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Chain Conformation and Solubility of Associating Polymers

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ABSTRACT: We consider a dilute solution of long polymers to which are attached, many monomers apart, $2N$ chemical side groups with a strong, saturating, two-body attraction ("stickers"). In an otherwise good solvent, the second virial coefficient between two such chains with $N = 1$ may be positive or negative, depending on the positions of the stickers on the chains (and on the dimension of space, d). Using results of des Cloizeaux (des Cloizeaux, J. *J. Phys. (Paris)* **1980**, *41*, 223) for interior chain correlations, we infer the scaling dependence of the virial coefficient on the chemical distance separating the stickers. We calculate the virial explicitly, to first order in $4 - d$, for the case when the stickers are at the chain ends. We argue that the conformation and solubility of a chain with many stickers ($N \gg 1$) may have a critical dependence on the arrangement of the stickers along the chemical sequence. A lower bound on an exponent Θ_2, describing interior chain correlations, is given.

1. Introduction

Flexible long-chain molecules containing a small fraction of strongly associating chemical groups are known to exhibit several unusual properties in dilute and semidilute solution.[1-3] At low values of the chain concentration, C, intrachain associations cause a reduction in chain size and a corresponding decrease in intrinsic viscosity[2] when compared with nonassociating precursor molecules. At high C, interchain associations are expected to affect both the second virial coefficient and the Huggins constant of the chains.

As the overlap threshold, C^*, is approached, the viscosity of the solution increases dramatically, leading eventually to the formation of a gel. Near $C = C^*$, the delicate balance between intrachain and interchain association is apparent in unusual rheological behavior such as shear thickening.[3]

Although the aim ultimately must be to understand the solution properties over the whole concentration range, we restrict ourselves in this paper to the study of dilute solution properties. However, our results for an important limiting case (that of strong, saturating associations between widely spaced chemical groups) allow a discussion of the phase diagram over the whole concentration range.

2. Perturbing about an Ideal Chain

Suppose we have a chain of S monomers, with $2N$ ($\ll S$) associating groups attached, in an otherwise good solvent (i.e., a good solvent for a precursor chain with $N = 0$). We wish to decide whether or not such a chain will collapse. A simple theoretical approach, due to Joanny,[4] is to assume that both the associating groups and the rest of the chain interact weakly and expand perturbatively about an ideal chain. One supposes a certain pairwise interaction $U(r)$ to act between all pairs of monomers (at spatial separation r) plus an additional (attractive) interaction $U'(r)$ acting only between the $2N$ substitutent groups. Providing that both interactions U and U' are of short range, the expansion to one loop of the perturbed mean square end-to-end distance $\langle R^2(U,U')\rangle$ is found to be[4]

$$\langle R^2(U,U')\rangle = R^2{}_0[1 + \zeta + 0(\zeta^2)] \tag{1a}$$

where the expansion parameter ζ obeys

$$\zeta = (A_2 + f^2A_2')a^{-d}S^{2-d/2} \tag{1b}$$

Here $R^2{}_0 = \langle R^2(0,0)\rangle \cong a^2S$ is the unperturbed, gaussian, value of the end-to-end distance; A_2 is the second virial coefficient of the interaction $U(r)$; A_2' (which is negative) is the second virial coefficient of the attractive interaction $U'(r)$; $f = 2N/S$ is the fraction of associating groups; and a is a monomeric length.

Equation 1b is just like the usual two-parameter expression for ζ[5] except that the dimensionless virial coefficient between monomers, A_2, has been replaced by a weighted average

$$\bar{A}_2 = A_2 + f^2A_2' \tag{2}$$

over the pairwise interactions between ordinary monomers and associating groups. A swollen coil is predicted for $\zeta \gg 1$, whereas a significant reduction in chain size is expected for $\zeta \lesssim -1$. If the associating groups are strongly attracting, so that the term f^2A_2' dominates on the right in eq 2, this gives the following criterion for a significant collapse of the chain radius (compared with a gaussian chain) in three dimensions:

$$f^2S^{1/2}|A_2'|a^{-3} \gtrsim 1 \tag{3}$$

It should, however, be emphasized that the above analysis is only appropriate when the effects of attraction and repulsion can be treated on an equal footing; in practice, this means that the associating groups must not be spaced too far apart along the chemical sequence. In what follows, we will be interested in the opposite limit, when the associating groups are so widely spaced that each intervening segment of "normal" polymer is itself long enough to show swollen chain behavior. In this limit, excluded-volume effects are strong and cannot be treated perturbatively; correspondingly, eq 3 is not the appropriate collapse criterion. Instead, the additional effects of widely spaced associating groups may be studied by using the known scaling properties of swollen chains. This approach results in important modifications to the above picture. For example, we will see below that for small f the associating interactions must be much stronger than indicated by eq 3 before the attractive groups have any significant effect on the overall chain size.

3. Perturbing about a Swollen Coil

In this section we develop an expansion in which we treat perturbatively the effects of widely spaced associating groups in an otherwise swollen coil. This work complements that discussed in the previous section but does not depend upon it.

We start with a discussion of correlations inside a swollen coil. Suppose we have two "marked" monomers, i and j, separated by s_{ij} steps on a swollen chain of step length a. These monomers have root mean square spatial

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separation $\bar{r} \cong as_{ij}^{\nu}$. The probability $P_b(\bar{r})$ that they are found within a short distance b of one another has been studied by des Cloizeaux using an expansion in $\epsilon = 4 - d$.[6] He found

$$P_b(\bar{r}) \cong \text{const } (b/\bar{r})^{d+\Theta} \qquad (4)$$

where the constant is dimensionless (of order unity) and where the value of Θ depends as follows on the placement of the markers.

