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Simple Models for Interactions of Linear Polymers in Dilute Solutions

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ABSTRACT: A simple mean-field approach that was introduced by DiMarzio for the description of the collapse transition of linear polymers in dilute solutions is extended to the case of interacting polymers. We discuss the potential of mean force between two identical molecules and the resulting second osmotic virial coefficient. In the good-solvent range, this approach yields results which are very similar to those of the Flory–Krigbaum theory. While the direct extension of DiMarzio's approach leads to unphysical behavior near or below the Θ-point, a modified treatment which combines elements of both his and Flory and Krigbaum's approach leads to results which are physically reasonable also in the latter case. The theory also yields information on how the average size of interacting molecules changes with their intermolecular separation; the results are in good qualitative agreement with simulation results given in the literature. The paper closes with a discussion of the potential of mean force between a linear polymer and a hard wall.

1. Introduction

Properties of polymer molecules in dilute solutions have been the subject of continuing interest since the pioneering work by Flory in the late 1940s.[1] Problems that have been studied in great detail both theoretically and experimentally are the molecular-weight dependence of the typical size of single molecules and the possibility of a collapse transition from an expanded coil to a collapsed globule state at a particular temperature, the "Θ-temperature". Much work has also been directed toward understanding the characteristic interactions between two polymer molecules with mutual overlap; the relevant quantity here is the effective interaction potential (or, in other words, the potential of mean force) which directly yields the osmotic second virial coefficient of the polymers in solution. On the theoretical side, the treatments of these problems range from mean-field type of approaches, which are more in the spirit of the original work of Flory and co-workers, to scaling analysis and rather sophisticated renormalization group methods, to numerical studies which include both molecular dynamics and Monte Carlo simulations. For a survey of the field, the reader is referred to a number of books and review articles.[2-5] Generally speaking, one can say that all these approaches have led to a rather detailed insight into the above-mentioned problems.

In the present paper we take up, once more, the problem of interactions of polymer molecules in dilute solutions. However, in doing so, we are *not* striving for more detail or sophistication but rather the opposite; we are trying to keep the discussion as simple as possible. Our work is motivated by a paper by DiMarzio[6] in which he describes a very simple approach to the polymer collapse transition which, within the limitations of mean-field theory, yields the correct qualitative features of both the extended and the collapsed state of a linear polymer. The same approach has recently also been successfully applied to star polymers.[7] Here we address the question of whether it is possible to extend this "simplest possible treatment"[6] to the case of interacting polymers. It is, of course, clear that one cannot expect such a simple approach to do much better than already existing, more elaborate treatments of the same problem. However, we believe that the discussion of both its merits and limitations is of interest because it may provide a better understanding of certain aspects of the problem. Moreover, we will see that it yields results for quantities that have so far only been studied by numerical simulations.

DiMarzio's treatment of the polymer collapse transition is probably the simplest example of the mean-field approaches (cf. ref 8 and references therein[9]) that have been developed as extensions of Flory's classical theory[1] of "real" chains in dilute solutions. DiMarzio treats a polymer molecule of end-to-end distance ("size") R as a penetrable sphere of diameter R that is characterized by a *constant* polymer–segment density throughout its volume. The statistical weight (probability) associated with a particular value of R is estimated by correcting the corresponding weight of an ideal, noninteracting chain with respect to interactions of and between segments; the latter are treated within the standard mean-field approximation. The statistical weight yields a size-dependent free energy, and it is assumed that the minimum of this free energy determines the average properties of the ensemble of all possible chain configurations. In particular, the average size is identified with the value that minimizes the free energy or, in other words, with the most probable value of R. A more detailed discussion of DiMarzio's approach will be given in section 2.

In section 3 we extend this approach to the case of two interacting (identical) polymer chains in solution. For fixed intermolecular separation r, we calculate the size-dependent statistical weight (and thus the corresponding free energy) of the two (possibly) overlapping molecules. Minimization with respect to size yields the overall free energy for given r ("saddle-point" approximation), and comparison with the free energy at infinite separation directly yields the potential of mean force. For comparison, we also consider the potential that is obtained if the interacting molecules do not "adjust" their size to their separation r; i.e., instead of minimizing the mutual free energy, we simply take the value which corresponds to the overlap of two molecules of optimum size in the isolated, "free" case. In the good-solvent range, i.e., at temperatures well above Θ, both potentials are found to be physically reasonable in the sense that they are very similar to the "classical" (mean field) result of Flory and Krigbaum.[10] In the Θ- and poor-solvent range, however, we obtain a rather unphysical behavior of the interaction potential as well as of the second virial coefficient. This unphysical behavior is found to mainly stem from the

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rather crude assumption of constant segment density throughout the volume occupied by the molecule.

In section 4, we introduce a somewhat modified approach which allows for spatial variations of the segment density. In analogy to the original work by Flory and Krigbaum, a Gaussian density is assumed. Unlike their theory, however, the present approach is not restricted to the case of good solvents. The reason for this is that higher order terms in the free energy, which were neglected by Flory and Krigbaum and which become important when the chains are compact, are now taken into account. In this respect, our treatment is closely analogous to that of Orofino and Flory[11] in the late 1950s. The result for the interaction potential is (again within the limitations of a mean-field theory) now physically reasonable for all solvent conditions, i.e., also for Θ and poor solvents (quasi-ideal and collapsed chains, respectively) if the molecules are not assumed to adjust their size to the intermolecular distance. In contrast, the potential associated with the saddle-point approximation for the mutual free energy still shows some physically unreasonable features in poor solvents.

Furthermore, the approaches discussed here yield—in a relatively natural way—results for the dependence of the size of the polymer molecules on their intermolecular separation. This dependency is of interest in that its knowledge, together with that of the intermolecular potential, can provide information on how the average polymer size changes with concentration in dilute solutions. As far as we know, the problem of how the size of two interacting polymers varies with separation has so far only been studied by numerical simulations.[12-14] The Gaussian density model leads to results which are in good qualitative agreement with those observed in these simulations.

For completeness, we remark that there are several approaches in the theory of (moderately) concentrated polymer solutions that are partly based on ideas similar to those discussed here. Examples are the "cell model theory" by Sanchez and Lohse,[15] which is based on the assumption that the intermolecular interaction energy is proportional to the volume of overlap of two (spherical) polymers (cf. our section 2), and the work by Fixman and Peterson,[16-18] who attempted to obtain both the free energy and the chain dimension behavior by using concentration-dependent interaction potentials and radial distribution functions.

In section 5 we discuss a way to extend DiMarzio's simple approach to the interaction of a single polymer molecule with an infinitely repulsive (hard) wall. This situation might be viewed as the limiting case of the interaction of a polymer with a large hard sphere. The knowledge of the corresponding interaction potential is thus of potential interest for cases involving interactions between colloidal particles and polymers in dilute solutions. The results following from our simple approach are compared to exact results for ideal chains[19] and with simple scaling predictions for "real" chains. Our results indicate that corrections to simple scaling behavior might be rather important, particularly in good solvents.

Section 6 contains concluding remarks.

2. DiMarzio's Approach to the Polymer Collapse Transition

In this section we introduce the basic features of DiMarzio's approach[6] to the collapse transition of linear polymers. At the same time, this section also serves an an introduction of the basic notation used throughout this paper.

The collapse transition of a polymer from an expanded coil to a collapsed globule is due to the competition between the repulsive and attractive parts of the (solvent-mediated) interactions between the segments of the polymer. In simple terms, the situation may be described as follows: In the good-solvent case, i.e., at temperatures T above the Θ-temperature (which is characterized by a net compensation of the overall effects of repulsion and attraction) the repulsive interactions, which essentially correspond to excluded-volume interactions between segments, are dominating and the chain is swollen. For long chains, the typical size R, which might be identified with the root-mean-squared displacement or the radius of gyration, is proportional to n^{ν}, with $\nu \approx 3/5$ in dimension $d = 3$ (n denotes the number of segments). In the poor-solvent case, i.e., at temperatures T below Θ, the attractive interactions dominate and the chain is collapsed into a globular state; the typical size scales like $n^{1/3}$ in $d = 3$. At the Θ-point, the chain behaves quasi-ideally; i.e., the size scales like that of an ideal chain with no interactions at all ($R \propto n^{1/2}$). [It should be remarked that the latter criterion actually is one of several possible definitions of the Θ-temperature; other definitions given in the literature refer, e.g., to the vanishing of the second osmotic virial coefficient. A discussion of the relation between these different definitions can be found, for instance, in ref 20]. For an overview of the status of the field, the reader is referred to the more recent review cited in the introduction; another useful reference is a review article written by Williams et al. in the early 1980s.[8]

DiMarzio's description of the collapse transition, which yields the basic qualitative features described above, i.e., both the 3/5 and 1/3 laws, corresponds to a simple mean-field (MF) approach that is very much like Flory's original treatment of real chains in good solutions (by which the latter derived the exponent 3/5). As we will see, one of the main advantages of DiMarzio's approach is that it is conceptually very simple—which is exactly the reason why we take it as the starting point for the discussion in this paper.

In the following we consider linear polymers with n segments of size l. For simplicity, it is assumed that the segments are spherical; with l taken to be their diameter, the volume of a segment is $v \equiv (\pi/6)l^3$. The length scale will be fixed by setting l equal to 1. The interactions that will be taken into account are excluded-volume interactions between all segments, and short-range interactions of segments between themselves and with surrounding solvent molecules.

DiMarzio's approach begins by classifying the different possible configurations of the molecules according to their "size" R, which is taken to be the end-to-end distance. In order to calculate average properties, for example the average size (the root-mean-squared end-to-end distance), DiMarzio develops estimates for the statistical weight $W(R)$ associated with a particular value of R; $W(R)$ may be written as

$$W(R) = \exp[-f(R)] \triangleq \exp[-F(R)/kT] \tag{2.1}$$

where $F(R)$ is the free energy of the (sub)ensemble of all molecules of size R, k is Boltzmann's constant, and T is the temperature. With $W(R)$ given (see below), averages over the whole ensemble could, in principle, be performed exactly by integrating over all R. For example, the mean-squared end-to-end distance is given by $\langle R^2 \rangle = \int_0^\infty R^2 W(R)\,\mathrm{d}R / \int_0^\infty W(R)\,\mathrm{d}R$. However, since these integrations typically cannot be performed in closed form, the quantities of interest are discussed in terms of a simple saddle-point argument involving the most probable value R_0, i.e., the value of R that maximizes W (or minimizes f, respectively). Thus, the average size is simply assumed to be given by R_0. The corresponding approximation for the overall free energy $\mathcal{F}$ similarly reads

$$\exp(-\mathcal{F}/kT) = \int W(R)\,\mathrm{d}R = \int \exp[-f(R)]\,\mathrm{d}R \approx \exp[-f(R_0)] \quad (2.2)$$

We will refer to this approximation when we discuss the potential of mean force of two interacting molecules (section 3).

