Unified Lattice Theory of Homopolymers of General Architecture: Dendrimers, Stars, and Branched Polymers

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We present a lattice theory of homopolymers of a variety of architectures. The effective χ has a strong concentration dependence, and χ_θ at the θ point is $(q/2)\ln(q-1)/(q-2)$ for all architectures, where q is the coordination of the lattice. We give the closed-form expressions for the entropy, the free energy, and the complete phase diagram. The latter is restricted to systems having no first-order transitions in athermal solutions.

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The synthesis of well-defined branched polymers, stars, and dendritic polymers [1–6] has become increasingly popular over the past ten years for a variety of reasons. One reason for this growing interest is the high number of functional groups in such architectures, along with their good solubilities and their biodegradability. Because these structures are more compact than linear chains (even in dilute solutions), connectivity of monomers in these structures enforces strong local correlations in the positions of monomers. These correlations not only reduce the configurational entropy but also change the local energy of interaction compared to linear chain structures. Since these correlations are neglected in the conventional Flory-Huggins theory [7], there is a strong need for a theory of polymers of arbitrary architectures which attempts to incorporate such correlations. Such a theory is lacking at present and, therefore, would be highly welcomed.

In the present Letter, we produce such a theory. We focus on two special architectural types: (A) a particular polydisperse solution of randomly branched polymers of *arbitrary functionalities,* and (B) a generalized monodisperse solution of dendrimers of *fixed functionalities* and of fixed size. These two types contain a variety of architectures like linear polymers, stars, regular dendrimers, etc. and can be either polydisperse or monodisperse. We show that, as a consequence of our theory, quantities of interest depend, and in some cases strongly, on the coordination number, $q = r + 1$, of the underlying lattice and that the conventional Flory-Huggins theory for athermal solutions emerges as $q \rightarrow \infty$. Since the "effective coordination q" is controlled by the flexibility of the polymer under investigation, the correction may be appreciable. For solutions with interactions, our theory is, in general, different from the conventional Flory-Huggins theory even as $q \rightarrow \infty$. We locate the θ point for various architectures and show that the χ parameter at the θ point is

$$\chi_\theta = (q/2)\ln(q-1)/(q-2), \tag{1}$$

regardless of the architecture. As $q \rightarrow \infty$, $\chi_\theta \rightarrow \frac{1}{2}$, the value obtained by Flory [7].

We show that the entropy $S = S_{\text{ath}} + S_{\text{int}}$, where

$$\begin{aligned} S_{\text{int}} = {} & \phi_{0u}\ln\phi_s^0 + \phi_{mu}\ln\phi_p^0 - \phi_p\ln\phi_p \\ & - \phi_s\ln\phi_s - \phi_c\ln(\phi_c/2), \end{aligned} \tag{2}$$

is the contribution due to interaction and has the same form for all architectures. Here $\phi_0 = 1 - \phi_m$ is the solvent density; ϕ_m is the monomer density; $\phi'_m = (\phi_c + 2\phi_p)/q = \phi_m - 2\phi/q$, $\phi_u = q/2 - \phi$ is the density of unbonded lattice bonds (i.e., bonds uncovered by polymers); $\phi_{mu} = q\phi'_m/2$ and $\phi_{ou} = q\phi_0/2$ are the densities of unbonded bonds attached to a monomer and to a solvent, respectively; ϕ is the density of bonds in polymers; and ϕ_p, ϕ_s, and ϕ_c are monomer-monomer, solvent-solvent, and monomer-solvent contacts. In an athermal state, $\phi_p = \phi_p^0 = \phi_{mu}^2/\phi_u$, $\phi_s = \phi_s^0 = \phi_{ou}^2/\phi_u$, and S_{int} vanish. Thus we observe that S_{int} is given in terms of only bond densities of various kinds, as one expects intuitively. For polydisperse branched polymers S_{ath}, the athermal part can again be broken into $S_{\text{ath,lin}}$ and $S_{\text{ath,br}}$:

$$\begin{aligned} S_{\text{ath,lin}} = {} & (\phi_1/2)\ln 2q/r + \phi\ln r - \phi_0\ln\phi_0 - \phi_1\ln\phi_1 \\ & - \phi_2\ln\phi_2 + \phi\ln\phi + \phi_u\ln(2\phi_u/q), \\ S_{\text{ath,br}} = {} & \sum \phi_k \ln(G_k/\phi_k), \quad k \geq 3, \end{aligned} \tag{3}$$

where

$$G_k = \binom{q}{k} \Big/ \binom{q}{2}^{k/2},$$

$\phi_1, \phi_2, \phi_3 \ldots$ are the densities of k-functional sites, i.e., end points, bifunctional sites, trifunctional branches, ... We note that the effect of the architecture is contained only in constants G_k. For dendrimers,

$$\begin{aligned} S_{\text{ath}} = {} & \phi_\tau \ln\binom{q}{\tau} + \phi_\sigma \ln\binom{r}{s} - \phi_n\ln\phi_n \\ & - \phi_0\ln\phi_0 + \phi_u\ln(2\phi_u/q), \end{aligned} \tag{4}$$

where $\phi_n = \phi/b$ is the number density of dendrimers, each containing b bonds. The effect of the architecture is contained in the constants

$$\binom{q}{\tau} \text{ and } \binom{r}{s},$$

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and the relations $\phi_\tau = \phi_n$, $\phi_\sigma = (b - \tau)\phi_n/s$, where $\tau = t + 1$ is the functionality of the core and $\sigma = s + 1$ is the functionality elsewhere except at the free end. Usually $\tau = \sigma$.

The dimensionless free energy, $\omega = -F/T$ (we set the Boltzmann constant $k_B = 1$), can also be broken into ω_{ath} and ω_{int}, the latter vanishing for athermal solutions,

$$\omega_{\text{int}} = (q/2)\ln(\phi_{ou}^2/\phi_u\phi_s),$$
$$\omega_{\text{ath}} = -\ln\phi_0 + (q/2)\ln(2\phi_u/q), \qquad (5)$$

for *all architectures.* The interaction energy, $\chi\phi_c/q$, according to Flory, is given in terms of the effective χ by $\chi_{\text{eff}}\phi_m\phi_0$. Hence, $\chi_{\text{eff}} = \chi\phi_c/q\phi_m\phi_0$ and has a complicated dependence on various densities and the temperature, since ϕ_c is a complicated function.

It should be stressed that even though various expressions given above have the same form for different architectures, the actual values are different for different architectures for the same parameters, for example, for the same χ. This is because, for the same set of parameters, the densities will, in general, have different values for different architectures.

The general problem on a lattice of N sites ($N \to \infty$), of course, cannot be solved exactly. Therefore, to proceed further, we make the following *approximation* which was initiated some time ago [8]: We replace the lattice by a Bethe lattice of the same coordination $q = r + 1$. This is an infinite tree. The dual cactus is obtained by surrounding each site of the lattice by a q-sided polygon obtained by connecting the midpoint of q bonds meeting at the site, as shown in Fig. 1, for $q = 4$. After this approximation, the problem is solved *exactly* by using standard methods [8,9]. Thus, excluded-volume effects and all correlations are treated exactly on this tree. In this regards, our theory goes beyond the conventional Flory-Huggins theory of linear polymers.

