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A Lattice Model for the Entropy of Mixing of a Polymer Solution at Arbitrary Concentrations

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ABSTRACT: The free energy of a polymer solution at arbitrary concentrations and temperatures was recently determined with a renormalization group approach and a field theoretic approach. These powerful methods involve sophisticated calculations and one may wonder if a lattice model could not reproduce some of their results. We here show that a good starting point is a double lattice with large cells of the order of the monomer–monomer screening length and small cells with a size comparable to that of a monomer or a solvent molecule. With that model we determine the entropic part of the free energy of the solution and we deduce from it the polymer osmotic pressure in an athermal solvent of arbitrary concentration. The results are quite simple and compare not so badly with the ones obtained with more complex approaches.

I. Statement of the Problem

When two kinds of molecules are mixed together, the entropy and energy of the assembly are not only the sum of the entropy and energy of the individual phases; they also involve an entropy of mixing ΔS and an energy of mixing ΔE. For a solution of n_p deformable polymers (with N monomers each) and n_s molecules of solvent, Flory and Huggins proposed the following expressions deduced from a lattice model:[1]

$$\Delta S/k_B = -n_p \log \phi - n_s \log (1 - \phi) \qquad (1a)$$

$$\Delta E/k_B T = \chi n_s \phi \qquad (1b)$$

where k_B is the Boltzmann constant, χ is the interaction parameter, and

$$\phi = n_p N/(n_s + n_p N) \qquad (2)$$

is the volume fraction of the monomers.

To find the above result, it was supposed that the monomers were uniformly distributed over the whole available volume. If acceptable for concentrated solutions, this hypothesis clearly fails at low monomer concentration where the macromolecules appear as individual coils which do not overlap. Flory solved this difficulty by introducing the concept of an excluded volume[2] where one can find the only monomers belonging to a given polymer. For very dilute solutions in an athermal solvent ($\chi = 0$), this excluded volume is of order R_F^3, where

$$R_F \sim aN^\nu \quad (\nu \simeq 0.6) \qquad (3)$$

is known as the Flory radius and a represents a typical dimension of a monomer (or a solvent molecule). The associated entropy of mixing is that of a dilute solution of hard spheres of radius R_F:[2]

$$\frac{\Delta S}{k_B} \simeq -n_p\left[\log \phi + \frac{R_F^3}{2Na^3}\phi\right] \qquad (4)$$

As a result, the low-concentration limit of the polymer osmotic pressure Π in an athermal solvent is

$$\frac{\Pi a^3}{k_B T} \simeq \frac{\phi}{N}\left(1 + \frac{1}{2}\frac{\phi}{\phi^*}\right) \quad (\phi \ll \phi^*) \qquad (5)$$

where

$$\phi^* = Na^3/R_F^3 \simeq N^{1-3\nu} \qquad (6)$$

is the volume fraction for which the polymer coils begin to overlap.

If the two extreme cases of very dilute and concentrated solutions are described with some confidence by eq 4 and 1, respectively, what about intermediate concentrations? Using field theoretic techniques, Muthukumar and Edwards[3] achieved a complete calculation of the free energy at arbitrary concentrations and temperatures. In particular, for high temperatures (athermal solvent) they recovered the des Cloizeaux scaling law for semidilute solutions[4]

$$\frac{\Pi a^3}{k_B T} \sim \phi^{3\nu/(3\nu-1)} \quad (\phi^* \ll \phi \ll 1) \qquad (7)$$

But these powerful field theoretic calculations, as well as the renormalization group calculations,[5] are rather difficult to follow and one may wonder if a modified form of the lattice model can reproduce some of their results.

The clue to this problem is perhaps the blob model proposed by de Gennes,[6] where a polymer is described as a succession of blobs of volume ξ^3. In field theoretic language, ξ^3 is the screening volume for the monomer–monomer interaction, but here we may simply picture a blob as what remains of Flory's excluded volume when the polymer coils partially overlap. The blob model can be translated into a lattice model with a cell volume ξ^3 intermediate between a^3 and R_F^3. Each of these large cells is itself divided into small cells of volume a^3 where one can find a monomer or a solvent molecule, as in the Flory–Huggins lattice. The result is a double lattice, pictured in Figure 1.