If the markers are at the chain ends

$$\Theta = \Theta_0 = \frac{\gamma - 1}{\nu} = \frac{\epsilon}{4} + \frac{9\epsilon^2}{128} + ...$$

If one marker is at a chain end and one is well within the chain

$$\Theta = \Theta_1 = \epsilon/2 - 3\epsilon^2/64 + ...$$

If both markers are well within the chain

$$\Theta = \Theta_2 = \epsilon - 15\epsilon^2/32 + ...$$

We can use this result to find a perturbative criterion appropriate to our chosen limit of widely spaced associating groups. This is most easily done in the context of a specific lattice model. We consider a self-avoiding chain of S steps on a lattice, subject to an (attractive) nearest-neighbor interaction energy $-U$ which acts whenever substituent monomers occupy adjacent lattice sites. In the absence of any associations, such a chain has a root mean square end-to-end distance $R \cong aS^{\nu}$.[7] For simplicity we consider the case when the associating groups are spaced regularly, f monomers apart, along the chemical sequence. We label the ith such group by s_i where $i = 1, 2, 3, ..., 2N$; in terms of the ordinary monomer labels, $s = 1, 2, 3, ..., S$, s_i stands for the substituent monomer at position $s = (i + {}^1/_2)/f$ in the chemical sequence. This model is appropriate whenever the interaction between associating groups is of a range comparable with the monomeric length a.

We now examine perturbatively the effect of the attraction U on the root mean square distance, $R(U)$, between the ends of the chain. To do this we first imagine switching on the interaction U between only two groups, s_i and s_j. Consider the total weight $P_{ij}(U)$ associated with configurations in which s_i and s_j are adjacent. In the absence of any attraction, we have from (4)

$$P_{ij}(0) \cong P_a(as_{ij}^{\nu}) \cong s_{ij}^{-(d+\Theta_2)\nu}$$

where $s_{ij} = |s_i - s_j|$ and where we assume the monomers in question to be well within the chain. The attraction increases this weight by a factor $e^{U/kT}$. Hence

$$P_{ij}(U) = P_{ij}(0) + \delta P_{ij}(U)$$

with

$$\delta P_{ij}(U) \cong -A_2'a^{-d}s_{ij}^{-(d+\Theta_2)\nu} \qquad (5a)$$

where A_2' now denotes $a^d[1 - e^{U/kT}]$.

Now, $\delta P_{ij}(U)$ is the extra weight associated with configurations in which s_i and s_j are adjacent in space. But this subensemble of configurations has a reduced value of the end-to-end distance, $R' \cong a\,[S - s_{ij}]^{\nu}$, when compared with the value $R \cong aS^{\nu}$ for the full ensemble of self-avoiding walks. In effect one has a chain of only $S - s_{ij}$ steps onto which is grafted a closed loop of s_{ij} steps; the root mean square radius R' scales like that of the shortened chain alone.

We thus obtain the perturbed root mean square end-to-end distance $R(U;i,j)$ resulting from the presence of a nearest-neighbor attraction $-U$ between groups i and j only:

$$R(U;i,j) = \frac{R + R'\delta P_{ij}(U)}{1 + \delta P_{ij}(U)}$$

Because $P_{ij}(0)$ is defined as a normalized probability, this expression contains no approximation. We next expand the denominator to give

$$R(U;i,j) = R + \delta R_{ij}\delta P_{ij} + 0(\delta P_{ij}^2)$$

where we have defined

$$\delta R_{ij} = R' - R \cong a[(S - s_{ij})^{\nu} - S^{\nu}]$$

Next we Taylor-expand $(\delta R)_{ij}$ for small s_{ij} to obtain

$$\delta R_{ij} = (-s_{ij}/S)F(s_{ij}/S)R \qquad (5b)$$

where $F(x)$ is a smooth function that tends to a constant at small x.

Finally we simply add up the perturbations to one loop order (i.e., to first order in A_2') arising when the interaction U is switched on between all pairs of associating groups s_i, s_j. This gives

$$R(U) = R + \sum_{i,j}\delta R_{ij}\delta P_{ij} + 0(A_2'^2)$$

Substituting the results (5a) and (5b) into this expression and performing the sum, we obtain the expansion

$$R(U) = R[1 + \zeta' + 0(A_2'^2)] \qquad (6a)$$

where the expansion parameter ζ' obeys

$$\zeta' = \sum_{i,j}\delta P_{ij}\delta R_{ij}/R$$

$$\cong A_2'a^{-d}\sum_{ij}s_{ij}^{-(d+\Theta_2)\nu}(s_{ij}/S)F(s_{ij}/S)$$

$$\cong A_2'a^{-d}[f^2S^{2-\nu(d+\Theta_2)} + f^{\nu(d+\Theta_2)}] \qquad (6b)$$

Now, we do not expect a weak attraction between associating groups to overcome the excluded-volume effect between the remaining monomers. Moreover, although we have discussed above the case of an attractive interaction ($U < 0$), the analysis leading to eq 6 is clearly applicable regardless of the sign of U, and we certainly do not expect a weak extra *repulsion* between widely spaced groups to change the swelling exponent ν. Accordingly, we expect the perturbation represented by ζ' to be irrelevant, in the sense that its magnitude should not grow indefinitely with S. This means that the power of S in eq 6, $2 - \nu(d + \Theta_2)$, must be negative, giving a rigorous bound: $\Theta_2 > 2/\nu - d$.

Using des Cloizeaux's[6] value of Θ_2, one finds $\nu(d + \Theta_2) \cong 2.18$ in three dimensions. For long chains the total perturbation represented by the attracting groups will therefore be small unless

$$-\zeta' \cong f^{2.18}[e^{U/kT} - 1] \gtrsim 1 \qquad (7)$$

This is an entirely different requirement from that found in (3) above. Most importantly, it is a local criterion, involving the average spacing (f^{-1}) between stickers but not the overall chain length S. This makes it a much stronger requirement on A_2' then eq 3 in the limit of a long chain. (Notice that a nonlocal and physically incorrect criterion would have been obtained had we used Θ_0 instead of Θ_2 in the calculation of ζ'.)

