Mean field theory of polymer crossover behavior

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An argument is presented that the exponent previously employed to describe crossover behavior of either a linear or randomly branched polymer from the theta region to the swollen or collapsed state is inconsistent with the mean field description of the polymer free energy. In place of the conventional exponent $\phi(d) = [2 - dv_\theta(d)]$, it is suggested that mean field theory compels use of the exponent $\psi(d) = [v_\theta(d)d - 1]$, where $v_\theta(d)$ is the index which describes the dependence of polymer length on molecular weight in the theta region. The consequences of this different choice of crossover index are discussed for crossover behavior of the polymer length and for phase separation behavior. Comparison of the results of the different predictions with both Flory–Huggins theory and ϵ-expansion calculations is included. For linear chains in two dimensions striking differences are found for the predicted behavior of the phase separation curve at high monomer concentrations.

I. INTRODUCTION

A polymer chain can adopt greatly different configurations in different regions of the temperature-composition phase diagram. The chain will be swollen in the good solvent region, adopt a more ideal configuration in the theta region, and collapse in the poor solvent region. A good deal of attention has been given to the crossover behavior of the polymer between these various regimes.

The purpose of this paper is to point out that the conventional argument for determining the crossover behavior is not consistent with the assumptions of mean field theory. We present an alternative argument for describing the crossover behavior within mean field theory and show that this has substantial significance for scaling behavior and for the predicted phase separation behavior of the linear and randomly branched polymer systems under consideration here.

The mean field theory of a polymer molecule in dilute solution is based on a Flory-type free energy of the form[1,2]

$$F(R) = \frac{R^2}{N^{2v_0}} + \frac{2vN^2}{dR^d} + \frac{wN^3}{dR^{2d}}, \tag{1.1}$$

where R is the radius of gyration and $v_0 = 1/2$ for a linear chain while $\bar{v}_0 = 1/4$ for a randomly branched polymer chain[3] (lattice animal). Here, N is the number of segments taken to be of unit length, $kT = 1$, d is the dimensionality of space, and v and w give the strength of the average repulsion between pairs and triplets of segments, respectively, within the polymer. In Eq. (1.1) we have neglected the entropy term[1] proportional to $\ln R$, which is sometimes included in the elastic free energy. Justification for omitting this term is presented in the Appendix.

Minimization of this free energy and direct analysis[4] permits determination of the chain size with length

$$R \sim N^{v(d)} \tag{1.2}$$

in the different regimes of polymer configuration. There is a critical dimensionality d_c above which the polymer behaves in an ideal manner $v = v_0$. In a good solvent $v > 0$; one finds

$$v = 3/(d + 2), \quad d_c = 4 \tag{1.3}$$

for a linear chain and

$$\bar{v} = 5/2(d + 2), \quad d_c = 8 \tag{1.4}$$

for a randomly branched polymer. At the theta point T_θ, $v = 0$; one finds

$$v_\theta = 2/(d + 1), \quad d_c = 3 \tag{1.5}$$

for a linear chain and

$$\bar{v}_\theta = 7/4(d + 1), \quad d_c = 6 \tag{1.6}$$

for a branched polymer. In a poor solvent $v < 0$, the polymer collapses and one finds

$$v_c = \bar{v}_c = (1/d) \tag{1.7}$$

for both the linear and branched polymer.

The crossover behavior of the polymer between these various regimes depends upon how the pair potential varies from net repulsion $(v > 0)$ to attraction $(v < 0)$ as a function of the dimensionless temperature $\tau = [(T - T_\theta)/T_\theta]$. In the vicinity of the theta temperature, one assumes

$$v(\tau) \sim \tau. \tag{1.8}$$

The scaling argument[5] for the crossover behavior is based on introduction of a *crossover exponent* $\phi(d)$ and introduction of a dimensionless function which has the appropriate asymptotic dependence to describe the proper polymer behavior in each regime. For example, in the case of crossover behavior of a linear chain to the good solvent regime, one assumes

$$R = N^{v_\theta} h(\tau N^\phi) \tag{1.9}$$

and that the dimensionless function $h(x)$ has the properties

$$h(x) \to 1 \text{ as } x \to 0; \quad h(x) \to x^m \quad x \gg 1$$

with the exponent m determined to give the correct behavior $R \sim N^v$ in the asymptotic regime; thus one finds $v = v_\theta + \phi m$.