II. A General Expression for the Entropy of the Solution

According to the blob model,[6] the n_p polymers distributed over the volume V of the solution

$$V = (n_s + n_p N)a^3$$

may be thought of as n_p sequences of N/n blobs of size ξ, each blob containing n monomers. To determine the entropy of the solution we must estimate (i) the number of independent random walks of n_p sequences of N/n contiguous blobs distributed on a lattice of cell size ξ and volume V and (ii) the number $\mathcal{N}_n(x)$ of independent self-avoiding walks distributed on a lattice of cell size a

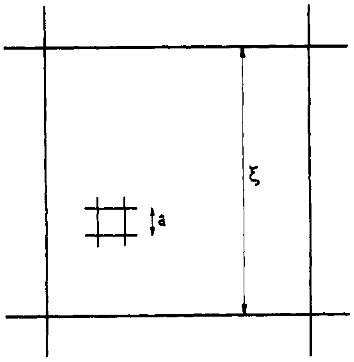

Figure 1. The two interpenetrating lattices. ξ is the screening length for the monomer–monomer interaction and a is the mean dimension of a monomer or a solvent molecule. The large cells are either full of solvent or occupied by a blob. The small cells are occupied either by a monomer or a solvent molecule.

and giving a gyration radius of order $\xi = ax$ to an n-monomer chain.

Let us suppose for a moment that the explicit form of $\mathcal{N}_n(x)$ is known. Then the number of independent configurations of the monomers inside a chain of N/n blobs is

$$x^3[\mathcal{N}_n(x)]^{N/n}$$

where the x^3 factor is due to the ξ^3/a^3 possible positions for the first monomer inside the first blob of the chain. Hence, for the n_p polymers present in the solution, the entropy associated with the monomer configurations *inside* the blobs is

$$\frac{S_m}{k_B} = n_p\left[\log x^3 + \frac{N}{n}\log \mathcal{N}_n(x)\right] \tag{8}$$

As for the entropy associated with the blob configurations, we just have to duplicate the Flory–Huggins calculation[1] since the blob density is almost constant over the volume V. But now the lattice cells have a volume ξ^3 and a polymer is a sequence of N/n blobs instead of N monomers. Hence there are

$$\frac{n_0!}{n_p!\left(n_0 - \frac{N}{n}n_p\right)!}\left(\frac{Z-1}{e}\right)^{n_p(N/n-1)} \tag{9}$$

distinct configurations, where

$$n_0 = V/\xi^3$$

is the number of cells of the blob lattice and Z its coordination number. Since the number of cells must exceed the number of blobs, the following inequality holds:

$$n_pN/n_0n < 1 \tag{10}$$

The entropy associated with the blobs is the logarithm of the independent configurations:

$$\frac{S_b}{k_B} = -n_p \log\frac{n_p}{n_0} - \left(n_0 - \frac{N}{n}n_p\right)\log\left(1 - \frac{n_pN}{n_0n}\right) + n_p\left(\frac{N}{n} - 1\right)\log\frac{Z-1}{e} \tag{11}$$

and the total entropy of the solution is

$$S = S_b + S_m$$

If we consider the entropy s per site (cell) of volume a^3, defined as

$$s = S/(n_s + n_pN)$$

we arrive at

$$-\frac{s}{k_B} = \frac{\phi}{N}\log\frac{\phi}{N} + x^{-3}\left(1 - \frac{x^3\phi}{n}\right)\log\left(1 - \frac{x^3\phi}{n}\right) - \frac{\phi}{n}\left(1 - \frac{n}{N}\right)\log\frac{Z-1}{e} - \frac{\phi}{n}\log \mathcal{N}_n(x) \tag{12}$$

where the monomer volume fraction ϕ is defined in (2).

In the blob model, the volume from which a given polymer expels all the other polymers is $\xi^3(N/n)$, while the volume forbidden to solvent molecules is Na^3. Let us consider the "relative excluded volume" u defined as

$$u = (\xi^3N/n)/(Na^3) = x^3/n \tag{13}$$

and which satisfies the inequality

$$1 < u < 1/\phi \tag{14}$$

if (10) is taken into account. It should be noted that $1/u$ represents the volume fraction of the monomers inside a blob and that $u\phi$ is the volume fraction of the blobs inside the solution. We hope that no confusion will arise between the quantity u, representing the volume excluded by a given polymer with respect to all the other polymers, and the excluded volume $(1 - 2\chi)a^3$, relative to a given monomer with respect to all the other monomers. With u instead of x, the above expression for the entropy per site finally becomes

$$-\frac{s}{k_B} = \frac{\phi}{N}\log\frac{\phi}{N} + \frac{\phi}{N}\log\frac{Z-1}{e} + \frac{\phi}{n}\left[\frac{1-u\phi}{u\phi}\log(1-u\phi) - \log\frac{Z-1}{e} - \log \mathcal{N}_n(u)\right] \tag{15}$$

