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Conformation of Star Polymers without Excluded Volume

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ABSTRACT: Nonideal behavior in the vicinity of the point where chains are attached together can significantly affect the dimensions of branched polymers. Several features of the branch point are considered, and their effect on the radius of gyration of star-shaped molecules is calculated. Two classes of behavior are found according to whether the description treats only specific geometrical properties of the monomers close to the junction or perceives the branch point more generally, as a region of reduced accessibility to more distant parts of the molecule. A new model is introduced within the latter category in which a repulsive potential surrounds the branch point and acts on all the monomers. For the special case of a hard-sphere potential an exact solution is found, from which a general relationship, $\langle S^2\rangle^{1/2} - \langle S^2\rangle_0^{1/2} \approx c$, is derived, linking the mean squared radius of gyration, $\langle S^2\rangle$, to its value in the unperturbed state, $\langle S^2\rangle_0$, and to a length, c, characteristic of the range of the potential. It is shown how the effect of the repulsive potential can be distinguished experimentally from local, geometrical properties of the branch point, and from the available data it is concluded that this repulsive nature of the branch-point region is the more important factor in determining the size of star-branched polymers.

Introduction

The simplest descriptions of polymer chain conformation are based on the random walk or Gaussian model. The central assumption of such theories is that in a statistical ensemble of chains of equal length, the distance r_{ij} between monomers i and j is governed by a Gaussian distribution whose variance is proportional to the number of monomers between i and j along the backbone of the chain, that is, $\langle r_{ij}^2\rangle = K|i - j|$. The effects of local interactions between a monomer and its first few closest neighbors are factored into the stiffness constant, K, but interactions between monomers well-separated along the chain are ignored. Chains that comply with the above considerations are referred to as "unperturbed" chains, and it follows directly from the Gaussian assumption that the mean squared radius of gyration, $\langle S^2\rangle$, is proportional to N, the total number of monomers in the chain.[1] All the statistical properties of unperturbed chains may be expressed in terms of the single parameter $\langle S^2\rangle$.

The random walk model is known from experiment to apply to flexible linear polymers in the molten state and is also a good approximation in polymer solutions at the Θ temperature, where the combination of solution entropy and interaction energy conspires to eliminate the effects of long-range binary interactions. More generally, however, the statistical properties of polymers in solution *are* influenced by two-body interactions, and the random walk model must be adjusted by the inclusion of a second parameter, the "excluded volume".[2]

An extension of the random walk concept to branched chains was provided by Zimm and Stockmayer,[3] who assumed that the Gaussian distribution for r_{ij} applies whether i and j are on the same branch or not. In other words, two subchains joined at a point to one or more others behave statistically, as if they were one continuous linear chain. However, in spite of the success of the random walk model with linear chains, its application to branched molecules is much less tenable. Two factors are important. First, the effect of intramolecular excluded volume is more significant in a branched molecule because the number of segment–segment contacts increases as the intramolecular segment density becomes larger. Second, the Gaussian assumption fails to recognize the singular nature of the branch point. When several branches are attached together, spatial crowding prevents lateral motion and forces the chains to radiate away from each other. This imposes rigid correlations upon the initial trajectories of the arms, and a local increase in stiffness is likely. Furthermore, the region around the branch point is less accessible to monomers from further out on the molecule because it is not easy to force a path through the anchored branches, so random walking near to the branch point is inhibited.

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The failure of the Gaussian model has been frequently illustrated by experiments on star-shaped polymers. It has been recently shown[4] that in the molten state the sizes of many-arm star polymers are considerably expanded compared with unperturbed molecules. This swelling must be attributed to the effect of the molecular core, since all orders of excluded volume are screened out in the melt. Steric screening of monomers near the star point is also believed to be responsible for the shift in concentration of the cloud point curve in star/linear polymer blends.[5] In solution, excluded volume causes star polymers to expand still further from their melt sizes.[6] In the case of Θ solutions, the swelling has been shown to arise from important, residual, three-body interactions, which are thought to cause a constant expansion, independent of molecular mass.[7] With many-arm stars, therefore, it is likely that the influence of the core is most important at low molecular masses, while excluded volume effects dominate at high masses. This crossover of behavior appears to be evident in the series of 12-arm stars of Huber et al.[8] and the 270-arm stars of Roovers et al.[9]

