Macromolecules **1999,** *32,* 7645−7654

Steady-State Permeation Rate of Homopolymer Chain Molecules through a Pore in a Barrier

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Received August 17, 1998; Revised Manuscript Received August 25, 1999

ABSTRACT: An analysis based upon the Rouse bead−spring model and the Smoluchowski many particle diffusion equation in the free draining limit is utilized to derive an expression for the steady-state permeation rate of homopolymeric chainlike molecules passing through a narrow pore with a cross-sectional area slightly greater than that of an individual chain segment in an otherwise impenetrable barrier that separates in general two different solvent environments. The analysis is also applied to determine the steady-state permeation rate of homopolymers diffusing across a planar liquid−liquid interface formed by two immiscible solvents. The planar interface corresponds to a pore whose cross-sectional area is much larger than the mean square end to end dimensions of the polymer molecule. The key results give the permeation rate, J, as a function of the degree of polymerization, N, the individual bead diffusion coefficient(s) D_i ($i = 1, 2$) in the different solvents and a localized pore or interfacial surface contact resistance, h. The polymer−pore permeation rate becomes $J \simeq D_R/N^3$ where $D_R = D_1D_2/(D_1 + D_2)$ whenever $h/D_R \gg 1$ and is consistent with the prediction of reptation dynamics.

I. Introduction

The permeation of flexible and rigid macromolecules and biopolymers through membranes and lipid bilayers is an event of considerable interest and importance in many chemical and biochemical applications and situations. Comprehension of the transport mechanisms of polymer molecule permeation through pores in membranes should prove valuable in drug delivery applications and in ascertaining the manner of incorporation of DNA, RNA, and viral molecules into cells.[1,2]

Here we investigate the steady-state permeation rate of flexible homopolymers threading themselves through small diameter orifices or pores in thin impenetrable barriers. Sung and Park[3] have considered the translocation of flexible polymer chains through a pore in a membrane by regarding it as a diffusion process across a free energy barrier. An excellent schematic drawing of the situation appears in Figure 1 of ref 3. Sung and Park described the translocation process in terms of the probability $P(n,t)$ that n segments of the polymer reside on the right (trans) side of the barrier at time t. $P(n,t)$ was assumed to satisfy a Fokker−Planck equation,[4] which corresponds to a Smoluchowski diffusion equation[5] with a thermodynamic driving force derived from the configurational entropy of the polymer chain as a function of the degree of penetration, n. Sung and Park assumed a diffusion coefficient or diffusivity that corresponds to diffusion of the center of mass of the chain and thus depends on the degree of polymerization, N.

The Sung and Park dynamical description of the polymer translocation process is limited by the tacit assumption that the trains of protruding polymer chain segments on each side of the barrier relax instantaneously to their equilibrium distribution of configurations while the polymer chain stochastically advances or retreats on a segmental basis through the pore. (At the very least the rate of diffusion of the protruding polymer segments is taken to be much greater than the rate of segmental permeation through the orifice.) This assumption permits a coarse graining where specifying n at a given time describes the dynamic state although this surely represents a limited perspective of the actual situation. A difficulty also arises in the Sung and Park interpretation of the diffusivity as a finite center of mass diffusion coefficient when instantaneous relaxation (with infinite segmental diffusion coefficients) occurs for the individual segmental motions of the chain. In the instantaneous relaxation approximation it seems plausible to include an N-independent pore-localized diffusivity factor which provides contact resistance to the passage of individual chain units across the pore surface.

Here a more detailed description of the configurational behavior of a polymer chain is included in the analysis of the steady-state permeation rate through an orifice in a barrier. Specifically a one-dimensional (1-D) Rouse bead−spring model is utilized eventually to describe the configurations of a homopolymer chain of N beads as it permeates the barrier.[6] The dynamics of the N bead chain is determined from a set of distribution functions $W_n(x_1, x_2, ..., x_N; t)$ which give the probability density for observing a configuration of the chain specified by the bead locations $(x_1, x_2, ..., x_N)$ measured relative to the orifice at time t for each degree of bead penetration, n $(0 < n \le N)$. The W_n are assumed to be solutions of an N-particle Smoluchowski diffusion equation subject to appropriate boundary conditions. Both individual bead-solvent diffusion coefficients and a bead−pore surface contact resistance can influence the permeation rate.[7]

In section II, the steady-state permeation rate of flexible homopolymer chains through an orifice in an otherwise impenetrable barrier is determined when instantaneous relaxation of the protruding trains of contiguous chain segments on opposite sides of the barrier prevails regardless of the degree of penetration, n $(0 < n \le N)$. In this limit only a finite contact resistance, h, which is independent of N, acts on the individual chain segments as they diffuse stochastically in either direction through the orifice. The direction of diffusion is, however, biased by a thermodynamic driving force which depends on n and is derived from the

10.1021/ma9812938 CCC: $18.00

corresponding equilibrium configurational entropy. The maximum possible steady-state permeation rate, J, is determined to be $J \propto h/N^2$ for completely flexible homopolymers in a Θ solvent environment. This result agrees within numerical factors to that obtained by Sung and Park for the reciprocal of the first mean passage time for polymer translocation provided an N-independent diffusivity is adopted.

In section III, the steady-state permeation rate for a specified concentration difference with which a flexible N-bead homopolymer diffuses across a thin interface formed by two immiscible solvents is determined using the many-bead diffusion equation approach and the 1-D Rouse model. The planar interface corresponds to a pore in a barrier in the limit where the cross sectional area of the pore is much larger than the average mean square end-to-end dimension of the homopolymer chain. Hence the chain diffuses as a coil rather than a thread across the interface.

The analysis presented in section III shares certain common features with the perhaps more difficult homopolymer chain−pore in a barrier permeation problem which is investigated in section IV for the more realistic situation where the individual beads experience finite diffusion coefficients in the barrier-partitioned solvent environments in addition to a pore surface−bead contact resistance. The steady-state permeation rate is found to be diminished in comparison to that obtained in section II due to the finite individual bead diffusion coefficients. In the absence of bead−pore surface contact resistance, the steady-state permeation rate tends to $J \propto D_R/N^3$ where D_R is a reduced diffusion coefficient. This result is consistent with the de Gennes reptation theory of the dynamics of constrained polymer chains.[5,8]

Throughout the present analysis both excluded volume effects and hydrodynamic interactions between diffusing polymer segments are not considered explicitly although their influences on the effective center of mass diffusion coefficient can be estimated as discussed in section V.[5,9] Also since the polymer translocation occurs in a single direction, a 1-D rather than a 3-D model for the diffusing homopolymer chains is employed for convenience rather than necessity in the forthcoming treatment.

II. Steady-State Permeation Rate for Homopolymer Diffusion through a Pore in a Barrier for the CASE of Instantaneous Relaxation of the Protruding Trains of Segments

Consider an ensemble of like systems each consisting of an N segment ideal freely jointed homopolymer chain which is partially threaded through an orifice or pore in an otherwise thin planar impenetrable barrier which divides generally different solvent environments. The cross-sectional area of the pore, while larger than that of the penetrating chain segment, is assumed to be sufficiently small that a polymer molecule can pass through only by a stochastic segmental threading process which can occur in either direction normal to the surface of the orifice. Thus, hairpin chain configurations which double back through the orifice are prohibited. The barrier is assumed to be sufficiently thin that only a single chain segment resides within the orifice at any instant.

When the two trainlike sections of the penetrant polymer molecules on opposite sides of the barrier relax instantaneously to their equilibrium distribution of configurations, the permeation process through the barrier may be described by specifying the segment length of either section as a function of time. Presumably instantaneous relaxation of the protruding polymer chain segments can be achieved in the absence of solvents (i.e., in vacuo) on opposite sides of the barrier. Let $w(n,t)\,\mathrm{d}n$ denote the probability of finding between n and $n + \mathrm{d}n$ ($N - n$ and $N - (n + \mathrm{d}n)$) polymer chain segments to the right (left) of the barrier at time t. All relevant information necessary to describe the permeation rate of polymer chains in the member systems of the ensemble resides in $w(n,t)$. Also let $w_e(n)$ represent the normalized equilibrium probability distribution function which gives the probability of observing a polymer chain which has $n(N - n)$ segments to the right (left) of the barrier.