The Flory–Huggins expression (1) is recovered (up to irrelevant terms linear in ϕ) if we merely let

$$n = u = 1 \tag{16}$$

that is to say if a blob is nothing but a single monomer. In fact, if $\mathcal{N}_n(u)$ was a constant $\mathcal{N}_0$ for any values of n and u, the minimization of (15) with respect to n and u would have led to the solution (16) provided

$$\frac{Z-1}{e}\mathcal{N}_0 > 1$$

The explicit form of $\mathcal{N}_n(u)$ thus plays a crucial role in selecting the couple (u, n) minimizing (15).

III. A Phenomenological Expression for $\mathcal{N}_n(x)$

The number $\mathcal{N}_n(x)$ of independent self-avoiding walks giving a gyration radius of order x to an n-monomer chain must reduce drastically when x tends to $n^{1/3}$ (collapsed chain) and when x tends to n (completely stretched chain), while it must present a maximum around $x = n^\nu$ when n is large enough. All these requirements are satisfied by Flory's expression:[2]

$$\log \mathcal{N}_n(x) \sim n - \frac{n^2}{x^3} - \frac{x^2}{n} = n\left[1 - \frac{n}{x^3} - \left(\frac{x}{n}\right)^2\right]$$

from which the celebrated value $\nu = {}^3/_5$ was deduced. But we know[7] that Flory overestimated both the "elastic" contribution x^2/n and the "repulsive" contribution n^2/x^3. In fact, from scaling arguments x can appear in $\mathcal{N}_n(x)$ only through the combination x/n^ν. If we again impose the above requirement of scarcity of states when $x \simeq n^{1/3}$ and

$x \simeq n$, we arrive at the scaling result

$$\log \mathcal{N}_n(x) \sim n - \left(\frac{n^\nu}{x}\right)^{3\alpha} - \left(\frac{x}{n^\nu}\right)^{\delta} = n\left[1 - \left(\frac{n}{x^3}\right)^{\alpha} - \left(\frac{x}{n}\right)^{\delta}\right] \quad (17)$$

where the exponents α and δ are linked to ν by the relations

$$\alpha = (3\nu - 1)^{-1} \quad (18a)$$

and

$$\delta = (1 - \nu)^{-1} \quad (18b)$$

It is remarkable that if we impose the supplementary relation

$$\delta = 2\alpha$$

we recover from (17) and (18) the Flory exponent $\nu = {}^3/_5$, although α in (17) does not have the mean field value ($\alpha = 1$) used by Flory. Moreover, the above argument can be easily extended to a d-dimensional space. In this case

$$\log \mathcal{N}_n(x) \sim n\left[1 - \left(\frac{n}{x^d}\right)^{\alpha} - \left(\frac{x}{n}\right)^{\delta}\right]$$

with $\alpha = (\nu d - 1)^{-1}$ and $\delta = (1 - \nu)^{-1}$. If we again impose that $\delta = 2\alpha$, we deduce

$$\nu = 3/(d + 2)$$

and we find that the exponents α and δ are always larger than the mean field values (i.e., $\alpha > 1$ and $\delta > 2$) when $d < 4$. Needless to say that if we can justify (17) and (18), we have yet no explanation for the supplementary relation $\delta = 2\alpha$.

It must be stressed that $\mathcal{N}_n(x)$ is not identical with $\mathcal{P}_n(x)$, the number of self-avoiding walks giving an end-to-end distance x to an n-monomer chain. Although both functions scale similarly for $x \gg n^\nu$, they are completely different at low x since $\mathcal{N}_n(x)$ is null for $x < n^{1/3}$ while $\mathcal{P}_n(x)$ is nonzero up to $x = 1$ whatever is n.