With reference to star-shaped polymers, Daoud and Cotton[10] have argued that in order to minimize the repulsive interactions between segments a star molecule adopts a conformation in which each of the f arms may be considered as constrained within a cone of solid angle $4\pi/f$ radiating from the star point, so that the mean separation of the arms increases with distance from the center. For length scales smaller than the mean arm separation the arms behave as isolated linear chain segments and obey the scaling laws appropriate for unbranched polymers. In the solution state the intersegment repulsion is due to excluded-volume interactions, and the validity of the Daoud–Cotton model has been proven by its success in describing experimental and Monte Carlo data. In the molten state, however, there are no repulsive interactions between segments, so there seems no justification for the model's basic assumption that outside the core region the arms try to keep as far apart as possible. Another limitation of Daoud and Cotton's model is that it neglects the effect of the core region on the conformation of the molecule as a whole, so it applies only to molecules of very large molecular mass.

The experimental and theoretical considerations listed above emphasize the need for a better understanding of how the conformation of branched molecules is influenced by the branch point. In this paper we take the random walk conformation as a basis and investigate how several different branch point properties influence the dimensions of star polymers. Strictly speaking, our calculations apply only to the molten state, since excluded-volume effects are ignored, but when the overall change in molecular conformation is not too large the core and excluded-volume effects can be treated as independent perturbations on the same Gaussian "ground state", so the magnitude of the core effect should be the same in solution as in the molten state.

Models for Star Polymers

(i) Displaced Random Walks. We consider first those models that account only for specific properties of the center of the star. Included in this category is the calculation by Mansfield and Stockmayer[11] for wormlike stars, which introduces the effects of correlations between the initial directions of the arms in an otherwise unperturbed molecule. The rotational isomeric state (RIS) model of star polymers[12] is a more sophisticated example of this genre, since it can incorporate the specific bonding of the atoms in the core. One further model, based on the freely jointed chain but with a number of rigid bonds connecting each arm to the star point, is introduced to investigate the effect of induced stiffness close to star center.

All the above-mentioned models treat the branch point as a constraint only on monomers close to it along the chemical sequence. Monomers further along each arm may wander back through this region without further constraint. When the degree of polymerization is large the only difference between these models is in the description of the bonds in the immediate neighborhood of the branch point, and for the most part the trajectories of the arms may be represented by random walks starting from a point displaced a certain distance away from that point. In Appendix A it is shown that, to first order, the mean squared radius of gyration of such molecules may be written quite generally as

$$\langle S^2\rangle - \langle S^2\rangle_0 = c^2 \tag{1}$$

where $\langle S^2\rangle_0$ is the mean squared radius of gyration of a Gaussian star with N monomers and c is a constant, independent of N, and with dimensions of length. Equation 1 is reminiscent of the parallel axis rule for the moment of inertia of a rigid body.

The form of eq 1 can easily be verified for the specific models referred to above. In the limit when the length of the arms is much greater than the persistence length, Mansfield and Stockmayer's calculation for wormlike stars reduces to

$$\langle S^2\rangle - \langle S^2\rangle_0 = \left(\frac{1-2f}{4f} - \frac{F}{2f^2}\right)b^2 \tag{2}$$

where F is the sum of the cosines of the angles between pairs of arms at the star point and b is the Kuhn length (twice the persistence length). Since F is never smaller than $-f/2$,[11] it follows that for wormlike stars c^2 is always negative. Thus, if the only modification to the Gaussian model is the introduction of directional correlations between the arms at the branch point, then the radius of gyration is reduced, and the length c has no physical meaning.

As regards the RIS model, two studies have been undertaken that are of relevance to the present discussion. The calculations of Mattice[13] for polyethylene stars with up to 20 arms showed that the ratio $\langle S^2\rangle/\langle S^2\rangle_0$ was a linear function of $1/N$, as expected from eq 1, and that the wormlike and RIS models were in good agreement. More recently, the RIS model was used by Huber et al.[8] to calculate the global dimensions of polyethylene stars with two types of arm linking. Their "combinatorial" star has the same property as a Gaussian star, namely, that the mean-squared distance between two monomers is independent of whether or not they are on the same or different arms. The "specific" center introduced by Huber et al. is a bonding sequence for 12-arm stars similar to that at the center of real stars. The results presented in ref 8 have been replotted in Figure 1 with the x and y axes proportional to $1/N$ and $\langle S^2\rangle/N$, respectively. According to eq 1, such a graph has a gradient of c^2 and an intercept of $\langle S^2\rangle_0/N$. The data are evidently consistent with this analysis for both combinatorial and specific star types, and the respective values of c^2 obtained by linear regression are −0.28 and 0.04 nm^2.