Equation 7 is appropriate for deciding whether associating groups of strength U produce a significant perturbation to the chain size (compared with a fully swollen chain) whenever f is so small that the sections of chain between associating groups are able to show swollen behavior.

It is interesting to compare the result (7) with that obtained by the uniform effective chain approach of Joanny, noted above. Here we may use the standard two-parameter expression[8] for $\langle R^2(A_2)\rangle$:

$$\langle R^2(A_2)\rangle \cong aS[S^{2-d/2}A_2a^{-d}]^{(2\nu-1)/(2-d/2)}$$

If we now replace A_2 by $\bar{A}_2$ from eq 2, we can determine the perturbative effect of the attractions at finite A_2 with A_2' small and S large. The resulting expression for ζ' is $\zeta' \cong f^2A_2'a^{-d}$. This approach therefore gives the correct qualitative (S-independent) behavior for ζ' but underestimates slightly the power of f.

Before proceeding, it is useful to generalize the contact probability, eq 4, as follows.[9,10] Suppose we have an arbitrary system of polymers in a good solvent and mark two chosen monomers. We again denote their average spatial separation by $\bar{r}$. In deriving eq 4 for monomers on the same chain we took $\bar{r} \sim as^\nu$, whereas for monomers on separate chains in a volume V, $\bar{r} \sim V^{1/d}$.

The excluded-volume interaction induces correlations between chain segments, which surpress the close approach of our marked monomers on some length scale L. The length L is given by the average separation of the markers ($\bar{r}$), the size of a swollen coil (R), or, in semidilute solution, the screening length (ξ), whichever is least. For $b \ll L$, eq 4 then becomes

$$P_b(\bar{r},L) \sim (b/\bar{r})^d(b/L)^\Theta \qquad (8)$$

The first factor, $(b/\bar{r})^d$, is just the probability that two markers confined to a volume $\bar{r}^d$ are within a distance b. The factor $(b/L)^\Theta$ reflects the extra entropic penalty of forcing sections of excluded-volume chain into close proximity. The choice of Θ is fixed by the number of chain sections emanating from the point of contact; $\Theta = \Theta_0$ if there are two sections, Θ_1 if there are three, and Θ_2 if there are four. Equation 8 will be used often below.

4. Saturating Associations

Equation 7 is expected to identify the onset of collapse for a chain with nonsaturating short-range associations. Often, however, steric and other interactions may cause the attraction between associating groups to saturate at some effective functionality (which might be adjustable by chemical means). For simplicity, we here suppose the groups to form dimers only. (However, our main conclusions apply also to higher values of the functionality.) Each group is thus a "sticker" to which one other sticker may be attached.[10]

An interesting limit is that of strong attractions or $-\zeta' \gg 1$. In this limit, we need consider only those configurations in which every sticker is paired. The partition function Z of an associating polymer or system of such polymers may then be written

$$Z = \sum_{\mathrm{c}} Z_{\mathrm{c}}$$

where c denotes a complete specification of sticker pairings (i.e., a list of pairs s_i, s_j in which each sticker appears exactly once) and Z_{c} is the partition function of the system of polymers constrained to have this set of pairings. All polymer properties (in an otherwise good solvent) then become independent of temperature, because the pairing of all stickers is an athermal constraint. We therefore expect (for small f) a universal dilute/semidilute regime in which physical quantities such as the osmotic pressure, Π, depend only on an overlap parameter, $CR^d = C/C^*$ (determined in the absence of stickers), on d, and on the number and relative spacing of the stickers along the chains.

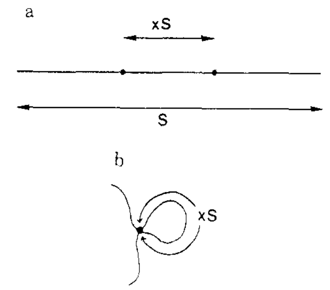

Figure 1. Chain with $N = 1$.

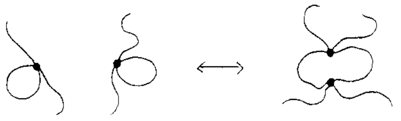

Figure 2. Interchain pairing for $N = 1$.

Consider, for example, the second virial coefficient of chains each with a single pair of stickers ($N = 1$). The arrangement of the stickers is take to be that of Figure 1, with a chemical distance xS between the stickers. Treating the pairing of stickers as an athermal constraint, we first obtain by eq 8 the partition function Z_1 of one such chain

$$Z_1 = Z_0P_a(x^\nu R) \sim Z_0(xS)^{-(d+\Theta)\nu} \qquad (9)$$

where Z_0 is the partition function of the chain with no stickers present. The virial coefficient, $G/2$, between two such chains may be obtained by considering the partition function Z of the two chains in a volume V. This Z is the sum of configurations in which each chain is stuck to itself plus those in which the chains are stuck to each other (Figure 2):

$$Z = Z_1^2(1 - V^{-1}G_0) + Z_2 \qquad (10)$$

Here the term $Z_1^2V^{-1}G_0$ is the number of "self-stuck" configurations disallowed by the mutual excluded volume of the two chains. Because this is effectively a hard-sphere repulsion,[5] we may write

$$G_0 = \mathbf{g}_0(x,d)R^d \qquad (11)$$

where $\mathbf{g}_0(x,d)$ is a dimensionless universal function, which depends rather weakly on x but strongly on d. Close to $d = 4$, $\mathbf{g}_0$ is of order $\epsilon = 4 - d$.

