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Equilibrium Partitioning of Flexible Macromolecules between Bulk Solution and Cylindrical Pores

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ABSTRACT: A Monte Carlo technique was used to investigate the effects of segment length and chain length on the partitioning of freely jointed chains between bulk solution and cylindrical pores. The results demonstrate that the partition coefficient, or equilibrium pore-to-bulk concentration ratio, of a chain with finite segment length can be substantially higher than that of a chain with an infinite number of infinitesimally short segments but with the same radius of gyration. These differences are prominent even for chains having more than 400 segments and become increasingly important as the radius of gyration of the macromolecule approaches and exceeds the pore radius. The effects of attractive interactions between chain segments and the pore wall, in the form of a square-well potential, were also investigated with the Monte Carlo technique. The introduction of small, attractive interaction energies produced dramatic increases in the partition coefficients of finite chains.

Introduction

The behavior of flexible macromolecules in finely porous materials plays an important role in separtion processes such as ultrafiltration and size-exclusion chromatography. The equilibrium distribution of macromolecules between bulk solution and the porous medium must be known in order to understand these processes. This equilibrium is usually expressed in terms of the partition coefficient or equilibrium pore-to-bulk concentration ratio.

In one of the earliest theoretical studies of the partitioning of flexible macromolecules, Casassa[1] derived expressions for the partition coefficient of a random-flight chain in pores of various shapes. Using an analogy to heat conduction, he found the partition coefficient, K, for a chain with radius of gyration $\langle s^2 \rangle_0^{1/2}$ in a cylindrical pore of radius R to be

$$K = 4 \sum_{i=1}^{\infty} (1/\alpha_i^2) \exp(-\alpha_i^2 \lambda_G^2) \qquad (1)$$

where $\lambda_G = \langle s^2 \rangle_0^{1/2}/R$ and the α_i are the roots of $J_0(\alpha) = 0$, J_0 representing the Bessel function of the first kind and of order zero. While the analysis is valid for a chain with an arbitrary distribution of segment lengths, the results were obtained for the limiting case of an infinite number of chain segments with vanishingly small mean length. (The boundary condition used in the derivation is physically reasonable only in this limit.) Casassa's concise and elegant result indicates the importance of the molecule-

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to-pore size ratio, λ_G, in partitioning. Casassa and Tagami[2] later extended this work to starlike, random-flight chains.

Daoud and de Gennes[3] have also studied the partitioning of polymer chains with infinitely many segments of vanishingly small length. Using scaling arguments, they confirmed the trends found by Casassa for ideal chains (i.e., in Θ solvents) and extended the analysis to good solvents. Unfortunately, this approach does not provide numerical coefficients, making quantitative comparisons impossible.

In another theoretical study of macromolecular partitioning, Giddings et al.[4] formulated expressions for the partitioning of rigid macromolecules in pores of simple shapes using statistical mechanical and geometrical arguments. One of the macromolecular shapes considered, that of a thin, rigid rod, can be viewed as the limiting case of a chain with a single segment. Giddings et al. expressed the partition coefficient for the rigid rod in a cylindrical pore in terms of combinations of elliptical integrals depending only on the segment-to-pore size ratio, l/R. Aubert and Tirrell,[14] using a linear elastic dumbbell model, calculated partition coefficients for polymer chains in pores of various geometries. For a cylindrical pore and $\lambda_G = 1$, K was approximately 0.2, some 2 orders of magnitude larger than the value obtained from eq 1, and similar to the results of Giddings et al.[4] for a rigid rod with $\lambda_G = 1$.