The scaling expression (17), intended to be valuable over the whole range $n^{1/3} < x < n$, is in fact a rather poor approximation around the maximum because the x^δ and $x^{-3\alpha}$ behaviors only hold far from it. Since we expect the result of the forthcoming variational calculations to give an equilibrium value for x around n^ν for an athermal solvent and in the range between $n^{1/3}$ and n^ν for poorer solvents, we must henceforth delete from (17) the x^δ contribution and find a more satisfying expression around $x \simeq n^\nu$. To this end, we finally adopt the simple expression deduced from (17) and scaling requirements

$$\log \mathcal{N}_n(x) = A\left[n - \left(\frac{n^\nu}{x}\right)^{3\alpha} - 3\alpha \log \frac{x}{n^\nu}\right] \quad (n^{1/3} \lesssim x \lesssim n^\nu) \quad (19)$$

where

$$A = \log \tilde{z}$$

and $\tilde{z}$ is the effective coordination number of the small cell lattice. The factor 3α in front of the logarithm is for convenience only since it locates the maximum of $\mathcal{N}_n(x)$ at $x = n^\nu$ exactly. From the above expression follows the number of independent configurations of a collapsed n-monomer chain,

$$\mathcal{N}_n(x = n^{1/3}) = n^A \quad (20)$$

It would be interesting to know from an exact calculation if the number of configurations in a collapsed state is really a power of n.

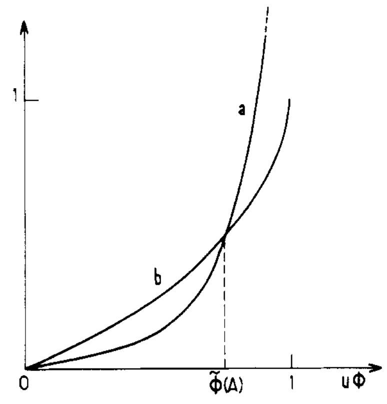

Figure 2. Graphical solution of eq 25. Curve a represents $A \log f_A(u\phi)$, where $f_A(u\phi)$ is defined in eq 26. Curve b represents $g(u\phi)$ defined in (27).

IV. Maximization of the Entropy

The coordination number of the monomer lattice cannot be widely different from that of the blob lattice. We shall henceforth suppose that

$$\log \tilde{z} \simeq \log (z - 1) \qquad (= A) \quad (21)$$

The scaling expression (19) can be rewritten with $u = x^3/n$ instead of x and the result is

$$\log \mathcal{N}_n(u) = A\left[n(1 - u^{-\alpha}) - \log \frac{u^\alpha}{n}\right] \quad (22)$$

With the simplifying hypothesis (21) and the scaling law (22) the entropy per site (15) becomes

$$-\frac{s}{k_B} = \frac{\phi}{N} \log \frac{\phi}{N} + \frac{\phi}{N}(A - 1) - A\phi(1 - u^{-\alpha}) + \frac{\phi}{n}\left[1 + \frac{1 - u\phi}{u\phi} \log (1 - u\phi) + A \log \frac{u^\alpha}{en}\right] \quad (23)$$

The problem is now to minimize (23) for a given value of the lattice parameter A and for a given volume fraction ϕ of the monomers. The minimization problem expressed by

$$\frac{\partial s}{\partial u} = \frac{\partial s}{\partial n} = 0$$

leads to the two equations

$$n = u^\alpha f_A(u\phi) \quad (24)$$

$$g(u\phi) = A \log f_A(u\phi) \quad (25)$$

where

$$f_A(u\phi) = 1 - \frac{1}{\alpha A}\left(1 + \frac{1}{u\phi} \log (1 - u\phi)\right) \quad (26)$$

and

$$g(u\phi) = 1 + \frac{1 - u\phi}{u\phi} \log (1 - u\phi) \quad (27)$$

A graphical solution of (25) is sketched in Figure 2. There is an irrelevant solution $u\phi = 0$ associated with a minimum of the entropy. The function $A \log f_A(u\phi)$ behaves like $u\phi/2\alpha$ when $u\phi$ tends to zero, while $g(u\phi)$ behaves like $u\phi/2$ in the same limit. Since α is greater than one (see definition (18) with $\nu \simeq {}^3/_5$), $g(u\phi)$ always lies above $A \log f_A(u\phi)$ near the origin. Conversely when $u\phi$ tends to one,

