

Monte-Carlo calculations of equilibrium partitioning of flexible chains into pores

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The partition coefficient K of flexible coils distributed between bulk solution and a cubic pore was calculated by the Monte-Carlo method on a simple cubic lattice. Self-avoiding walks up to 100 steps have been generated with the variable intersegmental energy simulating coils in solvents of various thermodynamical quality. The coefficient K decreases rapidly from 1 in large pores to negligible values at λ over 0.8, where λ is the ratio of the characteristic dimensions of the coil and pore. The partition curve is only slightly affected by solvent quality. The marked change of coil statistics with solvent is observed in the region of large confinement of coils by pores for $\lambda > 1$. This does not seem to be properly reflected by the scaling theory. However, the local 'conformational' structure of chains is not influenced by pore constraints. Implications of results for the static and dynamic measurements of partition equilibrium and for transport properties of macromolecules in porous media are discussed.

(Keywords: self-avoiding walks; partition coefficient; confined chain statistics; scaling theory; gel chromatography)

INTRODUCTION

Equilibrium partitioning of flexible molecules between bulk phase and microporous material is important in numerous separation techniques such as gel such as ultrafiltration. The prefix 'micro' refers to a pore such as ultrafiltration. The prefix 'micro' refers to a pore whose characteristic linear dimension is comparable to that of the partitioning species. The partition coefficient K is defined as the ratio of the average concentration inside the pore to the concentration of the bulk phase in equilibrium with it. At a very low concentration of solute, only the interactions between the pore and single, isolated particles are relevant. In a simple steric model, the pore walls behave as hard walls and geometrical hindrances of a particle in a small pore suffice to explain the partitioning effect. The inclusion of the attractive (adsorption) action of the pore walls or long-range repulsion is the next level of complication in the analysis of partitioning.

The description of the steric partitioning focused primarily on the dependence of the partition coefficient K on size and shape of solute and pore. Simple analytical expressions of solutes modelled as hard spheres in pores of regular shape¹ apply to the coefficient K . Steric partition is a result of the existence of excluded volume adjacent to the pore walls that is not accessible to the centre of the particles due to their finite size. Partition of rigid particles of various shapes inside pores of single and distributed sizes has been studied in great detail by Giddings *et al.*².

The rationalization of partitioning of flexible polymer-chain solutes is much less straightforward. Casassa³ derived the expressions for K by solving the differential equation for a probability of a random flight restricted by cavities of simple geometrical shape (sphere, slit, cylinder). The crucial result of the analysis, the

dependence of K on λ , the ratio of characteristic dimensions of coil and pore, has also been deduced in a slightly different form from a bead-spring dumbbell model of chains distributed into pores⁴. The statistics of a macromolecule in solution trapped in small pores were addressed qualitatively by the scaling theory⁵. The sensitivity of function K versus λ to the solvent remains an important unresolved question. The analytical solutions for the partition coefficient by the random-flight model correspond to the partition equilibrium at the theta state. However, most partition measurements are performed in thermodynamically good solvents where coils are expanded relative to the theta state due to the excluded volume.

Monte Carlo (MC) simulations on a lattice represent an attractive alternative to the evaluation of the partition coefficient K of flexible chains. The statistics of chains confined in a boundary of simple geometry make it possible to evaluate the effect of size and shape of pore on K and to compare the results with the analytical solutions. The simulations with the variable intramolecular excluded volume (coil swelling) enable us to estimate how solvent quality modifies the function of K versus λ . Moreover, the configurational properties of chains at the strong pore confinement, i.e. in pores smaller than the size of the coil, can be evaluated by simulations. In the present paper, this approach is illustrated by a cubic lattice simulation of partitioning of a flexible chain into a cubic pore of variable size. The coefficient K has been calculated for solutions with coils in the range from the expanded to the collapsed state. The effect of pore confinement on thermodynamic functions of chains and on the lattice-step orientation ('conformational' population) has been evaluated. Preliminary results of simulations and their application to the prediction of solute rejection on microporous membrane at ultrafiltration have already been reported⁶.