The positive character of c^2 associated with the specific star center used in the work cited above is a result of the extended nature of the branch point, which more

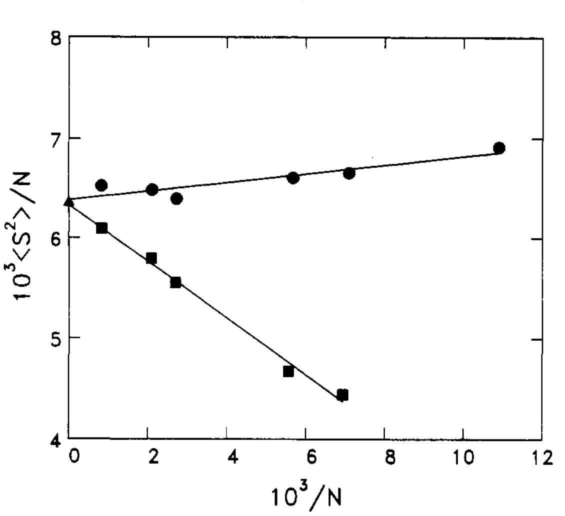

Figure 1. Data of Huber et al.[8] for 12-arm rotational isomeric state stars calculated with two types of branch-point structure: (■) combinatorial star with no defined branch-point geometry; (●) specific structure, related to the bonding sequence in real star polymers. The intercept point (▲) has been calculated from the values of $\langle S^2\rangle/N = 0.0269$ for a linear chain. The data are consistent with the form of eq 1 and yield c^2 values of -0.28 nm^2 and 0.04 nm^2.

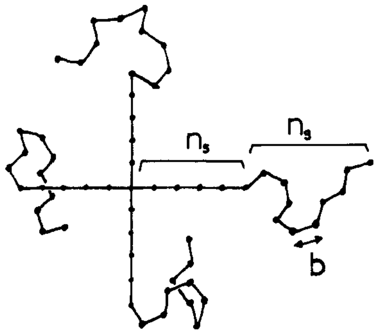

Figure 2. Rigid center model used to calculate eq 3, giving the effect of an increase in chain stiffness near to the branch point.

closely resembles reality than does the wormlike or Gaussian models. Another feature that may be associated with branch points is a local increase in chain stiffness brought on by crowding. We have calculated the radius of gyration of star molecules whose arms have n_g freely jointed bonds of length b, connected to the star point by n_s straight bonds of the same length (Figure 2). In the limit where $n_g \gg n_s$ this model yields

$$\langle S^2\rangle - \langle S^2\rangle_0 \approx \left(\frac{3f-1}{4f} + \frac{(f-1)}{f}n_s(n_s-2) - \frac{(2n_s-1)^2}{2f^2}F\right)b^2 \tag{3}$$

where F has the same meaning as before. Equation 3 has the same general form as eq 1, as anticipated, and when $n_s = 1$ it resembles quite closely eq 2 for wormlike stars. When there are two or more straight bonds $\langle S^2\rangle - \langle S^2\rangle_0$ is positive, and the length c is then characteristic of the size of the core. In this case the model may be likened to the RIS calculation with the specific center.

In summary: all the star polymer models described in this section have arms that might be regarded as "displaced random walks". These models may be identified by the molecular mass independence of the difference between the mean squared radius of gyration of the star and that of the unperturbed star (the latter being calculated within the random walk model from the size–mass relationship for linear chains of the same material).

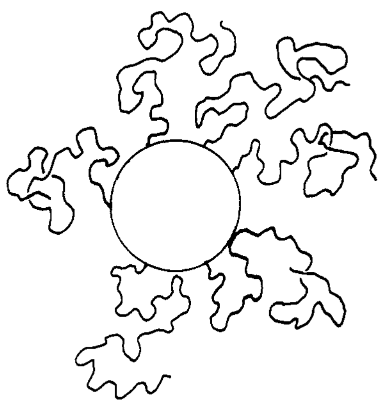

Figure 3. Impenetrable sphere model of a branch point. The arms are free to diffuse about at random as long as they do not enter the central sphere.