More recently, Priest[5] considered the system of a freely jointed chain in a cylindrical pore with the restriction that $l/R \geq 2$, i.e., under the condition that no segment can take on every orientation in the pore. With the assumption that the freely jointed chain consists of n points connected by segments of length l, the radius of gyration, $\langle s^2\rangle_0^{1/2}$, is given by[6]

$$\langle s^2\rangle_0^{1/2} = l[(n-1)(n+1)/6n]^{1/2} \tag{2}$$

Using an integral equation method, Priest solved for the partition function of such a chain to obtain

$$K = (\zeta/2\pi)^{n-1} \tag{3}$$

where ζ are eigenvalues that depend only on the ratio l/R. Because of the restriction on Priest's solution, it cannot be compared with Casassa's result at low molecule-to-pore size ratios and reasonably large values of n. However, at $\lambda_G = 1.5$ Priest's prediction for $n = 3$ is 4 orders of magnitude larger than the $n \rightarrow \infty$ limiting value of Casassa. Although this discrepancy will be considerably smaller at the n and λ_G values of most practical interest, the comparison demonstrates the potential importance of the ratio l/R. In systems of practical importance this ratio varies widely; for example, pore sizes in size-exclusion chromatographic materials vary from about 10^2 to 10^5 Å while effective segment lengths for polymer molecules are typically 5 to 40 Å. These figures yield a range of l/R values from 5×10^{-5} to 0.4. The primary purpose of the work described here is to examine and elucidate the dramatic effects of finite l/R and n on the partitioning of freely jointed chains in cylindrical pores.

As an extension of this problem, we have considered the effects of attractive, polymer–pore interactions on the partitioning of freely jointed chains in cylindrical pores. A number of authors have used lattice models to study the effects of polymer–pore interactions on finite[7] and infinite[8,9] chains in slitlike pores and on infinite chains in pores of square cross section.[10] While differences in pore geometry prevent quantitative comparison with the results of these studies, our understanding of interaction effects may be increased by qualitative comparison. The studies of Zhulina et al.[9] and Gorbunov et al.[10] are most useful for this purpose because these authors have considered energies of attraction in the regime where adsorption of polymer to the pore surface is not the dominant effect.

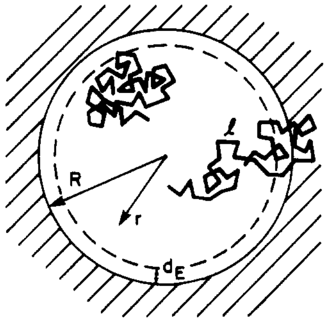

Figure 1. Cross-sectional view of cylindrical pore. Two freely jointed chains consisting of segments of length l are shown, one of which lies completely within the pore of radius R. There is an interaction region of thickness d_E adjacent to the wall.

Model Formulation and Computational Methods

Purely Steric Partitioning. The problem geometry is depicted in Figure 1. We consider a chain containing n mass points that are connected by rectilinear segments of length l. The chain is placed, hypothetically, in a pore of radius R with its center of mass at a radial position r. Some chain conformations will lie completely within the pore; others will not. The fraction of all chain conformations that lie within the pore at a given radial position is denoted by p. The partition coefficient is then given by

$$K = \int_0^R p(r) r \, \mathrm{d}r \Big/ \int_0^R r \, \mathrm{d}r \tag{4}$$

where the normalization factor in the denominator ensures that $K = 1$ when $p = 1$ everywhere. Equation 4 can be rewritten in terms of the dimensionless radial position $\beta = r/R$ as

$$K = 2 \int_0^1 p(\beta)\beta \, \mathrm{d}\beta \tag{5}$$

The Monte Carlo approach[11] was chosen to study this problem, since it allows a wide range of finite l/R values to be considered while at the same time letting n be varied. By calculating $p(\beta)$ and performing the required integration explicitly, rather than sampling positions within the pore randomly to arrive at the partition coefficient, we gain the detailed information about the radial distribution of macromolecules within a pore contained in $p(\beta)$. This information is needed, for example, to estimate the diffusive and convective fluxes of macromolecules through membrane pores.