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Table 1 Reduced intersegmental energy F , radius of gyration R_g and square of expansion coefficient α of 100-segment coils simulated in the various states

State	F	R_g	α^2
Expanded	-1.0	7.11	1.70
Athermal	0.0	6.43	1.39
Theta	0.26	5.46	1.00
Collapsed	0.5	3.63	0.44

COMPUTATIONAL TECHNIQUE

Polymer chains comprising 100 segments were generated on a simple cubic lattice in a cubic pore of variable dimension L using the procedure of Rosenbluth-Rosenbluth described in detail by McCrackin *et al.*⁷ In this method, the chains are constructed by adding segments with a step-by-step procedure based on scanning in each step for allowed continuations. The first segment is placed at random into an empty pore. In each of the next steps the continuation is selected at random avoiding the previously occupied sites. Since the number of allowed possibilities is known for each step they can be multiplied to obtain the weight w_k of the k th walk. The estimate of the partition function of a single chain from a sample of m walks is

$$Q^* = \frac{1}{m} \sum_{k=1}^m w_k \exp(P_k F) \quad (1)$$

where P_k is the number of contacts in the k th chain formed by the unbonded segments separated by one lattice distance. Interaction between these segments is given by $F = -\varepsilon/k_B T$, where ε is the attractive energy between unbonded segments, k_B is the Boltzmann constant and T is temperature. The chain contacts with the pore walls were not included in P_k because reflecting, but otherwise inert, walls were assumed.

The partition coefficient K was calculated as the ratio $K = Q_{cf}^*/Q_f^*$, where Q_{cf}^* and Q_f^* are the partition functions of the chain confined in a pore and the free chain outside the pore in bulk solution, respectively. Radius of gyration of the chain $R_g = \langle s^2 \rangle^{1/2}$ was calculated in an analogous way by the thermodynamic averaging of the self-avoiding random walks. The expansion coefficient $\alpha^2 = \langle s^2 \rangle / \langle s_0^2 \rangle$ is defined relative to the unperturbed dimensions in the theta state. Pore size and radius of gyration are expressed in units of the basic lattice modulus. Results for chains in bulk solvent ($L \rightarrow \infty$) were obtained by placing the first monomer of the chain into the middle of a sufficiently large pore. According to statistics up to 30 000 configurations were generated to obtain reliable mean values of K and R_g .

RESULTS AND DISCUSSION

The confinement of macromolecules by a cubic pore and their partitioning was examined for several representative strengths of the intrachain excluded volume specified by the reduced intersegmental energy F (Table 1). On a cubic lattice, the 'pseudo-ideal' chains with the dimensions corresponding to the theta state are generated when F equals 0.26 for a 100 segment chain⁸, i.e. when a slight attraction of segments is assumed to balance the intrachain volume exclusion. An additional increase of attraction to F of about 0.5 leads to the preference of

compact configurations termed as collapsed coil or globule. MC simulations in an athermal system where $F=0$ result in coil dimensions slightly expanded relative to the theta dimensions. At negative values of the parameter F , the chain expansion is enhanced by intersegmental repulsion. Variation of the intrachain excluded volume given by the parameter F at simulation can be used to estimate indirectly how the partitioning into pores would be influenced by changes of the coil size due to variable solvent quality.

Variation of chain confinement with the pore size

The effect of the pore size on the partition function of a chain in the expanded, athermal, theta and collapsed states is shown in Figure 1. The partition function Q refers to one segment and is reduced by the number of the unrestricted lattice random walks, i.e. by the factor $Z(Z-1)^{N-1}$ for an N segment chain on the lattice with the coordination number Z . The intrachain energy parameter F affects considerably both the absolute value of the partition function and its dependence on pore size. The partition function of free chains (for $L \rightarrow \infty$) reaches a maximum value for a collapsed coil characterized by an enhanced probability of segmental contacts. The difference between the present self-avoiding chain simulation and a random walk is properly reflected in a Q_f value less than unity for the theta chain.