The analysis we present suggests that the conventional mean field argument for determining ϕ is not consistent with the assumptions of the theory and that a correct argument leads to a different crossover exponent which we denote ψ. In

particular, we find for linear chains $\phi = \psi$ in $d = 3$ but $\phi(2) \neq \psi(2)$. For randomly branched polymers $\bar{\phi}(d) \neq \bar{\psi}(d)$ in either $d = 3$ or $d = 2$.

The body of this paper is devoted to presenting our reasoning on why the correct crossover exponent is $\psi(d)$, the implications of this exponent for crossover behavior and for the predicted phase separation, including critical behavior, for concentrated polymer solutions. A comparison of these mean field results with the predictions of Flory–Huggins theory and the predictions of calculations based on ϵ expansions is also included.

II. DETERMINATION OF THE CROSSOVER EXPONENT

A. The conventional argument

The conventional argument[6] for determination of the crossover exponent ϕ is based on identification of a *region* in the vicinity of the theta point where the pair interaction energy in Eq. (1.1) $E^{(2)} \sim [2\tau N^2/dr^d]$ is "small," i.e., of order unity or less. Within this region $R \sim N^{\nu_\theta}$ so that

$$E^{(2)} \sim (2_\tau/d)N^\phi \tag{2.1}$$

with

$$\phi(d) = 2 - d\nu_\theta(d) . \tag{2.2}$$

One must be sufficiently close to the theta point for this pair interaction energy to be small. This requires that $\tau \lesssim N^{-\phi}$ in the theta region where more nearly ideal behavior is to be expected.

For linear chains Eq. (2.2) predicts

$$\phi(d) = 2/(d + 1) , \quad d \leqslant 3 \tag{2.3}$$

and one obtains the expected ideal behavior $\phi(3) = 1/2$ in three dimensions. For $d = 2$, one finds $\phi(2) = 2/3$ which, it is important to note, is in good agreement with both simulation results[7] and the result of ϵ-expansion calculations.[8]
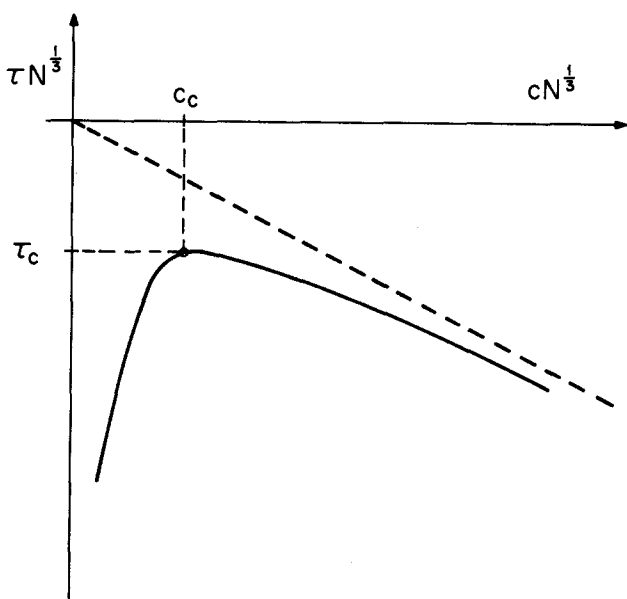

FIG. 1. Schematic prediction of phase separation boundary according to modified mean field theory for linear polymer chains in $d = 2$.

For branched polymer chains one obtains[5]

$$\bar{\phi}(d) = 2 - \bar{\nu}_\theta(d) = [(8 + d)/4(d + 1)] , \quad d \leqslant 6 \tag{2.4}$$

which yields ideal behavior in $d = 6$, $\bar{\phi}(6) = 1/2$, and $\bar{\phi}(3) = 11/16$, $\bar{\phi}(2) = 5/6$.