The procedure used to determine the partition coefficient using the Monte Carlo technique was as follows. A chain was generated by choosing vectors of fixed length and random direction and adding the segment vectors end-to-end until the chain was of the desired length. The direction of each segment vector was found by choosing randomly the orientation angles in a spherical polar coordinate system with its origin at the previous mass point, such that the vector end point would intersect all positions on a sphere of radius l with equal probability. When chain generation was completed, the center-of-mass of the chain was placed at a number of radial positions within the pore and it was tested to determine whether all of its segments fell within the bounding surface. If the entire chain fell within the pore, a success was recorded. This process was repeated for an ensemble of chains to yield the fractional success rate $p(\beta)$ as a function of the dimensionless radial position β. Integration of the fractional success rate over all radial positions as in eq 5 yielded the partition coefficient. All integrations were performed by using Simpson's rule.

The molecule-to-pore size ratio, $\lambda_G = \langle s^2\rangle_0^{1/2}/R$, was varied from 0.2 to 1.4. In most cases chains containing 20–800 mass points (corresponding to l/R values between 0.015 and 1.00) were considered. Because the determination of $p(\beta)$ follows binomial statistics, the fractional error in $p(\beta)$ is roughly proportional to $[Mp(\beta)]^{-1/2}$, where M is the number of chains tested (see Appendix). An analysis of the propagation of these errors into the partition coefficient showed that the fractional error in K depends on M in a similar way. Therefore, as the partition coefficient decreases (with increasing λ_G), the size of the test population must be increased accordingly to maintain accuracy. In this study the test population ranged from 8×10^4 to 5×10^6 chains. To within ca. 95% confidence, the reported partition coefficients from the Monte Carlo simulations for purely steric partitioning are accurate to within 2% for $\lambda_G \leq 0.8$ and 4% for $\lambda_G > 0.8$. A detailed error analysis is provided in the Appendix. At low values of λ_G, where computation was feasible, chains with as many as 6000 mass points were studied to examine the consistency of the Monte Carlo results with those of Casassa.[1] In addition, computations with values of n between 2 and 4 were performed for comparison with the results of Giddings et al.[4] and Priest.[5] In all cases $p(\beta)$ was calculated at 100 evenly spaced radial positions within the pore. All computations were done on the CDC CYBER 205 at the John von Neumann Center, Princeton, NJ. Limited, explicit vectorization of the Fortran code yielded substantial increases in computational efficiency. As a representative example of the computation time required for these calculations, partitioning calculations for $\lambda_G = 0.8$ and $n = 100$ with an ensemble of 6×10^5 chains required approximately 23 cpu minutes. Computation time was found to be roughly proportional to M, the number of chains tested.

Steric Partitioning with Attractive Chain–Pore Interactions. In order to study the effects of attractive interactions between the polymer and the pore wall, we considered the partitioning of freely jointed chains in cylindrical pores interacting with mass points by means of a square-well potential along the wall. As shown in Figure 1, the system geometry differs from the above case only in that there is an annular interaction region of thickness d_E adjacent to the pore wall. A mass point that lies in this interaction region is taken to have an energy E. Consequently, a chain that lies within the pore and has j mass points within the interaction region has a total energy of jE.

In calculating the partition coefficient, the chain generation and testing procedures were identical with those described above. However, when the testing of a chain was successful the number of mass points, j, between radial positions $R - d_E$ and R was determined. The success was then recorded with a Boltzmann weighting factor of $e^{j\epsilon}$, where $\epsilon = E/kT$ is the dimensionless attractive interaction energy per mass point, k is the Boltzmann constant, and T is the absolute temperature. Integration of the weighted fractional success rate was performed as before to obtain the partition coefficient.

This procedure allowed the partition coefficients for many interaction energies to be determined simultaneously. Values of ϵ up to 0.30 were considered. In most cases the interaction distance d_E was set equal to the chain segment length l; however, the sensitivity of the partition coefficient to d_E was investigated briefly. The choice of $d_E = l$ corresponds to interactions between the pore wall and segments within one lattice length of the wall in the lattice models mentioned above and provides the best basis for comparison with those models. Chains containing 20–400 mass points were studied. All other parameters were varied in the ranges used in the study of purely steric partitioning. Error estimates, outlined in the Appendix, indicate that the results presented here for steric partitioning with attractive interactions are accurate to within 6%.

