Tricritical Effect of Attractive and Repulsive Forces on a Single Polymer Coil in a Poor Solvent

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Values of the reduction in swelling of a single coil in a poor solvent are calculated for the continuous-polymer model, by use of the renormalized theory. These values are compared to light-scattering measurements of Perzynski, Adam, and Delsanti. The results support recent theoretical studies of anomalous effects associated with the tricritical state of a polymer chain and ultraviolet divergences. In fact, this comparison provides the first experimental evidence of the existence of a tricritical state for polymers near the θ temperature.

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When the temperature T of polymer solutions decreases, the effect of attractive forces between monomers becomes conspicuous: The sign of the second virial coefficient becomes negative and the size of the coil smaller than that of the equivalent Brownian coil. The reduction in swelling is, however, small and therefore attractive forces are not the only forces acting on the segments; stabilizing repulsive forces are also present and it is interesting to determine as exactly as possible the effect of these forces. This occurs in the vicinity of the Flory or θ temperature T_F, which in this paper is defined as the limit $T_F = T_c(N \to \infty)$, where $T_c(N)$ is the critical phase separation temperature of chains with N monomers.

We shall use the continuous model defined by the probability weight

$$P\{r\} = \exp\left\{ -\frac{1}{2}\int_0^S ds \left(\frac{d\mathbf{r}}{ds}\right)^2 - \frac{b}{2}\int_0^S ds \int_0^S ds'\, \delta(\mathbf{r}(s)-\mathbf{r}(s')) - \frac{c}{6}\int_0^S ds \int_0^S ds' \int_0^S ds''\, \delta(\mathbf{r}(s)-\mathbf{r}(s'))\delta(\mathbf{r}(s')-\mathbf{r}(s''))\right\}, \quad (1)$$

where $\mathbf{r}(s)$ is the configuration of the chain, and S the Brownian "area" of the chain, proportional to the molecular mass M. The coefficients b and c correspond respectively to the two-body and three-body interactions. The end-to-end mean square distance of the Brownian-model chain ($b = c = 0$) is

$$\langle R^2 \rangle = dS; \quad (2)$$

here $d = 3$. b is a function of T: At T_F, $b = 0$, and $b < 0$ for $T < T_F$. (It may look surprising that $b = 0$ for $T = T_F$ but actually b is not a pure two-body interaction and the elimination of short-range divergent three-body terms amounts to a shift of the two-body interaction parameter b.) We assume $c > 0$ to be independent of T. Therefore the real chain is not exactly Brownian at the θ temperature T_F.

The dimensionless interaction parameters are defined by

$$z = bS^{1/2}(2\pi)^{-3/2}, \quad y = c(2\pi)^{-3}. \quad (3)$$

Let R^2 be the average squared end-to-end distance of the coil. The swelling

$$\mathscr{X} = R^2/\langle R^2 \rangle \quad (4)$$

has been calculated by one of us for T near T_F by two different methods, using field theory[1] or, more directly, the continuous chain-model[2] (1), and renormalization theory.[3] A first-order perturbation calculation (linear approximation) gives

$$\mathscr{X}_L = 1 - 4\pi y + \tfrac{4}{3}z, \quad (5)$$

but the exact tricritical calculation yields

$$\mathscr{X} = A_0(y)(1 - \tfrac{148}{33}\pi h) + \tfrac{4}{3}z(h/y)^{4/11}A_4(y), \quad (6)$$

where A_0 and A_4 are regular functions[4] of y, with $A_0(0) = A_4(0) = 1$. Here h is the three-body osmotic coefficient[2] [the dimensionless third virial coefficient; in the linear approximation (5), one has simply $h = y$]. It depends on the molecular weight[1,2]:

$$h = 1/44\pi \ln(S/s_0), \quad (7)$$

where s_0 is a small cutoff area, corresponding roughly to the size of a monomer. Thus, in practice ($N >> 1$), we take $S/s_0 = N$, where N is the number of monomers of the coil.

For infinite chains, $h = 0$, and at their θ point T_F ($z = 0$), $\mathscr{X} = A_0(y)$. This residual swelling[4] cannot be measured, and it is appropriate to define the real swelling $\mathscr{X}_R = R^2/A_0(y)dS$:

$$\mathscr{X}_R = 1 - \tfrac{148}{33}\pi h + \tfrac{4}{3}z(h/y)^{4/11} \quad (8)$$