If we regard n as a continuous variable ($0 \le n \le N$), it is reasonable to expect $w(n,t)$ to satisfy the Smoluchowski diffusion equation

$$\frac{\partial w(n,t)}{\partial t} = h\left[\frac{\partial}{\partial n}\left(w_e(n)\frac{\partial(w(n,t)/w_e(n))}{\partial n}\right)\right] = h\left[\frac{\partial^2 w(n,t)}{\partial n^2} - \frac{\partial}{\partial n}\,[w(n,t)\beta F(n)]\right] \quad (1)$$

where $\beta F(n) \equiv \mathrm{d}(\ln w_e(n))/\mathrm{d}n$ with $\beta \equiv (k_B T)^{-1}$ where T is the absolute temperature and k_B is Boltzmann's constant. Here h, which is assumed to be independent of n, has dimensions of inverse time, and it represents the frequency with which a chain segment randomly diffuses forward or backward with localized contact resistance through the plane of the orifice in the barrier. It is important to emphasize that h only applies locally to the chain segment threading through the plane of the orifice. All other segments in the protruding train sections on opposite sides of the barrier are assumed to diffuse infinitely rapidly (i.e., relax instantaneously) to their equilibrium distribution of configurations. The term $h\,\partial^2 w(n,t)/\partial n^2$ in eq 1 corresponds to a random unbiased diffusion of chain segments in either direction through the pore. The remaining term $-h\,\partial[\beta F(n)w(n,t)]/\partial n$ corresponds to diffusion biased by a statistical thermodynamic driving force, $F(n) \equiv \beta^{-1}\,\mathrm{d}(\ln w_e(n))/\mathrm{d}n$, which tends to preferentially promote polymer chain penetration in the direction of lower free energy. At equilibrium, $w(n,t)$ becomes time independent and the flux $(-h(\mathrm{d}w(n)/\mathrm{d}n) + hw(n)\beta F(n))$ must vanish, which means that $w(n) = w_e(n)$.

For a flexible freely jointed polymer chain with the same internal energy for all configurations, $w_e(n)$ is proportional to the total number of configurations $Q(n)$, available to a polymer chain having $n(N - n)$ contiguous segments restricted to the right (left) hand side of an infinitesimally thin (absorbing) barrier. If self-excluded volume effects between chain segments are neglected, any configuration of a pore permeating chain with $n(N - n)$ segments to the right (left) of the barrier can be simulated by two particles undertaking independent one dimensional (1-D) random walks of n and $N - n$ steps of equal length normal to the barrier respectively on opposite sides of an absorbing barrier with each walk commencing at the orifice which is located at the origin. The number of paths, $Q(n)$, which the two particles can take without a return to the origin is known to be

$$Q(n) = \binom{n}{n/2}\begin{bmatrix}N - n\\(N - n)/2\end{bmatrix} \equiv n!(N - n)!/(n/2)!^2\left(\frac{N - n}{2}\right)!^2 \quad (2)$$

Also $w_e(n) = 2^{-N}Q(n)$ where 2^N represents the total number of paths a 1-D random walk can assume after N steps and $\sum_{n=1}^{N} w_e(n) = 1$.[10,11,12] When Stirling's approximation in the form $n! = (2\pi)^{1/2}n^{n+1/2}\exp(-n)$ etc. is employed to estimate the factorials in eq 2, one obtains

$$w_e(n) = \pi^{-1}[n(N - n)]^{-1/2} \quad (3)$$

If n is regarded as a continuous variable, it is easy to verify that the $w_e(n)$ given by eq 3 satisfies the normalization condition $\int_0^N w_e(n)\,dn = 1$. When the polymer segments experience different interaction energies with the solvents located on opposite sides of the barrier, then

$$w_e(n) = B[n(N - n)]^{-1/2}\exp(-na) \quad (4)$$

where ak_BT is the difference in solvent−polymer segment interaction energy between right- and left-hand-side solvents and B is a normalization constant. The Appendix provides an alternate derivation of eq 3 which is based on a Green function approach for one-dimensional diffusion in the presence of an absorbing barrier.

Equation 1 is solved easily in the steady state where $\partial w(n,t)/\partial t = 0$ is maintained in the ensemble through imposition of "source" and "sink" boundary conditions on $\psi(n) \equiv w(n)/w_e(n)$; $\psi(0) = 1$ and $\psi(N) = 0$. This corresponds to introducing chains from left to right in the member systems of the ensemble to replace those which have passed completely (left to right) through the orifice. The steady-state solution to eq 1 which satisfies $\psi(0) = 1$ and $\psi(N) = 0$ is for discrete segments

$$\psi(n) \equiv w(n)/w_e(n) = 1 - \sum_{j=1}^{n} r_j/R_N \quad (5a)$$

where $r_j \equiv w_e^{-1}(j)$, $R_N \equiv \sum_{j=1}^{N} r_j$, and $w_e(j)$ is given by eq 2. In the continuous chain segment limit the corresponding solution is

$$\psi(n) = 1 - \left(\int_0^n dn'/w_e(n')/\int_0^N dn'/w_e(n')\right) \quad (5b)$$

where $w_e(n)$ is given either by eq 3 or eq 4 when $a \neq 0$. For $a = 0$, utilizing eq 3, one obtains explicitly from eq 5b

$$\psi(n) \equiv \psi(m) = 1 - 2\pi^{-1}[\arcsin(m^{1/2}) - (m(1 - m))^{1/2}(1 - 2m)] \quad (6)$$

where $m \equiv n/N$ with $0 \leq m \leq 1$.

Of immediate interest is the steady-state flux

$$J = -hw_e(n)[\psi(n) - \psi(n - 1)] = h/R_N \equiv h\left(\sum_{i=1}^{N} w_e^{-1}(i)\right)^{-1} \quad (7a)$$

or for continuous segments

$$J = -hw_e(n)\frac{d\psi}{dn} = h\left(\int_0^N dn'/w_e(n')\right)^{-1} \quad (7b)$$

The flux is constant and gives the permeation rate of polymer chains as a function of the degree of polymerization, N. Substituting eq 3 into eq 7b gives

$$J = h/\pi N^2 \int_0^1 dm\; m^{1/2}(1 - m)^{1/2} = 8h/\pi^2N^2 \quad (8)$$

This result may be compared with the reciprocal of the mean first passage time $\tau^{-1} = 16h/\pi^2N^2$ obtained by Sung and Park[3] (see eq 16 of ref 3 with $h \equiv D/b^2$ in their notation). Equation 8 reveals that J decreases as N^{-2} for a flexible polymer chain whose protruding contiguous segments relax instantaneously to their equilibrium distribution of configurations. For a frictionless pore, $h \to \infty$, but a finite albeit indeterminate flux is possible in this limit since $\psi(n) \equiv w(n)/w_e(n) \to 1$ irrespective of n and $d\psi/dn \to 0$ (or $\psi(n) - \psi(n - 1) \to 0$).

Had the thermodynamic force $\beta F(n) = d(\ln w_e(n))/dn = -{}^1/_2(n^{-1} - (N - n)^{-1})$ been ignored (i.e., $F(n) = 0$ if $w_e(n) = 1$ for all n), then it follows from eq 5b that $\psi(m) = 1 - m$ and the corresponding steady-state flux, $J = h/N$, falls off as N^{-1} rather than N^{-2}. This flux applies for a rigid rodlike homopolymer permeating through a small pore in a barrier separating identical solvent environments. Comparison of eq 8 with $J = h/N$ indicates that the reduction in the number of available chain configurations and hence configurational entropy imposed by the barrier upon a flexible polymer chain acts to reduce its permeation rate by a factor of N^{-1} relative to that of a rigid rod homopolymer with the same N.

