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Mean Field Theory of Polymer Solutions: Concentration Dependence of Chain Dimensions

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ABSTRACT: A mean field theory for an incompressible polymer solution on a lattice is presented. Both excluded volume and attractive (van der Waals) interactions are included. The central concept is that of a screening length, x_s. Configurations of a chain which are larger than x_s have complete screening due to overlap with neighboring chains and so they have the statistics of ideal chains. Configurations smaller than x_s experience no overlap and thus have the statistics of isolated chains. The results of this model are developed in terms of the concentration dependence of the chain dimensions. These results are similar to, but in detail different from, the results of the recent scaling theories.[1-7] Chain dimensions show a power law relation with concentration in the semidilute region, but the power depends on molecular weight. Also, a slight expansion of chains in dilute Θ solutions is predicted. The agreement of these results with experiment is good.

I. Introduction

The statistical mechanics of polymer solutions have presented a challenge for scientists for well over 40 years. Even when considered as single chains, the polymer problem has not been solved exactly. Because the chains are long, an immense number of configurations are available to them. The enumeration of them is made more difficult because the chain cannot pass through itself—such hard-core repulsions give rise to the excluded volume effect. On top of this there are attractive, secondary forces (van der Waals) between chain segments as well as with the solvent. Such consideration of a single chain has application in dilute solutions in which the chains are essentially isolated from each other. However, the complexity becomes more severe when more than one chain is considered, that is, when the effects of concentration are included. At some point the region of space in which the segments of a chain are found will coincide with that of one or more other chains. Thus, the sizes of the coils will determine what interactions they experience. But these interactions will in turn influence the chain sizes. Such overlapping may cause the coils to contract away from one another (in good solvent) or to expand toward one another (in poor solvent). Those cases for which there is some overlap between chains, as well as some isolation, are called semidilute solutions, which have proved difficult to handle.

In the past decade, renewed interest in polymer solutions has been stimulated by both theoretical and experimental advances. Scaling theories, based on the renormalization group techniques used in the theory of phase transitions and critical phenomena, have been developed for single chains by de Gennes[1] and extended to semidilute solutions by des Cloizeaux[2] and Daoud and Jannink.[3,4] Such theories have also been derived recently by Kosmas and Freed[5] without the use of renormalization techniques. Good general reviews of these theories may be found in ref 6 and 7. Central to these developments is the concept of a screening length, first introduced by Edwards.[8] For distances shorter than the screening length, the intramolecular forces still have full effect, but at larger distances their effect is screened out by interactions with segments from other chains. As a result, power law expressions for chain dimensions and other functions can be determined.

The excitement generated by the new theories was partly due to the agreement they have had with the new experimental technique of small-angle neutron scattering (SANS). In order to see a single chain in a sea of similar chains (as in the bulk state or in semidilute and concentrated solutions) it is necessary to label the chain in some way. Photon scattering (light and X-ray) is due to electromagnetic forces, so the internal structure of a sample is seen by contrasts in electron density (X-ray) or polarization (light). But any labeling technique that causes a significant contrast in electron density (e.g., by attaching iodine to polystyrene[9]) also causes chemical changes, and so the labeled chain is no longer representative of the unlabeled chains. Neutrons are scattered, primarily, by interactions with the nuclei of the sample.[10] Isotopes of the same element may thus have different scattering properties, of which the most common example is the great difference in neutron scattering cross section between hydrogen and deuterium. When isotopic labeling is used, there should be no large chemical differences. Thus, for the first time, measurements of single-chain properties in concentrated systems have become possible.[11]

The theory presented here is based on mean field concepts. One basis is the seminal work of Flory[12] and Huggins[13] on polymer solutions, as well as later extensions of this approach.[14-16] Since fluctuations in segment density are not included in these theories, they work best in con-

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centrated solutions. There has been a wide variety of theories for the dilute solution as well; a full account is found in the text of Yamakawa.[17] This model also has roots in the lattice fluid theory of Sanchez and Lacombe,[42] which has been quite successful in describing the properties of polymer liquids and solutions. It has also been used to predict the properties of lower molecular weight substances and the compatibility of polymer blends. (It should be mentioned here that the present model differs from that in ref 43 chiefly in the way the local segment density is found; see section III.) More recently, efforts in dilute solution have been concentrated on the so-called collapse transition. When a dilute solution is cooled through its Θ temperature, isolated chains rapidly shrink in size. This has been observed in DNA,[18] polyelectrolytes,[19,20] and polystyrene.[19,21,22] Several new theories have been published on this transition.[23-29]

The gap between these dilute- and concentrated-solution theories is the target of the theory developed here. In section II the canonical ensemble partition function is developed. The crucial parameter here is the local segment density, which is determined as a function of concentration and chain size in section III. In section IV the chain dimensions are calculated for the solution, and the predictions are compared with experiment in section V. Finally, the theory is compared with the scaling theories in section VI.

II. Partition Function

A polymer solution is here modeled as a system of N_1 solvent molecules and N_2 r-mers (polymers of r segments) filling a lattice of $N_T = N_1 + rN_2$ sites. (Throughout this paper, parameters referring to solvent will be labeled with a subscript "1" and those referring to polymer with subscript "2".) Thus, the solution is assumed to be *incompressible* and the polymer to be *monodisperse*. Moreover, the volume of a solvent molecule and that of a chain segment are both taken as equal to the volume of a single lattice site. The volume fraction of polymer, ϕ_2, is then rN_2/N_T, and $\phi_1 = 1 - \phi_2$. The interaction energy of the solution is based on the nearest-neighbor interactions, $\{\epsilon_{ij}\} = \{\epsilon_{11}, \epsilon_{12}, \epsilon_{22}\}$. (These represent van der Waals interactions.) For example, ϵ_{12} is the segment–solvent interaction.

An important feature of this model is that the variation in the size of each chain is taken into account. This size is represented by the radius of gyration of the chain. Let $\{s_k\}$ be the set of the radii of gyration of all the chains. The canonical ensemble partition function can then be written as

$$Z(N_1,N_2,r,\{\epsilon_{ij}\},T) = \frac{1}{N_1!N_2!}\int \mathrm{d}\{s_k\}\ \Omega(\{s_k\},N_1,N_2,r,\{\epsilon_{ij}\},T) \times \exp(\beta E(\{s_k\},N_1,N_2,r,\{\epsilon_{ij}\},T)) \quad (1)$$

where Ω is the configurational partition function for the solution and E is its interaction energy. As is conventional, $\beta = (kT)^{-1}$. The integral is taken over all possible values for the chain sizes. The factorials in front of the integral account for indistinguishibility. As a simplification, it is also assumed that *the chains are independent of one another*; this means that

$$\Omega(\{s_k\}) = \Omega_1(N_1)\prod_{k=1}^{N_2}\Omega_{2,k}(s_k) \quad (2)$$

$$E(\{s_k\}) = \sum_{k=1}^{N_2}E_{2,k}(s_k) \quad (3)$$

The configurational partition function of the solvent is Ω_1, and $\Omega_{2,k}$ is that of the kth chain. Similarly, $E_{2,k}$ is the portion of the interaction energy that can be assigned to the kth chain (see below) which depends only on s_k. The independence of the chains assumed here means that the size of a particular coil does not depend on the size of its neighbors. The chain dimensions *do* depend on the presence of those neighbors, through the concentration; interactions between the segments of a chain and those of other chains which are within the coil volume are included in the theory (this is described in section III). In reality, the degree of such overlap depends on the sizes of the neighboring coils. This is a minor effect, however, which is ignored by using this assumption. The total partition function may then be rewritten as

$$Z(N_1,N_2,r,\{\epsilon_{ij}\},T) = \frac{1}{N_1!N_2!}\Omega_1(N_1)\prod_{k=1}^{N_2}\int \mathrm{d}s_k\ \Omega_{2,k}(s_k)\exp(\beta E_{2,k}(s_k)) \quad (4)$$

A. Configurational Partition Function. The method of counting configurations used here is somewhat different from that usually used;[12,13,40] that is, the chains will not be "laid down" on the lattice consecutively (first all of one chain, then all of a second, etc.), but rather in a nearly simultaneous fashion. The first segment of each chain is "laid down" first, then the second segment of each chain, etc., so that each chain is in essentially the same density field as it is "laid down" as every other chain. In the final step, the solvent molecules are added in to fill up the remaining empty sites.