The influence of the reduced intersegmental energy on the partition function of a coil confined in a pore, Q_{cf} , becomes even more pronounced (see Figure 1). The marked decrease of Q_{cf} occurs in the region where the chain diameter $2R_g$ exceeds the pore dimension L . For a given size of pore the Q_{cf} values diminish with the coil expansion. Thus, two parts on curves in Figure 1 can be distinguished. The first part, the region of large pores with the coil diameter smaller than the pore dimension L , is

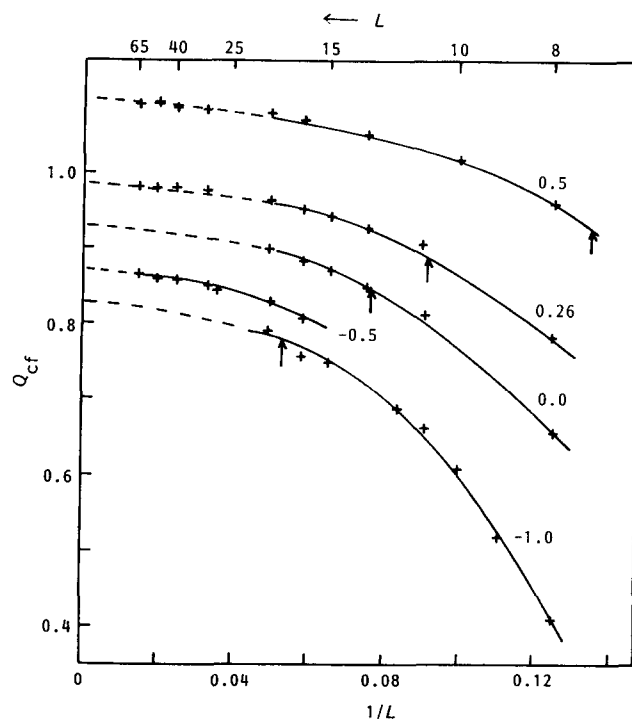


Figure 1 The plot of reduced partition function Q_{cf} expressed per segment versus the reciprocal of pore dimension L for coils of various reduced intersegmental energy F : (0.5) collapsed; (0.26) theta; (0.0) athermal; and expanded (-0.5 and -1.0) coils. Arrows indicate the coil diameter $2R_g$

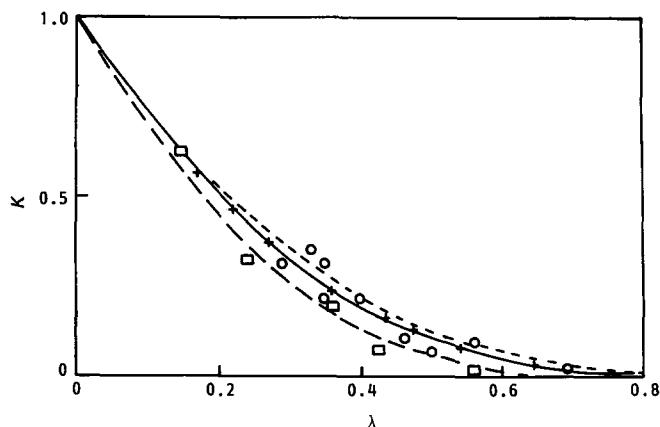


Figure 2 Variation of the partition coefficient K with $\lambda = R_g/a_p$. Some results of the simulation are represented as: (+) theta chain; $F=0.26$, a full line; (□) collapsed chain, $F=0.5$; (○) expanded chain, $F=-0.5$. Dashed curve corresponds to equation (2) of Casassa³, dotted curve is hard sphere relation $K=(1-\lambda)^3$

typical for the partitioning of coils into pores. Computations in this region require a generation of a large number of configurations and a considerable expenditure of computing time. In the simulation of the expanded coil, $F=-0.5$ has been chosen for this region. In the second portion of the curves in *Figure 1*, in the zone of small pores, a dramatic reduction of the number of chain configurations takes place. All the curves in *Figure 1* show a smooth convergence of the Q_{cf} values to the partition function Q_f of free chains.

