these aggregates may results from cross-links between PEO chains through the hydrated oxygen atoms.

Acknowledgment. Support of this work by the Natural Sciences and Engineering Research Council of Canada and the Department of Education of the Province of Quebec is gratefully acknowledged. The technical assistance of C. Vaillant is also acknowledged.

Registry No. PEO, 25322-68-3.

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Distribution of Random-Flight Polymer Chains in Solution near a Barrier†

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Received August 23, 1982

ABSTRACT: The problem of the equilibrium distribution of polymer chains in solution near an impenetrable but otherwise passive plane boundary is investigated with the assumption of random-flight statistics. Explicit expressions are obtained for the distributions of segments from specified positions (e.g., end segments and middle segments) along the contours of linear chains. A numerical integration leads to the total segment concentration profile in the depletion layer near the boundary. Some analytic properties of the segment profiles are discussed.

Introduction

When a flexible polymer chain in solution is placed near a nonabsorbing but impenetrable barrier, it is in an unfavorable entropy situation with respect to the bulk solution phase in that it is denied conformations that would be available to it in the absence of the barrier. The chain thereby experiences an effective repulsion from the barrier, and at equilibrium there exists near the barrier a depletion layer, in which the polymer chain-segment concentration increases from zero at the surface to approach the uniform value in the bulk phase. In the years since Asakura and Oosawa[1] first described this phenomenon, it has been invoked as the basis for the effect of dissolved polymer on stability of colloids[2-10] and for polymer fractionation by liquid size-exclusion (gel permeation) chromatography.[11,12] In chromatography, the net rejection of polymer chains from a micropore (the change in equilibrium polymer concentration between the pore and the bulk phase) and its dependence on chain length are of primary concern; but discussions of colloid effects focus more specifically on the character of the depletion layer. Another reason for interest in the depletion layer is that it is currently being studied directly by optical methods.[13]

In recent years several investigators have used computer simulation of lattice walks to model polymer chains in the depletion layer.[7-9] Such numerical approaches have the advantage that it is relatively simple to introduce the realistic complications of adsorption of polymer at the surface and interactions between chain segments. They have the disadvantage of not always affording the basic insight and revelation of subtle effects that even an extremely idealized analytic theory may provide.

In the following, we describe calculations of concentration profiles of polymer segments near a plane barrier (or large smooth colloidal particle). Since the derivation assumes random-flight statistics, the model can be applied rigorously only to a polymer in a Θ solvent. It has apparently not been noted that some simple analytic results

† Part of this work was presented at the IUPAC 28th Macromolecular Symposium, Amherst, MA, July 12–15, 1982.

0024-9297/84/2217-0601$01.50/0

are obtainable, even though an appropriate mathematical formulation has long been available from various sources, including our papers on the theory of exclusion chromatography of chain polymers.[11,12]

Distribution of Polymer in the Depletion Layer

We suppose that a random-flight linear chain of n segments with root-mean-square segment length b_0 is placed in a semiinfinite region $x > 0$ with one end at some point at distance x from the plane at $x = 0$. The plane is impenetrable to the polymer but otherwise noninteracting. The probability that the random-flight has not touched the boundary after n steps is[12]

$$P_{n,x} = \text{erf}\ (Ax) \tag{1}$$

where erf denotes the error function

$$\text{erf}\ y = \frac{2}{\pi^{1/2}}\int_0^y e^{-v^2}\,dv \tag{2}$$

and $A = (3/2nb_0^2)^{1/2}$. The quantity Ax is a dimensionless variable characterizing the ratio of distance x to an averaged chain dimension. Since $P_{n,x}$ is the probability of success in executing a random flight of n steps starting at x, it must be proportional to the concentration of chain-end segments at distance x from the wall in a solution containing many polymers identical with the test chain. Indeed, $P_{n,x}$ is equal to the dimensionless concentration $\rho(x)$ (or relative number density) of end segments normalized to unity as $x \to \infty$:

$$\rho_1(x) = \rho_n(x) = \text{erf}\ (Ax) \tag{3}$$

the subscript now designating the segment index along the chain.