The configurational partition function for the kth chain, $\Omega_{2,k}$, is based on that for an ideal chain. The total number of configurations for a phantom chain on a lattice of N_T sites and coordination number z is N_Tz^{r-1}. The number of configurations with size s is then $P_0(s)N_Tz^{r-1}$, where $P_0(s)$ is the ideal distribution function.[41] Because of the excluded volume, however, one must take into account those chain segments already on the lattice.[23] In general, the first segment has less than N_T open sites and the following segments have less than z. Let $\omega_k{}^{\mathrm{f}}$ be the number of ways to place the first segment of the kth chain, and $\omega_k{}^{(r-1)}$ the number of ways to place the rest of the segments. Therefore

$$\Omega_{2,k}(s_k) = P_0(s_k)\omega_k{}^{\mathrm{f}}\omega_k{}^{(\mathrm{r}-1)}(s_k) \quad (5)$$

since the eventual size of the coil should play no role in how the first segment is placed.

When the first segment of the kth chain is put on the lattice, the first segments of $k - 1$ other chains are already on the lattice, so $\omega_k{}^{\mathrm{f}} = N_T - k + 1$. The product of these factors over k is then

$$\prod_{k=1}^{N_2}\omega_k{}^{\mathrm{f}} = N_T!/(N_T - N_2)! \quad (6)$$

Just because the chain cannot "step back" onto itself, the number of possible ways to place any segment after the first is already reduced to $z - 1$. Moreover, this must be further reduced because of the presence of the segments which have already been placed on the lattice. This is accounted for by a survival factor, $1 - P_{kl}(s_k)$, where $P_{kl}(s_k)$ is the probability that a nearest-neighbor site is occupied when the lth segment of the kth chain is placed. This is taken to be the local density of segments (both from the kth chain and the others) at the time this segment is placed. (Here "local" is defined on the scale of the chain size. The density is assumed to be uniform within the volume of the chain.) Suppose that, after all the segments are on the lattice, the *local segment density* is $\hat{\phi}_2(s_k)$; then the local density when the lth segment is placed is

$[(l-1)/r]\hat{\phi}_2(s_k)$. The degree of intermolecular overlap depends on both chain size and concentration. The calculation of $\hat{\phi}_2(s_k,\phi_2)$ is done in section III.

The number of ways to place all the segments after the first on the lattice will just be the product of the survival factor over l:

$$\begin{aligned}\omega_k^{(r-1)}(s_k) &= \prod_{l=2}^{r}(z-1)(1-P_{kl}(s_k)) \\ &= (z-1)^{(r-1)}\prod_{l=2}^{r}\left(1-\left(\frac{l-1}{r}\right)\hat{\phi}_2(s_k)\right) \\ &= (z-1)^{(r-1)}\left(\frac{\hat{\phi}_2}{r}\right)^{(r-1)}\frac{(r/\hat{\phi}_2-1)!}{(r/\hat{\phi}_2-r)!} \qquad (7)\end{aligned}$$

This can be broken up into a factor independent of s_k, $\omega_0^{(r-1)}$, and one dependent on it, $\omega_x^{(r-1)}(s_k)$; they are conveniently written as natural logarithms

$$\ln \omega_0^{(r-1)} = -(r-1) + (r-1)\ln(z-1) + \frac{r}{\phi_2}\{(1-\phi_2/r)\ln(1-\phi_2/r) - (1-\phi_2)\ln(1-\phi_2)\} \quad (8)$$

$$\ln \omega_x^{(r-1)} = \frac{r}{\phi_2}(1-\phi_2)\ln(1-\phi_2) - \frac{r}{\hat{\phi}_2}(1-\hat{\phi}_2)\ln(1-\hat{\phi}_2) \quad (9)$$

(Stirling's rule has been used here, and we have dropped terms of order r^{-2}.)

After all the chains are on the lattice, there remain N_1 sites for N_1 solvent molecules. Therefore $\Omega_1(N_1) = N_1!$ Combining all the factors which are independent of s_k, we have (eq 6 and 8)

$$\begin{aligned}\Omega_0 &\equiv \Omega_1(N_1)\prod_{k=1}^{N_2}\omega_k^{\mathrm{f}}\omega_0^{(r-1)} \\ &= N_{\mathrm{T}}!\left(\frac{z-1}{N_{\mathrm{T}}}\right)^{N_2(r-1)} \qquad (10)\end{aligned}$$

so that Ω_0 is the part of the configurational partition function that is independent of $\{s_k\}$.

B. Interaction Energy. There are, in general, two domains in a polymer solution: one in which the chains are mixed with the solvent and the other which is purely solvent. The second of these becomes smaller the more concentrated the solution becomes, but even as the chains start to overlap there are regions of pure solvent in between them. Even though all the interactions in such regions are between solvent molecules, the amount of interaction does depend on the sizes of the coils because the sizes of the pure solvent domains do. As the chains expand or become more numerous (increases in s_k or ϕ_2), the pure solvent domain becomes smaller. There are thus two terms in $E_{2,k}(s_k)$; $E_{2,k}^{\mathrm{in}}(s_k)$, which arises from interactions inside the coil volume, and $E_{2,k}^{\mathrm{ex}}(s_k)$, which is due to those in pure solvent regions.

First, it is necessary to determine the volume pervaded by a coil of gyration radius s_k. Let ϕ_s be the *self-density* of such a chain, that is, the density of just those segments which are part of the chain inside its volume. This is to be distinguished from $\hat{\phi}_2$, which includes all the segments, even those from other chains, which are in the pervaded volume. This volume is proportional to s_k^3, so $\phi_s \sim r/s_k^3$. Turning this around, the volume pervaded is r/ϕ_s. Since $\hat{\phi}_2$ is the segment density in this volume, by mean field arguments[23] the total interaction energy in this volume, E_{T}, is

$$E_{\mathrm{T}} = \frac{r}{2\phi_s}(\hat{\phi}_1^2\epsilon_{11} + 2\hat{\phi}_1\hat{\phi}_2\epsilon_{12} + \hat{\phi}_2^2\epsilon_{22}) \qquad (11)$$

where $\hat{\phi}_1 = 1 - \hat{\phi}_2$ is the local solvent density. The number of segments in the volume is $\hat{\phi}_2(r/\phi_s)$; since r of them belong to the chain in question, $r/\hat{\phi}_2(r/\phi_s) = \phi_s/\hat{\phi}_2$ of the interactions can be ascribed to those segments so

$$E_{2,k}^{\mathrm{in}}(s_k) = \frac{r}{2\hat{\phi}_2}(\hat{\phi}_1^2\epsilon_{11} + 2\hat{\phi}_1\hat{\phi}_2\epsilon_{12} + \hat{\phi}_2^2\epsilon_{22}) \qquad (12)$$

How many solvent molecules are completely outside the regions circumscribed by the chains? To find the number which may be assigned to a chain of local segment density $\hat{\phi}_2$, consider what such a number would be if every chain had density $\hat{\phi}_2$; divide this number by N_2. If all the chains were of the same size, the total volume pervaded by the coils would be $N_2r/\hat{\phi}_2$ (and not N_2r/ϕ_s) because of overlap; see above. Since the solvent density in such regions is $\hat{\phi}_1$, there are $N_2(r/\hat{\phi}_2)\hat{\phi}_1$ solvent molecules there. The number outside such volumes, N_1^{ex}, is then

$$\begin{aligned}N_1^{\mathrm{ex}} &= N_1 - rN_2(\hat{\phi}_1/\hat{\phi}_2) \\ &= rN_2\left(\frac{\phi_1}{\phi_2} - \frac{\hat{\phi}_1}{\hat{\phi}_2}\right) \qquad (13)\end{aligned}$$