The extra term, Z_2, in eq 10 is the total number of new configurations made available by interchain pairing of stickers (Figure 2). This Z_2 may be estimated by using eq 8 as follows. We take two chains in a volume V with markers at the sticker positions. These have a partition function $Z_0^2 + 0(V^{-1})$. Now we choose one marker from each chain and stick them together. The new partition function, Z', is given approximately by $Z' \sim Z_0^2P_a(V^{1/d},R)$. Next we stick the remaining two markers: this contributes a further factor $P_a(x^\nu R)$. Hence

$$Z_2 \sim Z_0^2P_a(V^{1/d},R)P_a(x^\nu R)$$

$$= Z_1^2V^{-1}R^d\mathbf{g}_1(x,d) + 0(V^{-2}) \qquad (12)$$

where $\mathbf{g}_1(x,d)$ is another universal function:

$$\mathbf{g}_1(x,d) = VR^{-d}Z_2/Z_1^2 \qquad (13)$$

The limiting behavior of $\mathbf{g}_1$ for small x is

$$\mathbf{g}_1(x,d) \sim x^{(d+\Theta_2)\nu} \qquad (13a)$$

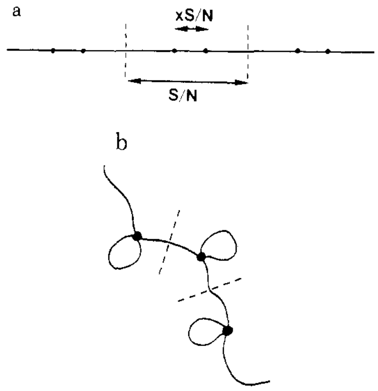

Figure 3. (a) Sticker arrangement with variable parameter x ($x \le 1/2$). (b) Locally paired "reference state".

Using (13) we may write

$$Z = Z_1^2(1 - V^{-1}G) + 0(V^{-2})$$

where the virial coefficient $G/2$ obeys

$$G = [\mathbf{g}_0(x,d) - \mathbf{g}_1(x,d)]R^d = \mathbf{g}(x,d)R^d \qquad (14)$$

The important point is that the two opposing contributions to G scale in the same way with the length S of the segments. Both parts are thus relevant in determining the universal dimensionless virial coefficient $\mathbf{g}(x,d)$ of long chains with $N = 1$.

Two limits are of interest. First, if x is very small, $\mathbf{g}_1(x,d)$ vanishes like $x^{(d+\theta_2)\nu}$ and is negligible. Hence $\mathbf{g}(x,d) \rightarrow g_0(x,d)$, which is always positive. Second, if x is fixed (say $= 1/2$) and d varies, for d near 4, $\mathbf{g}_0(x,d)$ is of order ϵ, whereas $\mathbf{g}_1(x,d)$ is of order unity. Thus, $\mathbf{g}(x,d)$ is negative (giving a net attraction between chains) close enough to $d = 4$.

In three dimensions, we expect $\mathbf{g}(x,d)$ to change sign at some value of x. This is not obvious, because $\mathbf{g}(x,d)$ could remain positive for all x, as it must be for small x. We have investigated this question by calculating $\mathbf{g}(x,d)$ for chains with a sticker at each end ($x = 1$) to order $\epsilon \equiv 4 - d$. The Appendix describes this calculation. As we noted above, $\mathbf{g}(1,d)$ is negative and of order ϵ^0 in $d = 4$; further, it actually becomes more negative as d is decreased toward 3. This is a result of the order-ϵ corrections to the attraction $\mathbf{g}_1$, which more than cancel the (order-ϵ) repulsion, $\mathbf{g}_0$. We therefore expect $\mathbf{g}(x,d)$ to have a zero at some x for all $d < 4$. A simple interpolation shown in Figure 4 suggests that $\mathbf{g}(x,d)$ is repulsive (positive) as long as x is less than about 0.4.

5. Chains with Many Stickers

We now turn to the case of large N; as in the previous section, we consider only the limit of large $-\zeta'$, in which we can treat the pairing of all stickers as an athermal constraint. The configuration of an associating chain with large N depends on a delicate balance between two types of entropy: the configurational entropy of the chain segments subject to a given set of sticker pairings, and the entropy associated with the fact that there may be many such pairing arrangements consistent with a given macroscopic chain conformation.

Consider, for example, the sticker arrangement of Figure 3. The locally paired state, Figure 3b, incurs the least entropy penalty from the excluded-volume interaction of the chain segments. However, there are very few pairing arrangements for which this is representative in determining the global chain characteristics. If we generalize our definition of the locally paired state slightly, we can include all states in which each sticker pairs only with a few chemically close neighbors ($\bar{p}$ such neighbors, say). All these states are roughly equivalent in determining the overall chain size; we can think of this approximate degeneracy as contributing a "sticker entropy" $\sim N \ln \bar{p}$.

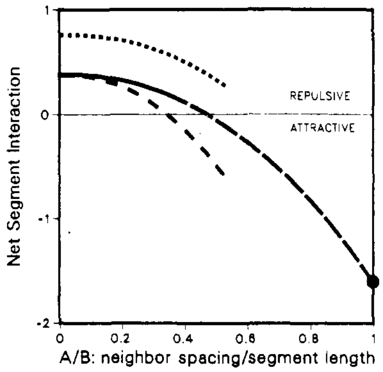

Figure 4. Estimate of the net interaction parameter for two associating segments of B monomers, each with a pair of stickers separated by A monomers in a good solvent with A and $B \gg 1$. The ratio A/B is denoted x in the text. The parameter is the mutual excluded volume of two such segments divided by the cubed root mean square end-to-end radius of a segment without stickers. The method of estimation is described at the end of the Appendix. The line crosses from repulsive to attractive at $x = 0.44$. The broken lines are guesses for the interaction parameter per segment when the segments are assembled into a long chain. The upper line was obtained by doubling the repulsive contribution; the lower line was obtained by doubling the attractive contribution. These broken lines terminate at $A/B = 1/2$, since nearest stickers in a chain cannot be more than half a segment apart.

We see that the sticker entropy for a locally paired state is much smaller than the corresponding entropy, $N \ln N$, associated with a completely random pairing arrangement. In contrast, a random pairing arrangement typically results in a global chain conformation that is highly compact, and this incurs a large entropy penalty from the excluded-volume constraints between chain segments.