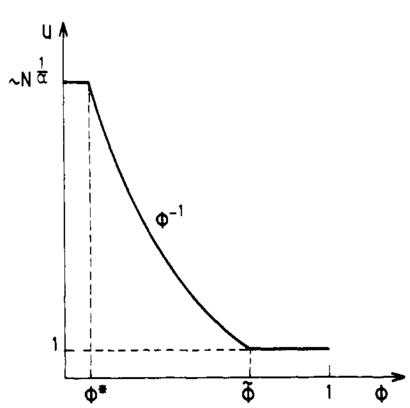

Figure 3. Relative excluded volume per polymer, u, as a function of the monomer volume fraction ϕ as deduced from the minimization of (23) with the constraints (14) and (31).

Table I
Values of $\tilde{\phi}(A)$ and $f(A)$, Respectively Defined by Eq 28 and 30, as a Function of the Lattice Parameter A Defined in Eq 21

A	$\tilde{\phi}(A)$	$f(A)$
1	0.805	1.96
1.5	0.75	1.43
2	0.70	1.27
100	0.60	1.004
∞	0.556	1

$g(u\phi)$ is finite while the other function diverges. There is thus a unique solution to (25) corresponding to a maximum of entropy:

$$u\phi = \tilde{\phi}(A) \tag{28}$$

with

$$0 < \tilde{\phi}(A) < 1$$

Consequently, the solution of (24) is

$$n = u^{\alpha} f(A) \tag{29}$$

where

$$f(A) = f_A(\tilde{\phi}) \tag{30}$$

The result of numerical calculations for a few A values (with $\alpha = 1.31$) is reported in Table I.

If we now take into account the constraints on the number of monomers per blob

$$1 < n < N \tag{31}$$

and on the relative excluded volume per polymer

$$1 < u < \phi^{-1} \tag{14}$$

we see that the solutions (28) and (29) cannot hold for arbitrary ϕ. On the low-ϕ side, the combination of (28) and (29) implies a large n. Since n cannot exceed N, the maximum of entropy is obtained with $n = N$ and a constant value for u given by (29); hence the solution.

$$n = N, \qquad u = \tilde{\phi}/\phi^* \qquad \text{when } \phi < \phi^* \tag{32}$$

where

$$\phi^* = \tilde{\phi}\left(\frac{f(A)}{N}\right)^{1/\alpha} \tag{33}$$

is of the order of the overlap volume fraction defined in (6). One may easily verify that the solution (32) exactly corresponds to the Flory result (3) since the polymer is now made of only one blob of size

$$\xi/a = (un)^{1/3} = f(A)^{-1/3\alpha} N^{\nu}$$

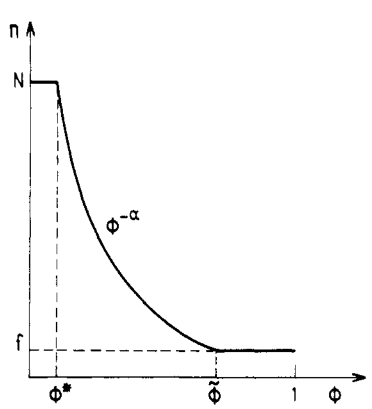

Figure 4. Number of monomers per blob, n, as a function of the monomer volume fraction ϕ as deduced from the minimization of (23) with the constraints (14) and (31).

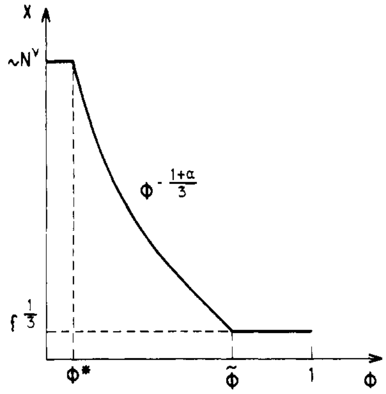

Figure 5. Adimensional size of a blob, $x = (un)^{1/3}$, as a function of the monomer volume fraction ϕ.

Conversely, on the high-ϕ side, the strict application of (28) would imply for u a value less than one, in contradiction with (14). Hence the maximum of entropy is in this case obtained with $u = 1$ together with a constant value for n deduced from (29)

$$u = 1, \qquad n = f(A) \qquad \text{when } \tilde{\phi} < \phi < 1 \tag{34}$$

The solution (34) clearly corresponds to the Flory–Huggins solution (16).