These results can be employed to determine the behavior of R as one leaves the theta *region*. For example, going out of the theta region, towards the good solvent region, one predicts via the scaling analysis described in the previous section

$$R \sim N^\nu \tau^{1/2[(d-1)/(d+2)]} , \quad d \leqslant 3 \tag{2.5}$$

for linear chains. In general, one finds

$$R \sim N^\delta \tau^{(\delta - \nu_\theta)/\phi} , \tag{2.6}$$

where δ is the appropriate exponent in the asymptotic regime, i.e., good (ν) or poor (ν_c) solvent states, and where the quantities ν_θ and ϕ should have bar superscripts for branched polymers.

B. The modified argument

The alternative argument we propose for determining the crossover exponent is based on recognition of the physical fact that in the theta *region*, triplet interactions $E^{(3)} = [wN^3/dR^{2d}]$ remain present and, by assumption, these interactions are net repulsions, i.e., $w > 0$. Accordingly, the appropriate criterion for the pair interactions to be inconsequential is not that $[E^{(2)}/kT]$ be small as in the conventional argument but rather that *the pair interaction energy be small compared to the triplet interaction energy*. Thus, the criterion we propose to define the theta region is $[E^{(2)}/E^{(3)}] \ll 1$. This criterion leads to a different crossover exponent $\psi(d)$. One finds

$$\frac{E^{(2)}}{E^{(3)}} \sim \frac{\tau R^d}{N} \sim \tau N^{\nu_\theta d - 1} \sim tN^{\psi(d)} . \tag{2.7}$$

For linear chains this yields

$$\psi(d) = \nu_\theta(d)d - 1 = [(d-1)/(d+1)] , \quad d \leqslant 3 \tag{2.8}$$

which leads to the expected classical result in $d = 3$ but gives a quite different prediction in two dimensions $\psi(2) = 1/3$ compared to the conventional argument $\phi(2) = 2/3$. Note that in one dimension, in contrast to the conventional prediction, the modified result correctly predicts no crossover behavior $\psi(1) = 0$, indicating that sufficient repulsions are present to force the linear polymer into the conformation of a rigid rod $\nu(1) = \nu_\theta(1) = 1$.

For the randomly branched polymer, identical reasoning leads to the result

$$\bar{\psi}(d) = \bar{\nu}_\theta(d)d - 1 = [(3d - 4)/4(d + 1)] , \quad d \leqslant 6 . \tag{2.9}$$

This result predicts ideal behavior, as expected, in $d = 6$. In two and three dimensions, the prediction is quite different from that of the conventional argument as presented by Daoud *et al.*[5] One finds $\bar{\psi}(3) = 5/16$ and $\bar{\psi}(2) = 1/6$ in contrast to $\bar{\phi}(3) = 11/16$ and $\bar{\phi}(2) = 5/6$.

The modified crossover exponent may be employed in scaling analysis in an identical manner to the conventional

exponent. In place of Eq. (2.6) one has

$$R \sim N^{\delta} \tau^{(\delta - \nu_{\theta})/\psi} . \tag{2.10}$$

For linear chains moving towards the good solvent regime one finds $R \sim N^{\nu} \tau^{[1/(d+2)]}$ in contrast to the prediction of the conventional argument, Eq. (2.5).

An appealing aspect of the approach which employs the crossover index ψ is that predicted temperature dependence as one leaves the theta region agrees with the temperature dependence expected in either the good or poor solvent region to which one is moving. For example, in the case of the transition to the good solvent region for linear chains in two dimensions, we predict $R \sim N^{3/4} \tau^{1/4}$. Use of the crossover exponent ϕ [see Eq. (2.5)] leads to the prediction $R \sim N^{3/4} \tau^{1/8}$. Thus there remains an unexplained crossover in temperature behavior from a $\tau^{1/8}$ dependence to a $\tau^{1/4}$ dependence on the good solvent side of the phase diagram when the exponent ϕ is employed.

There is an alternative line of reasoning which leads to the same conclusion that ψ is the correct crossover exponent within mean field theory. This reasoning is based on recognizing that the Flory-type free energy [Eq. (1.1)] should describe, as it stands, behavior in each regime and the transitions among them. Consistent application of mean field theory will give an unequivocal prediction for the crossover exponent. Here we show that consistent application of the mean field theory leads to the crossover exponent ψ, not ϕ.