The cactus is divided into generations $m = 0, 1, 2, \ldots$ (Fig. 1). The bond of the tree at the mth generation is called an mth bond. Note that a bond is shared by two polygons. Therefore, if K denotes the activity of a polymer bond, then each polymer bond in a polygon contributes $\sqrt{K}$ to the statistical weight. To describe interactions, we allow only the neighboring monomer-solvent pair interaction ε to be nonzero. Let $w = \exp(-\varepsilon/T)$ be the activity for such a contact. The Flory χ parameter is $\chi = -q\ln w$. For athermal solutions, we must set $w = 1$. We denote the contribution of all the polymers that lie above a given mth generation site such that a certain condition E is satisfied by $Z_m(E)$. We construct recursion relations (RR's) among these quantities and seek their fixed-point (FP) solution which describes the behavior in the bulk, i.e., near $m = 0$, the origin. This is a well-established technique in the field of statistical mechanics, see Ref. [9]. Therefore, we defer the details to a longer paper [10].

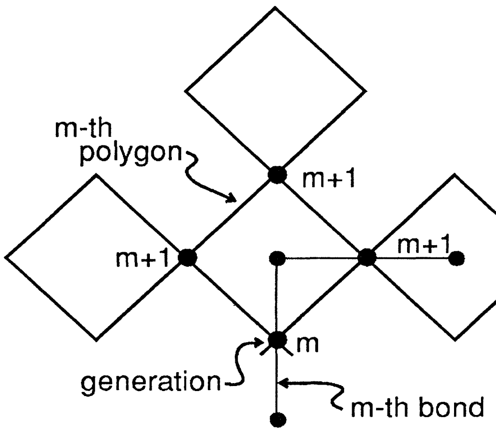

FIG. 1. The cactus for $q = 4$. The original bonds of the tree connect the centers of the two neighboring polygons.

(A) Branching polymers.—The polydispersity is produced by an *equilibrium* polymerization process, which is controlled by various activities. The athermal problem has been investigated recently [9]. Here, we consider arbitrary w. A bond on the lattice may be present (0) or absent (1) as a polymer bond. Let $Z_m(1) = X_m + Y_m$ and $Z_m = Z_m(0)$ denote the contribution when the mth bond is absent or present, respectively. In the former case, X_m denotes the contribution when no polymer is present, i.e., a solvent is present in the mth polygon [which lies between the mth and $(m + 1)$th generations]. The remainder is denoted by Y_m. We also introduce $U_m = wX_m + Y_m$ and $V_m = X_m + wY_m$, which are the contributions due to interaction between a polymer and a solvent, respectively, in an $(m - 1)$th polygon and an mth polygon not sharing a polymer bond. The RR's are evident (see Ref. [9]):

$$X_m = V_{m+1}^r, \quad Y_m = \sum{}' \binom{r}{k} w_k K^{k/2} U_{m+1}^{r-k} Z_{m+1}^k,$$

$$Z_m = \sum \binom{r}{k} w_{k+1} K^{(k+1)/2} U_{m+1}^{r-k} Z_{m+1}^k, \qquad (6)$$

where w_k denotes the activity for a k-functional site with $w_0 = w_2 = 1$. The prime over the sum denotes $k \geq 1$, otherwise $k \geq 0$. The FP solutions are obtained by setting $X_m = B_m x_0$, $Y_m = B_m(1 - x_0)$, and $Z_m = B_m x$. Introducing $y_0 = v/u$, $u = wx_0 + 1 - x_0$, $v = x_0 + w(1 - x_0)$, and $y = x\sqrt{K}/u$, we find from (6)

$$y = KQ_0/uQ_1, \quad y_0 = (y_0^r + wQ_1')/(wy_0^r + Q_1'), \qquad (7)$$

where

$$Q_1' = Q_1 - y_0^r = \sum{}' \binom{r}{k} w_k y^k,$$

and

$$Q_0 = \sum \binom{r}{k} w_{k+1} y^k.$$

Various densities ϕ_0, ϕ, and ϕ_k of solvents, polymer bonds, k-functional sites or branches $k \geq 1$, and pair densities ϕ_p, ϕ_s, and ϕ_c can be computed according to the procedures described in Ref. [9]:

$$\phi_0 = uy_0^q/Q_1Q_2, \quad \phi = qx^2/2Q_2,$$
$$\phi_k = \binom{q}{k} uw_k y^k/Q_1Q_2, \quad \phi_p = q(1 - x_0)^2/2Q_2, \qquad (8)$$
$$\phi_s = qx_0^2/2Q_2, \quad \phi_c = qwx_0(1 - x_0)/Q_2,$$

where $Q_2 = \mu + x^2$ with $\mu = v x_0 + u(1 - x_0)$.