(ii) Exclusion Zone around the Branch Point. None of the previous models take account of the effective repulsion between the star center as a whole and monomers situated many units away from it on the arms. We have modeled this phenomenon by defining a molecule comprised of an impenetrable sphere of radius r_0 onto whose surface f flexible arms are attached. Outside of the sphere the arms are free to adopt any configuration, as long as no monomer ventures inside the sphere (Figure 3). Though the hard-sphere potential is somewhat unrealistic for star polymers (it would perhaps be more appropriate for polymers adsorbed onto a spherical surface, such as surfactant molecule stabilizing a microemulsion), it has the distinction of being a one-parameter potential and should in any case be sufficient to account for the first-order deviations from the random walk model.

The static properties of this model are obtained by solving the diffusion equation with an infinite spherical potential, and details of the calculation are given in Appendix B. There, a power series expression is developed for the mean squared second moment, $\langle r^2\rangle$, of the monomer distribution about the star point. Although the experimentally measured quantity is $\langle S^2\rangle$, not $\langle r^2\rangle$, it might be expected that the expansion $\langle S^2\rangle/\langle S^2\rangle_0$ of the radius of gyration is very similar to that of the second moment, $\langle r^2\rangle/\langle r^2\rangle_0$. Equation B10 of the Appendix can therefore be written in terms of $\langle S^2\rangle$:

$$\frac{\langle S^2\rangle}{\langle S^2\rangle_0} = 1 + 2.15\left(\frac{3f-2}{6f}\right)^{1/2}\frac{r_0}{\langle S^2\rangle_0^{1/2}} + ... \tag{4}$$

The second-order term in the series is positive, so a reasonable approximation is to terminate the series after the first term and take the square root

$$\begin{aligned}\langle S^2\rangle^{1/2} - \langle S^2\rangle_0^{1/2} &\approx \frac{2.15}{2}\left(\frac{3f-2}{6f}\right)^{1/2} r_0 \\ &\approx c\end{aligned} \tag{5}$$

Thus, for a given number of arms, the difference between the real and unperturbed radius of gyration is independent of the molecular mass of the polymer. When f is large

$$c \approx 0.76 r_0 \tag{6}$$

so c may be identified with the range of the repulsive potential whose f dependence then determines the variation of swelling with degree of branching.

One may speculate as to the nature of this dependence of r_0 on f. One possibility is that the range of the potential corresponds to the distance away from the star point at which the arms attain a certain mean separa-

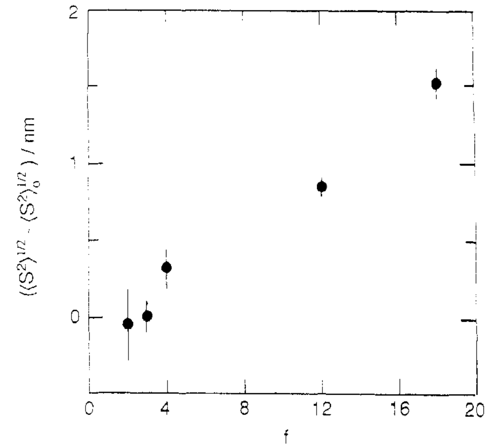

Figure 4. Small-angle neutron scattering results[4] for the radius of gyration of linear and star-branched polyethylenes in the molten state.

tion from each other. On the basis of this logic it follows that r_0 scales as $f^{1/2}$ and hence leads to a square root dependence of c on f. Alternatively, r_0 may scale with the radius within which the intramolecular segment density exceeds a certain value. For a rodlike star this hypothesis yields $r_0 \sim f^{1/2}$ again, whereas for a Gaussian star the result would be $r_0 \sim f$. We suggest, therefore, an intermediate scaling law of the form $r_0 \sim f^{m/2}$, where m is between 1 and 2. Thus

$$c \sim f^{m/2}, \quad f > 2, \ 1 \leq m \leq 2 \qquad (7)$$

It may be seen immediately that this repulsive potential model predicts a much more severe effect than does case (i), the displaced random walk, since from eq 4 we now have $\langle S^2\rangle - \langle S^2\rangle_0 \sim br_0N^{1/2}$. For the same reason it is not crucial in this model where on the surface the chains are presumed to be anchored, as this generates only displacement effects of the form (1).