The statistical weight $W(R)$ is written as a product of two terms:

$$W(R) = W_G(R)\,W_I(R) \quad (2.3)$$

The first term

$$W_G(R) = R^2 \exp[-(3/2)R^2/n] \quad (2.4)$$

corresponds to the usual Gaussian distribution of the end-to-end distance of ideal chains. It would be the only term present if there were no interferences between the segments. While (2.4) gives the correct result $\langle R^2 \rangle = n$, the value of R which maximizes W_G is given by $R_0^2 = (2/3)n$. To get rid of the "unwanted" prefactor 2/3, DiMarzio suggests maximizing $RW(R)$ rather than $W(R)$; this is formally equivalent to simply writing the Gaussian free energy $f_G(R) \equiv -\ln[W_G(R)]$ as

$$f_G(R) = (3/2)R^2/n - 3\ln(R) \quad (2.5)$$

The second term $W_I(R)$ in (2.3) corrects for the interactions present in the real, nonideal chain. It is estimated on the basis of the following simple picture: The polymer of size R (or, more precisely, the ensemble of all such polymers) is viewed as a "fuzzy" sphere of diameter R and uniform segment volume fraction

$$\phi = nv/V = n/R^3 \quad (2.6)$$

throughout its volume $V = (\pi/6)R^3$. Since the chain segments are assumed to be randomly distributed in V, correlations between segments along the chain are totally neglected. The resulting expression for $W_I(R)$

$$W_I(R) = \left[\prod_{j=1}^{n}\left(1 - \frac{(j-1)v}{V}\right)\right][\exp[-\chi n(1-\phi)]] \quad (2.7)$$

is now easily understood. The first term is the correction for excluded-volume interactions between segments. The jth factor of the product corresponds to the probability of inserting the jth segment assuming that the chain is constructed segment after segment beginning with one end. In this approximation, it only depends on the volume fraction created by the first $j-1$ segments. The second term accounts for the effect of additional short-range interactions between segments and solvent molecules. χ is the usual Flory parameter; in a lattice picture

$$\chi = \frac{z}{kT}[\epsilon_{ps} - (1/2)(\epsilon_{pp} + \epsilon_{ss})] \equiv \frac{z\Delta\epsilon}{kT} \quad (2.8)$$

where z denotes the number of nearest neighbors of a solvent molecule (s) or a polymer segment (p) and the $\epsilon_{\alpha\beta}$ are the corresponding nearest-neighbor interaction energies. Positive values of χ correspond to situations where contacts between polymer segments are energetically favorable (attractive case) while negative values of χ indicate that segment–segment contacts are energetically unfavorable (repulsive case).

Using the relation $\prod_{j=0}^{n-1}(1-j/N) = N!/[(N-n)!N^n]$ and applying Stirling's formula, one obtains the following expression for the free energy associated with $W_I(R)$:

$$f_I(R) = (V/v)[(1-\phi)\ln(1-\phi) + \phi + \chi\phi(1-\phi)] \equiv (V/v)g(\phi) \quad (2.9)$$

or, with $g(\phi)$ expanded in powers of ϕ

$$f_I(R) = (V/v)\left[(1/2-\chi)\phi^2 + \sum_{k=3}^{\infty}\frac{1}{k(k-1)}\phi^k\right] + n\chi \quad (2.10)$$

[Note that when the relevant values of R are of the order of $n^{1/3+\epsilon}$ ($\epsilon > 0$), $\phi \to 0$ as $n \to \infty$.]

In eq 2.10, the term of order ϕ^2 changes sign at $\chi = 1/2$. This corresponds to a point where—at least to this order in ϕ—repulsive and (effective) attractive interactions between segments compensate each other. Accordingly, the Θ-temperature is introduced via the relation

$$\xi \equiv 1/2 - \chi = (1/2)(1 - \Theta/T) \quad (2.11)$$

or, with (2.8), $\Theta = 2z\Delta\epsilon/k$.

With (2.5) and (2.9), the total free energy $f(R)$ reads

$$f(R) = f_G(R) + f_I(R) = (3/2)R^2/n - 3\ln(R) + (V/v)g(\phi) \quad (2.12)$$

or, after insertion of eq 2.6 for ϕ into (2.10)

$$f(R) = (3/2)R^2/n - 3\ln(R) + \xi n^2/R^3 + \sum_{k=3}^{\infty}\frac{1}{k(k-1)}n^k/R^{3(k-1)} \quad (2.13)$$

[For convenience, we have neglected the R-independent term $n\chi$ in (2.10), which is irrelevant for the following discussions.] Minimization of this expression with respect to R yields the desired quantity R_0. R_0 can, of course, easily be determined numerically for all temperatures and chain lengths of interest. In the following, however, we will only focus on the asymptotic, i.e., large-n, behavior for the three different cases of solvent quality:

(*i*) *Good-Solvent Case* ($T > \Theta$ *or* $\chi < 1/2$)

The ϕ^2 term of f_I is positive; i.e., like all higher order terms of f_I, it tends to expand the molecule. Making the ansatz $R_0 \sim n^\nu$ ($1/2 \le \nu \le 1$), one readily finds that ν takes the value 3/5 and that the asymptotic behavior of R_0 is determined only by the "elastic" Gaussian term and the $O(\phi^2)$ term of f_I; i.e., eq 2.13 can be approximated by

$$f(R) \approx (3/2)R^2/n + \xi n^2/R^3 \quad (2.14)$$

Minimization than explicitly yields

$$R_0 = \xi^{1/5}n^{3/5} \quad (2.15)$$

i.e., essentially the Flory result.

(*ii*) Θ-*Solvent* ($\chi = 1/2$)

By arguments similar to those under (i), one finds that the relevant terms in the free energy are both Gaussian terms plus the first nonvanishing term of f_I

$$f(R) \approx (3/2)R^2/n - 3\ln(R) + (1/6)n^3/R^6 \quad (2.16)$$

and the result for R_0 is

$$R_0 = bn^{1/2} \quad \text{with } b \approx 1.09 \quad (2.17)$$

The fact that the prefactor b is somewhat larger than 1 reflects the influence of the excluded-volume interactions which are, as we see, *not* completely compensated by the "χ-interactions" [Θ-chains are only *quasi*-ideal; for a more detailed discussion of this aspect, see, for instance, the work by Bruns[21-23] and references therein].

(iii) Poor-Solvent Case ($T < \Theta$ or $\chi > 1/2$)

In this case, the ϕ^2 term is negative; i.e., it tends to contract the chain. Stabilization occurs through the higher order terms of f_I. Once can show that the large-n behavior of R_0 is of the general form

$$R_0 = c(T)n^{1/3} \qquad (2.18)$$

The Gaussian contributions can be neglected with respect to f_I while all of the higher order terms of f_I should, in principle, be taken into account in order to estimate the prefactor $c(T)$ [note that $\phi = c^{-1/3}n^0$ with (2.18)]. However, assuming that $c^3 \ll 1$, one might provisionally neglect terms of order ϕ^4. Minimization of

$$f(R) \approx -|\xi|n^2/R^3 + (1/6)n^3/R^6 \qquad (2.19)$$

then leads to

$$c(T) = [3|\xi|]^{-1/3} \qquad (2.20)$$

This result is, however, only valid in a limited χ or temperature range [note that $c \ll 1$ requires that χ is much smaller than 5/6 or T much larger than 0.6Θ].

In his paper, DiMarzio generalized this approach also to arbitrary dimensions d, and he furthermore addressed the question of the order of the transition in the limit $n \to \infty$. Since we have already introduced the basic concepts and results needed for our treatment of interacting polymers, we are not going to comment on these additional results.

We conclude this section with a remark on how one can justify taking the end-to-end distance as the diameter of the "fuzzy" sphere described above. An explanation can be found in Flory's paper.[1] Flory, who derived the average size of an interacting chain under the assumption of a Gaussian segment density around the center of mass (cf. section 4) remarked that almost identical results are obtained when the "actual" Gaussian distribution is replaced by a uniform distribution within a sphere whose radius is very close to half the chain's end-to-end distance (this is the so-called "equivalent sphere"). Here, we may add a simple plausibility consideration which does not involve any knowledge about the effects of intrachain interactions. For the spherical molecule of diameter R, the squared radius of gyration, $S^2(R)$, is easily obtained by integrating s^2 over the distance s of the (uniformly distributed) segments from the center of mass: $S^2(R) = (1/V)\int_0^{R/2} s^2(4\pi s^2)\,\mathrm{d}s = (3/20)R^2$. Now, if we identify the overall average $\langle S^2\rangle$ with $S^2(R_0)$, we have

$$\langle S^2\rangle = (3/20){R_0}^2 \triangleq (3/20)\langle R^2\rangle \qquad (2.21)$$

which is indeed quite close to the well-known exact relation $\langle S^2\rangle = (1/6)\langle R^2\rangle$ for ideal chains.

3. Extension of DiMarzio's Approach to Two Interacting Polymers

In the following, the approach described in the previous section will be extended to the case of two interacting polymer molecules. For simplicity, we will only consider the case of two identical molecules; an extension to the more general case involving molecules of different chain lengths or χ-parameters is relatively straightforward. The main quantity of interest is the potential of mean force $U(r)$ between the two molecules (r is the distance between the centers of mass); it is defined as the change in free energy that arises when the molecules (A and B) are brought from infinite separation to the actual distance r:

$$U(r) \equiv \mathcal{F}_{\mathrm{A,B}}(r) - \mathcal{F}_{\mathrm{A,B}}(r{=}\infty) = \mathcal{F}_{\mathrm{A,B}}(r) - [\mathcal{F}_{\mathrm{A}} + \mathcal{F}_{\mathrm{B}}] \qquad (3.1)$$

$U(r)$ in turn determines the experimentally accessible second osmotic virial coefficient A_2:

$$A_2 \propto \frac{1}{n^2}B \qquad B \equiv \int_0^\infty \{1 - \exp[-U(r)/kT]\}(4\pi r^2)\,\mathrm{d}r \qquad (3.2)$$

where B is the excluded volume.

Part of the motivation for our investigation is the question of whether DiMarzio's simple approach also leads to physically reasonable results when it is extended to more complex systems than single polymers. Since DiMarzio's approach is not restricted to the case of good solvents, it would be interesting to extend it to the case of interacting polymers, thus allowing us to study the behavior of $U(r)$ (or A_2) in the vicinity of and below the Θ-point. In contrast to this, the "classical" MF result of Flory and Krigbaum for $U(r)$ (cf. below) is only applicable to the good-solvent case. Another interesting aspect is, as we have already mentioned in the Introduction, that the present approach also yields information on how the average size of interacting molecules depends on the intermolecular separation. The hope is that we might be able to explain, at least qualitatively, corresponding simulation results for lattice chains that have been published by Olaj and co-workers.[12]

Following the procedure outlined in section 2, we will describe the two polymers as spheres of diameter R_A and R_B. For a given distance r between spheres, we should, in principle, be able to estimate the statistical weight $W_{A,B}(R_A,R_B|r)$ for each possible combination of the two diameters. Saddle-point analysis then involves minimization of the corresponding free energy $f_{A,B}(R_A,R_B|r)$ with respect to both R_A and R_B. However, due to the symmetry between the identical molecules, the saddle-point values of R_A and R_B have to be equal. This allows us to consider, directly from the beginning, only situations with $R_A = R_B \equiv R$. For convenience, we will use the notation $W_2(R|r)$ instead of $W_{A,B}(R,R|r)$. The subscript 2 refers to the number of molecules; accordingly, the subscript 1 will henceforth refer to the statistical weight or the free energy of a single polymer as discussed in section 2.