We can proceed similarly to determine the concentration profile for segments other than those at the chain ends. We divide the chain of n segments into two subchains comprising m and $(n - m)$ segments. If segment m is placed at point x, the probabilities of successfully executing random flights of m and $(n - m)$ steps originating at x are independent, and the probability of a joint success is just a product of error functions, like that in eq 1, one for each subchain. Hence the concentration profile for the mth chain segments must be

$$\rho_m(x) = \text{erf}\left[\left(\frac{3}{2mb_0^2}\right)^{1/2} x\right] \text{erf}\left[\left(\frac{3}{2(n-m)b_0^2}\right)^{1/2} x\right] \tag{4}$$

The shape of the concentration profile for the mth segments is seen to depend on position m in the chain as well as on the chain length n. A quantity of greater interest, however, is the total (averaged) concentration profile due to all segments:

$$\bar{\rho}(x) = \frac{1}{n}\sum_{m=1}^{n}\rho_m(x) \tag{5}$$

which is again normalized to unity at large distances from the wall.

If the number of segments per chain is assumed large, we can let $u = m/n$ and $t = (3/2nb_0^2)^{1/2}x$ and write eq 5 in integral form:

$$\bar{\rho}(t) = \int_0^1 \rho(u,t)\,du = 2\int_0^{1/2}\rho(u,t)\,du \tag{6}$$

where

$$\rho(u,t) = \text{erf}\ (t/u^{1/2})\ \text{erf}\ [t/(1-u)^{1/2}] \tag{7}$$

Discussion

Some analytic properties of the segment concentration profiles derived above are of interest and are readily deduced. First, using the power series development of the error function,[14a] one finds that the initial dependence of $\rho(u,t)$ on t is quadratic except for $u = 0$, 1, where $\rho(u,t)$ reverts to a single error function, and

$$\left.\frac{\partial\rho(u,t)}{\partial t}\right|_{u=0} = \frac{d(\text{erf}\ t)}{dt} = \frac{2}{\pi^{1/2}}e^{-t^2} \tag{8}$$

which becomes $2/\pi^{1/2}$ at $t = 0$. Since the initial slope is finite but nonzero only at these two points, the initial slope of $\bar{\rho}$ with respect to t must be zero.

To establish the asymptotic behavior of the concentration profiles at large t, we can write $\rho(u,t)$ in terms of the error function complement

$$\text{erfc}\ x \equiv 1 - \text{erf}\ x \tag{9}$$

i.e.

$$\rho(u,t) = [1 - \text{erfc}\ (t/u^{1/2})][1 - \text{erfc}\ \{t/(1-u)^{1/2}\}] \tag{10}$$

perform the multiplication, and introduce an asymptotic series expansion[14b] for erfc x. It is then seen that for the chain-end distribution, the limiting dependence is just

$$\rho(0,t) \sim 1 - e^{-t^2}/(\pi^{1/2}t) \tag{11}$$

For $u \neq 0$, 1, the leading contribution to the deviation from unity is the sum of two terms of the form

$$(\beta/\pi^{1/2}t)e^{-t^2/\beta^2}$$

where β is $u^{1/2}$ or $(1 - u)^{1/2}$. Simple manipulations of the integral

$$\int_0^1 \text{erfc}\ (t/u^{1/2})\,du = \int_0^1 \text{erfc}\ [t/(1-u)^{1/2}]\,du \tag{12}$$

i.e., a transformation of the variable followed by an integration by parts, puts it in a standard form,[15a] the evaluation of which confirms the expectation that averaging over u leads to recovery of the simple form in eq 11 for the asymptotic behavior of $\bar{\rho}(t)$.