As a conclusion, the couple (u, n) maximizing the entropy (23) is given by (28) and (29) when $\phi^* < \phi < \tilde{\phi}$ and by (32) or (34) for low and high ϕ, respectively. The ϕ dependence of u, n, and $x = (un)^{1/3}$ is represented schematically in Figures 3–5.

V. Entropy of Mixing at Arbitrary Concentrations

The entropy of mixing is deduced from the entropy of the solution (23) when we discard all terms linear in ϕ and when we use the couple (u, n) which maximizes it. Taking (29) into account we get for the entropy of mixing per site the final expression

$$-\frac{\Delta s}{k_B} = \frac{\phi}{N}\log\phi + \frac{\phi}{fu^{\alpha}}\left[1 + \frac{1 - u\phi}{u\phi}\log(1 - u\phi) + A(f - 1 - \log f)\right] \tag{35}$$

where u is a function of ϕ, represented in Figure 3, and whose behavior is here rewritten for conciseness:

$$\begin{aligned} u &= (N/f(A))^{1/\alpha} \qquad 0 < \phi < \phi^* \\ u &= \tilde{\phi}(A)\phi^{-1} \qquad \phi^* < \phi < \tilde{\phi} \\ u &= 1 \qquad \tilde{\phi} < \phi < 1 \end{aligned} \tag{36}$$

where ϕ^* is defined in (33).

Once a value of the lattice parameter A is chosen, the values of $\tilde{\phi}$ and f follow from a simple numerical calculation (a few examples are listed in Table I); thus the fit with any other determination of Δs can be done through the variable A only. It is not difficult to see that in the limit of very dilute solutions ($\phi \ll \phi^*$), we get from (35) and (36)

$$-\frac{\Delta s}{k_B} \simeq \frac{\phi}{N}\left[\log \phi + \frac{\phi}{2}\left(\frac{N}{f}\right)^{1/\alpha}\right] \qquad (\phi \ll \phi^*) \quad (37)$$

which is the Flory expression (4) if

$$R_F = af^{-1/3\alpha}N^\nu$$

On the other hand, for concentrated solutions we get

$$-\frac{\Delta s}{k_B} = \frac{\phi}{N}\log \phi + \frac{1}{f}(1-\phi)\log(1-\phi) \qquad (\phi > \tilde{\phi}) \quad (38)$$

and we note that the Flory–Huggins result (1) would correspond to $f = 1$, i.e., to an infinite coordination number of both lattices (cf. Table I).

In the intermediate range of monomer concentration, (35) and (36) lead to

$$-\frac{\Delta s}{k_B} = \frac{\phi}{N}\log \phi + C\phi^{\alpha+1} \qquad (\phi^* < \phi < \tilde{\phi}) \quad (39)$$

where the constant C is related to the lattice parameter A, to $f(A)$, and to $\tilde{\phi}(A)$ by

$$C(A) = A(f-1)/f\tilde{\phi}^\alpha \quad (40)$$

VI. Polymer Osmotic Pressure: Comparison with Experimental Results

If we may neglect the energy of mixing (athermal solvent), the polymer osmotic pressure Π is linked to the entropy of mixing per site by

$$\frac{a^3\Pi}{k_BT} = \phi^2\frac{\partial}{\partial\phi}\left(-\frac{\Delta s}{k_B\phi}\right) \quad (41)$$

With our results (35) and (36) we get the surprisingly simple expression

$$\frac{a^3\Pi}{k_BT} = \frac{\phi}{N} - \frac{\phi}{fu^\alpha}\left[1 + \frac{1}{u\phi}\log(1-u\phi)\right] \quad (42)$$

where $u(\phi)$ is given in (36). Combining (42) and (36) we get for very dilute solutions ($u\phi \ll 1$)

$$\frac{a^3\Pi}{k_BT} = \frac{\phi}{N}\left[1 + \left(\frac{N}{f}\right)^{1/\alpha}\frac{\phi}{2}\right] \qquad (\phi \ll \phi^*) \quad (43)$$

We find back (5). For intermediate solutions ($u\phi = \tilde{\phi}$)

$$\frac{a^3\Pi}{k_BT} = \frac{\phi}{N} + \alpha C\phi^{\alpha+1} \qquad (\phi^* < \phi < \tilde{\phi}) \quad (44)$$

with the constant $C(A)$ given in (40). We find back (7). For concentrated solutions ($u = 1$)

$$\frac{a^3\Pi}{k_BT} = \frac{\phi}{N} - \frac{1}{f}(\phi + \log(1-\phi)) \qquad (\phi > \tilde{\phi}) \quad (45)$$

and again the Flory–Huggins expression corresponds to the case $f = 1$.