Thus we can say that the number of molecules in pure solvent regions due to the chain of size s_k is $r(\phi_1/\phi_2 - \hat{\phi}_1/\hat{\phi}_2)$ and

$$E_{2,k}^{\mathrm{ex}}(s_k) = \frac{r}{2}\left(\frac{\phi_1}{\phi_2} - \frac{\hat{\phi}_1}{\hat{\phi}_2}\right)\epsilon_{11} \qquad (14)$$

The total interaction from the chain is then

$$\begin{aligned}E_{2,k}(s_k) &= E_{2,k}^{\mathrm{in}} + E_{2,k}^{\mathrm{ex}} \\ &= \frac{r}{2\phi_2}\epsilon^* + \frac{r}{2}\Delta\epsilon(\hat{\phi}_2 - \phi_2) \qquad (15)\end{aligned}$$

where $\epsilon^* = \phi_1^2\epsilon_{11} + 2\phi_1\phi_2\epsilon_{12} + \phi_2^2\epsilon_{22}$ and $\Delta\epsilon = \epsilon_{11} + \epsilon_{22} - 2\epsilon_{12}$. The first term is the interaction energy from a homogeneous mixture of solvent and polymer, while the second term shows what differences arise due to the size of the coil.

C. Free Energy. The terms which are functions of s_k (eq 9 and 15) can be combined into a free energy which depends on chain size. Defining this free energy as

$$-\beta A(s_k) = \ln \omega_x^{(r-1)}(s_k) + \beta\frac{r}{2}\Delta\epsilon(\hat{\phi}_2 - \phi_2) \qquad (16)$$

gives

$$-\beta A(s_k) = r\left\{\chi(\hat{\phi}_2 - \phi_2) - \frac{1-\hat{\phi}_2}{\hat{\phi}_2}\ln(1-\hat{\phi}_2) + \frac{1-\phi_2}{\phi_2}\ln(1-\phi_2)\right\} = \beta a(\hat{\phi}_2) - \beta a(\phi_2) \qquad (17)$$

where $\chi = \beta\Delta\epsilon/2$ is the usual Flory interaction parameter[40] and

$$\beta a(\phi) = r\left\{\chi\phi - \frac{1-\phi}{\phi}\ln(1-\phi)\right\} \qquad (18)$$

Thus, the free energy clearly represents the difference between a system differentiated into regions defined by chain coils ($\hat{\phi}_2$) and a completely homogeneous one (ϕ_2).

Finally, the expression for the total partition function may be written as

$$Z(N_1,N_2,r,\{\epsilon_{ij}\},T) = Z_{\mathrm{FH}}(N_1,N_2,r,\{\epsilon_{ij}\},T)\prod_{k=1}^{N_2}Z_s(k,\phi_2,\chi,r) \qquad (19)$$

where Z_{FH} is just the Flory–Huggins partition function[12,13,40]

$$Z_{\mathrm{FH}}(N_1,N_2,r,\{\epsilon_{ij}\},T) = \frac{N_{\mathrm{T}}!}{N_1!N_2!}\left(\frac{z-1}{N_{\mathrm{T}}}\right)^{N_2(r-1)} \exp\left(\beta\frac{N_{\mathrm{T}}}{2}\epsilon^*\right) \tag{20}$$

and $Z_s(k)$ is that part due to the size distribution of the kth chain

$$Z_s(k,\phi_2,\chi,r) = \int \mathrm{d}s_k\, P_0(s_k)\, \exp(\beta a(\hat{\phi}_2(s_k)) - \beta a(\phi_2)) \tag{21}$$

But this will be the same for every chain, which is the result of their equivalent treatments in this development. Thus we can write

$$Z = Z_{\mathrm{FH}}(Z_s)^{N_2} \tag{22}$$

where

$$Z_s(\phi_2,\chi,r) = \int \mathrm{d}s\, P_0(s)\, \exp(\beta a(\hat{\phi}_2(s)) - \beta a(\phi_2)) \tag{23}$$

Notice that for a homogeneous system (as in the bulk), $\hat{\phi}_2 = \phi_2$ so $A(s) = 0$ and $Z_s = 1$. Then $Z = Z_{\mathrm{FH}}$ and the Flory–Huggins[12,13,40] or lattice fluid[42] result falls out. To complete the picture, what is needed is the dependence of $\hat{\phi}_2$ on s and ϕ_2, which is calculated in the next section.

III. Local Segment Density

In this mean field model, $\hat{\phi}_2$, the local segment density (that is, the density of segments in the volume pervaded by a chain) depends on the size of the chain, s, its length, r, and the polymer concentration, ϕ_2. (In general, of course, this would depend on the sizes of every chain as well as the positions of their centers of mass. However, as in section II, this is eliminated by using the mean field approximation and the assumption of chain independence.) The self-density of a chain, ϕ_s, has already been defined above as the fraction of the volume pervaded by a chain which is taken up by its own segments; thus $\phi_s \sim r/s^3$. For ideal chains, let $\phi_0 \equiv \phi_s$ $(s = \langle s^2\rangle_0^{1/2}) \sim r/\langle s^2\rangle_0^{3/2}$, where $\langle s^2\rangle_0$ is the mean-square radius of gyration for an ideal chain. Thus ϕ_0 is a quantity characteristic of the polymer, independent of the solvent. Since $\langle s^2\rangle_0 \sim r$, $\phi_0 \sim r^{-1/2}$. It is convenient to define $x = s/\langle s^2\rangle_0^{1/2}$ as a reduced radius of gyration, since then $\phi_s = \phi_0/x^3$. Because there is an upper limit on ϕ_s (when $\phi_s = 1$, every site is filled), $x \geq \phi_0^{1/3}$. Finally, an *intrinsic density*, ϕ_i, may be defined such that $\phi_0 = \phi_i r^{-1/2}$. Then ϕ_i is independent of r and depends only on the chemistry of the chain—what the monomer is, how much branching there is, chain stiffness, etc.

The local segment density can be calculated by a cell model.[43] Imagine that every chain has the same size and that the lattice is divided into cells, each of which has the volume of a chain, r/ϕ_s. Every chain is completely contained in a cell, but each cell may contain more than one chain. The maximum number of chains that a cell can contain is m, the largest integer less than or equal to $1/\phi_s$. If more than m chains were in a cell, the volume fraction would be greater than one, which is clearly impossible. (As mentioned in ref 43, the case of $m = 1$ corresponds to Fermi–Dirac statistics; for $m = \infty$, Bose–Einstein statistics. In general here, m is somewhere in between, which corresponds to Gentile statistics.[44])

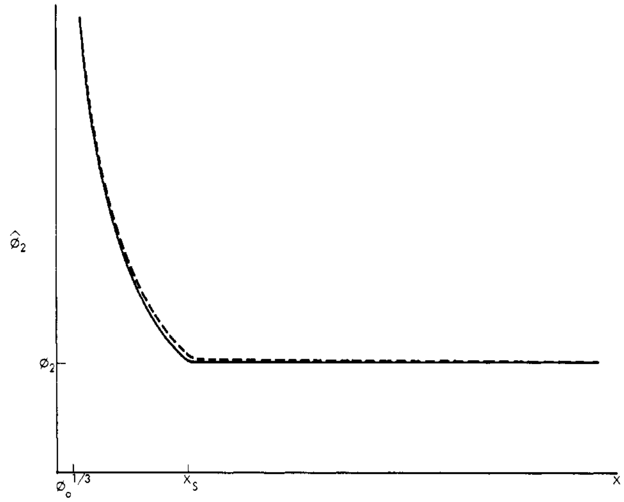

Figure 1. Dependence of local segment density, $\hat{\phi}_2$, on x: (---) as calculated from cell model; (——) from screening length approximation. x_s is the screening length.