The statistical weight $W_2(R|r)$ is now easily estimated. First, the Gaussian weight of a molecule is, by definition, not affected by the presence of the other one. Furthermore, at a given distance r, *inter*molecular interactions only come into play if the two spheres overlap. The volume V' of the overlap region is

$$\begin{aligned} V' &= [1 - (3/2)(r/R) + (1/2)(r/R)^3]V \qquad (R \geq r) \\ &= 0 \qquad (R < r) \end{aligned} \qquad (3.3)$$

We assume that a proportional number of segments of each molecule, namely, $n(V'/V)$, is found in the overlap region; the total polymer volume fraction in V' is then simply twice that in the nonoverlap region. Taking the overall statistical weight as the product of the Gaussian weights and those associated with the different partial volumes, we have

$$W_2(R|r) = [W_{1,\mathrm{G}}(r)]^2[W_{1,\mathrm{I}}^{(V-V')}(R|r)]^2 W_{2,\mathrm{I}}^{(V')}(R|r) \qquad (3.4)$$

Here, $W_{1,G}$ and $W_{1,I}$ correspond to the weights W_G and W_I given in the previous section; the superscripts V' and $(V - V')$ explicitly indicate the different partial volumes under consideration. Equation 3.4 leads with (2.9) directly to the following expression for the corresponding free energy:

$$f_2(R|r) = 2f_{1,G}(R) + 2[(V - V')/v]g(\phi) + (V'/v)g(2\phi) \qquad (3.5)$$

Obviously, eq 3.5 can be rewritten as

$$f_2(R|r) = 2f_1(R) + \Delta f(R|r) \qquad (3.6)$$

with $f_1(R)$ being the free energy of a single molecule as given by (2.12) and

$$\Delta f(R|r)(V'/v)[g(2\phi) - 2g(\phi)] \qquad (3.7)$$

explicitly denoting the change in free energy due to the mutual overlap of the two molecules. In view of the discussion at the end of section 2, we can also expand $f_2(R|r)$ in powers of ϕ; after substitution of n/R^3 for ϕ we find, in analogy to (2.13) for $f_1(R)$

$$f_2(R|r) = 3\frac{R^2}{n} - 6 \ln (R) + 2\xi\frac{n^2}{R^3}\left[1 + \frac{V'}{V}\right] + 2\sum_{k=3}^{\infty}\frac{1}{k(k-1)}\frac{n^k}{R^{3(k-1)}}\left[1 + (2^{k-1} - 1)\frac{V'}{V}\right] \qquad (3.8)$$

The further procedure for determining the potential $U(r)$ is now clear. Using the expression (3.3) for V' we minimize (3.8) [or (3.5)] with respect to R; the saddle-point (minimum) value of R will be denoted by $R_M(r)$ in order to distinguish it from R_0, the "optimal" size of an isolated molecule. $R_M(r)$ represents the "adjusted" size of one polymer molecule due to the presence of another molecule at distance r [obviously, $R_M(r \to \infty) = R_0$]. With both $\mathcal{F}_2$ and $\mathcal{F}_1$ approximated by their saddle-point values [cf. (2.2)], the interaction potential (3.1) is then simply given by

$$u(r) \equiv U(r)/kT \approx f_2(R_M|r) - 2f_1(R_0) \qquad (3.9)$$

In analyzing the behavior following from (3.9), it will be useful to compare our results with the classical result of Flory and Krigbaum (FK), which, in our notation, reads

$$u^{FK}(r) = \xi\left(\frac{3}{2\pi}\right)^{3/2}\frac{v}{2^{1/2}}\frac{n^2}{S_0{}^3}\exp[-(3/4)^2r^2/S_0{}^2] \qquad (3.10)$$

The FK potential is based on the assumption that the individual molecules can be described by Gaussian segment densities with fixed width S_0, where S_0 corresponds to the actual root-mean-squared radius of gyration ($\langle S^2\rangle^{1/2}$) of the chains; in principle, S_0 could be taken from any appropriate theory. In the present case, the identification

$$S_0 = (3/20)^{1/2}R_0 \qquad (3.11)$$

(cf. eq 2.21) appears to be the most reasonable choice for the comparison of u^{FK} with u. The way in which Flory and Krigbaum derived the result (3.10) will become clear in section 4, where we discuss an analogous approach; at this point, we only remark that the derivation involves an expression for the free energy which is essentially of the usual MF form [i.e., similar to (2.9)] but includes—as one might already guess from the presence of the prefactor ξ in (3.10)—only terms of order ϕ^2. Therefore, the theory is not expected to yield reasonable results for temperatures T near or below Θ where, as we have seen in section 2, higher order terms become increasingly important. In particular, the theory predicts that $u(r)$ is identically equal to zero at the Θ-temperature. Numerical simulations of Olaj et al., who discussed the properties of the pair potential U at and close to the Θ-point,[24,25] clearly show that this is, as expected, not the case. Furthermore, it should be mentioned that the FK theory also oversimplifies the behavior of the potential in the good-solvent regime. [See, for instance, the numerical investigation of the pair potential of athermal ($\chi = 0$) lattice chains by Olaj and Lantschbauer in the late 1970s.[26] A comparison of the FK second osmotic virial coefficient with those obtained by other, more advanced treatments can be found in ref 3 or 5.] However, in spite of its drawbacks, the FK result for good solvents might still be considered as being "qualitatively reasonable".

For comparison, we will also consider the potential which results when the overlap of two molecules of size R_0 separated by distance r does not result in an "adjustment" in their size (the spheres are "stiff"). This potential is given by

$$u^{st}(r) = f_2(R_0|r) - 2f_1(R_0) = \Delta f(R_0|r) \qquad (3.12)$$

cf. eqs 3.9 and 3.6. It should be noted that this corresponds to the simple approach discussed in the textbook by Hill,[27] although the discussion there was only for good solvents. Note that due to the definition of $R_M(r)$—the "adjusted size" of a molecule—the inequality $f_2(R_0|r) \geq f_2(R_m|r)$ is always fullfilled; therefore, $u^{st}(r)$ will always be larger than $u(r)$ given by (3.9).

We first consider the behavior of R_M and u in the case of good solvents. Under the (reasonable) assumption that, for all distances r, $R_M(r)$ still scales as $n^{3/5}$ as in the single-polymer case, we can proceed in analogy to section 2 (cf. eq 2.14); i.e., we only retain terms up to order $k = 2$ in eq 3.8 for the free energy of the two molecules. After insertion of eq 3.3 for V'/V, we thus obtain

$$f_2(R|r) \approx 3R^2/n + 2\xi(n^2/R^3)\left\{1 + H(r-R)\left[1 - \left(\frac{3}{2}\right)(r/R) + \left(\frac{1}{2}\right)(r/R)^3\right]\right\} \qquad (3.13)$$

where, for convenience, we have introduced a step function $H(x)$ which is 1 for $x \leq 0$ and 0 elsewhere. A closer inspection of (3.13) shows that, when $r > R_0$, $R_M = R_0$, and thus $u(r) = 0$. Hence, we will subsequently only consider the case $r \leq R_0$. It is now convenient to introduce the rescaled variables

$$\rho \equiv R_M/R_0, \qquad x \equiv r/R_0 \qquad (3.14)$$

Minimization of eq 3.13 with respect to R leads to the following equation for $\rho(x)$:

$$\rho^5 = 2 - 2(x/\rho) + (x/\rho)^3 \quad (x \leq 1) \qquad (3.15)$$

This equation can, of course, immediately be solved numerically; however, the essential behavior of $\rho(x)$ can also be obtained by a few simple analytical considerations. First, for $x = 1$, the only solution of (3.15) is $\rho = 1$; this is the situation where the spheres of diameter R_0 are "touching" each other. With decreasing x, ρ first slightly decreases until it reaches its minimum value, $\rho_m = (2[1 - (2/3)^{3/2}])^{1/5} \approx 0.982$, at the distance $x_m = (2/3)^{1/2}\rho_m \approx 0.802$. With further decrease of x, the size increases again, passing through its original value ($\rho = 1$) at $x_1 = (5^{1/2} - 1)/2 \approx 0.618$. Finally, at $x = 0$, the molecules are about 15% larger than their original size [$\rho(0) = 2^{1/5} \approx 1.15$].

This behavior [cf. Figure 1a, which shows $R_M(r)$ exemplarily for $n = 10^4$ and $T = 1.5\Theta$ ($\chi = 1/3$)] can be made plausible if one remembers that in the good-solvent regime, the effective interactions between the chain segments are repulsive. Initially (i.e., at distances $r < R_0$), when the molecules start to overlap, they "try to avoid" interchain contacts by reducing their size. Eventually, however, the repulsive interactions within the molecules prohibit further shrinking; since a rather large overlap is almost unavoidable for small values of r, the only way to compensate this

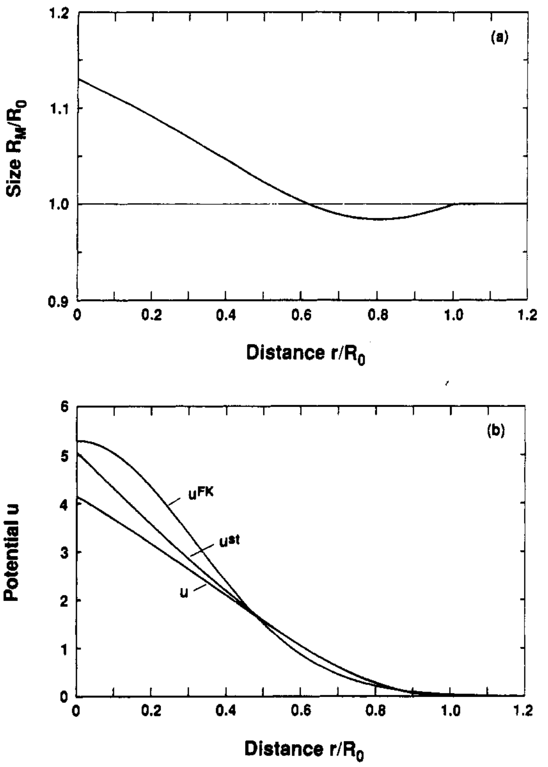

Figure 1. Interaction between two polymers in a good solvent [constant segment density model; $T/\Theta = 1.5$ ($\chi = 1/3$) and $n = 10^4$; $R_0 = 187.8$]. (a) Dependence of the size (end-to-end distance) of the molecules on their intermolecular separation r; (b) potential of mean force: Comparison between $u(r)$ (eq 3.9), $u^{st}(r)$ (eq 3.12), and the Flory–Krigbaum potential $u^{FK}(r)$ (eq 3.10).

unfavorable effect is to diminish the density in the overlap regime by expanding the whole molecule.

The same qualitative behavior as predicted above, i.e., a decrease in size at larger distances followed by an increase at smaller distances, has indeed been observed in numerical simulations of athermal lattice chains by Olaj et al.[12] These authors investigated the behavior of four- and five-way cubic lattice chains of 50 segments; besides athermal chains (which correspond to self-avoiding "walks"), they also considered chains under Θ-conditions. Later we will see that the numerically observed *shape* of the variation of $\rho(x)$ is better described by the approach discussed in section 4 which is based on the assumption of a more realistic variation of the density profile of the molecules than considered so far. However, we would like to point out that the absolute variations of ρ as predicted by (3.15) are actually quite close to those observed numerically. For instance, the data presented in Figure 2 of the paper by Olaj et al. (athermal five-way chains) correspond to values of $\rho(0) \approx 1.13$ and $\rho_m \approx 0.98$–0.99. Our predictions for characteristic distances (like x_m or x_1) are typically 10% too small. However, in view of the simplicity of the present approach (and the rather unrealistic assumption of spherical molecules with constant segment density), this discrepancy is not very surprising.