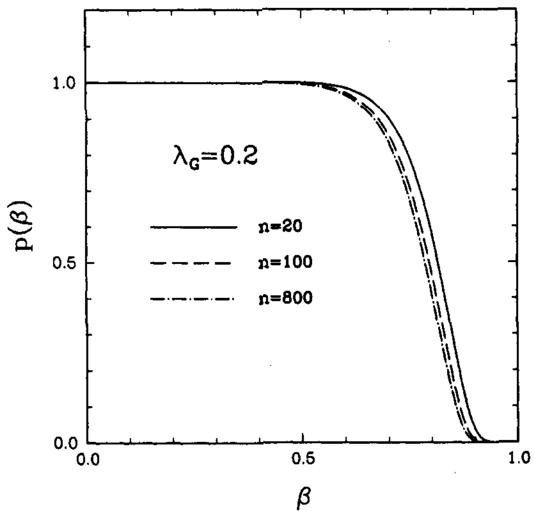

Figure 2. Fractional success rate $p(\beta)$ as a function of the dimensionless radial position β with molecule-to-pore size ratio $\lambda_G = 0.2$. The curves are the results of Monte Carlo simulations for chains containing 20, 100, and 800 mass points.

Results and Discussion

Purely Steric Partitioning. At low values of the molecule-to-pore size ratio, as in Figure 2 for $\lambda_G = 0.2$, the Monte Carlo simulations showed that the fractional success rate $p(\beta)$ was unity near the pore center, as expected, and remained close to unity until roughly $\beta = 1 - 2\lambda_G$. As β was increased further $p(\beta)$ dropped rapidly, reaching approximately 0.5 at $\beta = 1 - \lambda_G$ and zero at $\beta = 1 - 0.5\lambda_G$. In physical terms, relatively small macromolecules fit easily within the pore except in an annular region one to two radii of gyration in thickness, adjacent to the wall. While $p(\beta)$ profiles for chains of different n and l/R (at constant λ_G) differed slightly from one another at low λ_G values, they were qualitatively similar.

The effect of the number of mass points per chain (or finite step length) on the fractional success rate was much more dramatic at larger values of the molecule-to-pore size ratio. This is demonstrated in Figure 3. As can be seen, at $\lambda_G = 1.0$ chains with 20, 100, and 800 mass points (corresponding to l/R values of 0.55, 0.24, and 0.09, respectively) yielded very different $p(\beta)$ profiles. While the chains had identical radii of gyration, the chain with 20 mass points was able to access all regions of the pore more readily than the chains of 100 and 800 mass points. Even at the pore center line, where steric effects are weakest, the fraction of conformations fitting in the pore was nearly 3 times higher for 20-mass-point chains than for 800-mass-point chains. It should be noted, however, that at these high values of λ_G only a small fraction of all possible chain conformations fit within the pore.

Partitioning results when only steric interactions exist are summarized in Figures 4 and 5. Figure 4 demonstrates the effect of segment-to-pore size ratio (l/R) on the partition coefficient as a function of the molecule-to-pore size ratio (λ_G). Figure 5 sumarizes the same results on the purely steric partitioning of finite chains but in terms of number of points per chain (n). The results of Casassa[1]

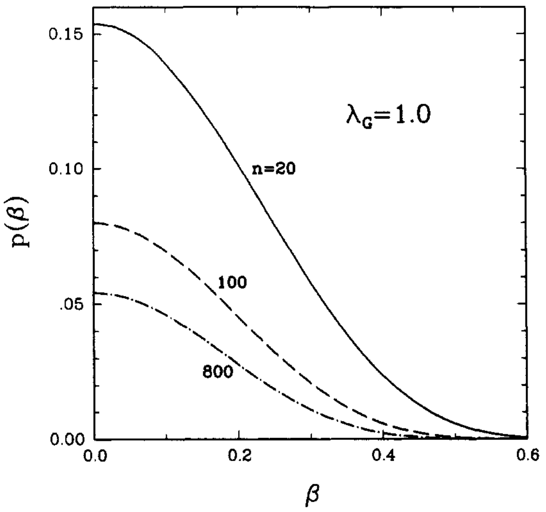

Figure 3. Fractional success rate $p(\beta)$ as a function of the dimensionless radial position β with molecule-to-pore size ratio $\lambda_G = 1.0$. The curves are the results of Monte Carlo simulations for chains containing 20, 100, and 800 mass points.