To evaluate the entropy S, we need to express various activities in terms of these densities. To this end, we express

$$y_0 = \sqrt{\phi_p}\,\phi_0/\sqrt{\phi_s}\,\phi_m', \quad y^2 = 2\phi_2 y_0^q/rq\phi_0. \tag{9}$$

From (7), we note that $Q_1 = \underline{Q_1' + y_0^r} = y_0^r/x_0$. Using $rK = u\phi_2 Q_1/\phi$, $(1 - x_0)/x_0 = \sqrt{\phi_p/\phi_s}$, and

$$w = \phi_c/2\sqrt{\phi_p\phi_s}, \tag{10}$$

we express K as follows:

$$\begin{aligned}\ln K = {} & \ln q/2r + r\ln\phi_0 + \ln\phi_2 + [(q-2)/2]\ln\phi_p \\ & - (q/2)\ln\phi_s - (q-2)\ln\phi_m' - \ln\phi. \end{aligned} \tag{11}$$

Similarly ($k = 1, 3, 4, \ldots$),

$$\begin{aligned}\ln w_k = {} & -\ln G_k + \ln\phi_k + [(k-2)q/2]\ln\phi_m' \\ & - (k/2)\ln\phi_2 - [(k-2)r/2]\ln\phi_0 \\ & + [(k-2)q/4](\ln\phi_s - \ln\phi_p). \end{aligned} \tag{12}$$

The set of Eqs. (10)–(12) comprises the complete set of *equations of state:* Given the activities, the densities are obtained by solving these, or vice versa.

The entropy is obtained by integrating the equations of state since, according to standard thermodynamic arguments [11], $\ln K = -\partial S/\partial\phi$, $\ln w = -\partial S/\partial\phi_c$, and $\ln w_k = -\partial S/\partial\phi_k$, $k = 1, 3, 4, \ldots$. The constant of integration is determined by setting $S = 0$ for the pure solvent system. This yields (2) and (3). The free energy ω is obtained by the Legendre transform: $\omega = S + \phi\ln K + \phi_c\ln w + \sum\phi_k\ln w_k$. Thus we obtain (5).

For linear chains, we must set $w_k = 0$ for $k \geq 3$. For an athermal solution, we set $w = 1$, i.e., $\phi_c = 2\sqrt{\phi_p\phi_s}$, see (10). This yields the first part of (3). By setting all but one w_k, $k \geq 3$, zero, we obtain a randomly branched system with a fixed functionality, and so on. Thus, a variety of systems can be described by (3) and (5).

For a single chain covering the entire lattice, $\phi = 1$ and $\phi_1 \to 0$. Hence, $S = \ln r - [(q-2)/2]\ln q/(q-2)$ and converges to the Flory expression for the entropy $\ln(r/e)$ as $q \to \infty$. For finite q, the Flory entropy is considerably lower than our entropy. In particular, for $q = 2$, we obtain the correct value of a zero entropy, whereas the Flory value is unphysical, i.e., negative.

(B) General dendrimers.—We consider a monodisperse solution of dendrimers in which $\sigma = s + 1$ different subbranches meet at each generation, except at the core where $\tau = t + 1$ branches meet. Each branch has D generations and $b_D = (s^D - 1)/(s - 1)$ bonds and each dendrimer has exactly $b = \tau b_D$ bonds. For $\sigma = 2$, we obtain stars. For $\sigma = \tau = 2$, we obtain linear chains. For $\tau = 1$, we obtain a branch of the dendrimer, etc.