{we have set

$$A_4(y)/A_0(y) \simeq A_4(0)/A_0(0) = 1;$$

we note, in particular, that the second term has a negative sign [see also Eq. (5)]}, in contradiction to Stephen's result[5] as was noted in Ref. 1, and we shall see that this nonobvious fact has interesting consequences. [The origin of these negative signs is well understood theoretically[2] (terms obtained by analytic continuation in dimension d)]. Let us note also that the coefficient of h in (8) contradicts that of Cherayil, Douglas, and Freed[6]: It is here ten times higher. When $z < 0$ the third term accounts for the reduction in swelling of the coil. Comparing Eqs. (8) and (5) we see that the coefficient of z in (8) is reduced by a tricritical factor $(h/y)^{4/11}$. It will be emphasized that *the experiments demonstrate the existence of this reduction* and this will be our main result. It is also of interest to compare Eqs. (8) and (5) to the formula *à la Flory,*[7]

$$\mathscr{X}_f^{5/2} - \mathscr{X}_f^{3/2} = \tfrac{1}{3}3^{3/2}z + 3^{1/2} \times 8y\mathscr{X}_f^{-3/2}, \tag{9}$$

where $\mathscr{X}_f$ is a global swelling. (The coefficients have been obtained by assumption that the monomer distribution is Gaussian). For a given set of values ($z < 0$, $y > 0$), the swellings obtained from (9) are very different from those given by (5) and (8). In particular, for $z > 0$, we have always $\mathscr{X}_f > 1$, whereas values $\mathscr{X}_L < 1$ and $\mathscr{X}_R < 1$ are possible.

We propose to compare results (5), (8), and (9) with light-scattering data[8,9] from Perzynski's thesis[9] concerning dilute solutions of polystyrene of mass $M_w = 1.26 \times 10^6$ in cyclohexane. However, we first need the values of b, c, and h and we shall determine them independently.

Values of b for the polystyrene-cyclohexane solution are derived from the swellings observed[10] at temperatures *above* T_F and from the precise theoretical swelling curve of des Cloizeaux, Conte, and Jannink.[11] The result

$$b = 2.918 - (896\ \text{K})/T\ \text{nm}^{-1} \tag{10}$$

is assumed to be valid for lower temperatures, and it gives $b = 0$, for $T = T_F = 34\,°\text{C}$, in agreement with the definition $T_F = T_c(S \rightarrow \infty)$. The values given by (10) are about 10% higher than the corresponding values of Ref. 10 obtained with the crude Flory swelling formula.

The value of c will be determined by comparison of experimental values of T_c to simple predictions of the Flory-Huggins approximation[12] (continuous version). Experiments give for polystyrene in cyclohexane[9]

$$10^3/T_c = 3.257 + 47/\sqrt{M}, \tag{11}$$

and therefore the critical value b_c of b is, as a result of (10),

$$b_c = -42/\sqrt{M}. \tag{12}$$

Now c can be obtained from the equation

$$c = b_c^2 S/4, \tag{13}$$

which follows from the critical-point equations $\partial\Pi/\partial C = 0$, $\partial^2\Pi/\partial C^2 = 0$, where Π is the osmotic pressure given in terms of the number C of chains per unit volume, by the *crude* equality

$$\Pi\beta = C + \tfrac{1}{2}bS^2C^2 + \tfrac{1}{3}cS^3C^3. \tag{14}$$

Since S and M are proportional, Eqs. (12) and (13) are consistent with our assumption that c is constant. To get it, we finally need the conversion relation

$$S = 2\langle\Lambda\rangle M, \tag{15}$$

where[13] for polystyrene $\langle\Lambda\rangle = 8.3 \times 10^{-4}$ nm^2/dalton. Thus we find for polystyrene in cyclohexane [see (3)]

$$c = 0.73, \tag{16}$$

$$y = 0.0029. \tag{17}$$

It is difficult to evaluate the error involved in approximation (14) and therefore the error in c. However, an independent similar value of c has been derived by Perzynski,[9] using directly the osmotic pressure measurements of Stepanek *et al.*[14] for semidilute solutions. It reads in our notation[15] $c = 0.76$.

We now need the value of h where $h = 1/44\pi \times \ln(S/s_0)$. Actually, S/s_0 is (approximately) the number of monomers of molecular mass $m = 104$. Thus, for the sample $M_w = 1.26 \times 10^6$, $S = 2090$ nm^2, and $S/s_0 = M_w/m = 1.21 \times 10^4$. Therefore,

$$h = 7.7 \times 10^{-4}. \tag{18}$$

Note that a logarithmic function like h varies slowly and therefore an error in s_0 has minor consequences. On the other hand, the swelling data of Perzynski[9] have been given for T in the range 301–308 K. The useful values of z are calculated by putting in (3) the corresponding values of b [given by (10)] and S (first column of Table I). Now, using these values of z, y (17), and h (18), we calculate the corresponding theoretical swellings $\mathscr{X}_f$(9), $\mathscr{X}_L$(5), and $\mathscr{X}_R$(8) (see Table I).