Minimization of the free energy, Eq. (1.1) with $w = 1$, leads to the resulting equation for R:

$$\left(\frac{R}{R_{\theta}}\right)^{2d+2} = [\tau N^{\psi}]\left(\frac{R}{R_{\theta}}\right)^{2} + 1 , \tag{2.11}$$

where we have introduced the notation

$$R_{\theta} = N^{\nu_{\theta}} \tag{2.12}$$

and employed the result

$$\nu_{\theta} = \frac{2\nu_{0} + 3}{2(d+1)} . \tag{2.13}$$

For branched chains, a superscript bar should be added.

Clearly, from Eq. (2.11) the mean field free energy leads to a description of the polymer dimension R in terms of a universal function which depends on the crossover exponent ψ:

$$R = R_{\theta} g(\tau N^{\psi}) . \tag{2.14}$$

It is an easy matter to show from Eq. (2.11) that the scaling function $g(x)$ has the desired asymptotic behavior; $g(x) \to 1$ as $x \to 0$ and $g(x) \to g^{\alpha}$ with $\alpha = [(\nu - \nu_{\theta})/\psi]$ for $x \gg 1$. For $x \ll 0$, toward the poor solvent region, Eq. (2.11) yields the behavior

$$R_{c} \sim |\tau|^{-1/d} N^{-(\psi/d)} R_{\theta} \sim |\tau|^{-1/d} N^{1/d} , \tag{2.15}$$

where R_{c} is the expected polymer length in the collapsed state.

We also note, although it will not be pursued here, that the same reasoning leads to modification of the conventional argument for crossover behavior for directed lattice animals.[9]

Finally, why would one advocate the adoption of the conventional criterion $\beta E^{(2)} \sim 1$ for crossover when strict

application of the Flory free energy leads to the modified criterion $E^{(2)}/E^{(3)} \sim 1$? The criteria are suggested by a heuristic argument that the end-to-end distance R_{E} of a chain (even in the presence of excluded volume) can be deformed by an energy kT. According to this view the appropriate criterion for the magnitude of the free energy change caused by a fluctuation is $\sim kT$. We believe this argument to be incorrect. The Flory free energy is expressed in terms of a variable R which is a rough measure of polymer size and not precisely R_{E} or any other particular variable. It corresponds most closely to the radius of gyration R_{G}. In most cases the averages of R, R_{G}, and R_{E} are not significantly different. But, when one seeks to estimate the energy required to cause a significant deviation of these variables, the difference is crucial. Even in the presence of repulsions R_{E} can fluctuate anywhere between $a \lesssim R_{E} \lesssim Na$ where a is the monomer size, but R or R_{G} is severely restricted in its fluctuations. Consequently, kT is not sufficient to distort R or R_{G} while it is adequate to distort R_{E}.

This point can be expressed more quantitatively as follows. When a force h, distorts a chain, the free energy is $\beta \mathscr{F}(R) = \beta F(R) - \beta hR$. A rough estimate of the energy required to significantly distort the chain is given by $\beta hR_{G} \sim \beta F(R_{G})$. For the end-to-end distance $\beta F(R_{E}) \sim R_{E}^{2}/R_{G}^{2}$ and consequently $hR_{G} \sim kT$ is the energy required to distort the chain. For the variable R, however, Flory theory for a linear chain with excluded volume gives $\beta hR_{G} \sim R_{G}^{2}/R_{0}^{2} \sim N^{(4-d)/(d+2)}$, and so an energy $hR_{G} \sim N^{(4-d)/(d+2)} kT$ is the typical energy required to distort R significantly.

III. PHASE SEPARATION BEHAVIOR

In this section, the consequences of the different crossover exponents ϕ and ψ for phase separation are discussed. We follow closely the analysis of Daoud et al.[5]

We assume that the free energy per unit volume in the critical region may be expressed as

$$F = N^{-\nu d} \theta^{d} f[(c/c^{*}), |\tau| N^{\psi}] , \tag{3.1}$$

where $f(x, y)$ is the scaling function and c is the monomer concentration. The quantity c^{*} is the monomer concentration which leads to overlap of the chains at a volume fraction of about unity

$$c^{*} = N^{1 - \nu_{\theta} d} . \tag{3.2}$$

The coexistence curve or the spinodal curve is found by successive differentiation of Eq. (3.1) with respect to c. One arrives at the relation

$$(c/c^{*}) = k(|\tau| N^{\psi}) . \tag{3.3}$$

At high concentrations it has been argued[10] that the coexistence curve should be independent of molecular weight. Accordingly, we assume that $k(x)$ has a power law behavior at large x and the exponent is determined by the condition of molecular weight independence. The result is

$$\tau \sim c^{[\psi/(\nu_{\theta} d - 1)]} \tag{3.4}$$

along the coexistence curve.