At first glance the effect of pore confinement on the partition function Q_{cf} in the region of partitioning where $L > 2R_g$ might seem surprisingly small. However, it should be realized that in the computation of the partition coefficient of a whole chain by the expression $K=(Q_{cf}/Q_f)^N$, minor variations in the ratio of the partition functions with L after raising to the N th power become sufficient to change K in the full range from unity to zero, i.e. from total to no partitioning into pores. *Figure 1* could be replotted to show the dependence of the coefficient K on the reciprocal pore dimensions L^{-1} where all curves would coincide at $K=1$ for infinitely large pores. Traditionally, however, instead of that function, a plot K versus λ is used in the representation of the steric partitioning, where $\lambda=R_g/a_p$ and a_p is an effective pore dimension; $L/2$ in our case. This function is shown in *Figure 2* with points from some simulations for the expanded, theta and collapsed chains. The unbroken line in *Figure 2* describes the data for the theta chain rather well. The scatter of points for the expanded and collapsed coil is slightly larger. However, the points for the expanded coil seem to be distributed roughly around the theta chain curve, whereas the points for the collapsed chain lie below this curve. The coefficient K becomes negligible for λ larger than about 0.8, i.e. far below $\lambda=1$ when the coil size matches the pore dimension.

Comparison with analytical theories

The prediction of the coefficient K from MC calculations is compared in *Figure 2* with the analytical theory of steric exclusion of flexible coils³. Casassa derived the dependence of K on λ by the calculation of distribution coefficients for random flight chains in cavities of simple geometrical forms. The coefficient K is determined by the fraction of unrestricted random-flight configurations starting in the space within a cavity that is

allowed in the presence of boundary, i.e. that do not intersect it. For a spherical cavity it is given as³

$$K = (6/\pi^2) \sum_{m=1}^{\infty} m^{-2} \exp(-m^2\pi^2\lambda^2) \quad (2)$$

This function is plotted in *Figure 2* as a dashed line.

A small difference in the function K versus λ between the theory of Casassa and MC simulations in *Figure 2* may be connected with the pore shape assumed in these treatments, which was sphere and cube respectively. However, a more fundamental difference between these two approaches derives from the fact that an analytical solution applies for the random-flight chains corresponding to the theta state and the coefficient K is determined by the entropic change only. In contrast, MC simulations provide a possibility to model the real chains with the nonzero intrachain excluded volume. In such a way the energy term is incorporated into the coefficient K and into ΔF^0 , standard free energy of transfer of one mol of chains from the bulk solution to the interior of the pore.

Finally, *Figure 2* shows the partition coefficient K calculated for hard spheres with radius R_g enclosed in a spherical cavity of radius a_p by the relation $K=(1-\lambda)^3$ (ref. 1). The hard sphere function is surprisingly similar to the curve from the MC simulation of the theta chains.

An important conclusion can be drawn from *Figure 2* on the effect of the solvent modelled through reduced intrachain energy F . In contrast to *Figure 1*, a difference in thermodynamic quality between a good solvent with $\alpha > 1$ and theta solvent does not play any significant role in the dependence of the coefficient K on λ . This effect could have some importance for λ higher than about 0.6 but in this region the absolute value of K is already very small. Hence, MC simulation seems to substantiate the procedure already frequently used in practice that the relations of Casassa³ for spherical and other idealized pores can also apply in good approximation to other solvents than the theta solvent.

Comparison with a scaling approach

All of the thermodynamic parameters deducible from the partition function Q_{cf} become sensitive to the parameter F and to the solvent quality when pore and coil dimensions are comparable. In this region, the behaviour of flexible chains dissolved in a good solvent and confined in pores was treated theoretically by the scaling method⁵. Repulsive interactions between monomers in a good solvent are taken into account in this approach and scaling law is predicted for the partition coefficient of an N -segment chain into slit pores in diluted solutions:

$$K = \beta \exp(-N/L^p) \quad (3)$$

The exponent p should be 2 and 5/3 for the theta and good solvent, respectively, and the prefactor β cannot be deduced from scaling arguments.