When the polymer segment-solvent interaction energies are different for the (different) solvents on opposite sides of the barrier (i.e., $a \neq 0$), then the steady-state flux becomes

$$J = -hw_e\frac{d\psi}{dn} = (h/\pi N^2)\left[\int_0^1 dm\; m^{1/2}(1 - m)^{1/2} \times \exp[Nam]\right]^{-1} \quad (9)$$

where we have employed eq 4 and eq 7b with $a \neq 0$. The integral appearing in eq 9 can be expressed as

$$\int_0^1 dm\; m^{1/2}(1 - m)^{1/2}\exp[Nam] = \pi(2Na)^{-1} \times \exp[Na/2]I_1(Na/2) \quad (10)$$

where $I_1(Na/2)$ is a Bessel function of imaginary argument.[13] Of primary interest are the limiting forms assumed by J as $Na \to 0$ and $Na \to \pm\infty$:

$$J \to (8h/\pi^2N^2)[1 - Na/2] \quad (Na \to 0) \quad (11a)$$

$$J \to 2\pi^{-3/2}(h/N^2)(Na)^{3/2}\exp(-Na) \quad (Na \to +\infty) \quad (11b)$$

$$J \to 2\pi^{-3/2}(h/N^2)(-Na)^{3/2}\exp(N|a|) \quad (Na \to -\infty) \quad (11c)$$

Thus, for small values of Na, J is enhanced (retarded) if $a < 0$ ($a > 0$) when compared to $J = 8h/\pi^2N^2$ when $a = 0$. As $Na \to \infty$, J decreases exponentially (see eq 11b) while as $Na \to -\infty$, which indicates a large attractive polymer segment−solvent interaction to the right of the barrier, J grows as $\exp(Na)$ (see eq 11c) and effectively overwhelms the resistance to permeation imposed by the orifice in the barrier. The limiting results of eq 11b and eq 11c are suspect, however, since excluded volume effects have not been included in this analysis and they should become increasingly important in determining isolated polymer chain configurations as the strength of the polymer segment−solvent interactions increases and significant deviations from Θ solvent behavior occur. For rigid rodlike homopolymers, the corresponding steady-state flux is given by

$$J = (h/N)(Na)(\exp(Na) - 1)^{-1} \tag{12}$$

It is apparent from eq 8 and eq 11 that the orifice in the barrier can function as a fractionation device which can separate flexible homopolymers of different values of N based on their different permeation rates under steady-state conditions. The fractionation can be influenced significantly by selecting solvents on opposite sides of the barrier which provide different interaction energies with the polymer segments.

III. Steady-State Permeation Rate of Homopolymer Chains Diffusing across a Planar Liquid−Liquid Interface or Phase Boundary

Before considering the polymer-barrier permeation problem when the individual segments diffuse at a finite rate, we pause here to investigate the related but perhaps simpler problem of diffusion of flexible homopolymer chains across a liquid−liquid interface under steady-state conditions since it generates some insight into the orifice in a barrier situation. The interfacial boundary is assumed to be infinitesimally thin and planar (e.g., the yz plane) and to suffer no physical distortion whenever a polymer molecule is engaged with it.

An individual polymer molecule is described in terms of a 1-D Rouse bead−spring model.[6] That is, a chemically homogeneous polymer molecule consists of a 1-D freely jointed chain of N identical beads connected by $N - 1$ segments which behave as Hookean springs of zero rest length. The beads act as drag points which provide viscous resistance to motion relative to the solvent and hence undergo Brownian motion while the connecting segments offer no such resistance and thus diffuse or relax infinitely rapidly in the solvent(s). The diffusion of such a polymer molecule involves the collective Brownian motion of all member beads of the chain. The possible configurations which the chain can assume are specified by giving the locations of the N beads (x_1, x_2, ..., x_N) measured relative to an origin in the yz plane at time t. Thus, in terms of an N-dimensional configuration space, each point (x_1, x_2, ..., x_N) depicts a possible chain configuration. The probability of a given chain configuration at time t is denoted by $W(x_1, x_2, ..., x_N; t)\, dx_1\, dx_2 \ldots dx_N$ where W is the probability distribution density in configuration space for a chain configuration where bead 1 lies between x_1 and $x_1 + dx_1$, bead 2 between x_2 and $x_2 + dx_2$ ..., etc.

At equilibrium the lengths of the Hookean springs connecting adjacent beads are distributed in a Gaussian manner and the N-particle probability density becomes

$$W_e(x_1, x_2, ..., x_N) = A \prod_{i=1}^{N-1} \exp[-\lambda(x_{i+1} - x_i)^2] \tag{13}$$

where λ is proportional to the stiffness constant of the springs, $\kappa \equiv k_B T/2\langle l^2\rangle$, where $\langle l^2\rangle$ is the mean-square length of a connecting link and A is a normalization factor.

The ratio of distribution functions, $\psi \equiv W/W_e$, at sufficiently long times where inertial effects are unimportant satisfies the N-particle diffusion equation

$$W_e \frac{\partial \psi}{\partial t} = \sum_{i=1}^{N} \frac{\partial}{\partial x_i}\left(D_i W_e \frac{\partial \psi}{\partial x_i}\right) \tag{14}$$

where D_i ($i = 1, 2, ..., N$) is the diffusion coefficient of the ith bead. The solution of eq 14 in the steady state where $\partial\psi/\partial t = 0$ is sought for an ensemble of similarly prepared systems of homopolymer chains diffusing across an interfacial boundary or (in the following section) through an orifice in an impenetrable barrier. The basic difficulty that is encountered in polymer diffusion problems of this type emanates from the restrictions that are imposed upon the number of available polymer chain configurations by the external constraints or boundaries. These restrictions are expressed mathematically in terms of boundary conditions which must be satisfied by either the distribution function(s) or its associated flux(es).

The precise influence of the interface upon the permeation of individual polymer chains diffusing across it depends on the physicochemical properties of the immiscible solvents forming the phase boundary. For instance the individual beads of an engaged polymer chain may experience different diffusion coefficients D_1 or D_2 as well as interaction energies E_1 or E_2 with solvent phases 1 or 2. Also the phase boundary itself may offer a contact resistance, h, to the permeation of individual beads across it. If the interface retards the diffusion of a polymer chain by exerting such resistance, a discontinuous drop in polymer concentration in configuration space develops across the interface.

The physical system consists of a thin diffusion column of length $2L$ which is filled with equal volumes of two immiscible solvents 1 and 2 so that the interfacial yz plane is at the center and perpendicular to the long axis of the column which is parallel to the x axis. The length L is taken to be comparable to or slightly greater than the average contour length of a fully extended polymer chain, making it unlikely but not impossible for a chainlike polymer molecule to be simultaneously engaged with the interface and either end of the column (i.e., $x = \pm L$). The column length is chosen to be comparable with and not significantly greater than the end-to-end dimensions of the homopolymer chain in an extended configuration in order to generate a permeation rate which is not merely dominated by the center of mass diffusion of the chain in the solvent environments on opposite sides of the interface or barrier. Throughout the selection $L = Npb$ is made where $b \equiv <l^2>^{1/2}$ and p is a numerical factor of 0(1). The bulk concentration of polymer molecules is maintained sufficiently dilute so that interactions between different polymer molecules are negligible and only a single polymer can be engaged with the interface over a time interval comparable to the reciprocal of the average permeation rate across the boundary.

Steady-state conditions are achieved by maintaining different bulk concentrations of polymer solute at opposite ends of the column. Thus, polymer molecules are introduced (removed) at the left (right) end of the column from an external source (sink) that sustains a constant bulk concentration level.

The steady-state flux, J, of polymer molecules across the phase boundary produced by a given polymer concentration difference maintained at opposite ends of the column is to be determined in order to obtain the corresponding permeation rate. It is assumed that a polymer molecule diffuses across the interface as a coil, without any restrictions upon the sequence with which the individual beads penetrate the phase boundary. This is in stark contrast to the sequential mode of chain penetration required for permeation through an orifice in a barrier.