The probability that a cell has n chains, c_n $(0 \leq n \leq m)$, is determined by s, ϕ_2, and χ. The cell model is solved by the method of Lagrange multipliers; for details see ref 43. One of the constraints on the system is that λ, the average number of chains in a cell, is just the number of chains, N_2, divided by the number of cells, ω. But $\omega = N_{\mathrm{T}}/(r/\phi_s)$ so

$$\lambda = \frac{N_2}{\omega} = \frac{rN_2}{N_{\mathrm{T}}\phi_s} = \phi_2/\phi_s \tag{24}$$

This is averaged over the whole lattice. However, $\hat{\phi}_2$ is the segment density inside the chains, so it is identified with the average number of chains in occupied cells $(n \geq 1)$:

$$\hat{\phi}_2 = \frac{N_2}{\omega(1-c_0)}\phi_s = \frac{\lambda}{1-c_0}\phi_s = \frac{\phi_2}{1-c_0} \tag{25}$$

since every chain has density ϕ_s in the cell model.

The results of such a calculation for $\hat{\phi}_2$ are shown as the dashed line in Figure 1. Here $\hat{\phi}_2$ is plotted vs. x for a given ϕ_2. There is very little dependence of this curve on temperature. To see how the x dependence comes about, consider two limits. As $\phi_2 \to 0$, the chains become isolated so $c_n = 0$ for $n \geq 2$. Thus

$$\sum_{n=0}^{m} c_n = c_0 + c_1 = 1$$

$$\sum_{n=0}^{m} nc_n = c_1 = \lambda \tag{26}$$

so $1 - c_0 = c_1 = \lambda$. Thus

$$\hat{\phi}_2 = \phi_2/\lambda = \phi_s \qquad (\phi_2 \to 0) \tag{27}$$

which is sensible; as the chains become isolated, the local density is just the self-density. On the other hand, as $\phi_2 \to 1$, every cell becomes occupied, so $c_0 = 0$ and $\hat{\phi}_2 = \phi_2$. As the chains overlap more and more, the solution becomes more homogeneous and the local density approaches the concentration, which is the global density.

It is appropriate to explain here why the cell model is not used to calculate chain dimensions or the partition function of the solution. When ϕ_2 becomes too large, that is, in the semidilute or concentrated regimes, the model breaks down. Consider an example. Suppose that the concentration is somewhat greater than 0.5, say $\phi_2 = 0.6$, and that the chains are of such a size that there is exactly one chain per cell $(\lambda = 1)$. Thus $\phi_s = 0.6$ also, so each chain occupies 60% of the cell it is in. Now keep $\phi_2 = 0.6$ but enlarge the chains (and so the cells) slightly so that $0.5 < \phi_s < 0.6$. Then $\lambda > 1$, and some cells must have at least two chains. But since $\phi_s > 0.5$, the maximum number of chains a cell can have, m, is one. Thus there is no way to arrange the chains into cells for these values of s and ϕ_2.

Indeed, the problem is more severe. For values of s and ϕ_2 near such impossible cases, there are very few arrangements possible (for example, the case where $\phi_s = \phi_2 = 0.6$ allows only one; exactly one chain per cell). Thus the probability of configurations is quite different in the cell model than it would be if partial overlap were allowed. The requirement that every chain be placed in a cell is too restrictive on a number of arrangements of chains. This, plus the need to make every chain the same size, makes the cell model unacceptable to be used generally here.

The local segment density may be found more simply in the following way. When the chain is at its minimum size ($x = \phi_0{}^{1/3}$), every part of its volume is filled with its own segments, so $\hat{\phi}_2 = \phi_s = 1$. As it expands somewhat, very few segments from other chains come into its volume so still $\hat{\phi}_2 \approx \phi_s$. However, once the chain is quite large, it overlaps to a large extent with its neighbors. The local segment density must then become the global density, ϕ_2. Where will the crossover between $\hat{\phi}_2 \approx \phi_s$ and $\hat{\phi}_2 \approx \phi_2$ occur? Because the number of segments inside the pervaded volume must be at least r, we have $\hat{\phi}_2 \geq \phi_s$ for all s; but also since segment density is higher near chain centers, $\hat{\phi}_2 \geq \phi_2$ for all s. Thus we assume that the crossover takes place near the point where $\phi_s = \phi_2$ at $x = x_s \equiv (\phi_0/\phi_2)^{1/3}$. The parameter x_s may be called a *screening length*, since for $x > x_s$, the intramolecular excluded volume interactions are screened by the presence of segments from other chains; for $x < x_s$, there is no screening. The solid line of Figure 1 is just the result of this screening length approximation

$$\begin{aligned} \hat{\phi}_2 &= \phi_s; \qquad x \leq x_s \\ &= \phi_2; \qquad x \geq x_s \end{aligned} \tag{28}$$

This gives almost exactly the same result as the cell model.

To clarify the meaning of this screening length, it is useful at this point to compare this model with the scaling theories.[1-7] In both the idea of a screening length is central. On a scale less than this length there are large fluctuations in segment density; on a scale greater than the screening length, the fluctuations disappear and the solution is homogeneous. In a polymer solution, there are two kinds of distributions which give rise to segment density fluctuations (assuming monodispersity of the polymer and incompressibility); the segment density varies from the center of the chain outward, and also the size of the chain will vary. In the scaling theories, the first of these distributions is considered. The screening length is the size of the so called "blob". A segment inside the blob has excluded volume interactions with other segments inside the blob, but interactions with segments outside are screened. In the mean field theory presented here, the chain cannot be broken up in this way; every segment of the chain interacts with all the others in the same way.

However, the scaling theories do not take into account the distribution of chain sizes. The radius of gyration is assumed to be a fixed quantity (at a given temperature and concentration) with the average value. This is just where the screening length described above, x_s, comes into play. For configurations of size less than x_s, there is no overlap and thus no screening of excluded volume interactions; the chain, therefore, has the characteristics of an isolated chain. Configurations of a chain which have a size larger than x_s do experience screening; their characteristics are those of an ideal chain.

The meanings of these two screening lengths are shown schematically in Figure 2. In Figure 2a, ζ, the screening length in the scaling theories, is defined as the point at which the segment density, ρ, is equal to the concentration ϕ_2.[11] Here R is the distance from the center of the coil. Similarly (Figure 2b), x_s is the size of a chain for which $\phi_s = \phi_2$. Thus, both denote the crossover between overlap and isolation, but they refer to different distributions.

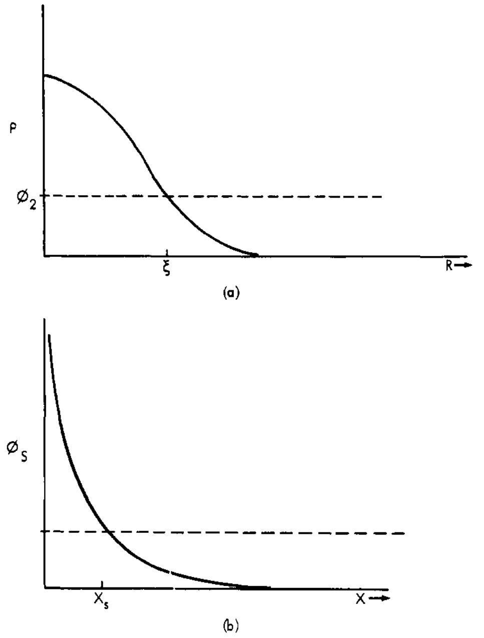

Figure 2. Comparison of (a) scaling and (b) mean field screening length.