Let us now consider the behavior of the potential $u(r)$ in the good-solvent regime. With (3.13) for $f_2(R|r)$, (2.14) for $f_1(R)$, and (2.15) for R_0, the potential (3.9) is given by

$$u(r) = \xi^{2/5}n^{1/5}\left\{3\rho^2 + \frac{2}{\rho^3}\left[2 - \frac{3}{2}(x/\rho) + \frac{1}{2}(x/\rho)^3\right] - 5\right\} \quad (x < 1) \quad (3.16)$$

with $\rho(x)$ being the solution of eq 3.15. Substitution of $\rho(x) \equiv 1$ directly yields $u^{st}(r)$; cf. eq 3.12. It should be remarked that (3.16) is of the same scaling form—namely, $u(r,n,\xi) = \xi^{2/5}n^{1/5}\hat{u}(x)$, where $\hat{u}$ is some function of the rescaled distance x—as the FK potential u^{FK} [eq 3.10 with (const)R_0 substituted for S_0; cf. (3.11)].

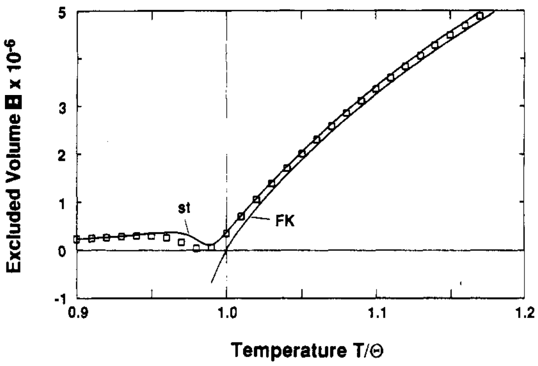

Figure 2. Excluded volume B vs temperature for chains of length $n = 10^4$ in the constant segment density model: Comparison between the excluded volumes following from $u(r)$ (□), $u^{st}(r)$, and $u^{FK}(r)$.

Figure 1b illustrates the behavior of the potential in the good-solvent case for $n = 10^4$ and $T = 1.5\Theta$. It is seen that the present approach leads to a behavior which is very similar to that of the FK theory. At smaller distances, where the difference between R_M and R_0 becomes more important, $u(r)$ takes, as expected, somewhat smaller values than $u^{st}(r)$, the potential derived under the assumption of nonadjustable molecule sizes. [Note that u^{st} reproduces the FK behavior rather closely.]

The similarity between the three different approaches is also reflected in the behavior of the excluded volume B. Figure 2 shows the temperature dependence of B as calculated from eq 3.2 with u, u^{st}, and u^{FK} for chains of 10^4 segments. At temperatures T well above Θ the different excluded volumes are indeed almost identical. This, however, is no longer the case when we consider the range of lower temperatures. As mentioned before, the FK theory—in which $B(T)$ vanishes exactly at $T = \Theta$—is not expected to be applicable for temperatures close to or below the Θ-point because excluded-volume interactions of higher orders are completely neglected. The present approach takes these interactions into account, but, as Figure 2 clearly shows, it nevertheless leads to unphysical results for $T < \Theta$ in that the resulting excluded volumes never take on negative values—in obvious contrast to experimental as well as simulation results. In order to understand the reason for this "failure", let us have a look at the behavior of $R_M(r)$ and $u(r)$ in the poor-solvent regime.

Expressions for the potential and the optimal size in poor solvents that are analogous to eqs 3.15 and 3.16 are readily obtained when we restrict ourselves to the situation (cf. the remarks following eq 2.20 in section 2) where it suffices to take only terms of second and third order in the density into account. In this case, eq 3.8, together with eqs 2.18 and 2.20 for R_0, yields

$$u(r) = 3\xi^2 n\left\{\frac{3}{\rho^6}\left[\frac{4}{3} - \frac{3}{2}(x/\rho) + \frac{1}{2}(x/\rho)^3\right] - \frac{2}{\rho^3}\left[2 - \frac{3}{2}(x/\rho) + \frac{1}{2}(x/\rho)^3\right] + 1\right\} \quad (3.17)$$

where $\rho(x)$ is the solution of the equation

$$\rho^3 = \left[4 - \frac{21}{4}(x/\rho) + \frac{9}{4}(x/\rho)^3\right]/[2 - 2(x/\rho) + (x/\rho)^3] \quad (3.18)$$

Again, u^{st} is simply obtained by setting $\rho \equiv 1$ in (3.17).

Figure 3 illustrates the behavior of $R_M(r)$ [$\rho(x)$, actually] and of $u(r)$ and $u^{st}(r)$ in poor solvents [$T = 0.9\Theta$ ($\chi = 5/9$),

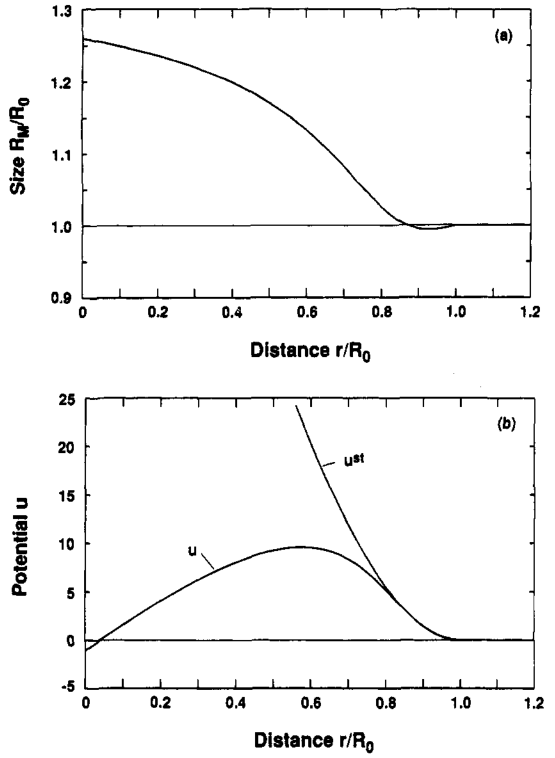

Figure 3. Interaction between two polymers in a poor solvent [constant segment density model; $T/\Theta = 0.9$ ($\chi = 5/9$) and $n = 10^4$; $R_0 = 40.9$]. (a) Dependence of the size (end-to-end distance) of the molecules on their intermolecular separation r. (b) Potential of mean force: Comparison between $u(r)$ (eq 3.9) and $u^{st}(r)$ (eq 3.12).

$n = 10^4$.] The reason why both potentials do not lead to a negative second virial coefficient is obvious: both do not show any relevant negative potential region at all. This behavior is unphysical; attractions between polymer molecules in poor solvents are to be expected, particularly at distances where the interacting molecules just start to overlap (i.e., at $r \approx R_0$). There, the formation of additional segment–segment contacts should be energetically favorable while excluded-volume interactions should not yet play a predominant role. Similarly, one would not expect the molecules to avoid mutual overlap as the (slight) decrease of $R_M(r)$ at distances r close to r_0 implies (Figure 3a); $R_M(r)$ is rather expected to increase steadily with decreasing distance.

The source of this unphysical behavior may be traced back to our use of a constant-density profile in which excluded-volume repulsions between segments are equally strong everywhere. In this model, single molecules are characterized by a *uniform* balance between segment–segment repulsions and attractions. In contrast to the good- or Θ-solvent case where the elastic Gaussian free energy, which depends on the size of the molecule, plays an essential role, the behavior of a single molecule in a poor solvent can be discussed solely in terms of the free energy f_I [cf. the discussion proceding (2.19)] and the segment density ϕ. [Note that, according to (2.9) and (2.6), f_I might be written as

$$f_I = ng(\phi)/\phi \qquad (3.19)$$

Thus, optimization with respect to R is, in the poor-solvent case, completely equivalent to optimization of f_I with respect to ϕ. In other words, the average behavior of a single molecule in the poor-solvent case is simply associated with the existence of a segment density $\phi_0 \equiv n/R_0{}^3$, which is the optimum with respect to segment–segment interactions. The consequence for situations where two molecules interact with each other is now easily understood: any overlap between two molecules, which locally doubles the density, leads first of all to an unfavorable, i.e., repulsive, situations.

Figure 3 also shows that the potential u goes through a maximum when r decreases and that, when both molecules overlap completely, u is very close to zero again. [Equations 3.17 and 3.18 yield the result that $u(r{=}0)$ is *exactly* zero; remember, however, that they describe the behavior in the asymptotic limit $n \rightarrow \infty$]. The case $r = 0$ is, within the approach discussed here, simply equivalent to the case of a single molecule with $2n$ instead of n segments. This "molecule" adjusts its size also to the optimal density ϕ_0 [note that this immediately explains the result $\rho(0) = 2^{1/d} = 2^{1/3}$ (cf. 3.18)) at complete overlap]. Because f_I is linear in n [(3.19)], the potential (3.9) simply vanishes. However, since one actually expects a strong repulsion between polymers at close intermolecular separations, this behavior of u should be considered as a pure artifact of the model. In this sense, then, the potential u^{st} appears to be more reasonable.

4. Interaction between Two Polymers: Gaussian Density Model

As we have seen in the previous section, the assumption of a constant polymer segment density leads to physically unreasonable results for temperatures close to and below the Θ-temperature. We should therefore allow for more realistic variations of the density profile within a molecule.

For instance, a simple way to improve on the approach discussed in section 3 would be to introduce as an additional degree of freedom a constant density gradient parallel to the axis of interaction.[28] Such an approach would take into account the lack of spherical symmetry in the density profile of a molecule that interacts with another one. By allowing for a decreased (i.e., locally lower than optimum) density in the overlap regime, additional intermolecular segment–segment contacts could more easily be formed, and this could give rise to an attractive region in the pair potential in Θ-like and poor solvents, which was missing in the constant-density model. There are, however, some problems associated with this simple approach. First, any variation in the strength of the gradient at fixed size R automatically changes the position of the center of mass of the molecule. There is also the problem that there is no obvious, intuitive way at hand to estimate the weight $W_{ideal}(R,G)$ of an ideal chain with end-to-end distance R and density gradient G. Finally, this approach would still be based on the picture of a polymer whose segments are confined to a well-defined, spherical volume.

In view of these objections we follow a different approach which is based on the assumption of a (spherically symmetric) Gaussian density profile. The expectation is that the lower density at larger distances also allows for an attractive regime in the interaction potential. While the assumption of a spherically symmetric profile is certainly still somewhat unsatisfying, the Gaussian form itself seems to be a much more reasonable choice than that of a simple sphere.

With respect to the assumption of a Gaussian profile, our approach is closely related to the original work by Flory[1] on single molecules and to the theory of Flory and Krigbaum[10] for interacting polymers. However, unlike these early treatments, our discussion will not be restricted to the case of good solvents. We will see that, in this regard, our approach partly parallels that of Flory and Orofino in the late 1950s,[11] who extended the FK theory by taking a third-order term in the free energy into account. These authors, however, were mainly interested in the effect of such a term on the second osmotic virial coefficient and did not discuss the behavior of the pair potential in any detail. Furthermore, since their treatment (like the FK theory) is not based on a variational approach, it does not provide any information on the dependence of the size of the interacting molecules on their intermolecular separation.