The simplest steady-state polymer diffusion problem arises when the column contains but a single solvent. It is well-known that a polymer molecule diffuses as if it were a compact particle and only center of mass diffusion contributes to its net transport from the high to low concentration ends of the column. It is, however, instructive to obtain this result from eq 13 and eq 14 by transforming into center of mass $X = \sum_{i=1}^{N} x_i/N$ and relative coordinates $s_i \equiv x_{i+1} - x_i$; $i = 1, 2,..., N - 1$. In terms of X and the $\{s_i\}$, eqs 13 and 14 become

$$W_e(\{s_i\}) = A\prod_{i=1}^{N-1}\exp[-\lambda s_i^{\,2}] \qquad (13')$$

and

$$D\sum_{i=1}^{N-1}\left(\frac{1\,\partial}{N\partial X} - \frac{\partial}{\partial s_{i+1}} + \frac{\partial}{\partial s_i}\right)\times \left\{W_e(\{s_i\})\left(\frac{1\,\partial\psi}{N\partial X} - \frac{\partial\psi}{\partial s_{i+1}} + \frac{\partial\psi}{\partial s_i}\right)\right\} = 0 \qquad (14')$$

The normalization constant A in eq 13′ is determined by requiring that $\int ... \int W_e(\{s_i\})\mathrm{d}s_1 \ldots \mathrm{d}s_{N-1} = 1$, where the integrations extend over all internal configurations of a flexible Gaussian polymer chain irrespective of the location of its center of mass. The source and sink boundary conditions at the ends of the column are conveniently expressed as

$$\int ... \int W(X = -L;\{s_i\})\, \mathrm{d}s_1 \ldots \mathrm{d}s_{N-1} \equiv C(-L)\int ... \int W_e(\{s_i\})\mathrm{d}s_1 \ldots \mathrm{d}s_{N-1} \equiv C(-L) = C_0 \qquad (15a)$$

and

$$\int ... \int W(X = L;\{s_i\})\mathrm{d}s_1 \ldots \mathrm{d}s_{N-1} \equiv C(L)\int ... \int W_e(\{s_i\})\mathrm{d}s_1 \ldots \mathrm{d}s_{N-1} \equiv C(L) = 0 \qquad (15b)$$

The solution to eq 14 subject to eqs 15a and 15b can be obtained by substituting $\psi \equiv W(X,\{s_i\})/W_e(\{s_i\}) \equiv C(X)$ into eq 14′ and imposing the cyclic boundary condition that $s_N = s_1$ so that $\sum_{i=1}^{N-1}(\partial/\partial s_i - \partial/\partial s_{i+1})W_e(\{s_i\}) = 0$ for sufficiently large N chains where edge effects are unimportant. The resulting steady-state diffusion problem thus reduces to solving

$$(D/N)\frac{\mathrm{d}^2C(X)}{\mathrm{d}X^2} = 0; \quad C(-L) = C_0, \quad C(L) = 0 \qquad (16)$$

and this is satisfied by

$$C(X) = (C_0/2)(1 - X/L) \qquad (17)$$

Since eq 16 describes the steady-state diffusion for Brownian particles with diffusion coefficient D/N, this verifies that a flexible polymer chain of N beads diffuses in a single viscous solvent as if it were a compact structureless particle with a steady-state flux of its center of mass given by

$$J = -[D/N]\frac{\mathrm{d}C}{\mathrm{d}X} = DC_0/2NL \qquad (18)$$

Consider now the situation where the column contains equal volumes of two immiscible solvents of a rather special nature. The individual beads of a diffusing polymer chain are assumed to possess different coefficients D_1 or D_2 in the two solvents

$$D_i = D_1u(-x_i) + D_2u(x_i); \quad i = 1, 2, ..., N \qquad (19)$$

where $u(x)$ is the unit step function ($u(x) = 1$, $x > 0$; $u(x) = 0$, $x < 0$). For simplicity, the immiscible solvents are assumed to provide identical bead-solvent interaction potentials.

The required relative distribution function, ψ, which determines the steady-state diffusion properties of flexible polymer chains, must satisfy eq 14 using eq 19 when $\partial\psi/\partial t = 0$ subject to the boundary conditions eqs 15a and 15b and the following conditions at the interface

$$-D_1W_e\frac{\partial\psi}{\partial x_i}\bigg|_{x_i = 0^-} = -D_2W_e\frac{\partial\psi}{\partial x_i}\bigg|_{x_i = 0^+}; \quad i = 1, 2, ..., N \qquad (20)$$

and

$$-D_1W_e\frac{\partial\psi}{\partial x_i}\bigg|_{x_i = 0^-} = hW_e[\psi(x_i = 0^-) - \psi(x_i = 0^+)]; \quad i = 1, 2,..., N \qquad (21)$$

Equation 20 represents N conditions of detailed balance, which prevent the accumulation of polymer molecules in any configuration having some bead in contact with the surface. The interfacial boundary conditions of eq 21 state that the net flux of an individual bead across the interface is proportional to the drop in concentration (i.e., probability density) that results when the bead crosses the phase boundary. The above interfacial boundary conditions must be satisfied for all possible chain configurations consistent with some designated bead localized at the interface.

The diffusion problem formulated above can be solved by selecting the following functional form

$$\psi \equiv W/W_e = \sum_{i=1}^{N}\{b_1x_iu(-x_i) + b_2x_iu(x_i)\} + d_0\left(1 - \sum_{i=1}^{N}u(x_i)/N\right) + d_1 \qquad (22)$$

where $u(x_i)$ is the unit step function and determining the constants b_1, b_2, d_0 and d_1 which satisfy eqs 14, 15a, 15b, 20, and 21. The proposed solution indeed becomes a linear function of the center of mass coordinate $X = \sum_{i=1}^{N}x_i/N$ whenever the polymer molecule completely resides in a single phase (i.e., either $x_i < 0$ for all i or x_i

> 0 for all i). Additionally ψ experiences a discontinuous decrease whenever any bead of the chain crosses the interface from left to right. Explicitly the solution is

$$\psi = C_0(1 + hL/D_R)^{-1}[-(h/N)\sum_{i=1}^{N}(x_iu(-x_i)/D_1 + x_iu(x_i)/D_2) + (1 - \sum_{i=1}^{n}u(x_i)/N) + hL/D_2] \quad (23)$$

where $D_R \equiv D_1D_2/(D_1 + D_2)$ represents a reduced bead diffusion coefficient. For the special case where the interface offers no contact resistance ($h \to \infty$)

$$\lim_{h\to\infty}\psi = -\left(\frac{C_oD_R}{NL}\right)(\sum_{i=1}^{N}(x_iu(-x_i)/D_1 + x_iu(x_i)/D_2)) + C_oD_R/D_2 \quad (24)$$

which is continuous at the interface for every bead ($x_i = 0$; $i = 1, 2, ..., N$).

The results for ψ given by eq 23 or eq 24 reveal that the steady-state transport of polymer molecules across the phase boundary depends only upon the diffusion of the center of the mass, appropriately generalized for chain configurations engaged with the interface by

$$X = \sum_{i=1}^{N}(D_1x_iu(-x_i) + D_2x_iu(x_i))/(\sum_{i=1}^{N}(D_1u(-x_i) + D_2u(x_i)))$$

The individual bead flux or equivalently the center of mass flux integrated over all internal configurations of the (Gaussian) chain is given by

$$J = \int...\int \mathrm{d}x^i\left(-D_iW_e\frac{\partial\psi}{\partial x_i}\right) = \left(\frac{hC_o}{N}\right)(1 + hL/D_R)^{-1} \quad (25)$$

where $\mathrm{d}x^i \equiv \mathrm{d}x_1 \ldots \mathrm{d}x_{i-1}\,\mathrm{d}x_{i+1} \ldots \mathrm{d}x_N$.

Clearly the permeation rate per unit concentration difference between source and sink, J/C_o, is at least inversely proportional to the degree of polymerization, N. As $h \to \infty$ or when $hL/D_R \gg 1$, $J/C_o \to D_R/NL$, and if $D_1 = D_2 = D$, $D_R = D/2$ and $J/C_o \to D/2NL$ which is eq 18 for a single fluid. If $D_R \to \infty$ or $hL/D_R \ll 1$, $J/C_o \to h/N$, which is independent of column length and varies inversely with N rather than N^2 which from eq 8 was the case for polymer chain permeation through an orifice in a barrier in the instantaneous relaxation limit.

