case we have considered here. However, the notion of chain rigidity is completely lost in this picture and the transition is smooth and continuous.

There is, however, a theoretical problem pointed out by de Gennes (25, 36) that at the Θ -point the third virial coefficient cannot be ignored; in the framework of the analogy between magnetic problems and polymer solutions, this implies that in a Landau free-energy expansion near the Θ -point, terms to sixth order have to be retained. (The coefficient of the sixth order term is proportional to the third virial coefficient and this form is known to give rise to a tricritical point.) The Θ -point is thus a tricritical point. It is known that for $d = 3$, tricritical exponents have the mean-field value but some logarithmic corrections have to be included in the probability of contact between two and three monomers.

The origin of such corrections can be perceived from the following crude argument (37): in three dimensions, the density of monomers surrounding a fixed monomer is $g(r) \sim 1/r$; if $c = g(r)$, the energy associated with the c^3 interaction is of the order of

$$\frac{F_3}{kT} \sim w^2 \int g^3(\mathbf{r}) d\mathbf{r} \sim w^2 \int \frac{1}{r^3} 4\pi r^2 dr$$

which shows logarithmic singularities. Some consequences of these have been analyzed (31, 36, 38, 39; J. Duplantier, to be published). They are probably not important enough to be seen in the variation of the coil size with temperature; local studies giving information on the statistics of monomer-monomer contacts would be best. None have been reported so far.

COMPARISON OF MF THEORY AND EXPERIMENTS FOR BINARY SYSTEMS

Mean-field theories account very well for the experimental results described in the first section: Bauer & Ullman (9), investigating the effect of molecular weight, verify that all their data can be represented by a single master curve if α is plotted as a function of $M\tau^2$, for a molecular weight range of three orders of magnitude; this also includes the results of Slagowski et al (5) and Nierlich et al (6). This last group recognizes two domains in the investigated temperature range: the Θ -region where R is approximately independent of temperature and the bad solvent region where they find a τ dependence very close to the predicted value of $-1/3$. There is a smooth cross-over between the two regions. Sanchez (29) has fitted satisfactorily the data of Slagowski et al (5) to his theory. All these experiments show a smooth variation of R_G with T , as expected for a flexible chain, and it was believed that no "transition" should be seen for polystyrene in cyclohexane (8, 10). However, Swislow et al (8, 10) did observe a sudden collapse of a high molecular weight chain at extremely low concentrations, described as the "coil-globule" transition. They fit their result to Sanchez's theory, to which they have added a supplementary term in the interaction energy corresponding to a reduction of the entropic freedom of the large benzene ring side chains of polystyrene when two segments come in contact; the collapsed region is reached only very close to the coexistence curve where they derive the temperature exponent for both R_G and R_H . They also claim that with low molecular weight polymers, the temperature range investigated corresponds to the onset of the coil-globule transition, and the stated exponent in Ref. (6) is only accidental.

The experimental determination of the exponent deserves further discussion. The great dispersion in the quoted values shows the difficulty of setting up an experiment in which the asymptotic region where exponents have a meaningful value has been reached. This region is limited in temperature by the coexistence curve. Although the molecular weight distribution attained by anionic polymerization is narrow, it is still sufficiently broad to allow for significant fractional separation according to molecular weight; thus the molecular weight distribution is shifted continuously to lower M as the temperature is lowered and the region of the coexistence curve for the nominal M is approached, and this can significantly affect the value of $\langle R_G \rangle_M$.

In view of the latest results of Swislow et al (8, 10), more experiments are clearly needed both in the polystyrene/cyclohexane system and in others where the flexibility of the chain is varied.

Experiments should be designed to characterize the statistics of local contacts and to show the consequences of the logarithmic singularities associated with tricritical phenomena. Hypochromism or fluorescence may be suitable methods.

We discuss above only three-dimensional systems; in two dimensions the situation is somewhat different and the predictions of the mean-field theory don't coincide with those associated with tricritical phenomena. Langmuir films of polymers can be deposited at a solvent/air interface (40), but single coil behavior requires extremely low overall concentrations and again very difficult experiments.

We have considered so far the somewhat ideal case of a flexible polymer in a solvent without any specific solvophilic or solvophobic interactions. When these exist the transition region is more easily reached; a fast contraction of the coil has been observed by light scattering and viscosity measurements for poly(acrylic acid) in dioxane (4) and more recently for polyacrylamide in acetone/water mixtures (41). In the latter system the variation of R_H with solvent composition follows a sigmoid curve.

Polymer gels are swollen in good solvent and collapse in poor solvent, very much like a collection of separate, independent coils [see (42a,b) for the collapse of a polyacrylamide *gel* in acetone-water mixture, compared with (41)].

A NEW EFFECT OF COLLAPSE IN A MIXTURE OF GOOD SOLVENTS

The collapse of a chain can occur in a mixture of good solvents, as well as in bad solvent. We present here some of the theoretical predictions and we hope to have experimental evidence for this new effect soon.