In ref 12 we pointed out (without making explicit mention of a concentration profile) that

$$\int_0^\infty [1 - P_{n,x}]\,dx = \bar{X}/2 \tag{13}$$

where $\bar{X} = (8nb^2/3\pi)^{1/2}$ is the quantity repeatedly calculated and discussed that has been called variously the "extent"[16] of a chain, the "span",[17] the "mean maximal size",[18] the "mean maximal projection",[19] or, more descriptively, the "mean projection onto an axis".[20] In terms of the concentration profile, the integral in eq 13 is a measure of the total deficiency of end segments in the depletion layer near the barrier. This deficit is the same as would be obtained by excluding end segments entirely from the region $0 < x < \bar{X}/2$ and having the uniform bulk-phase concentration of ends at all greater distances. Our reduced distance variable t is $2x/\pi^{1/2}\bar{X}$.

From the definition of the concentration profile, it is evident that the integral of $[1 - \rho(u,t)]$ with respect to t must be a measure of the total deficit in the depletion layer of segments from position u (mth segments) in the chains. Since the segment concentration is zero at the wall and the concentration of mth segments in the uniform bulk phase has to be the same for all m (all u), it follows that all segments give the same total deficit in the depletion region, i.e, the same integral of $[1 - \rho(u,t)]$:

$$\int_0^\infty [1 - \text{erf}\ (t/u^{1/2})\ \text{erf}\ \{t/(1-u)^{1/2}\}]\,dt = \int_0^\infty (1 - \text{erf}\ t)\,dt = 1/\pi^{1/2} \tag{14}$$

Although this result is deduced from the physical constraints of the problem, it must necessarily be verifiable mathematically; and indeed differentiation of the first

Table I
Total Segment Concentration Profile for Linear Polymer Chains in Solution near a Plane Barrier

t	$\bar{\rho}$	t	$\bar{\rho}$	t	$\bar{\rho}$
0	0	0.5	0.4971	1.0	0.8872
0.05	0.0094	0.55	0.5551		
0.1	0.0355	0.6	0.6091	1.1	0.9211
0.15	0.0749	0.65	0.6589		
0.2	0.1246	0.7	0.7041	1.2	0.9458
0.25	0.1816	0.75	0.7448		
0.3	0.2433	0.8	0.7811	1.3	0.9633
0.35	0.3075	0.85	0.8132		
0.4	0.3722	0.9	0.8414	1.4	0.9755
0.45	0.4358	0.95	0.8659		

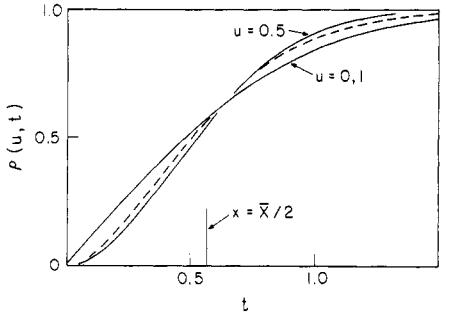

Figure 1. Chain-segment distributions in depletion layer for u = 0,1 (end segments) and u = 0.5 (middle segments). The dashed line is the overall concentration profile $\bar{\rho}(t)$. The abscissa at $1/\pi^{1/2}$ is marked to indicate the average thickness $\bar{X}/2$ of the depletion layer.

integral with respect to parameter u shows it to be independent of u. With $u = {}^1/_2$, an integration by parts transforms the first integral to a standard form[15b] that satisfies the equality. Then if the relation is true for $u = {}^1/_2$, it must be true for any u. Equation 14 demonstrates that the characteristic thickness of the depletion layer is the same (i.e., $\bar{X}/2$) whatever segment concentration profile is used to determine it. We have commented elsewhere[21] on the universality of the mean molecular projection as a measure of the depletion distance. An integration like that in eq 13 over a concentration profile of a single solute species at a noninteracting barrier gives half the mean projection of the molecule (particle) on an axis, independently of its structure.[22]

Since the integration in eq 6 apparently cannot be done analytically, a numerical method had to be used to obtain the segment densities $\bar{\rho}(t)$ given in Table I. Values of the error function were generated from an analytical approximation[14c] and used to calculate the integrand for a series of values of u at each chosen t. Integration was carried out in the range $0 < u < {}^1/_2$ by using Simpson's rule quadratures with fine enough divisions to ensure the accuracy of the fourth decimal in the tabulated values (at least 40 divisions for $t \leq 0.3$, 20 for $0.3 < t \leq 0.7$, and 10 for $t > 0.7$).