In order to investigate the competition between the two types of entropy, we consider the locally paired state (with $\bar{p} \cong 1$) as a "reference state" and try to discover whether or not it is stable against collapse.

The reference state, Figure 3b, may be treated as a chain of subunits, each with the geometry of Figure 1b. Therefore, to a first approximation, the global stability of the chain is governed by the sign of the second viral coefficient, G_s, between these subunits. From eq 14 we see that

$$G_s = \mathbf{g}(x,d)R_s^d \qquad (15)$$

where $R_s = R(2N)^{-\nu}$ is the swollen end-to-end distance of a chain of $S/2N$ monomers. As discussed in Section 3, $\mathbf{g}(x,d)$ may be positive or negative for different values of its arguments.

At a closer level of approximation, the global stability of the reference state depends not on G_s itself but on some effective virial $\bar{G}_s(x,d)$, which takes into account short-range three and higher body interactions between subunits.[11] To illustrate the difference between $\bar{G}_s$ and G_s, we observe that it would be equally valid to subdivide our reference chain into subunits in which the stickers were asymmetrically placed (i.e., we imagine sliding both stickers toward one end of the subunit, whilst keeping x fixed). The value of the "bare" virial, G_s, would change if we did this; indeed, if the repulsive and attractive contributions were in close balance, G_s could change sign. The effective virial, $\bar{G}_s(x,d)$, in contrast, would by definition remain the same. Thus the difference between G_s and G_s accounts for the change in the two-body virial between two subunits (well separated along the chemical sequence), which arises because each subunit is not really isolated but is instead joined onto its neighbors. Usually $\bar{G}_s$ and G_s should differ at most by a factor of order unity; however, if x is chosen so that the two contributions to $\mathbf{g}(x,d)$ in eq 14 are in close balance, $\bar{G}_s$ may be of opposite sign to G_s.

If $\bar{G}_s > 0$, the incorporation of short-range effects then corresponds to an increase of $\bar{p}$ from 1 (in the reference state) to a larger, but still N-independent, value. Once these effects are included, the locally paired reference state is stable against further collapse. The chain conformation for high N is then simple to describe: it is a swollen chain of our subunits (or, more strictly, of larger subunits containing about $2\bar{p}$ stickers each). The radius R' of such a chain scales as

$$R' \sim aN^{\nu}R_s \cong \text{const } aS^{\nu}N^0$$

or

$$R' = c(x,d)R \tag{15a}$$

where[7] $c(x,d)$ is a universal function. In general, c depends on the sticker arrangement (here parameterized by x) but not on N.

If, however, $\bar{G}_s < 0$, our reference state is unstable with respect to global collapse.

6. Collapsed State

The nature of the collapsed state may be investigated by calculating the free energy $F(V)$ of a chain with $2N$ stickers constrained to occupy a certain volume V and then choosing V so as to minimize F. The calculation of F can be done in two hypothetical stages; first a chain with $2N$ markers is isotropically squeezed into a volume V and then the markers are stuck together.

A simple limiting case arises when excluded-volume forces are absent. In this case we can show that the state with completely random sticker pairing is more stable than any locally paired state. First, if the pairing arrangement is to be random, the chain must be of such a size that two chemically adjacent markers can be at opposite sides of the constrained "globule" (Figure 5). Hence

$$a(S/N)^{1/2} \sim V^{1/d} \tag{16}$$

The elastic entropy penalty for squeezing an ideal chain into this volume is roughly that corresponding to N degrees of freedom: $\Delta F \simeq NkT$. If we now join up the markers in pairs, one marker in each pair is in effect confined to a volume a^d rather than to the volume V. This confinement applied to the N pairs of markers costs a free energy of order

$$NkT \ln (Va^{-d}) = NkT[d/2 \ln (S/N) + \text{const}]$$

In contrast, we have gained a sticker entropy of order $N \ln (N)$ from random pairing. Hence

$$\frac{F}{kT} \sim \text{const } N - \frac{d}{2}N \ln (S/N) - N \ln N \tag{17}$$

This must be compared with the free energy, F_0 of a locally paired reference state. The confinement of a sticker again costs a free energy of order $kT[d/2 \ln (S/N) + \text{const}]$, but the pairing entropy is only some constant amount $\ln (\bar{p}_0)$ per sticker. Thus

$$\frac{F_{\text{ref}}}{kT} \sim \text{const } N - \frac{d}{2}N \ln (S/N) - N \ln \bar{p}_0 \tag{18}$$

We see that

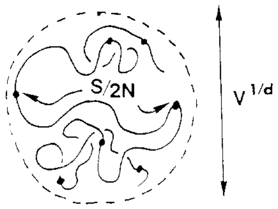

Figure 5. For random pairing, two chemically adjacent markers must be able to explore the whole globule independently.

$$F - F_{\text{ref}} \sim kT\,(\text{const } N - N \ln N) \tag{19}$$

and hence that in the absence of excluded volume the randomly paired state is stable at high N.

In the presence of excluded volume the results are very different; the cost of compressing the chain is much greater. When we isotropically squeeze the marked chain, its structure is like that of a semidilute solution. The monomer density becomes uniform beyond a screening length ξ, which depends only on the monomer concentration S/V. The free energy required for the squeezing process is proportional[5] to kT times the number n_b of correlation volumes or "blobs": $n_b \equiv V/\xi^d$. The compression also increases the pairing entropy from its value $\ln (\bar{p}_0)$ in the reference state to some larger value $\ln (\bar{p}(V))$. The net free energy of compression is of the order

$$\Delta F/kT \sim n_b(V) - N \ln (\bar{p}(V)/\bar{p}_0) \tag{20}$$

In the randomly paired state the typical distance between chemically adjacent markers is again comparable with the size of the globule $V^{1/d}$. This segment of the chain contains a fraction $1/N$ of the correlation volumes, arranged in a random walk. Thus

$$(n_b/N)^{1/2}\xi \sim V^{1/d} \tag{21}$$

or

$$n_b \sim N^{d/(d-2)} \tag{22}$$

Now using eq 8 to calculate the free energy cost of joining up the markers and subtracting the corresponding free-energy terms for the reference state, we find finally for $2 < d < 4$

$$F - F_{\text{ref}} \sim \{N^{d/(d-2)} - N \ln (N) + N \ln (\bar{p}_0/\bar{p}(V))\} \tag{23}$$

Thus, in contrast to eq 19, the randomly paired state is highly unfavorable for large N. This is a direct result of the high free energy cost of creating new semidilute blobs as the chain volume is decreased.