Noda and colleagues[8] measured the osmotic pressure of quasi-monodispersed α-methylstyrene in solution and found for dilute and semidilute solutions the two asymptotic behaviors

$$\frac{N\Pi a^3}{\phi k_BT} = 1 + K\frac{\phi}{\phi^*} \qquad \text{with } K_{\text{exptl}} = 1.12 \quad (46)$$

and

$$\frac{N\Pi a^3}{\phi k_BT} = K'\left(\frac{\phi}{\phi^*}\right)^{1.31} \qquad \text{with } K'_{\text{exptl}} = 1.50 \quad (47)$$

Our results (43) and (44) qualitatively agree with (46) and (47). Do they agree quantitatively with K_{exptl} and K'_{exptl}?

If we fit (43) and (46) (setting $K_{\text{theor}} = K_{\text{exptl}}$) we get from (44) a value for K'_{theor} varying from 4.5 (for $A = 1$) to 2.95 (for $A = 100$). Conversely if we fit (44) and (47) (setting $K'_{\text{theor}} = K'_{\text{exptl}}$) we get from (43) a value K_{theor} varying from 0.50 (for $A = 1$) to 0.67 (for $A = 100$). It is thus not possible for the present lattice model (involving the single parameter A) to fit simultaneously the two experimental results K_{exptl} and K'_{exptl}. But remember that we arbitrarily choose the maximum of $\mathcal{N}_n(x)$ at $x/n^\nu = 1.0$. It is actually possible (cf. concluding paragraph) to change the position of the maximum so as to achieve a better numerical agreement. But we cannot seriously do it before the exact position of the maximum is firmly established, both experimentally and theoretically.

VII. Comparison with Field Theoretic Results[10]

In a recent paper, Muthukumar and Edwards[3] derived expressions for the free energy of a polymer solution at arbitrary concentrations and temperatures. Their basic variables are the screening length ξ and the effective step length l_1 related to the mean square dimension of a polymer by

$$\langle R^2 \rangle = Nal_1$$

In the blob model, the polymer is an ideal chain of N/n blobs;[9] hence

$$\langle R^2 \rangle = (N/n)\xi^2$$

and consequently

$$\frac{l_1}{a} \equiv \frac{1}{n}\left(\frac{\xi}{a}\right)^2 = \left(\frac{u^2}{n}\right)^{1/3} \quad (48)$$

The results obtained in ref 3 can now be expressed with our variables u and n. In the high-temperature limit we have considered in this paper (negligible energy of mixing) Muthukumar and Edwards found

$$-\frac{\Delta s}{k_B} = \frac{\phi}{N}\log\phi + \frac{\phi}{N}\frac{S_1(\xi\rightarrow\infty)}{k_BT} - \frac{9}{16\pi}\frac{\phi}{u} + \frac{1}{24\pi un} + \phi^2 \quad (49)$$

where u and n are solutions of

$$6u\phi = \frac{27}{8\pi} + \frac{u}{n} \quad (50)$$

$$1 - \left(\frac{n}{u^2}\right)^{1/3} = \beta\left(\frac{n}{u^{5/4}}\right)^{4/3} \quad (51)$$

Equations 49–51 correspond to eq 1.6 and 1.3 of ref 3. In the above equations, β (denoted α in ref 3) is an unknown factor arising from the statistics of a single chain in an infinitely dilute solution and $S_1(\xi\rightarrow\infty)$ is the entropy of such a chain. When both n and u are large, the solution of (50) and (51) is

$$n = \beta^{-3/4}u^{5/4} \quad (52a)$$

$$u\phi = 9/16\pi \quad (52b)$$

Our results (28) and (29) agree with (52) when we let $\nu = {}^3/_5$, but notice that our possible $\tilde{\phi}(A)$ values always lie above $9/16\pi$. The agreement no longer exists for concentrated solutions where we found constant values for u

and n (cf. (34)) while (50) and (51) lead to a ϕ dependence of u and n in that domain. The situation is quite similar for the polymer osmotic pressure. A good agreement is found for semidilute solutions but for concentrated ones, a log $(1 - \phi)$ behavior is expected within the lattice model, while a ϕ^2 or $\phi^{3/2}$ dependence is obtained in ref 3. A possible solution to this dilemma is that eq 19 and 22, being scaling results, are valuable for large n only, and concentrated solutions are actually characterized by rather low n values.