Segment concentration profiles for end segments and middle segments are plotted in Figure 1 together with the averaged profile $\bar{\rho}(t)$. Despite the appearance of this illustration, plots of $\rho(u,t)$ for various values of u do not have a common intersection when the reduced distance variable t is about 0.65. To show in another way, and on an expanded scale, the rather complicated manner in which the concentration profiles for the individual segment populations differ from the averaged distribution, we plot in Figure 2 the difference $[\rho(u,t) - \bar{\rho}(t)]$. In effect, each curve describes the shape of a cross section of the $\rho(u,t)$ sheet at fixed t. Although the plots in Figure 1 show clearly that the averaged profile $\bar{\rho}(t)$ is much more like the $\rho(0.5,t)$ curve than the chain-end distribution $\rho(0,t)$, the fact that the curves in Figure 2 do not cross the abscissa at the same value of u shows that no individual segment profile duplicates $\bar{\rho}(t)$. An unexpected feature of Figure 2 is the maxima in the curves. They indicate that some of the segment profiles for $u > 0$ lie above the chain-end profile in the range of low t where the middle-segment profile is decidedly below $\rho(0,t)$, as is shown in Figure 1.

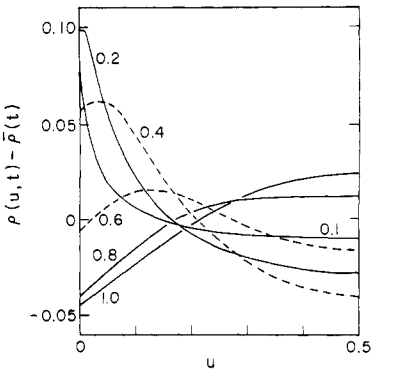

Figure 2. Deviation of $\rho(u,t)$ from the total segment concentration profile vs. u for values of reduced distance t as indicated.

Conclusion

It is tempting to speculate that the mathematical anomaly of the linear end-segment profile at the wall could be manifested by detectable effects in real systems: e.g., the depletion of interior segments relative to end segments might show up in preferential interaction of the latter with reactive sites on the wall.

We conclude with two remarks on matters that we expect to explore in greater detail elsewhere with the help of detailed quantitative calculations.

(A) A general treatment of the chain-segment distribution of branched random-flight chains is more difficult than the linear case discussed above. Even for the "regular star" molecule with f identical branches, each with n segments, calculation of the segment profile for an arbitrarily designated segment along the chain gives rise to integrals that apparently cannot be evaluated analytically. An exception is the branch node. Considering this at distance x from the wall as the origin of f random flights of n steps, we have by analogy with eq 4

$$\rho(x) = [\text{erf}\ (Ax)]^f \tag{15}$$

(B) Appropriately modified, the analysis given here also leads to the polymer segment distribution for dissolved chains confined within cavities with dimensions of the order of magnitude of the chain domain. In fact, although they are not so identified, eq 3, 6, 9, and 12 in ref 12 are expressions for the disbributions of linear-chain ends and star branch nodes inside pores of simple geometrical form.[23,24]

Acknowledgment. This work was supported by the National Science Foundation (Polymers Program, Industry–University Cooperative Research) under Grant DMR-8023213. The author is indebted to Hershel Markovitz for helpful discussion and for his patience as a sounding board.