Comparison with Experiment

The first experiments to indicate deviations from random walk statistics for branched polymers were light scattering measurements made on star polystyrenes[14] and polyisoprenes[15] in dilute solution at the Θ temperature. Since then, the radius of gyration of stars with greater than four arms has been shown repeatedly to exceed the corresponding unperturbed radius of gyration, and the effect is particularly severe at low molecular masses.

The explanation of this swelling in low molecular mass stars immediately requires a theory that goes beyond the wormlike model, which in accounting only for directional correlations at the star point, predicts a slight contraction in coil dimensions (eq 2). A comparison of the law for displaced random walk stars, eq 1, with that of the impenetrable sphere model, eqs 5 and 7, was recently facilitated by a small-angle neutron scattering study of low molecular mass polyethylene stars in the molten state.[4] An analysis of a series of 12-arm stars spanning over a decade in molecular mass showed that the quantity $\langle S^2\rangle - \langle S^2\rangle_0$ increased strongly with molecular mass, while $\langle S^2\rangle^{1/2} - \langle S^2\rangle_0^{1/2}$ was virtually constant. Thus, it was concluded that the most significant deviation from Gaussian statistics in molten star polymers is due to the relative impermeability of the region around the star point. On the assumption that eq 5 applied to all functionalities, with c a function of f, the values of c were determined and plotted against f. The results are reproduced in Figure 4. In ref 4 the points were arbitrarily fitted with a straight line, but the number of f values is small, and the data could equally be fitted to a weaker dependence on f. Equation 7, with $1 \leq m \leq 2$, is consistent with these results.

We have attempted a similar analysis with the series of 12- and 270-arm stars[8,9] mentioned earlier. Unfortunately, however, the radii of gyration were not measured with sufficient accuracy in either experiment to permit a meaningful test of eqs 1 and 5, and in addition it was difficult to make reliable corrections for the expansion due to excluded volume, either in Θ or good solvent.

Discussion and Conclusion

From the experimental evidence described in the last section it is concluded that the most important consideration in the description of the global dimensions of branched polymers wihtout excluded volume is the repulsive effect of the region around the branch point on the monomers that make up the rest of the molecule.

This statement is not meant to imply, however, that the RIS-type models discussed earlier should be rejected for other properties of branched polymers. The impenetrable sphere model makes no assumptions about the interior of the spherical center and so applies to properties dependent on long-range correlations within the molecule. To describe short-range effects, it is important to have a more accurate model of the architecture of the branch point. The scattering function of a star polymer at large angles, for instance, is strongly dependent on interferences between the arms near to the star point, as has been demonstrated by neutron scattering.[16] Thus, in the language of scattering practitioners, the impenetrable sphere model is applicable at low Q, while RIS-type models are more appropriate at high Q. A complete model of branch points should combine features of both approaches.

At the present time, data on short-arm stars without excluded volume are scant, and the conclusions reached here are based entirely upon the results of one neutron scattering study. However, in view of the surprisingly large swellings observed for the small, many-arm stars, there appears to be little justification for the neglect of such steric influences of branch points on the conformation of flexible polymers. Since theoretical descriptions of the bulk properties of polymers often depend on the molecular dimensions, it is important to know the swelling behavior of branched polymers if the theories are to be extended to such materials. It is hoped that the simple analysis presented in this paper might stimulate further experimental effort and thereby lead to a better understanding of the role of branching in polymer science.

Acknowledgment. We thank one of the referees for sending us a copy of refs 5 and 9.

Appendix A

Displaced Random Walk Models of Star Polymers. The derivation of eq 1 is a simple one and uses reasoning analogous to that which leads to the parallel axis rule for moments of inertia. For the present problem the moment of inertia is replaced by the squared radius of gyration, S^2, defined as the mean squared distance from the monomers to the center of mass of the molecule.