From eq 23 it is apparent that $\psi = C_o(1 + hL/D_R)^{-1}[1+ hL/D_2 - hX/D_1]$($\psi = C_o(1 + hL/D_R)^{-1}\,h(L-X)/D_2$) for chain configurations lying completely to the left (right) of the phase boundary. The difference of these two results evaluated at $X = 0$ is $C_o(1 + hL/D_R)^{-1}$, which represents the total depletion in bulk concentration of polymer across the phase boundary. The extent of the concentration drop for chain configurations which are interfacially engaged depends on the number of beads that have crossed to the right through the contribution $C_o(1 + hL/D_R)^{-1}(1 - \sum_{i=1}^{N}u(x_i)/N)$ in eq 23.

Determination of the steady-state permeation rate when the two solvents provide different interaction potential energies with the individual homopolymer beads is a somewhat more difficult problem which may require approximate variational or perturbative methods of analysis even if excluded volume effects are neglected. If ak_BT denotes the interaction energy difference between a chain bead and solvents 2 and 1, then each equilibrium configuration of an interfacially engaged polymer chain must be weighted by $W_e\exp[-a\sum_{i=1}^{N}u(x_i)]$ where W_e is given by eq 13 and $\sum_{i=1}^{N}u(x_i)$ represents the number of beads to the right of the interface for the given configuration.

Since the polymer chain is assumed to diffuse across the interface as a coil one must determine the number and segment lengths of all trains and loops of beads which protrude into phase 2 (e.g.) in order to deduce the correct Boltzmann weighting factor and this is a formidable task. The task, however, is not so difficult for the polymer−orifice in a barrier problem since only contiguous trains of beads protrude into the solvents on opposite sides of the barrier and for any degree of chain penetration the correct Boltzmann weighting factor can be determined easily.

IV. Steady-State Permeation Rate for Homopolymer Diffusion through an Orifice in a Barrier in the Finite Relaxation CASE

Here we investigate the steady-state permeation rate with which flexible chainlike homopolymers diffuse through an orifice in a thin barrier when the protruding segment trains relax at a finite rate to their equilibrium distribution of configurations for any degree of penetration. A 1-D bead−spring model is again utilized to describe the dynamics of the homopolymers each of which consists of N beads distributed uniformly along the contour of the chain. A polymer molecule is assumed to diffuse through the orifice only by a process of sequential bead by bead penetration. For example, whenever a particular bead of the chain is closest to the orifice (on either side) only that bead can diffuse in either direction through the pore while the other $N - 1$ beads cannot pass.

When the nth bead ($n = 1, 2, ..., N$) of a partially threaded polymer chain is closest to the orifice (located at the origin), then the relative distribution function(s)

$$\psi_n(x_1...x_n...x_N) \equiv W_n(x_1...x_n...x_N)/W_{en}(x_1...x_n...x_N); \quad n = 1, 2, ..., N$$

with $x_n \simeq 0$ must satisfy the many particle diffusion equations in the steady state

$$\sum_{i=1}^{N}\frac{\partial}{\partial x_i}\left[D_iW_{en}\frac{\partial\psi_n}{\partial x_i}\right] = 0;\ D_i = D_1u(-x_i) + D_2u(x_i) \quad (26)$$

subject to the requirements that for all $i \neq n$ ($i = 1, 2, ..., N$)

$$\frac{-D_i}{N}W_{en}\frac{\partial\psi_n}{\partial x_i}\bigg|_{x_i=0} = 0 \quad i \neq n \quad (27)$$

$$\frac{-D_1}{N}W_{en}\frac{\partial\psi_n}{\partial x_n}\bigg|_{x_n=0^-} = \frac{-D_2}{N}W_{en}\frac{\partial\psi_n}{\partial x_n}\bigg|_{x_n=0^+} \quad (28)$$

and

$$\frac{-D_1}{N}W_{en}\frac{\partial\psi_n}{\partial x_n}\bigg|_{x_n=0^-} = hW_{en}(\psi_n(x_n = 0^-) - \psi_n(x_n = 0^+)) \quad (29)$$

Again h represents an interfacial resistance offered by the orifice to the passage of an individual bead across it. If $h \to \infty$, then ψ_n becomes a continuous function of x_n at $x_n = 0$ in order to produce a finite flux by eq 29.

For chain configurations which are not threaded through the orifice, the equilibrium distribution function $W_{en} = W_e$ becomes independent of n and is given by eq 13. However for orifice-engaged configurations, the equilibrium distribution function for the nth degree of penetration, W_{en}, is assumed to be (for athermal solvents)

$$W_{en} \equiv W_{en}(x_1 ... x_n ... x_N) = 2^{-N}\binom{n}{\frac{n}{2}}\binom{N-n}{\frac{N-n}{2}} A \prod_{i=1}^{N-1} \times \exp[-\lambda(x_{i+1} - x_i)^2] \prod_{i=1}^{n-1} u(x_i) \prod_{i=n+1}^{N} u(-x_i) \quad (30)$$

for the discrete bead case and

$$W_{en} \equiv W_{en}(x_1 ... x_n ... x_N) = \pi^{-1}[n(N-n)]^{-1/2} A \prod_{i=1}^{N-1} \times \exp[-\lambda(x_{i+1} - x_i)^2] \prod_{i=1}^{n-1} u(x_i) \prod_{i=n+1}^{N} u(-x_i) \quad (30')$$

in the continuous bead limit where again $u(x_i)$ represents the unit step function. The normalization factor, A, and the spring constant, λ, have the same meaning as before in eq 13 with $A \equiv (\int ... \int \mathrm{d}x^n \prod_{i=1}^{N-1} \exp[-\lambda(x_{i+1} - x_i)^2])^{-1}$ where $\int ... \int \mathrm{d}x^n$ denotes integration over all bead coordinates except x_n. In the present analysis for allowed configurations W_{en} is given by the product of either eq 2 or eq 3 and eq 13. When W_{en} is integrated over all bead coordinates except x_n, one regains eq 2 or eq 3 for $w_e(n) = \int ... \int \mathrm{d}x^n W_{en}$ depending upon whether eq 30 or eq 30′ is employed for W_{en}. Furthermore, it follows that

$$\sum_{n=1}^{N} w_e(n) \equiv \sum_{n=1}^{N} \int .. \int \mathrm{d}x^n \, W_{en} = 1$$

or

$$\int_0^N \mathrm{d}n \; w_e(n) = \int_0^N \mathrm{d}n \int ... \int \mathrm{d}x^n \, W_{en} = 1$$

by direct substitution of eq 2 or eq 3 for $w_e(n)$ into the corresponding summation (integration) over n.

A further justification for the above selection of W_{en} (i.e., eq 30) follows. Presumably a more accurate estimate of W_{en} is

$$W_{en} = A'(n(N-n))^{-1/2} \prod_{i=1}^{n-1} G(x_{i+1}, x_i) u(x_i) \times \prod_{i=n}^{N-1} G(x_{i+1}, x_i) u(-x_{i+1}) \quad (30'')$$

where

$$G(x_{i+1}, x_i) = \left(\frac{\lambda}{\pi}\right)^{1/2} [\exp[-\lambda(x_i - x_{i+1})^2] - \exp[-\lambda(x_i + x_{i+1})^2]] = \left(\frac{\lambda}{\pi}\right)^{1/2} \exp[-\lambda(x_i - x_{i+1})^2]\{1 - \exp[-4\lambda x_i x_{i+1}]\}$$