As concentration increases, both of these sorts of fluctuations diminish in importance. As the chains overlap one another to a greater extent, the dropoff in segment density away from the center of the chain is balanced by the presence of segments from other chains in the volume pervaded by the chain. Also, changes in chain size have less effect, since the total density field becomes more homogeneous. However, these two effects fall off somewhat differently, so the predictions of the two models are somewhat different (for example, in the concentration and molecular weight dependence of chain dimensions on the semidilute region). A more complete theory would contain both effects.

The implications of the form of $\hat{\phi}_2$ in eq 28 can be seen in the behavior of $A(s)$, that part of the free energy which is dependent on chain size, and $P(s)$, the distribution of the radius of gyration, which is given by $P_0(s)e^{-\beta A(s)}$. Even though $\hat{\phi}_2$ itself has little temperature dependence, $A(s)$ is quite dependent on it. In Figure 3, $\beta A(s)$ is plotted vs. x for a dilute-solution case, where $\phi_2 = 0.001$, $r = 100$, and $x_s \approx 5$. Consider first the good-solvent case, where $\chi = 0$ ($T \rightarrow \infty$). This means that there are no net attractive forces and only the repulsive excluded volume forces come into play. Since there are more such interactions when $\hat{\phi}_2$ is large, regions of lower segment density have lower free energy. Thus, the free energy dependence on x mirrors that of $\hat{\phi}_2$; at low x, $A(s)$ is large, and it asymptotically goes to zero for large chains. This gives a heavier weighting to larger chains, and so they are expanded over ideal dimensions ($x = 1$) on average. (Also shown on Figure 3 is $-\ln P_0(s)$; since $-\ln P(s) = -\ln P_0(s) + \beta A(s)$, we can see how $\beta A(s)$ shifts the average dimensions.)

For a Θ solvent ($\chi = {}^1/_2$; $T = \Theta$) the dependence of $A(s)$ on x is similar, but $A(s)$ drops off more sharply. Lower segment density configurations are still favored, but not so strongly as for a good solvent since the attractive and

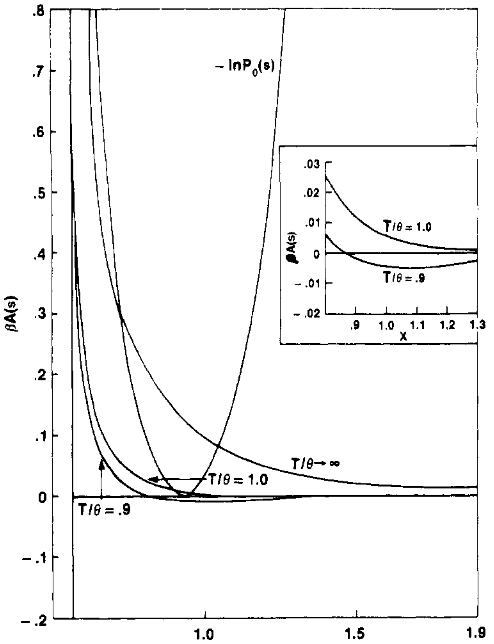

Figure 3. Dependence of free energy on chain size for $T/\Theta = 0.9$, $T/\Theta = 1.0$, and $T/\Theta \rightarrow \infty$. Also shown is $-\ln P_0(s)$, the ideal distribution ($\phi_2 = 0.001$, $r = 100$, $x_s \approx 5$).

repulsive forces nearly balance. To see this notice that (from eq 17)

$$\frac{\partial A(s)}{\partial \hat{\phi}_2} = -kTr\left(\chi + \frac{1}{\hat{\phi}_2} + \frac{1}{\hat{\phi}_2{}^2}\ln\left(1 - \hat{\phi}_2\right)\right) = kTr\left(\left(\frac{1}{2} - \chi\right) + \frac{\hat{\phi}_2}{3} + \frac{\hat{\phi}_2{}^2}{4} + \ldots\right) \quad (29)$$

Thus, for $\chi = {}^1/_2$, the attractive and repulsive forces exactly balance for $\hat{\phi}_2 = 0$ ($x \rightarrow \infty$), but not for $\hat{\phi}_2 > 0$. The ternary and higher order excluded volume interactions cause some small chain expansion at Θ. Such an effect has been predicted by de Gennes,[6] Sanchez,[23] and Oono.[45]

When $\chi > {}^1/_2$, the attractive forces are large enough to be dominant for small $\hat{\phi}_2$. For large x, the attractive interactions dominate (that is, there is a force to make large chains contract), while for small x, the repulsive ones do (there is a force to expand small chains). The minimum in $A(s)$ will occur for some finite x, as seen in Figure 3, where $A(s)$ is plotted vs. x for $\chi = 0.56$ ($T/\Theta = 0.9$). As temperature is lowered, the average chain size decreases.

The definition of dilute, semidilute, and concentrated solutions becomes clearer when $P(s)$ is examined. In Figure 4 the dependence of $P(s)$ on ϕ_2 for a good solvent is shown schematically. In Figures 4a and 4b are shown $P_0(s)$, the ideal distribution,[41] and $P_i(s)$, the distribution for an isolated chain,[23] respectively. Here α_0 ($= \langle x \rangle$ ($\phi_2 = 0$)) is the expansion factor at zero concentration (see below). Because the solvent is good, $\alpha_0 > 1$. By the screening length approximation, $P(s)$ will be some combination of these isolated and ideal distributions. Recall that when $x > x_s$, $\phi_2 = \phi_2$ so $A(s) = 0$ and $P(s) = P_0(s)$. This is equivalent to the statement that when the chains are so large, the intramolecular interactions are screened. But when $x < x_s$, $\phi_2 = \phi_s$ and $P(s) = P_i(s)$; small chains have no screening.

In dilute solution x_s ($\sim \phi_2{}^{-1/3}$) is large, since here a chain must be very large to overlap with its neighbors. Thus, the dilute region may be defined as that in which $x_s > \alpha_0$, as shown in Figure 4c. (The solid line is that portion of $P(s)$ from $P_0(s)$; the dashed portion that from $P_i(s)$.) Since only the largest configurations have screening, $P(s)$ is nearly the same as $P_i(s)$ and the dimensions are nearly those of an isolated chain.

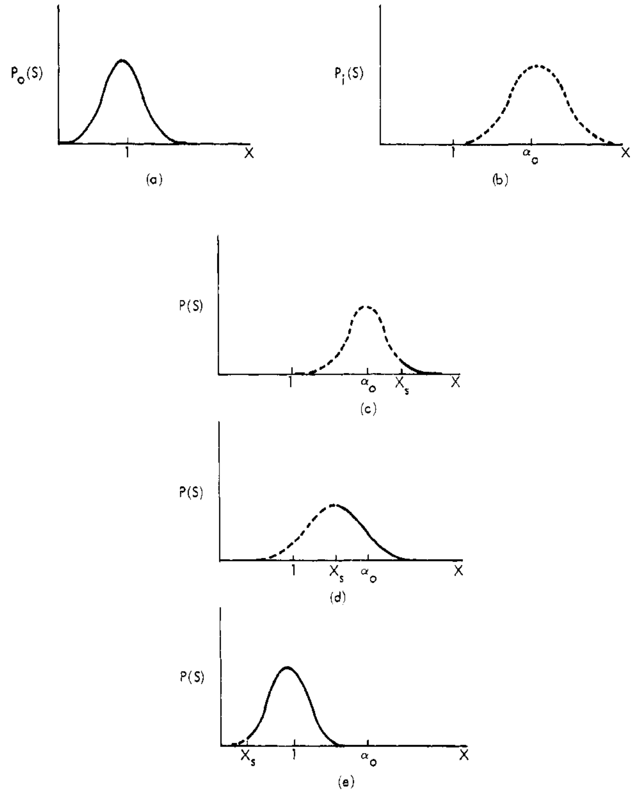

Figure 4. Dependence of $P(s)$ on concentration in good solvent: (a) ideal distribution, $P_0(s)$; (b) isolated chain distribution, $P_i(s)$; (c) dilute solution ($x_s > \alpha_0$); (d) semidilute solution ($\alpha_0 > x_s > a$); (e) concentrated solution ($a > x_s$).