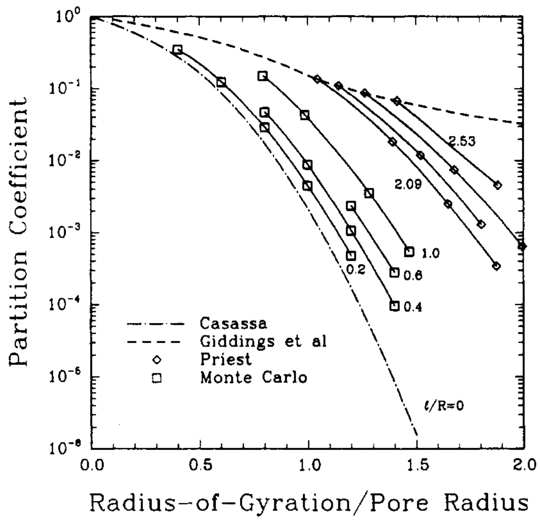

Figure 4. Steric partition coefficient K as a function of molecule-to-pore size ratio λ_G for various values of the step-to-pore size ratio l/R. Included are the analytical results of Casassa,[1] Giddings et al.,[4] and Priest[5] and the Monte Carlo results of this study.

and Priest[5] are shown, as well as that of Giddings et al.[4] for a rigid rod. As can be seen, the effect of finite segment length is very strong. At $l/R = 0.4$, a physically realizable value, the partition coefficient is up to an order of magnitude larger than in the limit $l/R = 0$. Even at a segment-to-pore size ratio as low as 0.09 the Monte Carlo results (not shown here) predict a partition coefficient (at $\lambda_G = 1.0$) that is nearly 40% larger than Casassa's limiting value. In practical systems, where the effective segment length is determined by the macromolecular structure, use of the partitioning result for a chain with an infinite number of vanishingly short segments will grossly underestimate the number of polymer molecules that penetrate the porous medium, especially when the pores become very small. This may be of partiticular importance in cases where the polymer of interest is relatively inflexible, in which an effective segment length may correspond to many monomer units. This phenomenon could make possible chromatographic separation of structurally different polymers of the same radius of gyration.

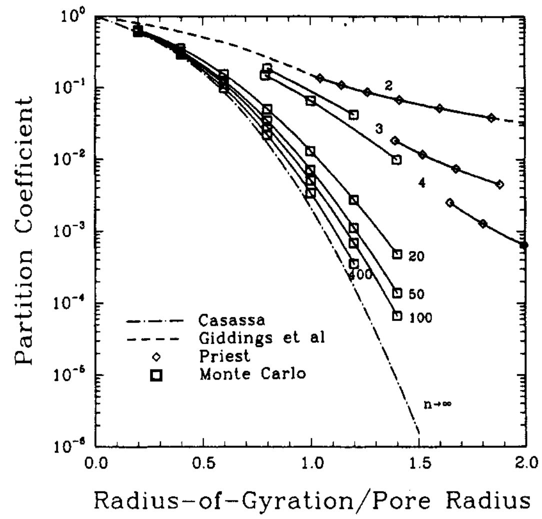

Figure 5. Steric partition coefficient K as a function of molecule-to-pore size ratio λ_G for various values of number of mass points per chain n. Included are the analytical results of Casassa,[1] Giddings et al.,[4] and Priest[5] and the Monte Carlo results of this study.