By studying the behavior of one chain P in solution in a mixture of two good solvents (A, B) in a range of temperatures and concentrations near the consolute point of AB ($T \sim T_c$, $c_A \sim c_{A_{crit}}$), one finds a surprising result (43). As T is reduced close to T_c , the chain collapses partially but reswells again at T_c and becomes ideal!

Solvent A and B are good solvents of P and one of them, say A, is slightly better than B. The Flory Huggins parameters χ_{BP} , χ_{AP} are both small and χ_{AP} is smaller than χ_{BP} . One sets (44) $D = (\chi_{BP} - \chi_{AP})a^3$. At T_c osmotic compressibility of the AB mixture diverges. Near T_c , the AB mixture reacts strongly to the small perturbation induced by the chain. One monomer, say monomer i , prefers A rather than B and creates a cloud richer in A. The size of the cloud is ξ , the coherence length of the AB mixture, which diverges at T_c . The increase of the A concentration around monomer i is fixed by the Ornstein-Zernike law $\delta c_A \sim (D/r)e^{-r/\xi}$.

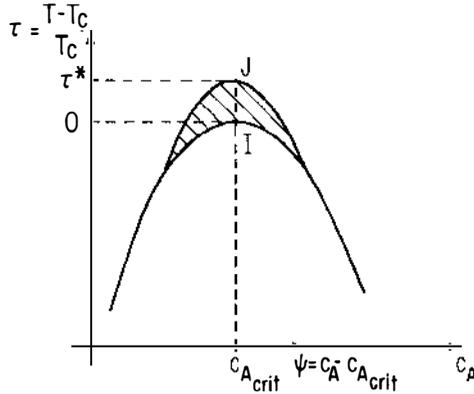


Figure 3 Coexistence curve of the Ab binary mixture. The hatched zone represents the domain of partial collapse.

This “A” cloud attracts a surrounding monomer, say j , and it leads to an attractive interaction between monomer i and j that is proportional to D and δc_A ,

$$W_{ij} = -k \frac{D^2}{r} e^{-r/\xi} \tag{21}$$

This interaction is similar to a screened coulomb interaction between charges of opposite signs. One has a competition between this attractive interaction and the excluded volume

$$\frac{1}{kT} W_{ij\text{Total}} = \nu_0 S(r_{ij}) - k \frac{D^2}{r_{ij}} e^{-r_{ij}/\xi} \tag{22}$$

(The additivity of the interaction is rigorous only if both terms are small. However, an analysis by the renormalization group method (45) leads to very similar results.) If the size of the chain R is larger than ξ , one can define an effective excluded volume by integration of Eq. 22

$$\tilde{\nu} = \nu_0 - 4\pi k D^2 \xi^2 \tag{23}$$

$\tilde{\nu} = 0$ defines the zone of collapse represented in Figure 3. We describe here the behavior between points J defined by $\tilde{\nu} = 0$, $c_A = c_{A\text{crit}}$ and the critical point I .

The mixing free energy F depends on two concentration variables. The first is c equal to the number of monomers inside the coil region $c = (\phi/\nu_0) = (N/R^3)$ where R is the radius of gyration. The second concentration variable is related to the concentration c_A of one of the solvents. One defines ψ as the difference between c_A and $c_{A\text{crit}}$, $\psi = c_A - c_{A\text{crit}}$. One needs also a temperature variable $\tau = (T - T_c)/(T_c)$ to measure the reduced temperature from the critical point.

Consider first the AB mixture at the critical concentration in the absence of any polymer. The free energy associated with fluctuations in ψ may be written in the form (46)

$$\frac{F}{kT} = \frac{1}{2} \chi^{-1} \psi^2 + \dots + \frac{1}{2} K |\nabla\psi|^2 \quad 24.$$

where χ is the osmotic compressibility diverging at T_c as $a^3 \tau^\gamma$ ($\gamma = 1.25$). The coefficient of the gradient term is finite at T_c ($K \sim a^5$). Equation 24 involves a characteristic length ξ for the spatial variation of ψ , which is given by

$$\xi = \sqrt{K\chi} \sim a\tau^{-\nu} \left(\nu = \frac{\gamma}{2} \right).$$

If we now add one polymer coil, we must introduce four modifications into Eq. 24:

$$F = \frac{1}{2} \chi_{(c)}^{-1} \psi^2 + \dots + \frac{1}{2} K |\nabla\psi|^2 - D\psi c + \frac{1}{2} v_0 c^2 + F_{el}. \quad 25.$$

We have three additional terms; a coupling term, which describes the preferential adsorption; the excluded volume term; and the elastic term, which turns out to be irrelevant here. The fourth modification is the shift of T_c inside the coil due to dilution effects. Monomers act as impurities and reduce the regular AB interactions. We have to take for χ

$$\chi^{-1} = a^3 (\tau + \alpha_1 a^3 c)^\gamma$$

which does not vanish anymore at $\tau = 0$, but at $\tau = -\alpha_1 a^3 c$.