Similarly, in a concentrated solution x_s is quite small, as the chain must coil up very tightly to avoid overlap. The crossover from the concentrated to semidilute region occurs when a significant number of the configurations are smaller than x_s. Since the ideal distribution, $P_0(s)$, is the same for all types of chains, the crossover may be defined as $x_s < a$, a constant. The value of a is somewhat arbitrary; here it is taken as 0.65, since P_0 ($x = 0.65$) is half the value at maximum. Since only a few configurations are smaller than x_s in this regime, $P(s) \approx P_0(s)$.

In semidilute solutions, x_s has a value between α_0 and a. This means that a good deal of the configurations are screened but also that about the same number are not. As shown in Figure 4d, $P(s)$ shows a maximum somewhere between α_0 and 1. It is in this region that the average chain dimensions change between the isolated and ideal value. This will be seen in the next section.

In a poor solvent, the same sorts of arguments may be used, but the results are quite different. This is due to the fact that the chains have a tendency to contract here, that is, $\alpha_0 < 1$. In Figures 5a and 5b we again show the ideal and isolated chain distributions, respectively. The dilute region (Figure 5c) will here be defined as $x_s > 1$, since it is in this region that nearly all configurations are not screened. Again, the concentrated region is defined by $x_s < \alpha_0$ (Figure 5e); here $P(s) \approx P_0(s)$. This is quite similar to the good-solvent cases. But, now, the intermediate region for poor solvents ($1 > x_s > \alpha_0$) is quite different from the semidilute region. In Figure 5d we notice that $P(s)$ is bimodal; instead of a single maximum between 1 and α_0, there are two maximums, one at $x = \alpha_0$ and the other at

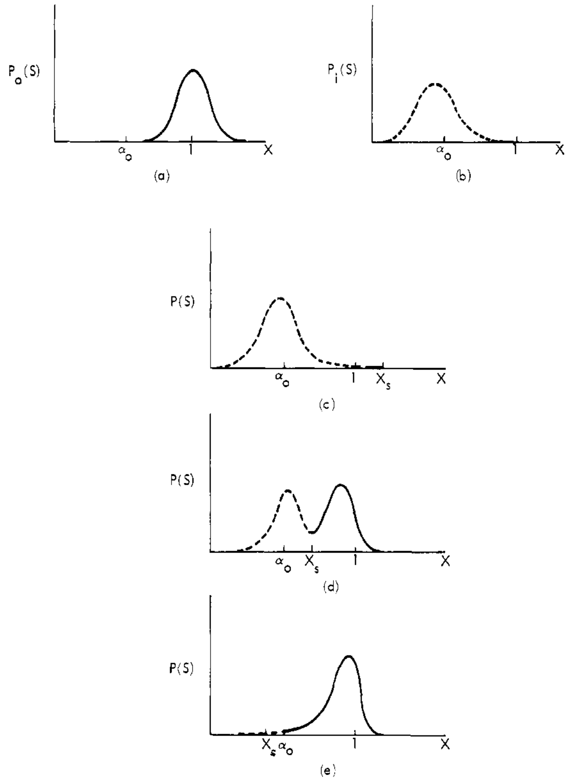

Figure 5. Dependence of $P(s)$ on concentration in poor solvent: (a) ideal distribution, $P_0(s)$; (b) isolated chain distribution, $P_i(s)$; (c) dilute solution ($x_s > 1$); (d) intermediate ($1 > x_s > \alpha_0$); (e) concentrated solution ($\alpha_0 > x_s$).

$x = 1$. This is an indication of the onset of phase separation. The solution separates into a dilute phase of collapsed, isolated coils and a concentrated phase of overlapping chains with nearly ideal dimensions. As shown in the next section, this is borne out by the chain dimension results.

IV. Expansion Factor

Now that the partition function has been completely determined, all the thermodynamic functions can be determined. For example, as discussed in ref 43, this model predicts that in good solvent the second virial coefficient is proportional to the $-{}^1/_5$ power of molecular weight, which has been observed in many experiments.[46-54] The quantity chosen here to illustrate the predictions of this model is the expansion factor, α, defined as

$$\alpha^2 = \langle x^2 \rangle = \frac{\int \mathrm{d}s\ s^2 P_0(s) e^{-\beta A(s)}}{\langle s^2 \rangle_0 \int \mathrm{d}s\ P_0(s) e^{-\beta A(s)}} \tag{30}$$

This is chosen because it has been the touchstone for the earlier theories[17] and the more recent scaling theories.[1-7]

In general, the concentration dependence of α^2 is as described above during the discussion of $P(s)$. Figure 6 is a plot of log α^2 vs. log ϕ_2 for good solvent ($\chi = 0$) and $\phi_i = 1.837$ (a geometrical factor for flexible linear chains). The three regions of concentration are quite distinct. At low concentration, α^2 has a nearly constant value, which is that of the isolated chain, α_0. Increases in ϕ_2 here result in very slight decreases in α^2, since only some of the larger configurations overlap. Significant changes in α^2 start at $\phi_2 = \phi^*$, the *crossover concentration*. This is where $x_s = \alpha_0$ so we have

$$\phi^* = \phi_0/\alpha_0^3 \tag{31}$$

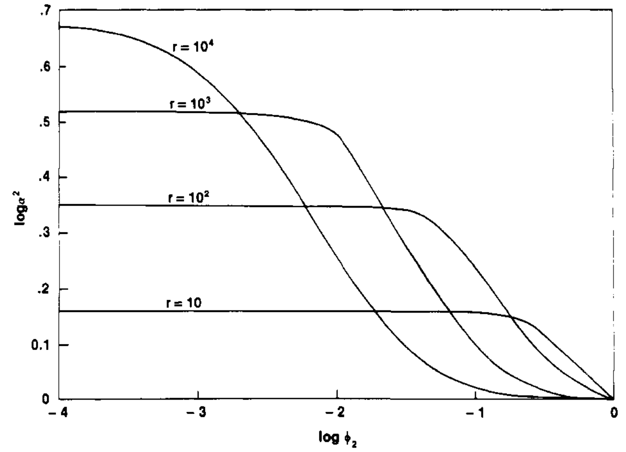

Figure 6. Chain length dependence of chain dimensions ($\chi = 0$, $\phi_i = 1.837$).

In good solvent $\alpha_0^2 \sim r^{1/5}$, so $\phi^* \sim r^{-4/5}$. At $T = \Theta$, α_0 is independent of r and $\phi^* \sim r^{-1/2}$. In poor solvent $\alpha_0^2 \sim r^{-1/3}$ so ϕ^* is independent of r.

At high concentrations also the dimensions vary little with ϕ_2. Here α has nearly reached the ideal chain value of 1. As the solution is diluted here, there is a slight rise in α^2 because very small configurations do not experience overlap. Their probability of occurring is thereby reduced, as discussed above. The crossover to the semidilute region, where the dimensions begin to increase significantly is at $\phi_2 = \phi^{**}$. This occurs for $x_s = a$. This value of a is discussed below; using it, ϕ^{**} can be written as

$$\phi^{**} = \phi_0/a^3 \tag{32}$$

Since a depends on the form of $P_0(s)$, it should not depend on r; thus $\phi^{**} \sim r^{-1/2}$ for all temperatures. Of course, ϕ^* and ϕ^{**} should not be considered as sharp cutoffs but rather as indications of broad regions over which crossover occurs.