We introduce X_m and Y_m as before, but divide $Z_m(0)$ into various parts as follows. Consider an mth polygon in which the mth bond is present. Either the core (c) or a free end (f) is at a higher generation. If this bond is k generations from the core (c) located in the $(m + k - 1)$th polygon, the contribution to $Z_m(0)$ is denoted by $Z_{m,k,c}$. If the free end (f) is in the $(m + k - 1)$th polygon, and the contribution is $Z_{m,k,f}$, the following RR's are obtained at $m = 0$:

$$\begin{aligned} Y_0 = {} & rV_1^{r-1} Z_{1,D,c}\sqrt{K} + \sigma\binom{r}{\sigma}U_1^{r-\sigma} \\ & \times \sum_k Z_{1,k,f}^{\sigma-1} Z_{1,D-k,c} K^{\sigma/2} + \binom{r}{\tau}U_1^{r-\tau} Z_{1,D,f}^{\tau} K^{\tau/2}, \\ Z_{0,1,f} = {} & \sqrt{K}\,U_1^r, \quad Z_{0,1,c} = \binom{r}{t} Z_{1,D,f}^{t} U_1^{r-t} K^{\tau/2}, \\ Z_{0,k,f} = {} & \binom{r}{s} Z_{1,k-1,f}^{s} U_1^{r-s} K^{\sigma/2}, \\ Z_{0,k,c} = {} & s\binom{r}{s} Z_{1,D-k+1,f}^{\sigma-2} Z_{1,k-1,c} U_1^{r-s} K^{\sigma/2}, \end{aligned} \tag{13}$$

with X_0 given in (6). For the *FP* analysis, we set $Z_{0,k,\nu} = B_0 x_{k,\nu}$, $\nu = f$ or c, with B_0 and x_0 defined as in (A). Introducing

$$\alpha = \binom{r}{s}^{1/s}\Big/u, \quad \beta = \binom{r}{t}\Big/u^t, \quad y_{k,\nu} = \alpha\sqrt{K}\,x_{k,\nu},$$

and $y = y_{1,f}$, we find that $y_{k,f} = y y_{k-1,f}^{s}$ and $y_{1,c} = \beta y (y_{D,f}/\alpha)^t$. Thus, $y_{k,f} = y^{b_k}$, $y_{k,c} = \beta^{k-1} y^{b_k'}/\alpha^t$, where $b_k = (s^k - 1)/(s - 1)$ and $b_k' = b - b_{D-k}$ (such that $b_D' = b$). From (13), we also note that $y = \alpha K/Q_1$, with Q_1 defined by $B_0 = B_1^r Q_1 u^r$ and $Q_1' = Q_1 - y_0^r = \beta\lambda y^b/u\alpha^\tau$, with $\lambda = q/\tau + (q-2)b_D$. Introducing $Q_0 = \alpha u$, we find that y_0 and y are given by (7). The partition function Z at the origin is $B_0^2 Q_2$ with $Q_2 = \mu + x^2$, $x^2 = 2\beta b_D y^{b+1}/K\alpha^{\tau+1}$. Various densities ϕ_0, ϕ, ϕ_p, ϕ_c, and ϕ_s can be calculated in the standard fashion and are given by (8) with the current choice of Q_0, Q_1, and Q_2. Because of the formal similarity, w and y_0 are given as before in (9) and (10). However, y is expressed differently: $\phi/\phi_0 = q\beta b_D y^b/\alpha^\tau u y_0^q$. Using this and $y = \alpha K/Q_1$, we find that

$$\begin{aligned}\ln K = {} & \ln q/2 + (1/b)\ln\phi_n G + qn\ln\sqrt{\phi_p}/\phi_m' \\ & + mq\ln\phi_0/\sqrt{\phi_s} - m\ln\phi_0, \end{aligned}$$

where $m = 1 + 1/b$, $n = m - 2/q$, and

$$G = \binom{r}{s}^{(\tau-b)/s}\Big/\binom{q}{\tau}.$$

Integrating $\ln K = -\partial S/\partial\phi$, $\ln w = -\partial S/\partial\phi_c$, with $S = 0$ for pure solvent, we obtain (2), (4), and (5) by the Legendre transform $\omega = S + \phi\ln K + \phi_c\ln w$.