Since $\psi = (\nu_{\theta} d - 1)$ [see Eqs. (2.7) and (2.9)] we find

$$\tau \sim c \tag{3.5}$$

for both linear and branched polymer chains independent of

dimension. This is in agreement with the results of Flory–Huggins theory and in sharp contrast to the results of Daoud *et al.* who base their analysis on the crossover exponent ϕ. Use of this crossover exponent leads to the prediction[5]

$$\tau \sim c^{[\phi/(\nu_\theta d - 1)]} \tag{3.6}$$

or by use of Eqs. (2.2) and (2.4),

$$\tau \sim c^{[(2 - d\nu_\theta)/(\nu_\theta d - 1)]}, \tag{3.7}$$

which exhibits a dependence on dimensionality. Note that for linear chains in $d = 3$, Eq. (3.7) predicts $\tau \sim c$ in agreement with Eq. (3.5). For linear chains in $d = 2$ or branched chains in $d = 2$ and $d = 3$, the predictions differ. In particular, for linear chains in $d = 2$ we propose that $\tau \sim c$ in the high concentration limit while the standard approach predicts $\tau \sim c^2$.

Predictions for the location of the critical point also differ in the two approaches. According to the free energy expression, Eq. (3.1), one expects

$$c_c \sim c^* \tag{3.8}$$

and

$$|\tau_c| \sim N^{-\psi}. \tag{3.9}$$

Since in our approach $c^* \sim N^{-\psi}$, we find $c_c \sim \tau_c$ which is in agreement with Flory–Huggins theory.[6] Our results differ from Flory–Huggins theory in the predicted molecular weight dependence because in the latter theory ideal behavior [$\psi = 1/2$] is always presumed to exist in the theta region. (The predicted phase diagram is schematically displayed in Fig. 1.)

The results of Daoud *et al.*[5] differ from those presented in Eqs. (3.8) and (3.9) since they find $c_c \sim N^{-\phi}$ and $|\tau| \sim N^{-\phi}$. For a linear chain in $d = 3$, $\psi(3) = \phi(3)$ so there is no difference in the prediction of the location of the critical point. In other cases there is a difference. In particular for a linear chain in $d = 2$, we predict $|\tau \approx \sim |c_c| \sim N^{-1/3}$ while Daoud *et al.* predict $|c_c| \sim N^{-1/3}$ and $|\tau_c| \sim N^{-2/3}$.

Finally, we note that the interesting heuristic argument presented by Daoud *et al.* to determine the high concentration limit for the coexistence curve can be utilized in our scheme as well. They propose that phase separation occurs when the volume fraction ϕ_v reaches some constant independent of N and τ. In the collapsed state,

$$\phi_v = (c/N)R_c^d, \tag{3.10}$$

where R_c is the appropriate chain length in the collapsed state. Use of Eq. (2.15) leads to $\tau \sim c$ in agreement with Eq. (3.5).

IV. DISCUSSION

In this article, we claim that *within mean field theory* the appropriate crossover exponent is ψ [Eq. (2.8)] and not ϕ [Eq. (2.2)] for linear polymer chains. For randomly branched polymer chains the appropriate quantity is $\bar{\psi}$ [Eq. (2.9)] and not $\bar{\phi}$ [Eq. (2.4)].