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(23) The equivalents of eq 2 and 3 in ref 12 have been rederived for the special case of linear chains by the same method we used [Dolan, A. K.; Edwards, S. F. *Proc. R. Soc. London, Ser. A* **1974**, 337, 509]. These relations are also implicit in the quite different development in ref 5. Using an approximate distribution function, Frank [Frank, F. C. *Faraday Discuss. Chem. Soc.* **1979**, *No. 68*, 7] has noted the qualitative difference between end-segment and middle-segment density profiles near a wall for linear chains confined between a pair of parallel planes. The corresponding exact results can be written by using eq 3 of ref 12. Gaylord et al. [Gaylord, R. J.; Paisner, M. J.; Lohse, D. J. *J. Macromol. Sci., Phys.* **1980**, *B17*, 473] give two expressions for the averaged segment density profile of chains confined between planes. However, the illustration in their Figure 2 does not show the correct quadratic form at the walls.
(24) In a sequel to ref 5, de Gennes uses scaling arguments to treat segment concentration profiles in the depletionlayer for semidilute solutions when there are interactions between the dissolved polymer and the wall [de Gennes, P.-G. *Macromolecules* **1981**, *14*, 1637]. Our treatment here is more limited and does not include behavior in the semidilute regime. We note also that Gaylord and Lohse have derived distribution functions for confined polymer chains when the statistics are not Gaussian [Gaylord, R. J.; Lohse, D. J. *J. Chem. Phys.* **1976**, *65*, 2779. Lohse, D. J.; Gaylord, R. J. *Ibid.* **1977**, *66*, 2843]. Recently, Aubert and Tirrell [Aubert, J. H.; Tirrell, M. *J. Chem. Phys.* **1982**, *77*, 553] have used an elastic dumbbell model of a macromolecule in discussing the depletion layer and flow of dilute polymer solutions in narrow channels.

Monte Carlo Calculations of the Hydrodynamic Radii of Polymers in Θ and Good Solvents†

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ABSTRACT: The inverse radius of a polymer chain at infinite dilution on cubic and face-centered lattices is computed with the formula $\langle 1/R \rangle = (1/N^2)\sum_{i \neq j}\langle 1/r_{ij} \rangle$. The chains are created by a Monte Carlo simulation in which both volume exclusion and the energetics of nearest-neighbor interactions are taken into account. Values of $\langle 1/R \rangle$ are calculated for various values of the interaction energy parameter, ϵ/kT. The qualitative features of $\langle 1/R \rangle$ so computed are shown to be consistent with the blob model predictions. The values of the hydrodynamic radius, R_H, computed from these values of $\langle 1/R \rangle$ are found to be in reasonable agreement with the temperature vs. diffusion coefficient data obtained by Pritchard and Caroline.

I. Introduction

The hydrodynamic radii of polymers are determined from their diffusion coefficients in dilute solutions measured by, for example, quasi-elastic light scattering. Their dependence on thermodynamic properties of the solution is obtained by changing the temperature of the solution or the type of solvent. In an earlier paper,[1] the hydrodynamic radius of a monodispersed polymer under the Θ condition was calculated with Kirkwood's approximation for the diffusion coefficients by an equilibrium Monte Carlo calculation of self-avoiding walks on a cubic lattice. This calculation was found to give better agreement with measured values than did values calculated from the Gaussian coil model of the polymer. These Monte Carlo calculations are extended in this paper to polymers in good solvents and to different lattices.

In Kirkwood's approximation,[2] the diffusion constant is given by

$$D_0 = \frac{kT}{N\xi} + \frac{kT}{6\pi\eta_0}\langle 1/R \rangle \tag{1.1}$$

where

$$\langle 1/R \rangle = \frac{1}{N^2}\sum_{i \neq j}\left\langle \frac{1}{r_{ij}} \right\rangle \tag{1.2}$$

†Dedicated to Walter Stockmayer on the occasion of his 70th birthday.