We first consider the properties of a single molecule (i.e., its average size and free energy). Configurations of single molecules may be classified according to their radius of gyration S, which is actually a better measure of the size or extent of a polymer than the end-to-end distance R. The reason is (cf. the discussion preceding eq 2.21) that S is directly related to the distribution of segments according to

$$S^2 = \frac{1}{n}\int \mathrm{d}\mathbf{s}\, s^2 \varphi(\mathbf{s}) \tag{4.1}$$

where $\varphi(\mathbf{s})$ is the local segment density at distance $\mathbf{s}$ from the center of mass. The normalization is $\int \mathrm{d}\mathbf{s}\ \varphi(\mathbf{s}) = n$. The local polymer volume fraction associated with φ is simply given by $\phi(\mathbf{s}) = \upsilon\varphi(\mathbf{s})$. In analogy with the discussion in section 2, the task is to estimate the statistical weight $W_1(S)$, or the corresponding free energy $f_1(S) = -\ln[W_1(S)]$, associated with a particular value of S.

First, it is assumed that the distribution of the radius of gyration of an ideal chain, i.e., $W_{1,\mathrm{G}}(S)$, is given by a Gaussian with second moment $\langle S^2\rangle = n/6$. In analogy to eq 2.5 the free energy $f_{1,\mathrm{G}}(S)$ is then given by

$$f_{1,\mathrm{G}}(S) = 9S^2/n - 3\ln(S) \tag{4.2}$$

It should be remarked that, in contrast to the case of the end-to-end distance where the Gaussian form is asymptotically exact, the actual distribution of S is of a more complicated form (cf. section 8 in ref 3). However, in view of the approximate nature of our approach, the assumption of a Gaussian appears to be reasonable enough.

Next, in order to determine the weight $W_{1,\mathrm{I}}(S)$ or the free energy $f_{1,\mathrm{I}}(S)$ which take the interactions between segments into account, we first have to make a reasonable choice for the distribution of segments at a given value of S, $\varphi(\mathbf{s}|S)$ [the corresponding volume fraction is $\phi(\mathbf{s}|S)$]. As mentioned above, we assume that the profile is Gaussian:

$$\phi(\mathbf{s}|S) = \upsilon\varphi(\mathbf{s}|S) = \upsilon n\left(\frac{3}{2\pi S^2}\right)^{3/2}\exp[-(3/2)s^2/S^2] \tag{4.3}$$

Note that (4.3) is properly normalized and fulfills eq 4.1. The assumption of a Gaussian is, of course, an approximation. It is mainly motivated by the fact that the *average* distribution of segments (i.e., that of all configurations irrespective of the radius of gyration) can be reasonably well described by a Gaussian.

Finally, we must calculate the free energy f_I associated with a given segment distribution $\phi(\mathbf{s})$. This is done in a straightforward extension of the simple MF approach discussed in section 1 (cf., for instance, Appendix B of ref 7). It is assumed that the total free energy is given by the volume integral of a local free energy density $\tilde{f}_\mathrm{I}[\phi(\mathbf{s})]$ which only depends on the local volume fraction $\phi(\mathbf{s})$. It is further assumed that the functional form of the infinitesimal free energy $\mathrm{d}f_\mathrm{I}(\mathbf{s}) = \tilde{f}_\mathrm{I}[\phi(\mathbf{s})]\ \mathrm{d}\mathbf{s}$ is the same as (2.9):

$$f_\mathrm{I} = \int \mathrm{d}\mathbf{s}\ \tilde{f}_\mathrm{I}[\phi(\mathbf{s})] = (1/\upsilon)\int \mathrm{d}\mathbf{s}\ g[\phi(\mathbf{s})] \tag{4.4}$$

In most cases, it will be difficult to perform this integral exactly (an exception is, of course, the "trivial" case treated in section 2). In such cases, it will be helpful to refer to the expansion of $g(\phi)$ in powers of ϕ which is given by eq 2.10; insertion into (4.4) yields

$$f_\mathrm{I} = \frac{1}{\upsilon}\xi I_2 + \frac{1}{\upsilon}\sum_{k=3}^{\infty}\frac{1}{k(k-1)}I_k \tag{4.5}$$

where

$$I_k \equiv \int \mathrm{d}\mathbf{s}\ [\phi(s)]^k \tag{4.6}$$

The integrals I_k are readily performed in the case of the Gaussian density (4.3). The free energy $f_{1,\mathrm{I}}$ associated with segment–segment interactions within a single molecule with radius of gyration S becomes

$$f_{1,\mathrm{I}}(S) = \xi\frac{\alpha}{2^{3/2}}\frac{n^2}{S^3} + \sum_{k=3}^{\infty}\frac{\alpha^{k-1}}{k(k-1)k^{3/2}}\frac{n^k}{S^{3(k-1)}} \equiv \sum_{k=2}^{\infty} f_{1,\mathrm{I}}{}^{(k)} \tag{4.7}$$

where

$$\alpha \equiv (3/2\pi)^{3/2}\upsilon = (3/2^5\pi)^{1/2} \tag{4.8}$$

Note that $f_{1,\mathrm{I}}(S)$ is of the same structural form as the free energy $f_{1,\mathrm{I}}(R)$ in section 2 (cf. eq 2.13).

With (4.2) and (4.7), the optimal size S_0 is readily obtained by minimizing the total free energy $f_1(S) = f_{1,\mathrm{G}}(S) + f_{1,\mathrm{I}}(S)$. We directly give the large-n results for the three different cases of interest:

(i) good solvent

$$S_0 = a\xi^{1/5}n^{3/5}, \qquad a = 2^{-1/2}(\alpha/3)^{1/5} \approx 0.399 \tag{4.9}$$

(This result is equivalent to that derived by Flory in ref 1.)

(ii) Θ-solvent

$$S_0 = b(n/6)^{1/2}, \qquad b \approx 1.11 \tag{4.10}$$

(iii) poor solvent

$$S_0 = c(n/|\xi|)^{1/3}, \qquad c = (1/3)(2^{2/3}\pi)^{1/6} \approx 0.315 \tag{4.11}$$

Let us briefly comment on how these results compare to those obtained in the previous section (eqs 2.15, 2.17, and 2.18–2.20). When we apply the identification $S_0 = (3/20)^{1/2}R_0$ (eq 2.21), the prefactors obtained in the constant segment density approach for the good- and poor solvent case are $a = 0.387$ and $c = 0.269$. The value of b in (4.10) should directly be compared to $b = 1.09$ in (2.17), because both measure the expansion with respect to the ideal chain. [Note that the comparison of the values of a and c obtained in both approaches is somewhat vague due to the question of whether one chooses $(3/20)^{1/2}R_0$ or $(1/6)^{1/2}R_0$ for $S_0(R_0)$. This vagueness, however, does not affect the qualitative picture.] The somewhat larger size in the Gaussian model can be attributed to the strong excluded-volume repulsion caused by the higher density in the center of the molecule.

We now consider the interaction between two molecules with given radius of gyration S at distance r. In analogy to the discussion in section 3, we first determine the free energy of the two molecules, $f_2(S|r) = 2f_{1,\mathrm{G}}(S) + f_{2,\mathrm{I}}(S|r)$. Minimization then yields the optimal size $S_\mathrm{M}(r)$, and the pair potential is finally determined from

$$u(r) = f_2(S_\mathrm{M}|r) - 2f_1(S_0) \tag{4.12}$$

The free energy of interaction, $f_{2,\mathrm{I}}(S|r)$, is given by (4.4), where ϕ now corresponds to the *total* polymer volume fraction resulting from the superposition of the densities of the two polymers:

$$\phi_{\text{tot}}(\mathbf{s}) = \phi(\mathbf{s}|S) + \phi(\mathbf{s}-\mathbf{r}|S) \tag{4.13}$$

The center of mass of one molecule has been chosen as the origin $\mathbf{s} = 0$; the vector $\mathbf{r}$ (with $|\mathbf{r}| = r$) denotes the position of the center of mass of the second one. With (4.13), the integral I_k (eq 4.6) can be written as $I_k = \sum_{j=0}^{k}\binom{k}{j}\int \mathrm{d}\mathbf{s}\, [\phi(\mathbf{s}|S)]^{k-j}[\phi(\mathbf{s}-\mathbf{r}|S)]^{j}$. The calculation of the integral is straightforward for the case of the Gaussian density (4.3), and insertion of the resulting expression for I_k into (4.5) shows that the free energy $f_{2,\mathrm{I}}$ can be written as

$$f_{2,\mathrm{I}}(S|r) = \sum_{k=2}^{\infty} f_{1,\mathrm{I}}{}^{(k)} \sum_{j=0}^{k} \binom{k}{j} \exp\left[-\frac{3}{2}\frac{(k-j)j}{k}\frac{r^2}{S^2}\right] \tag{4.14}$$

where the $f_{1,\mathrm{I}}{}^{(k)}$ are given by eq 4.7. In principle, eq 4.14 now allows for the calculation of the free energy $f_{2,\mathrm{I}}(S|r)$, and thus of $f_2(S|r)$ and $S_{\mathrm{M}}(r)$, up to any required order k.

Of course, we do not have a closed analytical expression for the pair potential $u(r)$ as given by (4.12); it has to be evaluated numerically following the "recipe" outlined above. A (semi)closed expression, however, can be given for the potential $u^{\mathrm{st}}(r)$ which results if we do not allow the molecules to adjust their size to the actual separation r; $u^{\mathrm{st}}(r)$ is, in analogy to eq 3.12 in section 3, given by $\Delta f(S_0|r)$, where $\Delta f(S|r) = f_{2,\mathrm{I}}(S|r) - 2f_{1,\mathrm{I}}(S|r)$ is the change in free energy associated with the interaction of two molecules of fixed size S. Subtracting eq 4.7 from 4.14), we immediately see that $\Delta f(S|r)$ is of the same form as (4.14), but with the second sum only running from $j = 1$ to $k - 1$. We thus have

$$u^{\mathrm{st}}(r) = \xi \frac{\alpha}{2^{1/2}}\frac{n^2}{S_0{}^3}\exp\left(-\frac{3}{4}\frac{r^2}{S_0{}^2}\right) + \sum_{k=3}^{\infty}\frac{\alpha^{k-1}}{k(k-1)k^{3/2}}\frac{n^k}{S_0{}^{3(k-1)}}\sum_{j=1}^{k-1}\binom{k}{j}\exp\left[-\frac{3}{2}\frac{(k-j)j}{k}\frac{r^2}{S_0{}^2}\right] \tag{4.15}$$

Comparison with (3.10) shows that the first term is identical with the Flory–Krigbaum potential $u^{\mathrm{FK}}(r)$. Higher order contributions to the FK theory have been discussed by Orofino and Flory,[11] who explicitly considered the additional interaction term that arises in the next higher order (ϕ^3); eq 4.15 with $k \leq 3$ is equivalent to their equation (10).