Evidently the chain must be considerably less collapsed than the randomly paired state requires. The natural balance point is a semidilute state whose average concentration is that of a segment between adjacent stickers. The number of blobs n_b is then of the order of the number of stickers N, and $\bar{p}(V)$ is greater than $\bar{p}_0$ by a fixed factor independent of V. Both terms in ΔF (eq 20) are of order NkT. This state corresponds roughly to a compact arrangement of our original swollen subunits. Such an arrangement gains entropy from "sticker exchange" (as shown Figure 2) between each subunit and its neighbors, withoiut the subunits interpenetrating so fully as to create too many new blobs.

An equally good way to describe this configuration is as a swollen "microgel" state, with $\sim S/2N$ monomers between tetrafunctional cross-links. The microgel obeys de Gennes' "C^* theorem"[5] for swollen gels: the blob size ξ is comparable with the swollen radius of a chain segment between cross-links. The typical radius R'' of the microgel is easily calculated (by blob arguments); $R'' \sim V^{1/d}$ where

$V \sim n_b\xi^d$ and hence

$$R'' \sim RN^{1/d-\nu} \sim aS^\nu N^{1/d-\nu} \qquad (24)$$

This should apply for large enough N whenever the effective interaction $\bar{G}_s$, defined below eq 15, is negative, while for $\bar{G}_s > 0$ the radius R' is independent of N (eq 15a).

We can certainly make $\bar{G}_s$ positive in three dimensions by choosing a sticker arrangement as in Figure 3 with small x, as section 4 shows. Unfortunately it is much harder to decide whether *negative* values of $\bar{G}_s$ are possible in three dimensions (though we do know that $\bar{G}_s < 0$ for any x close enough to $d = 4$). For the arrangement of Figure 3, the maximum value of x is $^1/_2$, so the calculation of $\mathbf{g}(1,d)$ in the Appendix does not help us directly in answering this question. In principle $\mathbf{g}(^1/_2,d)$ could also be calculated in an ϵ expansion, but even this would be inconclusive because of the imprecisely known relationship between G_s and $\bar{G}_s$.

At present, therefore, we can only conjecture that $\bar{G}_s \leq 0$ for some sticker arrangements in $d = 3$. In the following section, we assume this to be so and consider the consequences for the phase diagram of a dilute/semidilute solution of associating polymers.

7. Solubility and Phase Separation

We have seen that a chain with many stickers can to a large extent be described as a string of N (effectively impenetrable) subunits, each with the sticker geometry of Figure 1b, in the presence of some net interaction $\bar{G}_s$ between subunits. The behavior of the chain is governed by a single dimensionless interaction

$$\bar{\mathbf{g}} = \bar{G}_s R_s^{-d} \qquad (25)$$

which may be positive or negative depending on the sticker arrangement (and on d). For the simple geometry of Figure 3, we expect there to be some x, $x_\theta(d)$, at which $\bar{G}_s(x) = 0$. If so, we can rewrite eq 25 as

$$\bar{\mathbf{g}}(x) \propto \frac{x - x_\theta}{x_\theta} \qquad (26)$$

A similar parameterization in terms of measurable quantities should also be possible for more complicated arrangements of stickers, including random ones, and also in cases when the effective functionality exceeds 2; for any fixed functionality, however, in the limit of a large average separation between stickers, $\bar{\mathbf{g}}$ must be a universal functional of the relative sticker separations.

The existence of the dimensionless interaction $\bar{\mathbf{g}}$ between subunits allows us to apply directly some standard arguments,[5] developed to deal with ordinary chains, to predict certain features of the phase diagram for associating polymers. These features are shown in Figure 5. In going from ordinary chains to associating polymers, our subunits take over the role of monomers and N becomes a polymerization index. The Fixman-like parameter (cf. eq 2 above) is therefore

$$\zeta'' \cong \bar{\mathbf{g}}N^{2-d/2} \qquad (27)$$

The role of volume fraction on the horizontal axis (cf. ref 5, Figure IV. 8) is played by ϕ_s, the volume fraction of swollen subunits:

$$\phi_s \cong CR^dN^{-\nu d} \qquad (28)$$

An immediate consequence of the phase diagram in Figure 6 is that for $\bar{\mathbf{g}} < 0$ the dense microgel state can only be obtained at very low concentration. If N is large enough for the asymptotic law (eq 24) to be obeyed as $\phi_s \to 0$, phase separation will occur as ϕ_s is increased. Conversely, if N is chosen (with $\bar{\mathbf{g}} < 0$) so that the chain remains fully soluble over the whole concentration range, ζ'' must be small. Hence the overall chain size must be comparable with that of a chain of swollen subunits under "θ conditions". Such a chain is gaussian on scales larger than a subunit and therefore has a radius

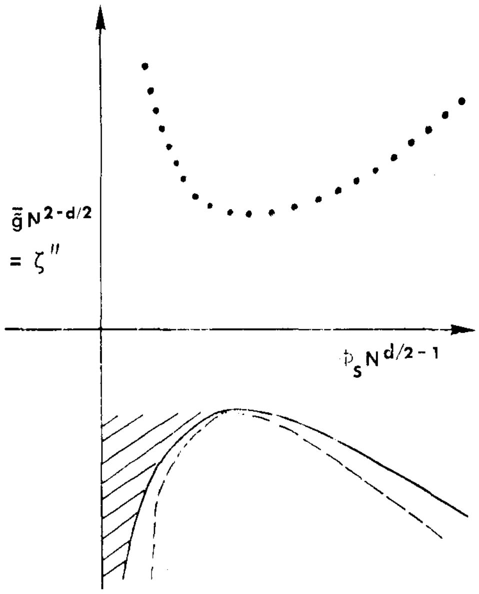

Figure 6. Phase diagram for associating polymers: (solid curve) coexistence; (dashed curve) spinodal; (dotted curve) crossover to semidilute; (hatched area) dilute microgel phase.