The partition coefficient, at constant molecule-to-pore size ratio, was found to be a linear function of l/R for $l/R \leq 0.15$, and linear extrapolation to $l/R = 0$ showed agreement with Casassa's predictions to within 1%. This finding, in combination with our ability to reproduce Giddings' rigid-rod results, provides strong evidence for the accuracy of our solutions. As λ_G increases, the Monte Carlo results begin to diverge strongly from Casassa's limiting value. Surprisingly, a chain of 50 mass points, which would be a reasonable approximation to an infinitely long chain in most bulk solution calculations, has a partition coefficient more than 16 times higher than the "infinite n limit" at $\lambda_G = 1.4$. Even a chain of 400 points differs from Casassa's limiting value by a factor of 2.

While the partitioning results presented in Figures 4 and 5 clearly demonstrate the importance of finite l/R and n on the partition coefficient, the numerical Monte Carlo solutions are not in a form that allows easy evaluation. For this reason, an empirical correlation of the Monte Carlo results was sought. At constant λ_G, ln K was found to vary linearly with the step-to-pore size ratio l/R, especially for $l/R \leq 0.5$. Based on this finding, the following approximating function was derived:

$$\ln K = \ln\,[K(l/R{=}0)] + (l/R)(0.49 + 1.09\lambda_G + 1.79\lambda_G^2) \quad (6)$$

In the above expression $K(l/R{=}0)$ represents the limiting value of Casassa shown in eq 1. Equation 6 approximates the partition coefficients from our Monte Carlo simulations to within 6% for $\lambda_G \leq 1.0$ and 25% for $\lambda_G > 1.0$. Therefore, in cases where l/R does not approach zero, this relation provides a significant improvement over Casassa's solution.

Steric Partitioning with Attractive Chain-Pore Interactions. Figure 6 demonstrates the effect of an attractive square-well potential near the wall of the pore on the partition coefficient for a chain of 50 mass points. The results for other values of n were qualitatively similar. As ϵ, the dimensionless attractive interaction energy per mass point (expressed as a fraction of kT), is increased, the partition coefficient increases substantially. This effect is most dramatic at large values of the molecule-to-pore size ratio. For example, at $\lambda_G = 1.0$ the partition coefficient for a 50-mass-point chain in a pore with $\epsilon = 0.2$ is 18 times larger than when there is no attractive interaction. Thus, chemically different polymers of similar size can be separated based on their relative attraction for the porous medium. It is also of particular interest that at approxi-

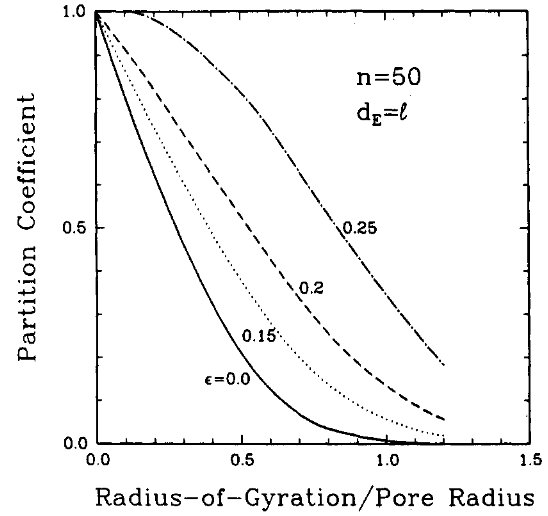

Figure 6. Partition coefficient K as a function of the molecule-to-pore size ratio λ_G for various values of the dimensionless, attractive interaction energy ϵ. The curves are the results of Monte Carlo simulations for chains containing 50 mass points and with the thickness of the interaction region d_E equal to the step length l.

mately $\epsilon = 0.2$ the partitioning curves change their curvature at low λ_G values from concave upward to concave downward. This effect can be seen clearly in the partitioning curve for $\epsilon = 0.25$ in Figure 6. This suggests that when large enough interaction energies exist there will be little separation of macromolecules on the basis of size alone if pore sizes are chosen such that $\lambda_G \leq 0.3$. Another significant trend worth noting is that the introduction of an attractive interaction energy exaggerates differences in the partition coefficients of chains with the same radii of gyration but different mass-point number. That is, as ϵ is increased the partitioning curves of different n values spread apart. This effect may be particularly relevant to polymer fractionation, where attractive interactions between the column packing material and the polymer might be exploited to enhance the size-based separation.