Figures 4–6 illustrate the behavior of $S_{\mathrm{M}}(R)$ and $u(*\mathrm{r})$ in good, Θ-like, and poor solvents, respectively. As in section 3, we have chosen the example of chains with $n = 10^4$ segments. The behavior of the resulting excluded volumes B is shown in Figure 7, which should be compared to Figure 2 in section 3. The discussion of the excluded volume will be interwoven in the discussion of Figures 4–6.

We first consider the good-solvent case. Figure 4 ($T = 1.5\Theta$, $n = 10^4$) is the analogue of Figure 1.

As Figure 4a shows, the qualitative behavior of $\rho_{\mathrm{s}} \equiv S_{\mathrm{M}}(r)/S_0$ is very similar to that of $\rho = R_{\mathrm{M}}(r)/R_0$; cf. Figure 1a. The main difference is that the Gaussian-density model leads to a "smoother" variation of ρ_{s} with distance in the contact region between molecules; this smooth variation is indeed very similar to the behavior observed in the simulations by Olaj et al. If we consider the asymptotic behavior for $n \rightarrow \infty$, the analytical expression which—in analogy to eq 3.14 for $\rho(x)$—determines the behavior of ρ_{s} as a function of the rescaled distance $x_{\mathrm{s}} \equiv r/S_0$ in the good-solvent situation is given by

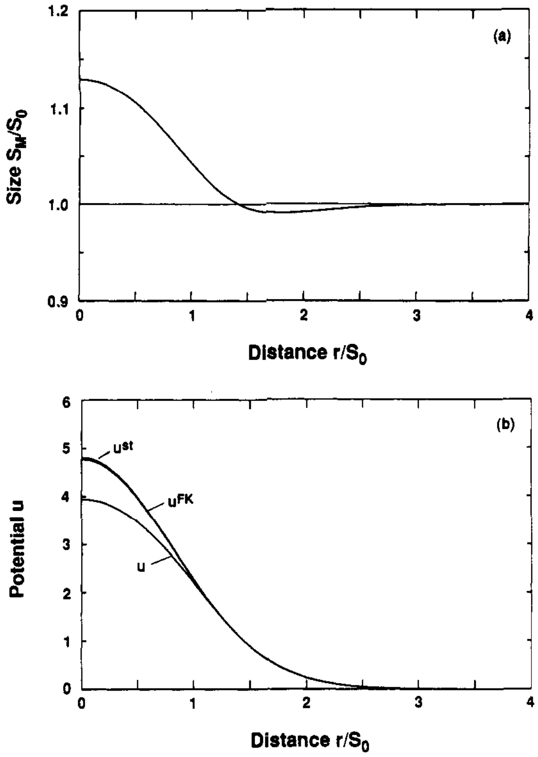

Figure 4. Interaction between two polymers in a good solvent [Gaussian-density model; $T/\Theta = 1.5$ ($\chi = 1/3$) and $n = 10^4$; $S_0 = 75.3$]. (a) Dependence of the size (radius of gyration) of the molecules on their intermolecular separation r. (b) Potential of mean force: comparison between $u(r)$ (eq 4.12), $u^{\mathrm{st}}(r)$ (eq 4.15), and the Flory–Krigbaum potential $u^{\mathrm{FK}}(r)$ (eq 3.10).

$$\rho_{\mathrm{s}}{}^5 = 1 + \left[1 - \tfrac{1}{2}(x_{\mathrm{s}}{}^2/\rho_{\mathrm{s}}{}^2)\right]\exp\left[-\tfrac{3}{4}(x_{\mathrm{s}}{}^2/\rho_{\mathrm{s}}{}^2)\right] \tag{4.16}$$

As one readily sees, ρ_{s} takes its minimum value, $\rho_{\mathrm{s,m}} = [1 - (1/2)\exp(-5/2)]^{1/5} \approx 0.989$, at $x_{\mathrm{s,m}} = (10/3)^{1/2}\rho_{\mathrm{s,m}} \approx 1.81$; this may be compared with the corresponding values in the constant-density model, which are $\rho_{\mathrm{m}} \approx 0.982$ and $x_{\mathrm{s,m}} \approx (20/3)^{1/2}x_{\mathrm{m}} \approx 2.07$; cf. section 3. ρ_{s} takes the value 1 again at $x_{\mathrm{s,1}} = 2^{1/2} \approx 1.41$ [1.60, for comparison]. The value at complete overlap, $\rho_{\mathrm{s}}(x_{\mathrm{s}}{=}1) = 2^{1/5} \approx 1.15$, is the same as before. It is seen that the characteristic distances are somewhat smaller than those in the constant-density model, which themselves were already a little bit smaller than those of the simulations.

The behavior of the interaction potential, Figure 4b, is as expected. While there is no significant (in this case actually no observable) difference between $u^{\mathrm{st}}(r)$ and $u^{\mathrm{FK}}(r)$ (because the higher order terms in u^{st} become irrelevant in good solvents when n is large), the potential u as given by (4.12) is less repulsive at smaller distances where the adjustment of the molecule size is more pronounced. However, the effect on the behavior of the second virial coefficient at temperatures well above Θ is again not very drastic as shown in Figure 7.

Of greater interest is, of course, the behavior near and below Θ. First of all, as Figure 7 shows, the Gaussian-density model indeed leads, both for u and u^{st}, to negative second virial coefficients in the poor-solvent regime, which is definitely an (at least qualitative) improvement over the constant-density model. In order to understand this better, let us first have a closer look at the behavior in a Θ-like solvent ($T/\Theta = 0.992$, $n = 10^4$), which is shown in Figure 5. The temperature $T = 0.992\Theta$ is approximately the one where the second virial coefficient vanishes for chains of this particular number of segments; cf. Figure

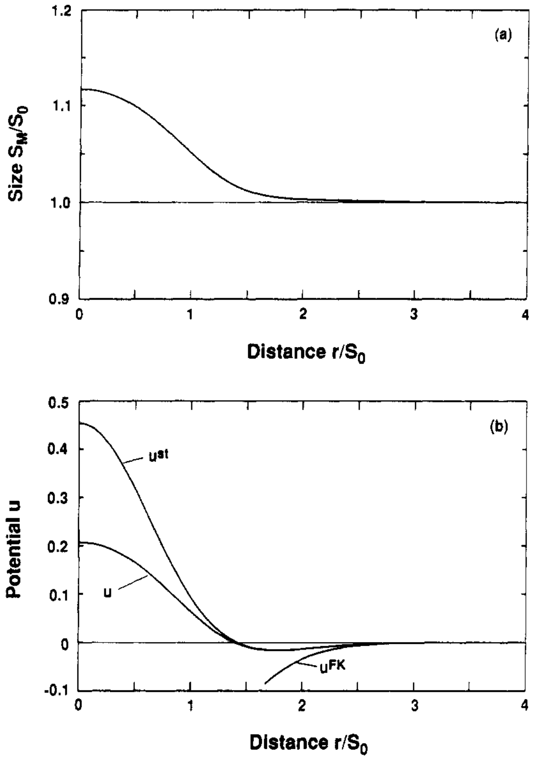

Figure 5. Interaction between two polymers in a Θ-like solvent [Gaussian-density model; $T/\Theta = 0.992$ and $n = 10^4$; $S_0 = 41.5$]. (a) Dependence of the size (radius of gyration) of the molecules on their intermolecular separation r. (b) Potential of mean force: comparison between $u(r)$ (eq 4.12), $u^{st}(r)$ (eq 4.15), and the Flory–Krigbaum potential $u^{FK}(r)$ (eq 3.10).

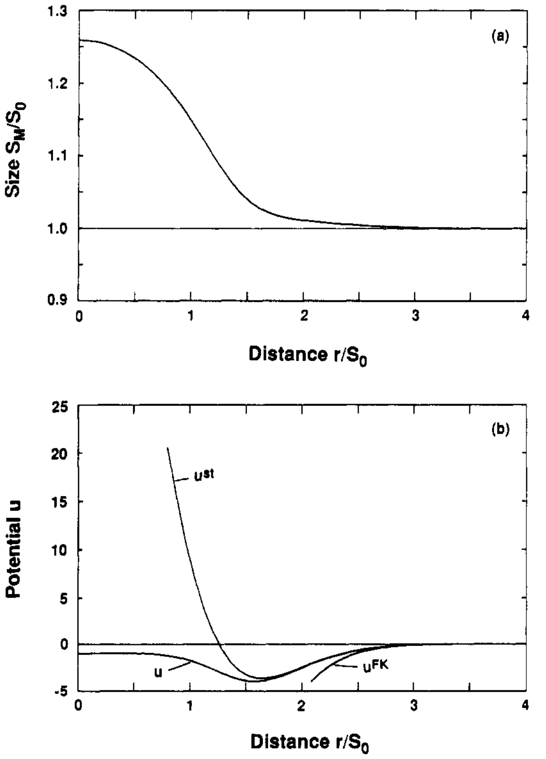

Figure 6. Interaction between two polymers in a poor solvent [Gaussian-density model; $T/\Theta = 0.9$ ($\chi = 5/9$) and $n = 10^4$; $S_0 = 18.8$]. (a) Dependence of the size (radius of gyration) of the molecules on their intermolecular separation r. (b) Potential of mean force: comparison between $u(r)$ (eq 4.12), $u^{st}(r)$ (eq 4.15), and the Flory–Krigbaum potential $u^{FK}(r)$ (eq 3.10).

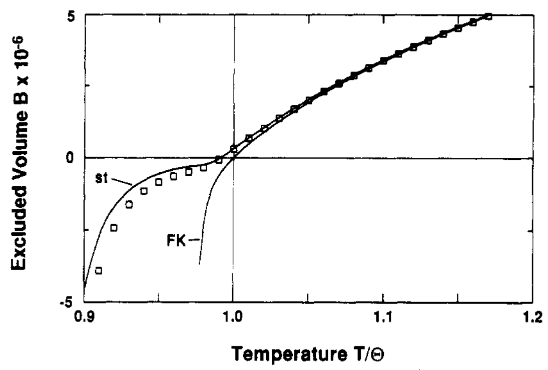

Figure 7. Excluded volume B vs temperature for chains of length $n = 10^4$ in the Gaussian-density model: Comparison between the excluded volumes following from $u(r)$ (□), $u^{st}(r)$, and the Flory–Krigbaum potential $u^{FK}(r)$ (eq 3.10).

If we look at the interaction potential (Figure 5b) first, we see that both u and u^{st} have—as they should—an attractive regime at larger distances and a repulsive part at smaller distances. In the case of u^{st}, the attractive part is obviously due to the FK term, which has been (partly) shown in Figure 6b; the repulsive higher order terms dominate the behavior at small values of r.

Figure 5a shows that the optimal size of the interacting molecules starts to increase right when they begin to interact. This is consistent with the attraction seen at this distance. The final value of S_M/S_0 at complete overlap is somewhat smaller than in the good-solvent situation (and also smaller than in the poor-solvent case; cf. Figure 6a); the same effect has been observed in the simulations by Olaj et al. It is related to the comparatively small overall effect of segment–segment interactions in the vicinity of the Θ-point. The simulations for Θ-chains ($n = 50$) by Olaj et al. show a feature that is not predicted by the present approach: an initial slight increase of the size is, as the molecules approach each other, followed by a slight decrease before the chains finally expand again at smaller distances. We refrain from speculating whether this "oscillation" would also occur in chains that are much larger than the ones studied numerically. The investigation of Olaj et al. into the behavior of the components of the radius of gyration parallel and perpendicular to the axis of interaction shows that the variation of the *overall* size is a result of an interplay between the parallel and perpendicular size changes. In other words, the change in the *shape* of the interacting molecules plays a major role (see also ref 13). For instance, in the Θ case, the initial slight increase and decrease in size are mainly due to the behavior of the parallel component; the perpendicular component actually first decreases when the molecules begin to interact. In view of this, one cannot expect that an approach that keeps the shape fixed and deals with only one size parameter is able to predict variations which are as subtle as those mentioned above.