$$R''' \sim N^{1/2}R_s \sim RN^{1/2-\nu} \qquad (29)$$

The "θ regime" in which this result applies can in principle be approached even when N is large by choosing a sticker arrangement for which $\mathbf{g}$ is very small (e.g., $x \to x_\theta$ in eq 26). This is, of course, very similar to the way in which the θ point can be approached for an ordinary chain by varying the temperature, although there is no temperature dependence in the strongly associating systems we have been discussing. Instead, the role of temperature is played by a parameter (such as x) characterizing the sticker arrangement.

We have seen that (for the particular case of the sticker arrangement in Figure 3) starting from evenly spaced stickers, a decrease in x favors solubility by enhancing the stability of local pairing. This suggests that randomness in the sticker placements, leading to a distribution of large and small gaps between stickers, should have the same effect. Thus, for random sticker arrangements, there is the possibility of a coil–globule transition controlled by the degree of disorder. Several other variants may be considered. We could envisage an arrangement like Figure 3 but modified so that groups A and B of different chemical species occupy alternate substituent positions. These might be chosen so that A and B stick to each other but not A to A or B to B. It is easy to see that in the (bare) virial $g(x,d)$, given by (14), this would leave the repulsive part g_0 unaffected but reduce the attractive component g_1 by a factor of exactly $^1/_2$. Hence this replacement would strongly favor the swollen state. In contrast, increasing the functionality of the stickers would presumably have the opposite effect, due to the extra combinatorial terms in the exchange entropy.

8. Conclusions

In order to study the conformation and thermodynamic properties of associating polymers in solution, we have described an idealized model in which the number of monomers between associating groups is very large, the associating interaction is both local and very strong (but saturating), and the solvent is otherwise good. Even this simplified model exhibits some subtle properties which, although temperature independent, are highly reminiscent of those found for ordinary chains near the Flory θ temperature.

Our results indicate that the global conformation of an associating polymer in three dimensions may have a surprising critical dependence on the way the associating groups are arranged along the chemical sequence. Thus the placement of these groups may constitute a new "geometric" method for controlling the solvation properties of a polymer. The present model demonstrates this controllability without invoking a balance between energy and entropy; the model is athermal. Thus this geometric mechanism is expected to create θ conditions in a robust way without the usual sensitivity to such factors as temperature or impurities.

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Appendix: Calculation of $\mathbf{g}(1,d)$ to Order ϵ

This calculation may be performed by using one of several renormalization schemes.[12-14] That of des Cloizeaux,[14] which is already formulated in terms of a virial series, turns out to be the most convenient.

Our calculations concern the partition functions of loop polymers, but we express the relevant length scales in terms of the mean square end-to-end distances ("areas") of linear chains. A linear Brownian chain[14] of area $\tilde{S}$ has a mean square end-to-end distance of $r^2 = \tilde{S}d$. The same chain under swollen conditions has $R^2 = {}^{\mathrm{e}}\tilde{S}d$. The ratio ${}^{\mathrm{e}}\tilde{S}/\tilde{S}$ exists in perturbation theory for $d < 4$

$$ {}^{\mathrm{e}}\tilde{S}/\tilde{S} = 1 + \beta z + 0(z^2) \tag{A1} $$

where[14] $\beta = 2/\epsilon - 1 + 0(\epsilon)$ and the expansion parameter z obeys

$$ z = b\tilde{S}^{2-d/2}(2\pi)^{-d/2} \tag{A2} $$

where b is proportional to the excluded volume between two monomers.

We now define the partition function $Z_0(\tilde{S})$ of a Brownian loop made by joining the ends of a Brownian chain. (This is not to be confused with the Z_0 of eq 9 in the text.) Normalizing by the partition function of the original chain, we have

$$ Z_0(\tilde{S}) = (2\pi)^{-d/2}\tilde{S}^{-d/2} \tag{A3} $$

We may also define a partition function $Z(\tilde{S})$ of the same loop with excluded-volume interaction

$$ Z(\tilde{S}) = Z_0(\tilde{S})[1 + \alpha z + 0(z^2)] \tag{A4} $$

where α is calculated below.

We next consider the partition function Z_n of a dilute gase of n excluded-volume loops of unswollen area $\tilde{S}$ in a volume V. For the moment, we do not allow interchain sticking. Thus Z_n has the virial expansion

$$ Z_n = (VZ(\tilde{S}))^n[1 - (1/2)n(n-1)V^{-1}G_0 + 0(V^{-2})] \tag{A5} $$

where G_0 is the mutual excluded volume of two chains.

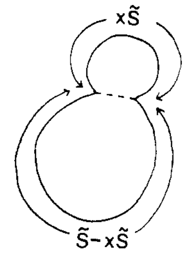

Figure 7. Diagram contributing term $0(z)$ in eq A12.

From this we may deduce the osmotic pressure Π

$$ \Pi = C[1 + CG_0/2 + ...] \tag{A6} $$

where $C = n/V$.

Following ref 14 we write this as

$$ \Pi = C[1 + (2\pi)^{d/2}({}^{\mathrm{e}}\tilde{S})^{d/2}gC/2] \tag{A7} $$

and identify $G_0 = (2\pi)^{d/2}({}^{\mathrm{e}}\tilde{S})^{d/2}g$.