This modification has major consequences for the predictions of polymer behavior. First, there is a different prediction for the scaling behavior of linear chains in $d = 2$ and of randomly branched chains in both $d = 2$ and $d = 3$ as the system moves from the theta region to either the good or poor solvent region. Second, use of the exponent ψ predicts

high concentration phase separation behavior for both linear and branched polymer chains below critical dimensionality of the form $\tau \sim c$. This is in agreement with Flory–Huggins theory and in sharp contrast with the predictions that follow from use of the crossover index ϕ. We predict that the critical point for polymer phase separation is located by the relations $c_c \sim \tau_c$ and $c_c \sim N^{-\psi}$ for both linear and branched polymers. The first relation is in agreement with Flory–Huggins theory, the second is not. In contrast, use of the crossover index ϕ predicts $c_c \sim N^{-\psi}$ and $|\tau_c| \sim N^{-\phi}$. These are all substantial differences.

We do not intend to claim that mean field predictions based on ψ are better than predictions based on ϕ compared to reality. After all there is no reason to believe that mean field theory is an adequate description for all aspects of polymer behavior. Moreover, for linear chains in two dimensions there is support for use of the value $\phi(2) = 2/3$ in the critical regions from both simulation results[7] and ϵ-expansion calculations[8] which suggest the tricritical crossover exponent $\phi_t(2) = 0.6364$.

Consistent application of the mean field results compared to consistent application of the results of ϵ expansion can be quite striking. A particularly striking case is a linear polymer in two dimensions which conveniently is the situation most likely to be amenable to experimental test. Here, it is already known that the mean field prediction[11] $\nu_\theta(2) = 2/3$ differs markedly from the results of ϵ-expansion[12] calculation $\nu_\theta^t(2) = 0.505$. In the critical region according to the scaling discussion for the free energy in the previous section one predicts approximately

$$\tau \sim c^{[\phi_t/(\nu_\theta^t d - 1)]} \sim c^{64} \tag{4.1}$$

if one consistently employs ϵ-expansion values for ϕ and ν_θ. In contrast, consistent use of mean field values predicts the linear relationship $\tau \sim c$.

This sharp difference evidently arises because of the factor $(\nu_\theta d - 1)^{-1}$ which appears in the exponent and it will be manifest in other physical situations where the same factor appears. The concentration dependence of the surface pressure π of a polymer monolayer which has been examined experimentally[13,14] presents another example since $\pi \sim c^y$ with $y = [(d\nu_\theta/(d\nu_\theta - 1)]$.

In the high concentration limit we believe the appropriate crossover index to employ is ψ and not ϕ within the context of mean field theory. This leads to the different predictions for the behavior of τ vs c along the phase boundary. We do not believe that an acceptable way to proceed in this region is to employ mean field values for ν and ν_θ and the crossover index ϕ which seems correct because of its resemblance to ϕ_t.

Substantial discrepancies between the predictions of a Flory-type mean field and more refined methods is disturbing in polymer chemistry. The agreement which is found in certain key quantities, e.g., $\nu(3) = 3/5$ and $\nu_\theta(3) = 1/2$ has led to an expectation that mean field theory is quite reliable for practical use. An improved understanding of the limitations of mean field theory compared to ϵ-expansion techniques (and vice versa) is very much to be desired. An especially important question concerns the identification of the

region within which the Flory-type mean free theory cannot be expected to hold and the proper description requires analysis supercrossover behavior from the tricritical exponent ϕ_t to ψ.

APPENDIX

For a linear chain the Flory free energy including the spatial entropy term which is proportional to $\ln R$ (this term comes from the volume element in the configurational integral) is

$$F(R) = -d \ln R + \frac{dR^2}{2N} + \frac{vN^2}{R^d} + \frac{wN^3}{2R^{2d}} . \quad (A1)$$

Minimizing the energy yields

$$0 = -\frac{1}{R} + \frac{R}{N} - \frac{vN^2}{R^{d+1}} - \frac{wN^3}{R^{2d+1}} . \quad (A2)$$

Introducing the expansion factor α by $R = N^{1/2}\alpha$ into Eq. (2) gives

$$\alpha^{2d}(\alpha^2 - 1) = \alpha^d vN^{2-d/2} + wN^{3-d} . \quad (A3)$$

The spatial entropy term has replaced α^2 by $(\alpha^2 - 1)$ in Eq. (A3).

It has been argued[15] that when v and w are small, this term becomes significant. This may especially be expected to be the case when considering the transition from θ to collapsed behavior in $d = 2$. Here, we specialize to the $d = 2$ case and show that $\psi(2)$ is still the correct crossover exponent to use within mean field theory.