The transition from $\alpha \simeq \alpha_0$ to $\alpha \simeq 1$ takes place between ϕ^* and ϕ^{**} in the semidilute region. One notices immediately on looking at Figure 6 that dimensions here do depend on r, unlike the results of the scaling theories.[1-7] In the semidilute region a significant portion of the chains are still characterized by the isolated distribution, which depends on r. Since the chains are here allowed to take on all possible sizes, the small isolated chain sizes make a contribution which is a function of r. This is true until the concentrated region is reached.

There is an approximate power law dependence of α^2 on ϕ_2 in the semidilute region, albeit with an exponent that depends on r. This exponent, l, is the slope of the log α^2 − log ϕ_2 curve in this region, so l can be found from the values of α_0^2, ϕ^*, and ϕ^{**}

$$l = \frac{2 \log \alpha_0}{\log \phi^* - \log \phi^{**}} \tag{33}$$

or, since $\phi^* = \phi_0/\alpha_0^3$

$$l = -\frac{2 \log \alpha_0}{3 \log \alpha_0 + \log (\phi^{**}/\phi_0)} \tag{34}$$

First consider two cases. Suppose that the chains are modeled as spheres which can contract or expand but never overlap (soft impenetrable spheres). This is the model of Rudin and Wagner.[55] Then $\phi_2 = \phi_s$ for all $\phi_2 > \phi^*$, since all the spheres are touching. Thus, $\alpha^2 = 1$ when $\phi_2 = \phi_0$, so $\phi^{**} = \phi_0$. This gives $l = -{}^2/_3$. Since there is no overlap, this is the steepest possible slope.

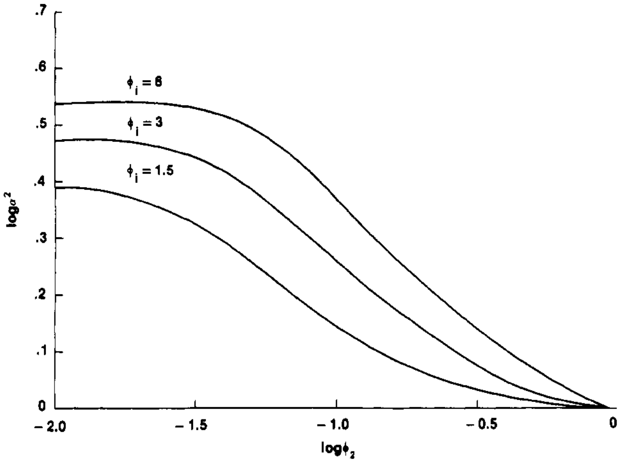

Figure 7. Intrinsic density dependence of chain dimensions ($\chi = 0$, $r = 250$).

As a second example, suppose that, for $\phi_2 > \phi^*$, chain dimensions were independent of r so that ϕ^{**} is a constant, independent of r. Since $\alpha_0^2 \sim r^{1/5}$ and $\phi_0 \sim r^{-1/2}$, for large r the slope is

$$l = \frac{-\frac{1}{5}\log r}{\frac{3}{10}\log r + \frac{1}{2}\log r} = -\frac{1}{4} \qquad (35)$$

which is the scaling result.[1-7] In this model, ϕ^{**}/ϕ_0 equals a constant, a^{-3}. The condition on a is that, in the ideal case, there are very few configurations such that $x < a$. Here, $P_0(s) = (x^6 e^{-7/2x^2})^{1/2}$ has been used;[41] in this case, P_0 ($x = 0.65$) is half the maximum value of P_0, which occurs at $x = (6/7)^{1/2}$. Since only 11% of the configurations are smaller than this, we use this value of a to define ϕ^{**}. Thus we have

$$l^{-1} = -1.5\left(1 - \frac{\log a}{\log \alpha_0}\right) \qquad (36)$$

If we also use (from isolated chain calculations[23])

$$\alpha_0^5 - \alpha_0^3 = \tfrac{3}{14}\phi_i r^{1/2} + O(1) \qquad \text{(good solvent)} \quad (37)$$

we find exactly the slopes calculated by this model. Since α_0 depends on r and ϕ_i (chemistry), so will the slope in the semidilute region. As $\alpha_0 \rightarrow 1$, $l \rightarrow 0$, since the chains have ideal dimensions then over the whole concentration range. When α_0 increases (because either r or ϕ_i increases) l becomes more negative; that is, there is a steeper drop in the dimensions. As $\alpha_0 \rightarrow \infty$, $l \rightarrow -2/3$, which, as mentioned in the soft, impenetrable sphere example, is the steepest possible slope. (That dimension depends on r in the semidilute region has received some support from viscosity measurements.[56])

It may seem somewhat contradictory that the long-chain limit for the overlapping chains should give the same slope as the soft, impenetrable spheres. The chains become more and more penetrable as x increases (the average self-density of an isolated chain, ϕ_2, is ϕ_s ($x = \alpha_0 = \phi_0/\alpha_0^3 \sim r^{-4/5}$). However, because the longer chains are larger, they have more overlap and so more screening. (Since $x_s \sim \phi_2^{-1/2} r^{-1/6}$, the screening length for long chains is quite small.) Thus, they approach ideal conditions much more rapidly.

As indicated by eq 37 for dilute solutions, chain dimensions increase with increasing intrinsic density, ϕ_i. This is shown over the whole concentration range in Figure 7 for good solvent (here $r = 250$, $\chi = 0$). The greater the segment density, the greater is the number of excluded volume interactions, so the chains must be expanded on average. This means that branched molecules are predicted to show a larger expansion factor than linear molecules of the same molecular weight. This has also been predicted by Kholkov.[57]

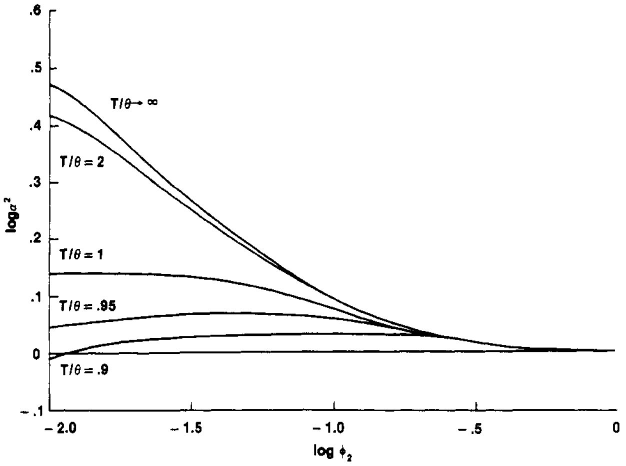

Figure 8. Temperature dependence of chain dimensions ($r = 100$, $\phi_i = 1.837$).

Finally, the dependence of α^2 on χ (temperature and solvent quality) is shown in Figure 8 for $r = 100$ and $\phi_i = 1.837$. The trends are as expected from the discussion of the dependence of $A(s)$ on χ above. At low concentrations, isolated chain behavior is seen.[23] The behavior for temperatures between Θ and the critical point for phase separation is interesting. Initially, as concentration increases, the dimensions at such temperatures increase. This is because of the dominance of the attraction the chains have for one another (which, at lower temperatures, leads to phase separation). The chains actually expand beyond the ideal size and then shrink after some concentration. At high concentrations, α^2 is nearly independent of χ, since the segment density field is nearly homogeneous. It is also interesting to note that the dilute-solution dimensions at $T = \Theta$ are *not* ideal, but that $\alpha^2 > 1$. From isolated chain theory[23]

$$\alpha_0^8 - \alpha_0^6 = \phi_i/7 + O(r^{-1/2}) \qquad (\Theta \text{ solvent}) \quad (38)$$

The ternary and higher order excluded volume interactions cause chain expansions even at $T = \Theta$.

V. Comparison with Experiment

As mentioned in the Introduction, one of the great impetuses for the increased interest in polymer solutions is the advent of new experimental techniques by which chain dimensions can be measured over the complete concentration range. Because of the labeling techniques used in small-angle neutron scattering, it is possible to "see" a single chain in a sea of many similar chains.[10] One of the first uses of the technique was to measure chain dimensions of bulk polymers[58,59] and soon thereafter of semidilute and concentrated solutions.[11] Although much has been done, much remains to be done, such as measurements of dimensions in Θ solvents and an investigation of the molecular weight dependence of α^2 in semidilute solutions.