The physical quantity measured by Perzynski, Adam, and Delsanti is precisely the gyration swelling $\mathscr{X}_G = R_G^2/R_G^2(T_1)$ where R_G^2 is the average squared radius of gyration, and T_1 a reference temperature. The value of T_1 ($T_1 = 35\,°\text{C}$) chosen by Perzynski is not far from $T_F = 34\,°\text{C}$ (see Table I and Fig. 1[16]).

Consider first the temperature $T_{\mathscr{X}}(S)$ at which the end-to-end swelling is unity. Its limit is the Flory temperature $T_{\mathscr{X}}(S \rightarrow \infty) = T_F = 34\,°\text{C}$. For finite molecular weights, the Flory model gives $T_{\mathscr{X}}(S) < T_F$ (Fig. 1), a result which could look natural. However, a quite different result is obtained by use of the continuous model, which takes into account the ultraviolet

TABLE I. The various swellings calculated or measured for different temperatures, for polystyrene of mass $M_w = 1.26 \times 10^6$ in cyclohexane. Parameter b is calculated from Eq. (10), and z from Eqs. (3) and (14). $\mathscr{X}_F$ is the Flory swelling (9). $\mathscr{X}_L$ is calculated from (5), $\mathscr{X}_R$ is the renormalized swelling calculated from (7) and (8), $\mathscr{X}_G$ is the experimental swelling taken from Perynski's thesis, and $\mathscr{X}_{G,L}$ and $\mathscr{X}_{G,R}$ are respectively the linear and renormalized gyration swellings (18) and (19).

T	$10^2 b$			End-to-end swelling		Gyration swelling		
(K)	(nm^{-1})	z	$\mathscr{X}_f$	$\mathscr{X}_L$	$\mathscr{X}_R$	$\mathscr{X}_G$	$\mathscr{X}_{G,L}$	$\mathscr{X}_{G,R}$
308	0.89	0.026	1.08	1	1.01	1	1	1
307	0	0	1.04	0.96	0.99	0.97	0.967	0.98
306	−1.05	−0.0305	0.97	0.92	0.96	0.95	0.928	0.955
305	−2.01	−0.058	0.88	0.884	0.942	0.931	0.893	0.934
304	−2.98	−0.086	0.75	0.845	0.915	0.912	0.857	0.912
303	−3.95	−0.115	0.46	0.81	0.89	0.855	0.82	0.89
302	−4.92	−0.143	0.29	0.77	0.87	0.81	0.784	0.867
301	−5.87	−0.17	0.22	0.73	0.85	0.756	0.75	0.846

divergences. Figure 1 shows that $T_{\mathscr{X}}(S) > T_F$, for S finite. A consequence is that the "dividing line" introduced by de Gennes[17] is found to be exactly in the opposite half-space from what was initially predicted. Note in Fig. 1 that for our sample, the linear theory yields $T_{\mathscr{X}}(S) - T_F = +1\,°\mathrm{C}$ and the renormalized one gives $+0.5\,°\mathrm{C}$.

The most interesting result concerns the curve of reduction in swelling. Figure 1 immediately shows that the Flory model is unrealistic. The continuous model represents much better the experimental reduction in swelling. We take here for the theoretical curves the reference temperature T_1 of the experimental data where $\mathscr{X}_G = 1$; this is achieved, according to the considerations just above, by shifting the line $\mathscr{X}_R$ to the right by 0.5°, and $\mathscr{X}_L$ by 0°. Then Fig. 1 shows that the slope of $\mathscr{X}_L$ is too large. On the contrary, *a good agreement is found with the renormalized curve* $\mathscr{X}_R$ (for $303\ \mathrm{K} \leq T \leq T_F$).

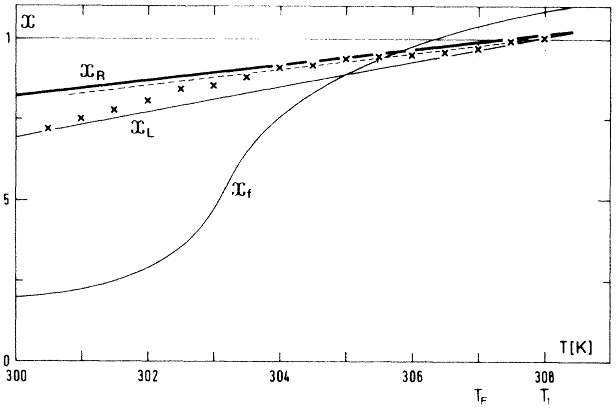

FIG. 1. Calculated end-to-end swelling for values of the parameters z, y, and h given in text. $\mathscr{X}_f$, swelling derived from the Flory theory [Eq. (9)]. $\mathscr{X}_L$, swelling in the continuous model: linearized theory [Eq. (5)]. $\mathscr{X}_R$, swelling in the continuous model: renormalized theory [Eq. (8)]. Crosses, experimental values obtained by Perzynski (Ref. 9) for the gyration swelling $\mathscr{X}_G$ of polystyrene in cyclohexane, $M_w = 1.26 \times 10^6$. Dashed line, theoretical reduction in swelling after shift of $\mathscr{X}_R$ to the right in order to obtain $\mathscr{X}_R = \mathscr{X}_G = 1$; at the same temperature $T_1 = 35\,°\mathrm{C}$.