We could proceed to write g as a series in z and analyze this series to find a fixed point g^* appropriate to long chains. In fact, to order ϵ, $g^* = \epsilon/8$,[14] independent of the chain geometry.[15]

We now calculate the correction to g resulting from interchain sticking. For two chains (with stickers at the ends) in a volume V

$$ Z = V^2Z(\tilde{S})^2[1 - V^{-1}(2\pi)^{d/2}({}^{\mathrm{e}}\tilde{S})^{d/2}g] + 2VZ(2\tilde{S}) \tag{A8} $$

where the extra term, $2VZ(2\tilde{S})$, is just the partition function of a loop of size $2\tilde{S}$ in a volume V multiplied by a factor of 2 for the two ways in which the stickers can pair between chains to make such a loop.

We now use the results of Section 4 to write

$$ Z = V^2Z(\tilde{S})^2[1 - V^{-1}(2\pi)^{d/2}({}^{\mathrm{e}}\tilde{S})^{d/2}(g - g')] \tag{A9} $$

where

$$ g' = (2\pi)^{-d/2}({}^{\mathrm{e}}\tilde{S})^{-d/2}[2Z(2\tilde{S})/Z(\tilde{S})^2] \tag{A10} $$

Comparing this with eq 13 and using $R^2 \equiv {}^{\mathrm{e}}\tilde{S}d$, we identify

$$ \tilde{\mathbf{g}}(1,d) = (2\pi/d)^{-d/2}(g^* - g'^*) \tag{A11} $$

where g'^* is the fixed-point value of g'. This we can calculate to order ϵ.

In (A10) we write

$$ Z(\tilde{S}) = Z_0(\tilde{S})[1 + \alpha z + 0(z^2)] $$

$$ Z(2\tilde{S}) = Z_0(2\tilde{S})[1 + \alpha' z + 0(z^2)] \tag{A12} $$

where the terms in z arise from the exclusion of configurations with one self-intersection (Figure 7); i.e.

$$ \alpha z = (1/2)b\int \mathrm{d}s'\,\mathrm{d}s''\,G(s',s'') \tag{A13} $$

where

$$ G(s',s'') = \int P[R(s)]\delta(R(s') - R(s'')) $$

and

$$ P[R(s)] = Q[R(s)]/\int Q[R(s)] $$

with $Q[R(s)] = \exp\{-{}^1/{}_2\int_0^{\tilde{S}}\mathrm{d}s\,(\partial R/\partial s)^2\}\delta(R(\tilde{S}) - R(0))$.

We find

$$ \alpha = -\int_0^{1/2} x^{-d/2}(1-x)^{-d/2}\,\mathrm{d}x \tag{A14} $$

and, by a similar calculation

$$ \alpha' = 2^{\epsilon/2}\alpha \tag{A15} $$

The integral in (A14) exhibits a short-range divergence that we eliminate by taking a principal value.[14] Integrating the remainder by parts gives

$$\alpha = 8 - (2 + \epsilon/2) \int_0^{1/2} x^{1-d/2}(1 - x)^{-d/2-1}\, \mathrm{d}x + 0(\epsilon)$$
$$= 8 - (2 + \epsilon/2)\left[\frac{2}{\epsilon}\left(\frac{1}{2}\right)^{\epsilon/2} + J + 0(\epsilon) \right] \tag{A16}$$

where

$$J = \int_0^{1/2} x^{-1}[(1 - x)^{-3} - 1]\, \mathrm{d}x$$
$$= 5/2 + \ln 2$$

Hence

$$\alpha = 2 - (4/\epsilon) + 0(\epsilon) \tag{A17}$$

Now substituting (A12) and (A15) into (A10) gives

$$g' = 2(2\pi)^{-d/2}({}^{\mathrm{e}}\tilde{S})^{-d/2}\frac{Z_0(2\tilde{S})}{Z_0(\tilde{S})^2}[1 + (2^{\epsilon/2} - 2)\alpha z + 0(z^2)]$$

and using also (A3), (A1), and (A17), we obtain

$$g' = 2^{1-d/2}\{1 + (2^{\epsilon/2} - 2)\alpha z - (d/2)\beta z\}$$
$$= \tfrac{1}{2}\{1 + (\epsilon/2) \ln 2 + (1 - 2 \ln 2 + 0(\epsilon))z\} \tag{A18}$$

We now wish to find g'^{*}. This is done[14] by writing z in terms of g and then setting $g = g^*$. To this order, we merely set $z = \epsilon/8$ in (A18).

Hence

$$g'^{*} = 1/2 + (\epsilon/8)[1/2 + \ln 2] \tag{A19}$$

and

$$\mathbf{g}(1,d) = (2\pi/d)^{-d/2}[-1/2 - (\epsilon/8)\{-1/2 + \ln 2\}] + 0(\epsilon^2) \tag{A20}$$

As expected, for $\epsilon \rightarrow 0$ $\mathbf{g}(1,d)$ is negative and of leading order ϵ^0. However, the coefficient of ϵ is also negative. Hence $\mathbf{g}(1,d)$ becomes more negative with decreasing d and is almost certainly negative for $d = 3$.

We may make a crude estimate of $\mathbf{g}(x,d)$ using this result, the known nonassociating limit $\mathbf{g}(0,d)$, and the form (eq 13a) of $g'^{*}(x)$ for small x. We assume that the repulsive term $g^*(x,d)$ is independent of x, as it is in order ϵ. (Even in the complementary limit where the chains are taken as hard spheres whose size is the ideal radius of gyration, $g^*(x)$ would only decrease by a factor of $2^{3/2}$ as x goes from 0 to 1.) We assume that g'^{*} varies as $x^{\nu(d+\theta_2)}$ for all x. Thus

$$\mathbf{g}(x,d) \cong \mathbf{g}(0,d)[1 - Cx^{\nu(d+\theta_2)}]$$

Choosing C to make $\mathbf{g}(1,d)$ agree with eq A20 and taking $\mathbf{g}(0,d) = \epsilon/8$ (as noted after eq A7), we obtain the estimate of Figure 4.

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