The measurement of the concentration dependence of chain dimensions in good solvent was done by Daoud et al.[11] on polystyrene in carbon disulfide. In the semidilute region (the crossover concentration is approximately 7.5%), α^2 shows a power law relation with ϕ_2 with an exponent of $-1/4$, within experimental error. This agrees with the scaling theory predictions. However, the data also agree nearly as well with the present theory, as shown in Figure 9. Here the data of Daoud et al.[11] are plotted along with the prediction of this model for $\chi = 0.25$ (based on the

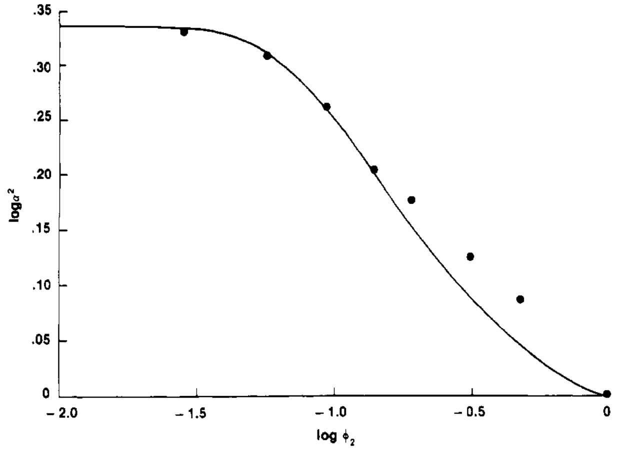

Figure 9. Comparison of theory (——) with data of Daoud et al.[11] (●).

cited value of A_2), $r = 150$ (based on a characteristic ratio of 7), and $\phi_i = 2.75$. The agreement is to within experimental error.

The extremely high value of the zero-concentration expansion factor is difficult under either model. If the value of $\alpha_0{}^2 = 2.79$ is accepted, then the crossover concentration is at 1.5%, instead of the 7.5% expected by the authors. Based on "blob" model calculations of Akcasu and Han,[60] $\alpha_0{}^2 = 1.98$ for this case, which is close to the mean field prediction as well. It should be noted that the zero-concentration measurement was performed in a manner different from those at finite concentration.

A SAXS study has been done by Hayashi, Hamada, and Nakajima[9,61,62] on polystyrene in toluene, a good solvent. Some of the chains were tagged with iodine to provide contrast in electron density for the X-ray scattering. A much sharper decrease in chain dimensions with concentration is noticed. However, it should be pointed out that such labeling changes the chemistry and physics of the chains and may lead to association and segregation effects not seen in unlabeled polymer. The interpretation of such experiments is therefore questionable.

Other evidence concerning chain dimensions in solution can be obtained from Monte Carlo simulations.[63-72] There have been a large number of such studies, looking at chains on a variety of lattices as well as chains off lattice. Because the number of possible configurations goes up rapidly with chain length, the longest chains considered so far are of $r \approx 120$. The general result from such studies is that chain dimensions do depend on r for such short chains, with a steeper drop of dimensions in the semidilute region as r increases, as predicted herein. For example, the work of Bishop et al.[72] gives exponents of −0.05 for $r = 5$ and −0.22 for $r = 70$. These values are still below the $-{}^1/_4$ predicted by scaling. Whether more negative exponents are reached for still longer r is still to be determined.

There has been less work done on chain dimensions in Θ solvents. Some SANS work indicates that chains in dilute solutions at the Θ temperature are slightly expanded compared to chains in the bulk.[58,59,73-75] Hayashi, Hamada, and Nakajima[76] have also performed SAXS measurements on polystyrene in *trans*-decalin, which is a Θ solvent at 21 °C. They find that α^2 is nearly constant with respect to concentration, but there is quite a bit of scatter in these data. (Recall the caveats mentioned above for SAXS experiments at high concentrations.) Recently, Nose and Chu[77] have performed some light scattering experiments on a high molecular weight (10^7) polystyrene in *trans*-decalin. For $T = \Theta$, the dimensions decrease with increasing temperature, as predicted by this model. The temperature at which the zero-concentration dimensions become ideal is several degrees below Θ. Slagowski et al.[78] and Bauer and Ullman[79] have measured the dimensions of PS in dilute solution near and below Θ by light scattering, and these results fit the mean field isolated chain theories well.[23,80] Moreover, chain expansion at Θ has been observed in computer experiments by Okamoto,[71] Olaj and Pelinka,[81] and Curro and Schaeffer.[82]

To see how experiment matches the predictions of the effect of ϕ_i, the intrinsic density, experiments comparing branched and linear molecules are useful. Light scattering experiments of Candau, Rempp, and Benoit[83] and also of Zilliox[84] on polystyrenes in cyclohexane have shown that branched molecules are more expanded than linear ones at $T = \Theta$. Moreover, the temperature for which the dimensions become ideal is lower for the branched molecules. The same result comes from computer simulations on star and comb molecules done by Mazur and McCrackin.[85] This is all as predicted by this theory.

VI. Summary

The best way to summarize the model presented here is to compare it with the scaling theories.[1-7] The mean field theory developed here considers the polymer solution as incompressible and on a lattice. It represents an improvement over the Flory–Huggins[12,13] and lattice fluid[42] theories in that the effect of concentration on the local density of segments, $\hat{\phi}_2$, is considered. The distribution of chain sizes (radii of gyration) is found and then the average chain dimensions are calculated. The central role is played by a screening length, x_s, which is a function of chain length, the structure of the chain, and concentration. When the chain is larger than the screening length, it overlaps neighboring chains to a large extent so that intramolecular effects are screened out. If the chain is smaller, there is no screening. Thus, fluctuations in segment density within the volume pervaded by the chain are ignored (because it is mean field), but density fluctuations due to the distribution of chain size are explicitly considered. In scaling theories the first effect is included while the second is not. There the screening length is a measure of segment density fluctuations in the coil volume.

In terms of chain dimensions, these two approaches give the same general results—the existence of three concentration regions, dilute, semidilute, and concentrated solutions. The exact dependences of α^2 on ϕ_2 and r vary somewhat. In good solvents this mean field theory predicts an approximate power law dependence of α^2 on ϕ_2 in semidilute solutions, with the exponent a function of r; for scaling the exponent is $-{}^1/_4$ for all r. In Θ solutions scaling predicts dimensions independent of concentration; the prediction of this mean field model is that chains are slightly expanded in dilute solution and shrink to ideal values as concentration increases. This model also predicts that branched molecules are more expanded than linear molecules of equivalent molecular weight.

The experimental evidence discussed in the preceding section does not provide clear support for either model. The SANS data go along with both; clearly there is a need here for more extensive measurement at a number of molecular weights and temperatures. The computer experiments lend some support to the mean field theory, but since the chains studied are so short, they are outside the range of validity for the assumptions made for the scaling theories. In Θ solvents as well the computer experiments, and also some light scattering work, agree with the predictions of the model here. Again, however, there is a need for a study of Θ dimensions by SANS.

To model a polymer solution well, it is critical to accurately know the segment density of the solution and its fluctuations. Such fluctuations come from two sources in incompressible, monodisperse solutions: fluctuations over the volume that the chain pervades and fluctuations in the size of the chain. A complete theory would account for both, but this is difficult since the two effects are strongly coupled. The key to handling both may be in the dynamics of the solution. The effects described herein result from the ability of the chains to have a wide variety of sizes. The importance of such effects may be determined by how effectively (or how rapidly) the chains can sample such a distribution. This in turn depends on such factors as entanglements which have not been included here. If they were, a more complete theory may well be produced.

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