We have used the results of MC simulations to test the scaling theory predictions. The double logarithmic plot of the relation in equation (3) for the theta, athermal and good solvents is shown in *Figure 3*. Apparently, the scaling law, equation (3) is obeyed in the narrow range of comparable dimensions of coils and pores around $\lambda=1$. However, for a stronger pore confinement, when the chain diameter is much higher than the pore dimension L and also for very large pores, the exponential factor in the scaling relation equation (3) is no longer dominant. The

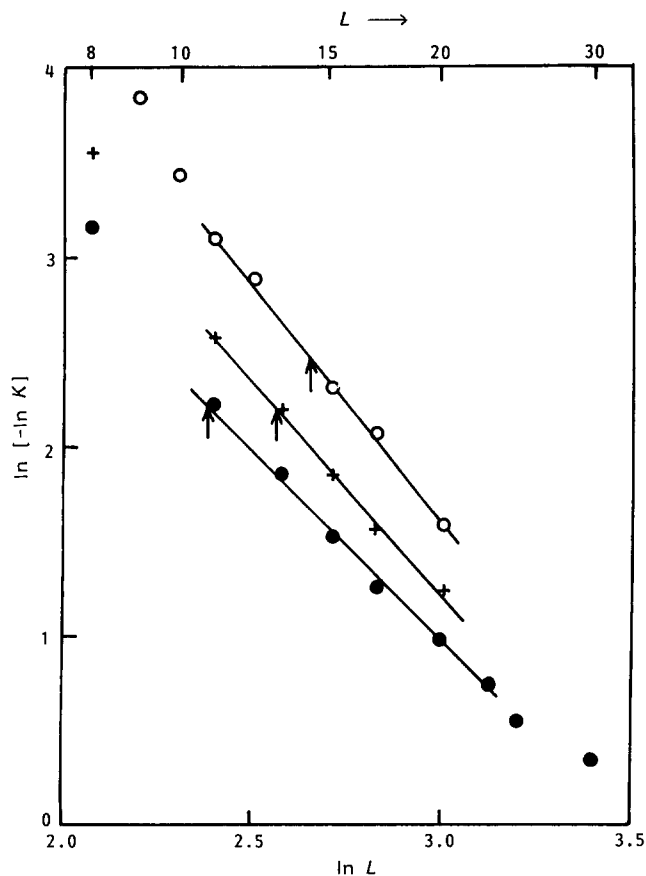


Figure 3 Double logarithmic plot of the scaling relation between K and L , equation (3): (●) for theta chains, $F=0.26$; (+) for athermal chains, $F=0.0$; (○) for expanded chains, $F=-1.0$; arrows indicate the coil diameter $2R_g$

prefactor β also depends on L , which results in the deviation of the plots in *Figure 3* from straight lines in the regions mentioned.

The exponent p from the straight line region of the function plotted in *Figure 3* is about 2.0, 2.2 and 2.5, respectively, for theta, athermal and good solvents. Although the first figure is in full accord with the scaling theory, the increase of the exponent with solvent quality is contrary to scaling predictions. The dependence of the coefficient K on L^2 for random flight coils is corroborated by the analysis⁹ of Casassa's relation, equation (2). The second term in the series is less than 0.001 of the first as soon as L is less than $6R_g$ and becomes negligibly small for L values less than coil diameter $2R_g$. Because the partition coefficient K in random-walk statistics is given only by the configurational entropy difference, ΔS^0 , between free chains outside the cavity and confined chains, equation (2) implies that ΔS^0 is proportional to L^2 in the theta system. Such a dependence of the entropy ΔS^0 was confirmed by MC simulations on a body-centred cubic lattice for 1000-segment chains enclosed by a sphere⁹. In a related simulation with the different type of chain confinement by two parallel plates, Ishinabe¹⁰ found the exponent p to be between 1.8 and 2.1 for the athermal system in the intermediate range of the chain confinement. In the analysis of equation (3) and *Figure 3* one should keep in mind that absolute values of the partition coefficient K to which these functions apply are extremely low. For example, a typical value of K corresponding to the middle of ordinate in *Figure 3* is about 10^{-4} .