with $\lambda = (2\langle l^2\rangle)^{-1}$ (see eq 13) and A' is a normalization constant which renders $\int \mathrm{d}x^n \, W_{en}(x_1, x_2, ..., x_{n-1}, ..., x_N) \equiv w_e(n) = \pi^{-1}[n(N-n)]^{-1/2}$ which is eq 3. As mentioned in the Appendix, the function $G(x_{i+1}, x_i)$ represents a Green's function for the propagation of a flexible chain connector between successive beads i and $i+1$ along the chain in the presence of an absorbing barrier at $x = 0$. Clearly $G(x_i, x_{i+1}) = 0$ whenever $x_i = 0$ and/or $x_{i+1} = 0$ since the factor $[1 - \exp(-4\lambda x_i x_{i+1})]$ vanishes identically. Also if $4\lambda = 2/\langle l^2\rangle$ is sufficiently large and it becomes larger as the continuum bead limit is approached, then $\exp[-4\lambda x_i x_{i+1}] \ll 1$ for $x_i \neq 0$ and $x_{i+1} \neq 0$, and to a reasonable approximation for almost all allowed configurations

$$1 - \exp[-4\lambda x_i x_{i+1}] \cong u(x_i) u(x_{i+1}) \quad \text{for } x_i > 0,\ x_{i+1} > 0$$

or

$$1 - \exp[-4\lambda x_i x_{i+1}] \cong u(-x_i) u(-x_{i+1}) \quad \text{for } x_i < 0,\ x_{i+1} < 0$$

and

$$G(x_{i+1}, x_i) \cong \left(\frac{\lambda}{\pi}\right)^{1/2} \exp[-\lambda(x_i - x_{i+1})^2] \times \{u(x_i) u(x_{i+1}) + u(-x_i) u(-x_{i+1})\}$$

Hence in this approximation one obtains eq 30 or eq 30′ for W_{en} with $A \equiv A'(\lambda/\pi)^{(N-1)/2}$.

The requirement imposed by eq 27 can be satisfied by assuming that $\psi_n \equiv \psi_n(x_n)$ is a function solely of bead coordinate x_n. Also both eq 30 and eq 30′ reveal that W_{en} is spatially a function of only the $N-1$ relative coordinates $s_i \equiv x_{i+1} - x_i$ ($i = 1, 2, ..., N-1$) and not x_n for any value of n. This suggests that $W_n(x_1 ... x_n ... x_N)$, which represents the probability density that a member system of the polymer chain-barrier ensemble possesses a chain with the nth bead nearest the orifice in a configuration denoted by $(x_1 ... x_n ... x_N)$ can be expressed as

$$W_n(x_1 ... x_n ... x_N) \equiv W_n(x_n, \{s_i\}) = \psi_n(x_n) W_{en}(\{s_i\}) \quad (31)$$

where $\{s_i\}$ ($i = 1, 2, ..., N-1$) denotes the set of $N-1$ relative bead coordinates.

Equation 26 for each n ($n = 1, 2, ..., N$) can then be expressed in terms of x_n and the $\{s_i\}$ as

$$\frac{\partial}{\partial x_n}\left[D_n W_{en}(\{s_i\}) \frac{\partial \psi_n(x_n)}{\partial x_n}\right] + \sum_{i=1}^{N-1}\left(\frac{\partial}{\partial s_i} - \frac{\partial}{\partial s_{i+1}}\right) \times \left\{D_i W_{en}(\{s_i\})\left(\frac{\partial \psi_n(x_n)}{\partial s_i} - \frac{\partial \psi_n(x_n)}{\partial s_{i+1}}\right)\right\} = 0 \quad (32)$$

and since by eq 30 $W_{en} \simeq \prod_{i=1}^{N-1} \exp[-\lambda s_i^2]$ is independent of x_n, eq 32 reduces to

$$\frac{\partial}{\partial x_n}\left[D_n \frac{\partial \psi_n(x_n)}{\partial x_n}\right] = 0 \quad n = 1, 2, ..., N \quad (33)$$

and eq 27 is identically satisfied.

In terms of the center of mass coordinate $X \equiv \sum_{i=1}^{N} x_i/N$, eq 33 becomes

$$\frac{1}{N}\frac{\mathrm{d}}{\mathrm{d}X}\left[\frac{D}{N}\frac{\partial\psi_n}{\partial X}\right] = 0 \quad n = 1, 2, ..., N \qquad (33')$$

where $D \equiv D_1 u(-X) + D_2 u(X)$. This result suggests that a homopolymer chain whose configurations are constrained by its passage through a narrow orifice which localizes at least a single bead or segment possesses a center of mass diffusion coefficient given by D/N^2 and a center of mass flux $-(D/N^2)\partial\psi_n/\partial X$. The N^{-2} dependence of the center of mass diffusion coefficient is consistent with the predictions of the reptation theory of polymer dynamics in polymer melts and in the presence of fixed obstacles of which a pore in a barrier is an example.[5,8] The individual bead flux through the orifice is larger than the center of mass flux by a factor of N and is $-(D_n/N)W_{\mathrm{e}n}\partial\psi_n/\partial x_n|_{x_n=0}$ where $D_n \equiv D_1 u(-x_n) + D_2 u(x_n)$ for any chain configuration. Thus, the appearance of the factor N^{-1} in eqs 27−29 is justified.

Steady-state conditions are achieved by maintaining a constant source and sink concentration of polymer molecules on opposite sides of the barrier for each member system of an ensemble of similarly prepared systems over a sufficiently long time duration. Summing eq 31 over n and integrating over all relative coordinates gives[14]

$$\sum_n \int ... \int \mathrm{d}s_1 ... \mathrm{d}s_{N-1}\, W_n(x_n,\{s_i\}) = \sum_n \psi_n(x_n) \int ... \int \mathrm{d}s_1 .. \mathrm{d}s_{N-1}\, W_{\mathrm{e}n}(\{s_i\})$$

and for configurations which are not engaged with the orifice $W_{\mathrm{e}n}(\{s_i\}) = W_{\mathrm{e}}(\{s_i\})$ which is given by eq 13 and since $\int ... \int \mathrm{d}s_1 ... \mathrm{d}s_{N-1}\; W_{\mathrm{e}}(\{s_i\}) = 1$

$$\sum_n \int ... \int \mathrm{d}s_1 ... \mathrm{d}s_{N-1} W_n(x_n,\{s_i\}) = \sum_n \psi_n(x_n) \equiv \psi(X)$$

In terms of $\psi(X)$, the boundary conditions can be expressed as

$$\psi(-L) = C_{\mathrm{o}}\ (\text{all } x_n \le 0); \quad \psi(L) = 0\ (\text{all } x_n \ge 0) \qquad (34)$$

The center of mass locations $X = \pm L$ are assumed to be near enough to the orifice that at least a terminal chain *segment* can make contact with it.

When $D_1 = D_2 = D$ and $h \to \infty$, eqs 26−29 and eq 33 are satisfied by

$$\psi_n(x_n) = -b'x_n + d' \quad n = 1, 2, ..., N \qquad (35)$$

where b' and d' are constants which may be determined by setting

$$\psi(X) = \sum_{n=1}^{N} \psi_n(x_n) = -N(b'X - d')$$

and utilizing eq 34 to obtain $b' = C_{\mathrm{o}}/2NL$ and $d' = b'L = C_{\mathrm{o}}/2N$. Hence

$$\psi(X) = \sum_{n=1}^{N} \psi_n(x_n) = \frac{C_0}{2}(1 - X/L) \quad \text{or}$$

$$\psi_n(x_n) = \frac{C_0}{2N}(1 - x_n/L) \quad n = 1, 2, ..., N \qquad (36)$$

The corresponding steady-state permeation rate is

$$J = \sum_{n=1}^{N} \int ... \int \mathrm{d}x^n\, W_{\mathrm{e}n}\left[-(D/N^2)\frac{\partial\psi(X)}{\partial X}\right] = \sum_{n=1}^{N} \int ... \int \mathrm{d}x^n\, W_{\mathrm{e}n}\left[-(D/N)\frac{\partial\psi_n(x_n)}{\partial x_n}\right] = DC_0/2N^2L \qquad (37)$$

where eq 36 has been utilized. If $L \propto N$, then $J \propto D/N^3$, which is consistent with the corresponding result obtained from the reptation theory of polymer dynamics.[8] Note that the $\psi_n(x_n)$ ($n = 1, 2, ..., N$) given in eq 35 are continuous across the orifice when $h \to \infty$. For finite values of h, the corresponding $\psi_n(x_n)$ exhibit discontinuous behavior across the orifice (i.e., at $x_n = 0$).