Figure 6, which is the analogue of Figure 3, illustrates the poor-solvent case ($T = 0.9\Theta$, $n = 10^4$). $S_M(r)$ shows a similar behavior to the Θ case; the main difference is that the expansion of the chains is much more pronounced. The value at complete overlap is (in the asymptotic limit) the same as in the constant-density model, $S_M(0)/S_0 = 2^{1/3}$. This is, of course, not surprising; in the present MF approach, the situation $r = 0$ is always equivalent to a single molecule of $2n$ segments, independently of the actual choice of the density profile. As far as we know, no results for the change in size of molecules interacting with each other in poor solvents are available in the literature. It is clear that corresponding simulations would be much

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7. [It should be noted that, in this MF approach, the difference between this temperature and Θ decreases when n increases; they become equal in the asymptotic limit.]

more demanding than those for good or Θ-solvents where the molecules are less compact. Our results appear to be physically reasonable; nevertheless, it would be interesting to compare them with "reality".

Figure 6b shows the behavior of the interaction potentials in the poor-solvent case. The result for $u^{st}(r)$ is physically appealing; the potential is characterized by an attractive part at larger distances and by a strong repulsion at smaller ones. The repulsion can be attributed to the fact that the molecules are collapsed and rather compact. In contrast, the potential $u(r)$ (eq 4.12) exhibits an anomalous behavior at smaller distances; it remains negative, taking a value close to zero at complete overlap (exactly zero when n goes to infinity). This behavior explains the difference between the excluded volumes associated with u^{st} and u at temperatures below Θ (Figure 7). Again, we are not aware of any direct observations (like simulations) of the pair potential in poor solvents. The absence of any strong, hard-core type of repulsion, however, is certainly an unphysical feature. It thus appears that the saddle-point approach, which leads to resonable results for the size of interacting molecules, is not really appropriate—at least not in poor solvents—when it is applied to the interaction potential.

5. Polymer at a Hard Wall

In this section we discuss a way to extend DiMarzio's approach to the case of a polymer interacting with a hard (i.e., infinitely repulsive) wall. In analogy to the previous discussions, we are interested in the behavior of the potential of mean force, $u_{HW}(z)$, and the corresponding second virial coefficient, where z denotes the distance of the center of mass of the molecule from the wall.

The interaction of a polymer with a hard wall (HW) might be considered as the limiting case of the interaction of a polymer with a large hard sphere. Such interactions are of interest in cases whiich involve excluded-volume interactions between colloidal particles and polymers in (dilute) solutions. Examples would be the precipitation of colloidal particles/proteins from polymer solutions or the partitioning of proteins in polymeric two-phase systems.

In the case of dilute solutions, one is first of all interested in the second osmotic virial coefficient A_2 which follows from the potential of mean force between the polymer and the hard sphere. If the size of the hard sphere is much larger than the (average) size of the polymer, the excluded volume B associated with A_2 (cf. eq 3.2), takes the following simple form:

$$B \rightarrow V_{HS} + A_{HS}\tilde{R} \qquad \tilde{R} \equiv \int_0^\infty dz\,\{1 - \exp[-u_{HW}(z)]\} \tag{5.1}$$

V_{HS} and A_{HS} denote the volume and the surface area of the hard sphere; $\tilde{R}$ might be considered as an effective hard-sphere radius of the polymer molecule.

Results for the excluded volume between hard spheres and *ideal* chains have been reported by Hermans.[19] He obtained

$$\tilde{R} = (2/3\pi)^{1/2}n^{1/2} \triangleq 0.38R_0 \tag{5.2}$$

for chains of n segments. We are not aware of any comparable treatments for chains with intramolecular interactions, i.e., more specifically, of approaches which go beyond the usual scaling assumption that the effective hard-sphere radius is simply proportional to the typical size of the molecules:

$$\tilde{R} = \text{const} \times R_0 = \text{const} \times n^{\nu} \tag{5.3}$$

In the following, we attempt a first step in that direction.

Discussing the problem in the framework of the present approach means that we first have to classify the configurations of the chain (which is at fixed distance z from the wall) in an appropriate way; i.e., we have to choose one (or more) parameters which suitably characterize their size or shape. Let $\{R\}$ denote the set of all chosen parameters. The task is to estimate the statistical weight

$$W_{HW}(\{R\}|z) = W_G(\{R\})\; W_{HW+I}(\{R\}|z) \tag{5.4}$$

where W_G denotes, as before, the weight of the ideal, Gaussian chain without any interactions, while W_{HW+I} corrects for the exclusion of "forbidden" configurations due to the presence of the HW and for the internal segment–segment interactions. Of course, W_{HW+I} will depend on the assumptions made about the distribution of segments associated with a given set $\{R\}$.

In the following, we will only discuss a straightforward extension of the simple approach of section 2. The molecules, which are described as spheres with constant segment density, will thus only be characterized by a single size parameter (the diameter of the sphere, R). In principle, it would, of course, be better to assume a more realistic density profile. In particular, one should try to take the effect into account that the chains get flatter with decreasing center-of-mass distance z; i.e., one should distinguish between parameters $R_\perp$ and $R_\parallel$ which measure the extension of the chain perpendicular and parallel to the wall. Any future approach attempted at improving the present rather simple and qualitative treatment should definitely incorporate such an extension.

Two different approaches will be considered. The first one, in the following denoted as (A), corresponds to taking the picture of a constant segment density literally. This means that we assume that each partial volume ΔV of the sphere V contains *exactly* $\Delta n = n(\Delta V/v)$ segments. The same picture has implicitly been used in the treatment of the interaction between two polymers in section 3 [remember that we assumed that the overlap volume V' contains exactly $2n(V'/V)$ segments]. Applied to the present problem, we consequently would have to exclude all values of R which lead to a nonvanishing overlap with the wall (i.e., $W_{HW+I}(R|z) = 0$ if $R > 2z$). In terms of the free energy

$$\begin{aligned} f_{HW}^{(A)}(R|z) &= f_1(R) \qquad \text{if } R \le 2z \\ &= \infty \qquad \text{otherwise} \end{aligned} \tag{5.5}$$

where $f_1(R)$, as before, denotes the free energy of a single molecule (cf. section 2). Obviously, $R_M(z)$, the value of R that minimizes $f_{HW}^{(A)}(R|z)$ is given by R_0 if $z \ge R_0/2$ and by $2z$ if $z < R_0/2$ [see also the plots of $f_{HW}^{(A)}(R|z)$ in Figure 8a]. Thus, the interaction potential, $u_{HW}(z) = f_{HW}(R_M|z) - f_1(R_0)$ is simply given by

$$\begin{aligned} u_{HW}^{(A)}(z) &= f_1(2z) - f_1(R_0) \qquad \text{if } z < R_0/2 \\ &= 0 \qquad \text{otherwise} \end{aligned} \tag{5.6}$$

An obvious shortcoming of this simple approach is that certain allowed (real) configurations of "size" (i.e., end-to-end distance) $R > 2z$ are neglected (namely, those which mainly extend parallel to the wall), while configurations with end-to-end distance $R < 2z$ which extend beyond the wall are not excluded. The former configurations are the ones which actually determine the properties of the ensemble when z is small. Therefore, we cannot expect that this approach will lead to any reasonable description at small distances. However, we should keep in mind that the behavior of the second virial coefficient is mainly determined by the behavior of the potential at larger distances where the repulsion is still comparatively small.

In the case of an ideal chain, (5.6) is given by

$$u_{\mathrm{HW}}^{(\mathrm{A})}(x) = (3/2)(x^2 - 1) - 3 \ln (x) \qquad (5.7)$$

cf. eq (2.5). For convenience, we have introduced the rescaled distance $x \equiv z/(R_0/2)$. Equation 5.7 allows us to compare our simple approximation with Hermans' (asymptotically) exact result. The integral (eq 5.1) that determines the effective hard-sphere radius $\tilde{R}$ associated with eq 5.7 is easily evaluated:

$$\tilde{R} = (R_0/2)\left[1 + \frac{5}{9} - \frac{2}{9}\exp(3/2)\right] \approx 0.28R_0 \qquad (5.8)$$

Comparison with (5.2) shows that the present approach underestimates the effective hard-sphere radius of an ideal polymer at a HW by about 26%. Unfortunately, Hermans' approach does not provide information about the potential $u_{\mathrm{HW}}(z)$ itself. The reason is that he calculates the excluded volume by summing over the contributions of chain configurations with fixed position of the first segment instead of those with fixed center-of-mass distance z. This method has the advantage that one can readily apply standard methods of diffusion/random-walk theory to calculate the probability that a chain is excluded by the wall.

The second approach (B) is a refinement of (A). Instead of excluding all values $R > 2z$, we try to estimate the probability that none of the polymer segments falls into the "forbidden" region beyond the HW. The volume of the part of the sphere which extends beyond the wall is

$$V_{\mathrm{e}}(z) = \left[\frac{1}{2} - \frac{3}{2}(z/R) + 2(z/R)^3\right]V \qquad (5.9)$$

If we provisionally neglect interactions between the segments, assuming that they are independently distributed in V, the probability that none of the polymer segments falls into the forbidden region is simply given by

$$[1 - V_{\mathrm{e}}(z)/V]^n \qquad (5.10)$$

Intrachain interactions come into play through the (increased) segment density in the remaining "allowed" volume $V_{\mathrm{a}} = V - V_{\mathrm{e}}$. If we assume a constant density all over V_{a}, we would, however, encounter the problem that the center of mass is shifted with respect to its initial position. A simple way to restore the condition of a fixed center of mass is provided by a rather crude symmetry argument: we simply make the approximation that configurations which do not have any segments in V_{e} are also not allowed tohave any segments in the corresponding volume at the opposite end of the sphere. Formally, this approximation simply corresponds to replacing V_{e} in (5.10) by $2V_{\mathrm{e}}$; accordingly, the available volume is reduced to $V - 2V_{\mathrm{e}}$. In total, this approach (B) leads to the following expression for the free energy, $f_{\mathrm{HW}}^{(\mathrm{B})}$:

$$\begin{aligned} f_{\mathrm{HW}}^{(\mathrm{B})}(R|z) &= f_1(R) \qquad (R \leq 2z) \\ &= f_{1,\mathrm{G}}(R) - n \ln [1 - 2V_{\mathrm{e}}/V] + [(V - 2V_{\mathrm{e}})/v] \times \\ &\qquad g[\phi = nv/(V - 2V_{\mathrm{e}})] \qquad (R > 2z) \qquad (5.11) \end{aligned}$$

The second term on the right-hand side for $(R > 2z)$ corresponds to the probability (5.10) with V_{e} replaced by $2V_{\mathrm{e}}$; the third term is the free energy f_1 associated with the interactions of n segments in a volume $V - 2V_{\mathrm{e}}$ (cf. eq (2.9).