Phase diagram.—The interaction energy in both cases is given by $\phi_c\ln w$. Using (10) and $q\phi_0 = 2\phi_s + \phi_c$ and $q\phi_m = 2\phi + 2\phi_p + \phi_c$, we find that $(1 - w^2)\phi_c^2/w^2 + 2\phi_c\phi_u - q^2\phi_0\phi_m' = 0$. Therefore, ϕ_c is a complicated function of w and various densities. This gives rise to a "complicated" concentration dependence in χ_{eff}. For $q \to \infty$, $\phi/q \to 0$, we have $\phi_c \to q\phi_0\phi_m$, for $w \approx 1$. In this case, χ_{eff} is concentration independent near $w = 1$. In general, this is *not* true.

Because of the complications produced by first-order transitions [9] in the presence of branching in system (A) when $w = 1$, we consider the system (B) and polydisperse linear chains below. We first consider the monodisperse system (B). Here, $Q_0 = \alpha u$ and $Q_1' = cy^b$ with $c = \beta\lambda/u\alpha^\tau$, which is independent of y. Also, $u/x_0 = w + (1 - x_0)/x_0 = w + Q_1'/y_0^r$. From (7), we find

$$(w - y_0)Q_1' = y_0^r(wy - 1), \tag{14}$$

which shows that y_0 lies in the range of $\{\min(w, 1/w), \max(w, 1/w)\}$, due to the positivity of y_0 and Q_1'. The equation $y = KQ_0/uQ_1$ yields

$$KQ_0/(1 - w^2) = yy_0^r/(y_0 - w), \tag{15}$$

where y must be expressed in terms of y_0 by using (14). For $w > w_\theta = \sqrt{r'/r}$, $r' = r - 1$, to be determined below, we find that there is no singularity in (15) for finite b. A singularity appears as $b \rightarrow \infty$ for $K = K_c$, given by

$$\binom{r}{s}^{1/s} K_c = w^{1-r}.$$

This gives the curve C in Fig. 2 in the K-w plane. For $w < w_\theta$, however, the system exhibits first-order transitions between the solvent-rich phase and polymer-rich phase, these transitions terminating in a line of critical points for any choice of b, when the three solutions of (15) merge into one. This happens at $w = w_c(M)$ given by $w^4(1 + Mr)^2 - 2w^2M(q + Mrr') + M^2r'^2 = 0$, with $M = mb = b + 1$, the total number of monomers in a dendrimer. (The larger root of these is unphysical since it gives rise to $y_0 > 1/w$ and must be discarded.) The lower root gives a line C' of critical points in Fig. 2. As $M \rightarrow \infty$, $w_c(M) \rightarrow w_\theta$, and this yields χ_θ in (1). At the θ point, C turns into line F of first-order transitions. Thus, the θ point represents a tricritical point as originally pointed out by de Gennes [12] in the context of linear polymers. The hatched surface represents the surface of first-order transitions. From the quadratic equation, it is easy to see that for large M, we have $w_c(M) \cong w_\theta - 1/r\sqrt{M}$, and hence, $\chi_c(M) = \chi_\theta + q/r\sqrt{M}$. For $M = 1$, $w_c(1) = r'/q$, which occurs at $K = 0$. For arbitrary M, it is easy to show that $\chi_c(M) \rightarrow (\sqrt{M} + 1)^2/2M$ as $q \rightarrow \infty$, as expected [12].