It should be pointed out that the results of these Monte Carlo simulations are extremely sensitive to the thickness of the interaction region d_E. For example, to get a tenfold increase in the partition coefficient of a 100-mass-point chain at $\lambda_G = 0.8$, an ϵ value of only 0.07 is required when $d_E = 2l$ as compared with 0.22 when $d_E = l$. Thus, any quantitative conclusions based on these calculations should be made with caution.

It is, however, useful to compare the interaction effects predicted by our model with those of previously reported lattice models. As mentioned earlier, these models assume that only segments in lattice sites adjacent to the pore wall interact with the wall, which is comparable to our assumption of $d_E = l$. On the basis of their lattice model calculations, Zhulina et al.[9] and Gorbunov et al.[10] have identified a critical interaction energy, ϵ_c, at which the entropic loss due to steric interactions is exactly offset by the energy of favorable polymer–pore interactions, such that the partition coefficient is unity. For large pores, where the effects of finite chain length are smallest, these authors found this critical interaction energy (expressed as a fraction of kT) to be between 0.18 and 0.21 for infinite chains in both slitlike and square pores. In comparison, our results indicate that the critical interation energy for large cylindrical pores is approximately 0.25–0.27 (see also Figure 6 for $\epsilon = 0.25$ at low values of λ_G). To the extent that the different model systems can be compared, these values of the critical interaction energy are indistinguishable. For smaller pores, our results indicate that the magnitude of the critical interaction should increase, in agreement with the predictions of Gorbunov et al. for a pore of square cross section. Below the critical interaction energy the increases in the partition coefficient predicted from our Monte Carlo simulations are qualitatively similar to those inferred from the work of Gorbunov et al.[10] when compared on the basis of equal ϵ/ϵ_c. For example, both models predict more than an order of magnitude increase in the partition coefficient at $\lambda_G = 1.0$, over that in the purely steric case, when an interaction energy of $\epsilon/\epsilon_c = 0.75$ is introduced. It is clear from this comparison that attractive chain–pore interactions have similar effects in pores of various shapes.

Although the present results are restricted to cylindrical pores, we expect the effects of chain structure (i.e., finite n and l/R) to be similar in pores of other geometries. Casassa[1,12] has derived expressions for the partition coefficients of a rigid rod ($n = 2$), a once-broken rod ($n = 3$), and a chain with an infinite number of vanishingly small segments ($n \rightarrow \infty$, $l/R \rightarrow 0$) in pores consisting of the void between two parallel, infinite planes. Comparison of his results on the basis of equal radii of gyration shows very substantial differences in the partition coefficients of these chains, which suggests strongly a significant effect of finite n and l/R in that pore geometry.

Of more general significance, this study provides an example of a situation in which, due to the presence of an additional length scale (the pore radius R), the common assumption that a chain of a few hundred segments can be adequately approximated by the $n \rightarrow \infty$ limit is incorrect. This finding, in addition to its importance in polymer separation problems, might play a significant role in other systems, such as colloid stabilization, where there are external length scales. In such systems, the details of chain structure may be an important consideration.

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Appendix: Error Estimation

When partitioning is purely steric the determination of $p(\beta)$ should follow binomial statistics. For a given number of chains tested M, the variance in $p(\beta)$ is

$$\sigma^2 = p(1 - p)/M \qquad \text{(A.1)}$$

For a linear combination of observations $\{x_i\}$ of the form

$$Y = \sum_{i=1}^{m} a_i x_i \qquad \text{(A.2)}$$

the variance in Y is given by[13]

$$\sigma^2{}_Y = \sum_{i=1}^{m} a_i{}^2 \sigma^2{}_i + 2\sum_{i=1}^{m} \sum_{j=i+1}^{m} a_i a_j \sigma_i \sigma_j \rho_{ij} \qquad \text{(A.3)}$$

where $\sigma^2{}_i$ is the variance of observation x_i and ρ_{ij} is the correlation coefficient between observations x_i and x_j. Because the numerical integration procedure represents the partition coefficient as

$$K \approx h \sum_{i=1}^{m} b_i \beta_i p(\beta_i) \qquad \text{(A.4)}$$

where h is the integration step size and the b_i are numerical coefficients, the variance in K was expressed in the form of eq A.3 with $a_i = hb_i\beta_i$ and the σ_i given by eq A.1. When the errors were estimated, the $p(\beta)$ values calculated in the