Distribution of chain conformations

Variation of the reduced intersegmental energy F may influence not only the overall configurational properties of a coil such as radius of gyration R_g or the expansion coefficient α but also a local orientation of individual lattice steps. Such 'conformational' statistics on the lattice should obviously differ from the similar statistics in real polymers but the comparison could be instructive. We divided the mutual orientation of three subsequent steps on a simple cubic lattice into four groups (*Figure 4*). Three steps in one direction define a linear (L) conformation. A 'square' planar structure is denoted as *cis* (C). All other planar conformations with side steps represent *trans* (T) conformations. Finally, a conformation with the last step in the direction perpendicularly to the plane of the first two steps is denoted as *gauche* (G). Populations of the above groups of conformations are shown in *Figure 4* as a function of pore dimension L for the theta and expanded coils.

Inspection of *Figure 4* reveals that conformational populations are only slightly affected by pore confinement even in the region where coil diameter $2R_g$ exceeds the pore dimension L . This curious behaviour can be rationalized when one realizes that chain encounter with a cavity boundary can be avoided by a change of orientation of only a one of 100 segments, located for example in the middle of the chain. In other words, a 1% change of populations p_i due to a suitable single bond 'conformational' transition can prevent the contact of a chain with a pore wall. *Figure 4* also suggests a minor influence of solvent on conformational preferences. The population of a *trans* conformation in an expanded coil is enhanced relative to the theta system and this increase is compensated by a reduction of *gauche* and *cis* conformations. Pore constrictions on the length of some conformational sequences can also be evaluated. For example, the distribution curve for the length of either

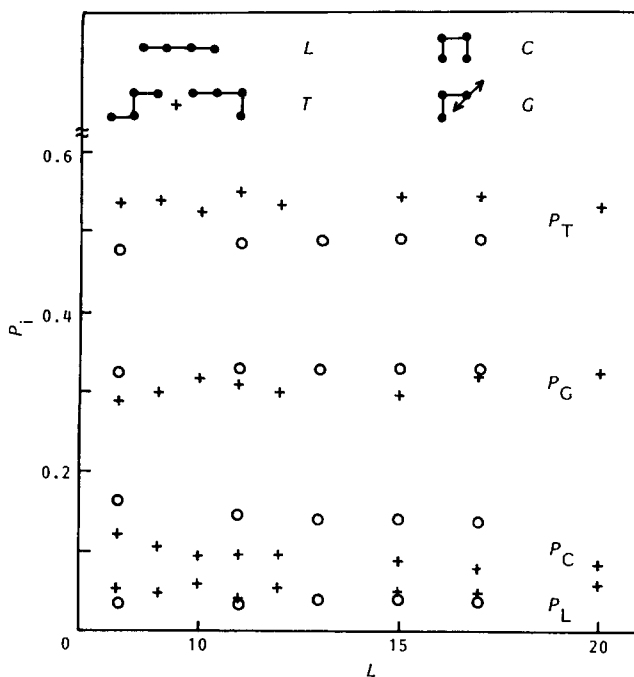


Figure 4 Schematic illustration of linear (L), *trans* (T), *cis* (C) and *gauche* (G) lattice conformations and their probability p_i in a chain as a function of pore dimension L for the theta coil: (○) $F=0.26$ and for expanded coil: (+) $F=-1.0$

trans or linear steps in the theta system suggests that the two step sequence is the most frequent. A probability of longer sequences is gradually reduced and is less than 1% for ten step sequences and longer. The pore confinement brings about only a lesser broadening of this distribution curve.

To date, no information is available on the conformational preferences of a real polymer trapped into micropores. In contrast to the results of lattice calculations in Figure 4, a negligible influence of the excluded volume on the single bond conformational populations p_i is commonly assumed for real polymers. For example, in a treatment of long range interactions in polyethylene¹¹, the probability of *trans* bonds was kept constant (over 60%) and the coil expansion by a good solvent was achieved by a marked enhancement of the length of *trans* bond sequences.