For $d = 2,1$ Eq. (A3) becomes

$$\alpha^4(\alpha^2 - 1) = N(v\alpha^2 + w) . \quad (A4)$$

We proceed to analyze Eq. (A4) for various cases.

1. $v > 0$

The right-hand side of Eq. (A4)$\rightarrow \infty$ as $N\rightarrow\infty$ and consequently $\alpha\rightarrow\infty$ as $N\rightarrow\infty$. Equation (A4) thus simplifies to $\alpha^6 \approx Nv\alpha^2$ in this limit and $\alpha \sim v^{1/4}N^{1/4}$ or $R \sim v^{1/4}N^{3/4}$. This is the good solvent result and the $\ln R$ contribution is irrelevant.

2. $v = 0$

In this case Eq. (A4) becomes

$$\alpha^4(\alpha^2 - 1) = Nw . \quad (A5)$$

The right-hand side of Eq. (A5)$\rightarrow \infty$ as $N\rightarrow\infty$ and consequently $\alpha\rightarrow\infty$ as $N\rightarrow\infty$. Thus Eq. (A5) simplifies to $\alpha^6 \sim Nw$ in this limit and $\alpha \sim w^{1/6}N^{2/3}$ or $R \sim w^{1/6}N^{2/3}$. This is the θ solvent result and again the $\ln R$ contribution is irrelevant.

There exists a crossover from θ to good solvent behavior for small v when $V\alpha^2 \approx w$ or $vN^{1/3} \approx w^{2/3}$. Since $v \sim \tau$, analysis identical to that given in Sec. II B leads the crossover exponent in $\psi(2) = 1/3$ as expected.

3. $v = -|v|$

In this case Eq. (A4) becomes

$$\alpha^4(\alpha^2 - 1) = N(-|v|\alpha^2 + w) . \quad (A6)$$

This is the regime where the spatial entropy term is expected

to be significant. The argument goes as follows: collapse occurs when $(-|v|\alpha^2 + w)$ becomes zero. At this point the right-hand side of Eq. (6) is zero independent of N, $\alpha = 1$, and consequently $|v| = w$. This argument would suggest that θ solvent behavior is observed for $|v| < w$, and at $|v| = w$ a collapse occurs.

The above argument is fallacious and does not take into account the limiting behavior of how $(-|v|\alpha^2 + w)\rightarrow 0$ as $N\rightarrow\infty$. This is of great importance as the right-hand side of Eq. (A6) includes a prefactor N which diverges. A closer analysis of Eq. (A6) suggests that for all $v = -|v| < 0$ as $N\rightarrow\infty$ collapse occurs with $\alpha^2 = w/|v|$ and for small $|v|$ there exists a crossover from θ to collapse with a crossover exponent $\psi(2) = 1/3$.

Clearly as $N\rightarrow\infty$, α cannot diverge for in this case $\alpha^6 \sim -|v|N\alpha^2$ and the left- and right-hand sides of the equation have opposite signs. Suppose instead that α tends to a constant (the condition for collapse) as $N\rightarrow\infty$, i.e., $\alpha^2(N) = a + b/N + c/N^2 + \cdots$. Substitution into Eq. (A6) yields a solution if $a = w/|v|$, $b^2 = w^2(|v| - w)/|v|^4$, etc. Thus Eq. (A6) yields collapse with $R \sim (w/|v|)N^{1/2}$ for $d = 2$ for all $v = -|v| < 0$, though there exist corrections to scaling at small N. For the special value of the parameter $|v| = w$, $a = 1$ and all $b = c = \cdots = 0$, and thus all corrections to scaling disappear.

For small values of $|v|$, θ behavior will be observed so long as $|v|\alpha^2 \ll w$, or as $\alpha \sim w^{1/6}N^{1/6}$ in the θ regime, so long as $|v|N^{1/3} \sim w^{2/3}$. In other words, as $|v| \sim |\tau|$, $\psi(2) = 1/3$ is again the correct crossover exponent to use.

We find that inclusion of the term $d \ln R$ in the free energy does not change any of the considerations presented in the body of the paper for linear chains. A similar conclusion holds for randomly branched polymers.

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