Suppose now that $D_n = D_1 u(-x_n) + D_2 u(x_n)$ for each n and that h remains finite, then the $\psi_n(x_n)$ exhibits a discontinuity at $x_n = 0$. It is reasonable to assume that a possible solution to eq 33 consistent with eqs 27−29 and eq 34 has the form

$$\psi_n(x_n) = b_{1n}x_n u(-x_n) + b_{2n}x_n u(x_n) + c[1 - \sum_{j=1}^{N} r_j u(x_j)/R_N] + d \qquad (38)$$

where $r_j \equiv w_{\mathrm{e}}^{-1}(j)$ and $R_N \equiv \sum_{j=1}^{N} r_j$ with $w_{\mathrm{e}}(j)$ given by eq 2 or eq 3 and $u(x_j)$ is again the Heaviside unit step function. Note that

$$\psi_n(x_n = 0^-) - \psi_n(x_n = 0^+) = cr_n/R_N \equiv cw_{\mathrm{e}}^{-1}(n)/\sum_{j=1}^{N} w_{\mathrm{e}}^{-1}(j)$$

represents the discontinuity of $\psi_n(x_n)$. The coefficients b_{1n}, b_{2n}, c, and d are to be determined by satisfying eqs 27−29 and eq 34. Insertion of eq 38 into eq 28 leads to the set of relationships

$$D_1 b_{1n} = D_2 b_{2n} \quad n = 1, 2, ..., N \qquad (39)$$

Also substitution of eq 38 into eq 29 leads to

$$b_{1n} = \frac{-hcNr_n}{D_1 R_N}; \quad b_{2n} = \frac{-hcNr_n}{D_2 R_N} \quad n = 1, 2, ..., N \qquad (40)$$

and

$$\psi_n(x_n) \equiv W_n/W_{\mathrm{e}n} = \frac{-hcNr_n}{R_N}\left[\frac{x_n u(-x_n)}{D_1} + \frac{x_n u(x_n)}{D_2}\right] + c[1 - \sum_{j=1}^{N} r_j u(x_j)/R_N] + d \qquad (41)$$

Also

$$\sum_{n=1}^{N}\int\ldots\int \mathrm{d}x^n W_n = \sum_{n=1}^{N}\psi_n(x_n)\int\ldots\int \mathrm{d}x^n W_{\mathrm{e}n} = \sum_{n=1}^{N}\psi_n(x_n)w_{\mathrm{e}}(n) = \frac{-hcN}{R_N}\sum_{n=1}^{N}\left(\frac{x_n u(-x_n)}{D_1}+\frac{x_n u(x_n)}{D_2}\right) + c\sum_{n=1}^{N}w_{\mathrm{e}}(n)\left[1-\frac{\sum_{j=1}^{N} r_j u(x_j)}{R_N}\right] + d \quad (42)$$

where we recall that $\sum_{n=1}^{N} w_{\mathrm{e}}(n) = 1$ and $r_n w_{\mathrm{e}}(n) = 1$ by definition. For chain configurations where all the beads lie to either side of the barrier, $\sum_{n=1}^{N}\int\ldots\int \mathrm{d}x^n\ W_n$ becomes a function of $X = \sum_{n=1}^{N} x_n/N$, $\psi(X)$, and eq 42 reduces to the following limits for $X < 0$ with all $x_n \leq 0$ or $X > 0$ with all $x_n \geq 0$

$$\psi(X < 0) = \frac{-hcN^2X}{D_1R_N} + c + d \quad (43a)$$

$$\psi(X > 0) = \frac{-hcN^2X}{D_2R_N} + d \quad (43b)$$

Employing the source and sink boundary conditions of eq 34 in eqs 43a and 43b generates a pair of linear equations which are solved easily for c and d and

$$d = hN^2Lc/D_2R_N; \quad c = C_0(1 + hN^2L/D_{\mathrm{R}}R_N)^{-1} \quad (44)$$

The steady-state permeation rate is

$$J = -\frac{D_2}{N}\int\ldots\int \mathrm{d}x^N\ W_{\mathrm{e}N}\frac{\partial\psi_{\mathrm{N}}(x_{\mathrm{N}})}{\partial x_N}\bigg|_{x_N = 0^+} = hc/R_N = (hC_0/R_N)[1 + hN^2L/D_{\mathrm{R}}R_N]^{-1} \quad (45')$$

where eq 41 and eq 44 have been utilized. This result also follows immediately from

$$J = -(D_1/N^2)\frac{\partial\psi}{\partial X}\bigg|_{X=0^-} = -(D_2/N^2)\frac{\partial\psi}{\partial X}\bigg|_{X=0^+}$$

where either eq 43a or 43b is employed for $\psi(X < 0)$ or $\psi(X > 0)$, respectively. The sum $R_N \equiv \sum_{j=1}^{N} w_{\mathrm{e}}^{-1}(j)$ has been evaluated in the continuous bead limit in sec II and from eq 7b and eq 8 $R_N = \pi^2N^2/8$.

Substitution of the explicit result for R_N and $L = pNb$ in eq 45′ where again p is a scale factor of 0(1) and $b = \langle l^2\rangle^{1/2}$ gives

$$J/C_0 = \frac{8h}{\pi^2N^2}\left[1 + \frac{8hNpb}{\pi^2D_{\mathrm{R}}}\right]^{-1} \quad (45)$$

When both $D_1 \to \infty$ and $D_2 \to \infty$, $J/C_o \to 8h/\pi^2N^2$, which is the result obtained in section II (eq 8) for the limiting case where the trains of segments protruding in the solvents on opposite sides of the barrier relax instantaneously to their equilibrium distribution of configurations as the chain threads itself through the orifice. This agreement in the limiting behavior provides motivation for the selection made for the orifice discontinuity contribution to $\psi_n(\mathrm{x}_n)$ in eq 38. Indeed if $\psi_n(x_n) = b_{1n}x_nu(-x_n) + b_{2n}x_nu(x_n) + c[1 - \sum_{j=1}^{N} u(x_j)/N] + d$ had been selected rather than eq 39 as an approximation to $\psi_n(x_n)$ and the subsequent analysis leading to eq 45 were repeated, one obtains

$$J^*/C_0 = \frac{2h}{N^2}[1 + 2hNpb/D_{\mathrm{R}}]^{-1} \quad (46)$$

This result reduces to $J^*/C_o = 2h/N^2$ rather than $J/C_o = 8h/\pi^2N^2$ in the $D_1 \to \infty$ and $D_2 \to \infty$ limit. Thus, $J^*/C_o > J/C_o$ as $D_i \to \infty$ $i = 1, 2$, which suggests that the steady-state permeation rate is reduced when proper account is taken of the configurational entropy of the polymer chain constrained by the orifice.

It is apparent from eq 45 that for finite values of D_1 and D_2 the finite relaxation rates of the individual beads of the chain act to reduce the overall steady-state permeation rate from its maximum value $8h/\pi^2N^2$. If $8hNpb/\pi^2D_{\mathrm{R}} \gg 1$, where $D_{\mathrm{R}} = D_1D_2/(D_1 + D_2)$ for finite h, $J/C_o \propto D_{\mathrm{R}}/N^3$ and the permeation rate is in fact determined by the finite diffusion rate of the individual beads in their respective solvent environments, and this result is consistent with the reptation theory of polymer dynamics.[5,8]

V. Concluding Remarks

The principal results of this analysis are eq 25 and eq 45 which give the steady-state permeation rates per unit concentration difference, J/C_o, of flexible N unit homopolymers diffusing respectively across a planar interface and through an orifice in a barrier under Θ-solvent conditions and in the free-draining limit where hydrodynamic interactions between different diffusing segments along the chain are neglected. Both eqs 25 and 45 involve a combination of two contributions: (1) a localized contact resistance which acts at either the interfacial or orificial surface and (2) an effective diffusion of the center of mass of the chain in a direction in opposition to the applied concentration gradient and normal to either the interfacial or orificial surface. Whenever $h/D_{\mathrm{R}} \ll 1$ ($h/D_{\mathrm{R}} \gg 1$) the permeation rates given in eqs 25 and 45 are dominated by the contact resistance (center of mass diffusion) contributions.