Suppose that each of the f arms radiates away from the star point with some specific bonding sequence that transforms, at a certain radius, into a pure random walk (as illustrated in Figure 2). When averaged over an ensemble of similar molecules the mean squared distance from

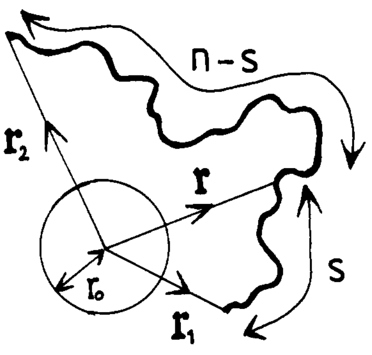

Figure 5. Notation used in the calculation of the molecular radius of gyration in the impenetrable sphere model. The ends of the chain segment have position vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ relative to the center of the sphere, and the position vector $\mathbf{r}$ corresponds to a point at a contour length s along the chain.

a particular monomer, j, to the center of mass can be decomposed into the sum of two terms:

$$\langle S_j^2\rangle = \langle R_{0c}^2\rangle + \langle r_j^2\rangle \tag{A1}$$

where $\langle R_{0c}^2\rangle$ and $\langle r_j^2\rangle$ are, respectively, the mean-squared distances from the centre of mass and from monomer j to the beginning of the random walk section of the arm. The mean squared radius of gyration, $\langle S^2\rangle$, is now obtained be taking the average of eq A1 over all the N monomers in the molecule:

$$\langle S^2\rangle = \frac{1}{N}\sum_j(\langle R_{0c}^2\rangle + \langle r_j^2\rangle) \tag{A2}$$

In eq A2, $\langle R_{0c}^2\rangle$ is the same for all j and so can be taken out of the sum, and the $\langle r_j^2\rangle$ contribution from the N_c monomers in the non-Gaussian central part of the molecule is proportional to N_c/N, so can be neglected if $N \gg N_c$. The remaining terms in the sum are identical with those of a random walk star with $N - N_c$ monomers, so that

$$\langle S^2(N)\rangle = \langle R_{0c}^2\rangle + \langle S^2(N-N_c)\rangle_0 + O(N_c/N) \tag{A3}$$

$\langle S^2(N)\rangle_0$ is the radius of gyration of a Gaussian polymer and is proportional to N, so

$$\langle S^2(N-N_c)\rangle_0 = \langle S^2(N)\rangle_0 - \langle S^2(N_c)\rangle_0 \tag{A4}$$

The amalgamation of eq A3 and A4 gives, to first order

$$\langle S^2\rangle - \langle S^2\rangle_0 = c^2 \tag{A5}$$

as required, with c^2 independent of N. The sign of c^2 is determined, in the limit of large N, by the competition between the terms $\langle R_{0c}^2\rangle$ from eq A3 and $-\langle S^2(N_c)\rangle_0$ from eq A4.

Appendix B

Impenetrable Sphere Model. The problem of f linear chains attached to an impenetrable sphere is perhaps most easily visualized as a Monte Carlo calculation: random walks are generated starting on the surface of a sphere, and any walk that involves an incursion into the spherical exclusion zone is rejected. Here, the problem will be solved by an equivalent, but analytic, method.

A statistical weight $W_n(\mathbf{r}_1,\mathbf{r},\mathbf{r}_2;s)$ is associated with a particular configuration of the chain of n monomers that starts at $\mathbf{r}_1$, finishes at $\mathbf{r}_2$, and has monomer s located at $\mathbf{r}$. The situation is illustrated in Figure 5. Once W_n has been determined, the segment density distribution is evaluated from

$$\phi(\mathbf{r}) = \frac{\sum_{s=1}^{n}\int d\mathbf{r}_2\int d\mathbf{r}_1\, W_n(\mathbf{r}_1,\mathbf{r},\mathbf{r}_2;s)}{\sum_{s=1}^{n}\int d\mathbf{r}\int d\mathbf{r}_2\int d\mathbf{r}_1\, W_n(\mathbf{r}_1,\mathbf{r},\mathbf{r}_2;s)} \tag{B1}$$

whence the second moment follows from

$$\langle r^2\rangle = \int r^2\phi(\mathbf{r})\, d\mathbf{r} \tag{B2}$$

Hereafter, s will be treated as a continuous variable, and so the sums will be converted to integrals.