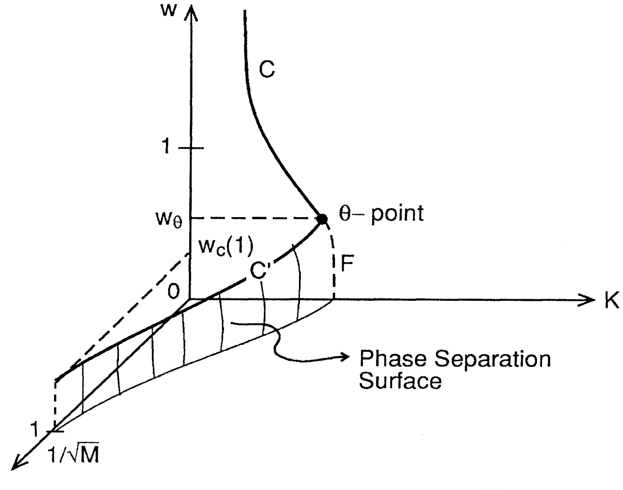

FIG. 2. The schematic diagram in K-w-$(1/\sqrt{M}$ or $w_1)$ space for polydisperse linear chains and monodisperse generalized dendrimers (linear polymers, stars, dendrimers, etc.).

A similar phase diagram with identical χ_θ is also obtained for polydisperse linear chains where w_1 plays the role of $1/\sqrt{M}$.

In summary, we have developed a new and unified theory for a variety of architectures and two particular types of dispersity. The athermal part S_{ath} of S depends on architecture and dispersity; see (3) and (4). As interactions ($w \neq 1$) are introduced, S_{int} has the same form in all cases; see (2). This is also true for ω_{ath} and ω_{int}; see (5). For $w = 1$, our theory reduces to the usual Flory-Huggins theory as $q \rightarrow \infty$. For $w \neq 1$, this is not true in general (see the discussion regarding χ_{eff} above), because the Flory-Huggins theory violates the relation (10) for $w \neq 1$, a relation also obtained by Rushbrooke [13] for simple fluids. This failure of the Flory-Huggins theory has important consequences that will be discussed at length elsewhere. Here, we only point out a few important consequences. (i) Since $\phi_c = q\phi_m\phi_0$ in the Flory-Huggins theory, $\partial\phi_c/\partial w = 0$, whereas one knows that ϕ_c must increase as w increases. (ii) S_{int} must depend on w and vanish only at $w = 1$. In the Flory-Huggins theory, $S_{\text{int}} \equiv 0$. Flory's conjecture [7] that $S_{\text{int}} \equiv \chi_s\phi_m\phi_0$, with χ_s as the entropic parameter contributing to χ, must be incorrect, as this S_{int} does not depend on w and, hence, does not vanish at $w = 1$.

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[1] *Macromolecule Design: Concept and Practice,* edited by M. Mishra (Polymer Frontiers International Inc., NY, 1993).
[2] A. Halperin, M. Tirrel, and T. P. Lodge, Adv. Polym. Sci. **100**, 31 (1990).
[3] Y. Tsukahara, K. Tsutsumi, Y. Yamashita, and S. Shimada, Macromolecules **23**, 5201 (1990).
[4] I. Gitsow, P. T. Ivanova, and J. M. J. Frechet, Macromol. Rapid Commun. **15**, 387 (1994).
[5] S. Beachaouch, B. Coutin, and H. Sekiguchi, Macromol. Rapid Commun. **15**, 125 (1994).
[6] M. Antonietti and T. Nestl, Macromol. Rapid Commun. **15**, 111 (1994).
[7] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, NY, 1959).
[8] P. D. Gujrati, Phys. Rev. Lett. **53**, 2453 (1984).
[9] P. D. Gujrati, J. Chem. Phys. **98**, 1613 (1993).
[10] P. D. Gujrati (unpublished).
[11] P. D. Gujrati, Phys. Rev. E (to be published).
[12] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).
[13] G. S. Rushbrooke, Proc. R. Soc. London A **166**, 296 (1938).