The shift of T_c modifies the coherence length ξ inside the coil

$$\xi_{int} = \sqrt{\frac{K}{(\tau + \alpha_1 a^3 c)^\gamma a^3}} < \xi_{ext}$$

As the chain collapses, c increases and ξ_{int} decreases, leading to an increase of \tilde{v} (Eq. 23). This effect is responsible for the reswelling of the chain near T_c .

We have to find ψ inside the coil and c for a fixed value of ψ_c outside the coil. We limit the derivation to the case $\psi_c = 0$. We need two equations that are the equality of the chemical potential for the two species A and B. At $c_A = c_{A,crit}$, these equations are simply

$$\frac{\partial F}{\partial \psi} = 0 \quad 26.$$

$$\frac{\partial F_{ch}}{\partial c} = 0, \quad 27.$$

where $F_{ch} = \int F d_3 r$ is the chain volume free energy per chain.

Eq. 26 leads to

$$\psi = Dc_x. \quad 28.$$

Inserting the Result 28 into Eq. 25, one finds

$$F = \frac{1}{2} v_{eff} c^2 \quad 29.$$

with

$$v_{eff} = v_0 - \frac{D^2}{(\tau + \alpha_1 \phi a^3)^\gamma a^3} = v_0 - \frac{D^2 \xi_{int}^2}{K}.$$

We remark that v_{eff} is larger than $\tilde{v} = v_{eff}(c = 0)$ given by Eq. 23.

The free energy per chain is given by

$$F_{ch} = \frac{1}{2} v_{eff} c N. \quad 30.$$

For $\tau > \tau^* = (d^2/v_0)^{1/\gamma}$ (corresponding to $v = 0$), F_{ch} has a minimum for $c = 0$, but we have to include F_{el} and $R = R_0 = Na^{1/2}$. For $\tau < \tau^*$, F_{ch} has a minimum which gives the equilibrium concentration c_e inside the coil. c_e is independent of N and $R = (N/c_e)^{1/3}$ obeys a collapsed $N^{1/3}$ law. We see from Figure 4 that decreasing τ from τ^* (point *J*) to $\tau = 0$ (point *I*), c_e increases but decreases again. At $T = T_c$, the minimum is again at $c_e = 0$ and the chains are swollen again at ($R = N^{1/2}a$). This situation of partial collapse and reswelling is a remarkable result due to the shift of T_c inside the coil.

One concludes that this process is very different from the collapse in a poor solvent:

1. v_{eff} depends upon c .
2. The third order terms are not needed to obtain a minimum of F_{ch} and are irrelevant.
3. The renormalization group analysis [Ref. (43)] shows that at scales smaller than ξ , the chain is swollen in contradistinction with the usual collapse where the chain is locally ideal.

The main result is this unusual property of deswelling-reswelling. One needs experiments to confirm these theoretical predictions. Light scattering experiments are excluded, because of the turbidity due to critical AB concentration fluctuations. It can also be tested by using a gel swollen in an AB mixture. Similar properties of partial collapse and the possibility of a reswelling are also predicted for a polymer chain in a nematogenic solvent (47).

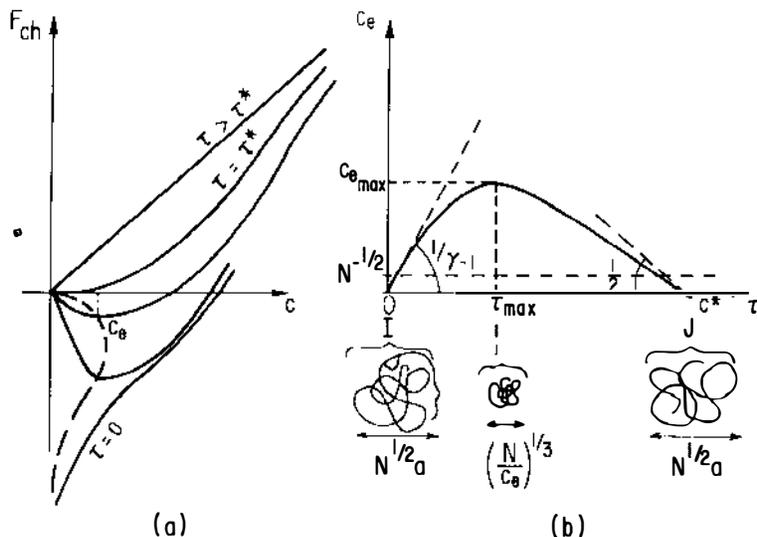


Figure 4 (a) The free energy per chain as a function of c has a minimum at $c = c_c$ for $0 < \tau < \tau^*$. (b) c_e as a function of τ and corresponding chain configuration. The chain is ideal at point J but also at point I.

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