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Monte Carlo simulations were used as estimates of the true fractional success rates and the correlation coefficient ρ_{ij} was taken as unity (its maximum value) for all i and j. With the assumption of a normal distribution of the error, approximate 95% confidence limits are given by $K \pm 2\sigma_K$. In all of our calculations errors associated with numerical integration were negligible in comparison with the statistical errors.

Unfortunately, estimation of the errors in partition coefficients when there are attractive interactions is more difficult. The determination of $p(\beta)$ no longer follows binomial statistics because there are now $n + 2$ possible "states" a chain can occupy (failure or success with zero to n mass points in the interaction region) as compared with two "states" (failure or success) in the purely steric partitioning case. In addition, the exponential weightings employed in the calculation of $p(\beta)$ tend to exaggerate statistical fluctuations, especially at large n and high interaction energies where peaks appeared in the $p(\beta)$ profiles. Recognizing this, we estimated the additional error in the partition coefficient due to the introduction of the interaction energy as the difference between an approximate maximum partition coefficient and the partition coefficient calculated by the usual procedure. The maximum partition coefficient was estimated by performing the integration using the trapezoidal rule between local maxima in the $p(\beta)$ profiles (including a correction for the larger integration step size). This additional error was added to the error estimate for the purely steric partition coefficient to obtain the overall error in partition coefficients when attractive interactions are present.

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Confined Star Polymers

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ABSTRACT: The behavior of star polymers confined to a narrow slit in a good solvent is investigated by using scaling ("blob") analysis. In the confined star we distinguish (1) an interior region with spherical symmetry in which the confinement has no effect, (2) an intermediate region where the global spherical symmetry is lost, but the blob structure is still three-dimensional, and (3) an exterior region characterized by cylindrical symmetry. The concentration profile and the radius of the isolated star are obtained as well as its confinement free energy. Concentration effects are discussed. For this system we find six regimes rather than the five found for confined linear chains.

I. Introduction

The interest in polymer confinement is twofold: On the applied side, it is relevant to the study of polymer solution in porous media,[1] wetting by such solutions,[2] etc. From a theoretical point of view, the emphasis is on the various crossovers between three- and two-(one) dimensional behavior, which are associated with confined polymers. Most research efforts in this area have been directed toward the understanding of *linear* macromolecules under confinement.[3] In the following we will consider the theory of confined *star* polymers.

In recent years there has been an increased interest in branched polymers.[4] Of the various kinds of branched polymers, star-branched polymers may be synthesized so as to obtain well-characterized stars at varying numbers of arms (functionality). It is thus possible to probe their configurational properties as a function of their molecular weight and functionality. Such investigations were carried out on dilute star polymer solutions using static and dynamic light scattering as well as intrinsic viscosity measurements.[5]

Early theoretical studies of star polymers assumed Gaussian statistics. Their predictions, however, were not in good agreement with experimental results on stars with high functionalities. A scaling theory developed by Daoud and Cotton[5–7] generally accounts for the experimental results in this regime. Nevertheless, both experiment and a renormalization group study of Miyake and Freed[8] suggest that the Daoud–Cotton (DC) model is only valid for high functionalities (>7). On the other hand, for high functionalities, one may worry about spurious effects due to the complicated structure of the center. It is possible to avoid this difficulty if we replace the star polymers by colloidal particles stabilized by grafted linear polymers.[6,10] Bearing these considerations in mind, we will base our discussion on the DC model. We will consider a solution of star polymers, in good solvent, confined to a slit, i.e., between parallel plates. The slit walls will be assumed to

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