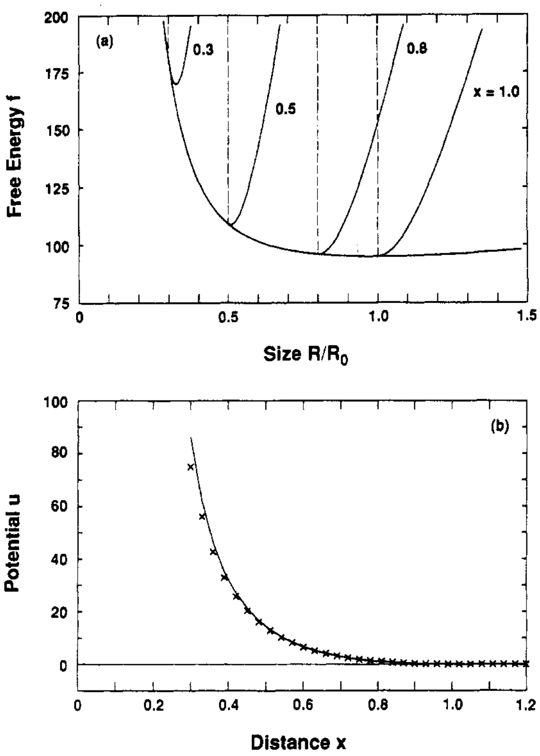

Figure 8. Polymer at a hard wall [$n = 10^3$, $T/\Theta = 5$ ($\chi = 0.1$); $R_0 = 56.7$]. (a) Free energy $f_{\mathrm{HW}}^{(\mathrm{B})}(R|z)$ vs polymer size R for different values of $x = z/(R_0/2)$; cf. eq (5.11). For comparison, we have indicated the behavior of $f_{\mathrm{HW}}^{(\mathrm{A})}(R|z)$ (eq 5.5, dashed lines). (b) Potential of mean force: comparison between $u_{\mathrm{HW}}^{(\mathrm{A})}(z)$ (solid line) and $u_{\mathrm{HW}}^{(\mathrm{B})}(z)$ (×).

Figure 8a illustrates the behavior of $f_{\mathrm{HW}}^{(\mathrm{B})}(R|z)$ for different values of $x = z/(R_0/2)$ [for $n = 10^3$ and $\chi = 0.1$ ($T/\Theta = 5$)]; for comparison, the behavior of $f_{\mathrm{HW}}^{(\mathrm{A})}(R|z)$ has also been indicated. It is seen that particularly for the larger distances, the value of R which minimizes $f_{\mathrm{HW}}^{(\mathrm{B})}$ is very close to $R_{\mathrm{M}}^{(\mathrm{A})}(z) = 2z$. Since the potential is calculated within the saddle-point approximation, approaches A and B lead accordingly to a very similar behavior of $u_{\mathrm{HW}}(z)$. Figure 8b shows the behavior of both $u_{\mathrm{HW}}^{(\mathrm{A})}(z)$ and $u_{\mathrm{HW}}^{(\mathrm{B})}(z)$ for $n = 10^4$ and $\chi = 0.1$. Essentially the same observation is made for other values of χ and similarly large values of n. The differences between $u_{\mathrm{HW}}^{(\mathrm{A})}$ and $u_{\mathrm{HW}}^{(\mathrm{B})}$ at smaller values of z are a bit more pronounced when the solvent quality is poor; these differences, however, which occur at values of u_{HW} which are rather large, have only a minor effect on the virial coefficient. Differences between the two approaches will, of course, show up when free energies are calculated by actually performing the integrals over all values of R; cf. (2.2). The observation that the saddle-point approximation is rather insensitive to the difference between the two approaches gives another indication that this approximation should be indeed be viewed with some caution. In the following, we will therefore mainly discuss the more qualitative aspects of the present approach. In view of the similarity of (A) and (B), we will, for convenience, only refer to the simpler approach (A).

We are mainly interested in the qualitative behavior of the effective hard-sphere radius $\tilde{R}$ in the different cases of good, Θ, and poor solvents. The approach is the following: in each case we will only consider the terms in the free energy $f_1(R)$ that are of relevance for $n \to \infty$ (cf. the discussion in section 2). When we calculate $u_{\mathrm{HW}}(z)$ in this way, we should, of course, be aware that the resulting expressions will only be valid for distances z that are not too small compared with $R_0/2$; with decreasing distance higher order terms in the density will always eventually become important. Since it is the initial increase of the potential which determines the behavior of $\tilde{R}$, $\tilde{R}$ will furthermore be evaluated on the basis of an expansion of u_{HW} in the vicinity of $x = z/(R_0/2) = 1$. Since this expansion is equivalent to the expansion of $f_1(R)$ around its minimum R_0, it takes the general form

$$u_{\mathrm{HW}}(x) = K(1-x)^2 + O[(1-x)^3] \qquad (5.12)$$

with $K > 0$. Taking only the first term into account, we can readily evaluate $\tilde{R}$:

$$\tilde{R} \approx (R_0/2)[1 - (1/2)(\pi/K)^{1/2} \operatorname{erf}(K^{1/2})] \qquad (5.13)$$

In order to get a feeling for this approximation, let us first consider the ideal case. The expansion of (5.7) reads $u_{\mathrm{HW}}(x) \approx 3(1-x)^2$; (5.13) thus leads to $\tilde{R} \approx 0.25R_0$, which is about 10% smaller than (5.8).

We now explicitly consider the cases of good, Θ, and poor solvents: Using eq 5.6 for u_{HW} and the results of section 2 for $f_1(R)$, we first determine the corresponding expansion factor K (eq 5.12). Insertion of K into (5.13) then yields the effective hard-sphere radius $\tilde{R}$.

(*i*) *Good Solvent*: With (2.14) and (2.15), (5.6) yields

$$u_{\mathrm{HW}}(x) = (1/2)\xi^{2/5}n^{1/5}[3x^2 + 2/x^3 - 5] = (15/2)\xi^{2/5}n^{1/5}(1-x)^2[1 + O(1-x)] \qquad (5.14)$$

The large-n behavior of $\tilde{R}$ is with (5.13) then given by

$$\tilde{R} \approx (R_0/2)[1 - \text{const} \times \xi^{-1/5}n^{-1/10}] \qquad (n \to \infty) \qquad (5.15)$$

a result that indicates a rather slow approach to the asymptotic value of the effective hard-sphere radius [$(R_0/2)$ in this approximation].

(*ii*) Θ-*Solvent* ($T = \Theta$): With (2.16) and (2.17)

$$u_{\mathrm{HW}}(x) = (3/2)b^2(x^2 - 1) - 2\ln(x) + (1/x^6 - 1)/(6b^6) \approx 5.22(1-x)^2[1 + O(1-x)] \qquad (5.16)$$

Equation 5.13 yields $\tilde{R} \approx 0.33R_0$, which should be compared to $0.25R_0$ for the ideal chain in the same approximation. Not unexpectedly, the additional interactions in the Θ-chain lead to a larger ratio between the effective hard-sphere radius and R_0.

(*iii*) *Poor Solvent* (*Cf.* (*2.18*)–(*2.20*)):

$$u_{\mathrm{HW}}(x) = (3/2)|\xi|^2 n[1/x^6 - 2/x^3 + 1] \approx (27/2)|\xi|^2 n(1-x)^2[1 + O(1-x)] \qquad (5.17)$$

We thus obtain, in analogy to (5.15)

$$\tilde{R} \approx (R_0/2)[1 - \text{const} \times |\xi|^{-1}n^{-1/2}] \qquad (n \to \infty) \qquad (5.18)$$

Compared to the good-solvent case, $\tilde{R}$ approaches the asymptotic value $R_0/2$ rather quickly.

The above results are, of course, based on rather drastic approximations. Nevertheless, they indicate that—particularly in the good-solvent case—corrections to the simple scaling ansatz (5.3) might be of considerable importance even for longer chains. We expect that this would similarly be the case for polymers interacting with other hard objects.

The treatment we have presented here could certainly be improved in many respects. As mentioned above, one should first of all allow for more realistic variations of the segment density. It seems to be promising to consider an approach which explicitly distinguishes between the extension of the chain perpendicular and parallel to the wall. As we have seen, the saddle-point approximation for the potential of mean force appears to be a somewhat questionable feature; however, an improved approach could, at least, yield interesting information on how the size and shape of the polymer changes with its distance from the wall. Simulations, similar to those by Olaj et al.[13,25,26] for interactions between chains, would, of course, also be of interest.

6. Conclusion

We have discussed simple models for the interaction between linear polymers in (dilute) solution and for the interaction of a polymer with a hard wall. The models are extensions of a simple MF approach introduced by DiMarzio for the description of the polymer collapse transition. The basic feature of the approach (and its extensions) is that the polymer molecules are characterized by a size parameter (their end-to-end distance or radius of gyration) and an associated segment-density profile. The statistical weight associated with a certain size and profile, which yields a size-dependent free enegy, is estimated within the standard MF approximation, and it is assumed that average quantities of the ensemble of all chain configurations are solely determined by the minimum of this free energy. In particular, the average size of the molecule is identified with the value which minimizes the free energy, and the overall free energy of the ensemble is taken to be the corresponding "saddle-point" value.

We have considered two different models of the segment-density profile. In the first, the molecules are described as spheres with constant segment densities, following DiMarzio's original treatment. The extension of this approach to the case of two interacting molecules leads to reasonable results for the potential of mean force between the two molecules in the case of good solvents but to unreasonable results in poor solvents. In the second model, therefore, we have introduced a modified approach in which the molecules are described by a more realistic Gaussian-density profile. In that, the approach is analogous to the Flory–Krigbaum theory. However, unlike the FK theory, its validity is not restricted to good solvents; the reason is that higher order interactions between segments (which become important in Θ and poor solvents) are, at least approximately, taken into account. The approach leads to reasonable results for the pair potential and the osmotic second virial coefficient for all solvent conditions if the molecules are not assumed to adjust their size (i.e., to minimize the mutual size-dependent free energy) with respect to the intermolecular distance. In contrast, the pair potential associated with the saddle-point of the mutual free energy still shows some physically unreasonable features in poor solvents. While the applicability of the MF/saddle-point approach to the pair potential is thus questionable, the approach nevertheless yields physically reasonable results for the variation of the (average) size with the intermolecular distance. For athermal and Θ-chains, the results were found to be in good qualitative agreement with simulation results given in the literature.

The simple constant-density model has also been applied to the problem of a polymer molecule interacting with a hard wall. We have discussed the potential of mean force between the molecule and the wall and the behavior of the effective hard-sphere radius of the polymer. The results indicate that corrections to a simple scaling behavior might be rather important, particularly in good solvents.

Our investigations have shown both the merits and the shortcomings of the MF/saddle-point approach. While it does not lead to completely satisfying results with respect to the potential of mean force, it nevertheless appears to be a rather useful tool to predict average configurational properties (size, shape, etc.) of the polymers. It would therefore be of interest to extend this work by taking more realistic density profiles into account, i.e., profiles which are more suited to the particular situation of the polymer(s) than the ones discussed here. Simulations of the pair potentials in poor solvents as well as of the potential of a polymer at a hard wall would also be of great interest in order to check the ideas presented in this paper.

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