The $\mathbf{r}_1$ and $\mathbf{r}_2$ integrals are immediately separable, since for noninteracting chains the W_n must obey the law of joint probability:

$$W_n(\mathbf{r}_1,\mathbf{r},\mathbf{r}_2;s) = G(\mathbf{r}_1,\mathbf{r};s)G(\mathbf{r},\mathbf{r}_2;n-s) \tag{B3}$$

The function $G(\mathbf{r}_1,\mathbf{r};s)$ represents the probability that if a chain of s segments has one end at $\mathbf{r}_1$, then the other end will be in a volume $d\mathbf{r}$ at $\mathbf{r}$. Technically, G is Greens' function for the problem, and satisfies a diffusion, or Schrödinger, equation:[17]

$$\frac{b^2}{6}\nabla^2 G - \frac{\partial G}{\partial s} = U(\mathbf{r})G - \delta(\mathbf{r}-\mathbf{r}_1)\delta(s) \tag{B4}$$

where b is the segment length and U is the potential. The δ function on the right-hand side of eq B4 expresses the condition that the segment at the chain end $s = 0$ is fixed at $\mathbf{r} = \mathbf{r}_1$. The equation need only be solved for the region outside the sphere where $U = 0$; within the sphere G must be zero. Also, since the geometry of the problem is spherically symmetric, eq B4 may immediately be integrated over a solid angle and recast in the form

$$\frac{b^2}{6}\frac{\partial^2 u}{\partial r^2} - \frac{\partial u}{\partial s} = -\frac{1}{r}\delta(r-r_1)\delta(s) \tag{B5}$$

where $u = Gr$. The full solution for G may be obtained by means of a Laplace transformation and is

$$G(\mathbf{r}_1,\mathbf{r};s) = \frac{1}{rr_1}\left(\frac{3}{2\pi sb^2}\right)^{1/2}\left\{\exp\left(-\frac{3(r-r_1)^2}{2sb^2}\right) - \exp\left(-\frac{3(r+r_1-2r_0)^2}{2sb^2}\right)\right\} \tag{B6}$$

The first Greens' function in the product of eq B4 is a special case of eq B6 in which $r_1 = r_0$. In fact as r_1 tends to r_0, G becomes proportional to $(r_1 - r_0)$ and finally vanishes *at* $r_1 = r_0$. However, since G always occurs in ratios like eq B1, the prefactor cancels, and only the r-dependence need be retained. The limiting form is

$$G(\mathbf{r}_1,\mathbf{r};s) \propto \frac{(r-r_0)}{rs^{3/2}}\exp\left(-\frac{3(r-r_1)^2}{2sb^2}\right) \tag{B7}$$

The second term of the product in eq B4 for W_n may similarly be written

$$G(\mathbf{r},\mathbf{r}_2;n-s) \propto \frac{1}{rr_2(n-s)^{1/2}}\left\{\exp\left(-\frac{3(r_2-r)^2}{2(n-s)b^2}\right) - \exp\left(-\frac{3(r_2+r-2r_0)^2}{2(n-s)b^2}\right)\right\} \tag{B8}$$

Equations B7 and B8 are sufficient to enable $\phi(\mathbf{r})$ to be calculated from eq B1, and hence the more relevant quantity $\langle r^2\rangle$ can be found.

The integration is laborious, but straightforward, and gives the exact result for $\langle r^2 \rangle$:

$$\langle r^2 \rangle = \frac{1}{2} n b^2 \frac{(1 + \alpha x + \beta x^2 + \gamma x^3)}{(1 + \delta x)} \tag{B9}$$

where

$$x = \frac{r_0}{n^{1/2} b}$$

$$\alpha = \frac{46}{9}\left(\frac{3}{2\pi}\right)^{1/2}$$

$$\beta = 2\left(1 + \frac{8I}{\pi^{1/2}}\right)$$

$$\gamma = 4(3/2\pi)^{1/2}$$

$$\delta = 2(3/2\pi)^{1/2}$$

and I is the multiple integral

$$I = \int_0^\infty dt \int_0^\infty dy \frac{t^{3/2}}{(1 + t)^2} y^2 \exp(-ty^2) \operatorname{erf}(y) = 0.3316$$

When $x = 0$, expression B9 reduces to $(1/2)nb^2$. This is just $\langle r^2 \rangle_0$, the mean squared second moment of a Gaussian polymer about its midpoint, as may be derived with the Wang–Uhlenbeck theorem.[2] Since x is expected to be much less than unity, it is sufficient to write eq B9 as a power series and to retain only the first few terms:

$$\langle r^2 \rangle / \langle r^2 \rangle_0 = 1 + 2.15x + 2.02x^2 + \ldots \tag{B10}$$

Finally, it should be remarked that in the above calculation the segment density inside the hard sphere has been neglected. It can be shown, however, that if a realistic segment density is included in the calculation, the correction to eq B10 is at worst second order in x, so results (5) and (6) are still valid to first order.

References and Notes

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