Implications for processes in porous media

In a more general part of the discussions we will focus our attention on the results for large pores and the coefficient K . MC simulations are a versatile tool for the study of the partitioning equilibrium. They can be used to establish new relationships of K versus λ , in addition to the already existing analytical functions, for chains of various sizes and flexibilities and for an arbitrary size and shape of pore.

CONCLUSIONS

In this paper we concentrated on the unresolved problem of the solvent influence on the relation between K and λ . For cubic pores, our results on a simple cubic lattice do not show any significant effect of the thermodynamic quality of the solvent on partition. Provided this finding could be generalized to other pore shapes, it would support the universality of the K versus λ plot regardless of the type of solvent. That would be very fortunate, because in practice mainly good solvents are used in partition measurements for solubility reasons.

The possibility of agreement between the results of calculations in Figure 2 (either from MC simulation or from analytical theory) with experimental data from static or dynamic (gel chromatography) measurements should be viewed with scepticism¹². An incomplete representation of real polymers by lattice simulations, idealization of a pore model in calculations, pore nonuniformity in microporous materials and polydispersity of measured solutes, are only a few of the numerous factors affecting the comparison of theory and experiment. That is also a reason why the question of solvent influence on the partitioning curve K versus λ could not be answered experimentally. Furthermore, it is extremely difficult to secure the partitioning of solute by the steric exclusion only in experiments. The contributions of solute adsorption on pore walls and finite concentration of solute could affect considerably the partition coefficient in static¹³ and dynamic¹⁴ measurements. Prediction of the coefficient K in cases where both factors are operating has been accomplished to date for hard-sphere solutes only.

Results concerning the partition coefficient K are relevant not only to equilibrium situations but also indirectly to transport properties in porous media, as is viscosity⁴, restricted diffusion¹⁵ and solute rejection in ultrafiltration¹⁶. In restricted diffusion, the transport of solute through pores is controlled by two phenomena.

First, there is a partitioning of the solute at the end of the pore and second, pore walls increase the viscous drag on a solute molecule as it moves through the liquid within the pore with the intrapore diffusion coefficient D_p . The effective diffusion coefficient in the pore is given by the product $D_{\text{eff}} = KD_p$. The coefficient D_{eff} is usually smaller than the corresponding value in bulk solution D . Our calculations may help to establish the dependence of D_{eff}/D on λ for slit-like pores analogous to already existing relations for cylindrical pores¹⁵. Besides, since our results in Figure 3 do not support the scaling theory predictions concerning the pore size exponent p in good solvent, it seems that some reservation should be raised to analysis of the restricted diffusion using equation (3) recently made for a dilute solution of polystyrene¹⁷.

In ultrafiltration, porous membranes selectively reject solute molecules from a solution. This rejection is characterized by a reflection coefficient σ defined as the fraction of macromolecules held back by the membrane. The value of σ , between 0 and 1, depends on the interaction between the solute and membrane matrix. The coefficient σ is related to the partition coefficient K in a very good approximation by the expression¹⁶.

$$\sigma \approx (1 - K)^2 \quad (4)$$

This relation, based on the rigid solutes theory, was established for different sizes and shapes of both solute and pore and is supported by some experimental data. The partition curve from MC simulation in Figure 2 has been converted using equation (4) to a plot of coefficient σ versus λ in slit-like pores⁶. The membrane rejection was predicted to rise rapidly and the rejection was almost complete at λ over 0.7. Again, the coefficient should be insensitive to the solvent used in ultrafiltration. However, the predictions of σ for flexible coils based on equation (4) are apparently applicable only to ultrafiltration at the weak flow condition. At a higher flow velocity, the deformation of coils in the solvent gradient may take place¹⁶. As a consequence, the chains originally unable to enter the pore due to their size, can pass through a pore after their elongation. Then, coefficient σ is also a function of solvent flow rate and undeformed chain characteristics, such as R_g , cannot be used in the correlation of σ with the ratio λ .

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