What is a bit more surprising is that the lattice model expression (15) for the entropy is rather different in its structure from the result (49) of field theoretic calculations. Since S_1 is the analogue of our $\mathcal{N}_n(u)$, one sees that within the lattice model (i) no isolated ϕ^2 term is found, (ii) a $(un)^{-1}(1 - u\phi) \log (1 - u\phi)$ term is found instead of $(un)^{-1}$, and (iii) a ϕ/n term is found instead of ϕ/u. The last two discrepancies are probably not crucial insofar as, due to (28) or (36b), we get a $(un)^{-1}$ term for the large range $\phi^* < \phi < \tilde{\phi}$ and, due to (29), the ϕ/n term is equivalent to ϕ/u^α. But it is hard to see how an isolated ϕ^2 term could be deduced from a lattice model.

VIII. Concluding Remarks

The double-lattice model (DLM) pictured in Figure 1 is a natural extension of the Flory–Huggins lattice; the two basic ingredients of the DLM are Flory's excluded volume and de Gennes' blobs. The entropy of mixing (35) and the polymer osmotic pressure (42) deduced from the DLM have rather simple expressions; they are most conveniently written in terms of u, the relative excluded volume per polymer (or blob).

The special case of DLM we presented here is very simplified. If hypothesis (21) is suppressed and if the maximum of $\mathcal{N}_n(u)$ is located at

$$n = Bu^\alpha$$

then the entropy of the solution becomes

$$-\frac{s}{k_B} = \frac{\phi}{N} \log \frac{\phi}{N} + \frac{\phi}{N}(A - 1) - \tilde{A}\phi(1 - u^{-\alpha}) + \frac{\phi}{n}\left[1 - A + \frac{1 - u\phi}{u\phi} \log (1 - u\phi) + \tilde{A}B \log \frac{u^\alpha}{n}\right] \quad (53)$$

where

$$A = \log (Z - 1)$$

and

$$\tilde{A} = \log \tilde{Z}$$

Our simple expression (23) corresponds to $A = \tilde{A}$ (cf. (21)) and $B = 1$. The three-parameter expression (53) would perhaps better fit with experimental results, but remember that B cannot be taken as a true parameter (at variance with the lattice parameters A and $\tilde{A}$) and in the absence of any firmly established value for B, we deliberately chose to work with the one-parameter expression (23) since it is very simple and it keeps all the basic features of (53).

It is rather surprising that the DLM leads to an expression for the entropy of mixing which is rather different from that deduced with field theoretic methods. Despite this, the results concerning the osmotic pressure are quite similar, except for concentrated solutions. We have no explanation yet for these discrepancies.

If not perfectly rigorous, the DLM is undeniably simple and can prove useful for numerical simulations of polymer solutions. It now remains to find the energy of mixing along the same lines.

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Thermodynamics of Flow-Induced Phase Separation in Polymers

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ABSTRACT: The thermodynamics of a liquid–liquid phase separation as a way of explaining flow-induced structure formation in polymer solutions is presented. The effect of the flow field is taken into account by using two fundamentally different approaches: the reduced flexibility and the stored free energy approach. The basis of both models is clarified, and phase diagrams are constructed for the reduced flexibility case. The binodal curves are shown to become broader compared with the quiescent phase diagrams and can be shifted to higher temperatures depending on the values of the flexibility parameters.

Introduction

It has been recognized for some time that flow-induced liquid phase structure formation may be involved in a number of phenomena ranging from rheological characterization to oriented phase transformation. In the latter case, studies of high molecular weight polyethylene fiber growth in Poiseuille[1] and Couette[2] flow geometries have established that fiber crystallization at elevated temperatures is preceded by the formation of amorphous gel-like liquid precursor phases. A similar suggestion has been made in studies of rigid systems such as poly(ethylene terephthalate)[3] and others[4] and could be implied from the

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