We can still improve the comparison by calculating the theoretical gyration swelling.[2] The linear approximation is

$$\mathscr{X}_{G,L} = R_G^2/R_G^2(T_1) = 1 + \tfrac{134}{105}(z - z_1), \qquad (19)$$

where z_1 is the value of z for the reference tempera-

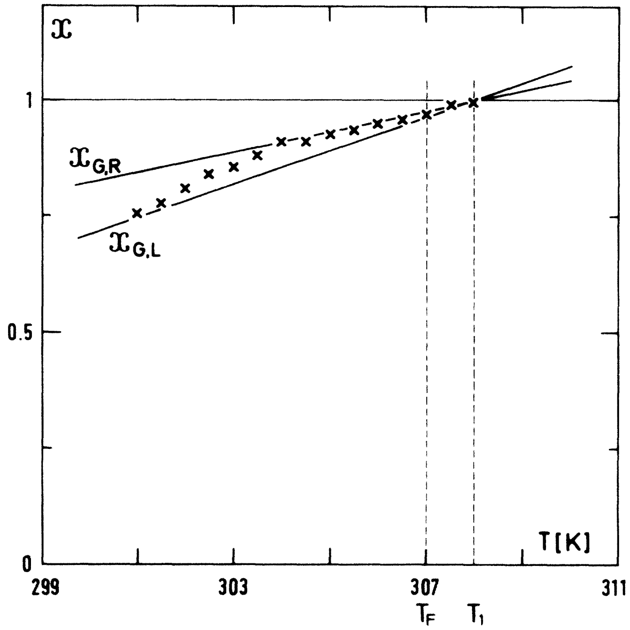

FIG. 2. Calculated gyration swellings for values of the parameters z, y, and h given in text; crosses, measured gyration swelling, as in Fig. 1. Calculated and measured swellings are normalized to unity at the same temperature $T_1 = 308$ K.

ture $T_1 = 35\,^\circ\mathrm{C}$. On the other hand, the renormalized gyration swelling[2,18] reads

$$\mathscr{X}_{G,R} = 1 + \tfrac{134}{105}(h/y)^{4/11}(z - z_1). \qquad (20)$$

(Note that the numbers $\frac{134}{105} = 1.2762$ and $\frac{4}{3} = 1.3333$ are rather close.) $\mathscr{X}_{G,L}$ and $\mathscr{X}_{G,R}$ are given in Table I and Fig. 2. Again the line $\mathscr{X}_{G,L}$ is too steep and $\mathscr{X}_{G,R}$ is in good agreement with the data. Thus, *the main observable effect is the renormalization of the coefficient of z in* $\mathscr{X}_{G,R}$ *(or* $\mathscr{X}_R$*) by a tricritical factor* $(h/y)^{4/11} \simeq 0.62$.

Let us finally consider the range of validity of the tricritical theory. It is predicted[1,2] to be valid for T close enough to T_F:

$$|z| \lesssim h^{1/2}(y/h)^{4/11} \times \mathrm{const}. \qquad (21)$$

Thus using (17) and (18), we find $|z| \lesssim 0.045 \times \mathrm{const}$. The constant in (21) is not exactly known, but, assuming that its value is unity, we find from Table I that (21) gives 305 K $< T \leqslant T_\mathrm{F}$. Actually a good agreement is found in the range 303 K $< T \leqslant T_\mathrm{F}$ (Fig. 2). Note[15] that 303 K is the critical phase separation temperature of our sample. Below 303 K, the reduction in swelling is stronger, as expected (collapse).

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[4] We have found (Refs. 1 and 2) $A_0(y) = 1 + \frac{16}{33}\pi y + \ldots$, and in this article we have $y = 2.9 \times 10^{-3}$, and so $A_0(y) \simeq 1.0044$.

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[16] This figure is taken from the forthcoming book by J. des Cloizeaux and G. Jannink, "Polymères en solution : leur modélisation et leur structure" (Editions de Physique, to be published).

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[18] One has, using direct renormalization theory (Ref 2),

$$R_G^2/dS = A_0(y)\left[1 + \frac{541}{33 \times 4}\pi h\right] + \frac{134}{105} z \left(\frac{h}{y}\right)^{4/11} A_4(y)$$

and, linearizing all the small quantities,

$$\mathscr{X}_{G,R} = R_G^2/R_G^2(T_1) = 1 + \tfrac{134}{105}(z - z_1)(h/y)^{4/11}.$$