Explicitly, when $h/D_{\mathrm{R}} \ll 1$, eq 25 and eq 45 respectively reduce to $J/C_o - h/N$ and $J/C_o \simeq 8h/\pi^2N^2$, and both these results follow immediately from eq 7 using either $w_{\mathrm{e}}(n) = 1$ (for the interface) or eq 3. Clearly in this limit, J/C_o is determined by h and the reciprocal of the equilibrium distribution function of an engaged polymer chain summed over all possible degrees of penetration. The selections chosen for $w_{\mathrm{e}}(n)$ are consistent with Θ-solvent environments where excluded volume interactions are neutralized.[5,15] When non-Θ-solvent conditions prevail, a $w_{\mathrm{e}}(n)$ different from eq 3 must be utilized which takes account of excluded volume contributions. For good athermal polymer−solvent combinations the excluded volume-corrected equilibrium configurational distribution function, $w_{\mathrm{e}}^*(n)$, is expected to satisfy $w_{\mathrm{e}}^*(n) < w_{\mathrm{e}}(n)$ for all n because certain configurations become disallowed and the corresponding permeation rate is smaller than $8h/\pi^2N^2$ when $h/D_{\mathrm{R}} \ll 1$. Explicit inclusion of excluded volume effects and ascertaining their effect upon permeation rates of chainlike polymers is a contemplated extension of the present work.

In the opposite limit where $h/D_{\mathrm{R}} \gg 1$ eqs 25 and 45 respectively reduce to $J/C_o \to D_{\mathrm{R}}/N^2pb$ and $J/C_o \to D_{\mathrm{R}}/N^3pb$ where we have set the effective column length to be proportional to the polymer chain contour length (i.e. $L \simeq Npb$). The permeation rates in this limit depend only upon the rate of diffusion of the center of mass of the chain. The dependence of J/C_o on N can be ascertained to within numerical factors by application of the Einstein relationships expressed as $J/C_o \simeq \tau^{-1} \simeq D_c/\langle x^2\rangle_c$ where τ is a mean permeation time, D_c is the center of mass diffusion coefficient and $\langle x^2\rangle_c$ is the mean square distance the center of mass of the polymer chain must traverse for translocation across the barrier. One anticipates, however, that $\langle x^2\rangle_c$ can be estimated to within numerical factors by the mean square end to end distance spanned by the polymer chain. For flexible, free-draining polymer chains in a Θ solvent, $\langle x^2\rangle \propto N$ and $D_c = D_R/N$ or $D_c = D_R/N^2$ for freely diffusing or reptating chains, respectively. Thus, the limiting results of eqs 25 and 45 when $h/D_R \gg 1$ are apparent.

If hydrodynamic interactions between the individual diffusing polymer chain segments were to be included as in the Zimm approach,[5,9,15] then in a Θ solvent environment one anticipates $D_c = D_R/N^{1/2}$ and $D_c = D_R/N^{3/2}$ for polymer chains diffusing across a planar interface and through a pore in a barrier, respectively. The corresponding dependencies of J/C_0 on N are expected to be $J/C_o \propto D_R/N^{3/2}$ and $J/C_o \propto D_R/N^{5/2}$ in the limit $h/D_R \gg 1$. For non-Θ-solvent conditions, excluded volume effects must be considered. For good solvent environments one anticipates that $\langle x^2\rangle \propto N^{2\nu}$ where $\nu \simeq 3/5$ and $D_c \propto D_R/N^{\nu}$ (interface) or $D_c \propto D_R/N^{1+\nu}$ (orifice in a barrier). Thus, when $h/D_R \gg 1$ one anticipates that $J/C_o \propto D_R/N^{3\nu} \propto D_R/N^{1.8}$ and $J/C_o \propto D_R/N^{1+3\nu} \propto D_R/N^{2.8}$ for the interfacial and pore permeation rates, respectively, when hydrodynamic interactions are considered in good solvents. A more detailed analysis is both contemplated and required to determine the N dependence of the permeation rate when h and D_R are comparable (i.e., $h/D_R \simeq 1$), and both hydrodynamic and excluded volume interactions must be considered.

In many cases of physical interest involving the permeation of macromolecules and biopolymers through membranes, it is believed that the process is assisted by adsorption or adhesion of polymer molecule segments to “chaperone” molecules located on the side of the membrane where the penetrant species eventually translocates.[3] Thus, the direction of diffusion of the permeating macromolecules may be strongly biased through specific interactions with complementary molecular species prevalent in one of the membrane-partitioned solvents. If polymer segment−chaperone molecule adsorption is a primary means of interaction between the moieties, this feature should be included in determining the effective thermodynamic force which can act to bias the direction of diffusion. Inclusion of such polymer−chaperone molecule adsorption behavior which may be energetically favorable and entropically unfavorable also suggests a possible extension of the present analysis.

Appendix

The probability distribution function $w_e(n)$ can also be obtained from

$$w_e(n) = \lim x_1^* \rightarrow 0,\ x_2^* \rightarrow 0 \left\{K\int_0^{\infty} dx_1 \int_{-\infty}^{0} dx_2\, G(x_1,x_1^*;\ n) G(x_2,x_2^*;\ N - n)\right\} \quad \text{(A-1)}$$

where $G(x_i,x_i{}^*;\ n_i)$ $i = 1,2$ with $n_1 \equiv n$ and $n_2 \equiv N-n$ represent Green’s functions for propagation of a point particle which diffuses as a one-dimensional random walk between initial point x_i^* and terminal point x_i after n_i steps each of length l such that no intermediate step passes through the origin. Also $K \equiv l^2/2x_1^*x_2^*$ is a normalization constant which renders $\int_0^N w_e(n)\, dn = 1$. The Green’s functions $G \equiv G(x_i,x_i^*;\ n_i)$, $i = 1, 2$ ($0 < x_1 < \infty$, $0 \leq n_1 \leq n$) ($-\infty < x_2 < 0$, $0 \leq n_2 \leq N - n$) satisfy

$$\frac{\partial G}{\partial n_i} = \frac{l^2}{2}\frac{\partial G}{\partial x_i{}^2} \quad \text{(A-2)}$$

subject to the initial condition $G(x_i,x_i^*;\ n_i = 0) = \delta(x_i - x_i^*)$ and the boundary condition $G(x_i = 0,x_i^*;\ n_i) = 0$ for all n_i, $i = 1, 2$, at the impenetrable absorbing barrier at the origin. The solution of eq A-2 subject to the indicated conditions is

$$G(x_i,x_i^*,n_i) = (2\pi n_i l^2)^{-1/2}[\exp[-(x_i - x_i^*)^2/2n_i l^2] - \exp[-(x_i + x_i^*)^2/2n_i l^2]] \quad \text{(A-3)}$$

In the limit $x_i^* \rightarrow 0$, eq A-3 reduces to

$$G(x_i,x_i^*;\ n_i) \rightarrow (2\pi n_i l^2)^{-1/2}(2x_i x_i^*/n_i l^2) \exp[-x_i{}^2/2n_i l^2] \quad \text{(A-4)}$$

with $n_1 = n$ and $n_2 = N - n$. Substitution of eq A-4 into eq A-1 and performing the integration gives $w_e(n) = \pi^{-1}n^{-1/2}(N - n)^{-1/2}$, which is identical to eq 3.

If in eq A-3 one sets $n_i = 1$, $x_i^* = x_{i+1}$ and $\lambda = {}^1/_2 l^2 \equiv {}^1/_2\langle l^2\rangle$, then

$$G(x_i,x_{i+1}) = \left(\frac{\lambda}{\pi}\right)^{1/2}[\exp[-\lambda(x_i - x_{i+1})^2] - \exp[-\lambda(x_i + x_{i+1})^2]]$$

which is the Green’s function for propagation introduced in eq 30″ for successive beads i and $i + 1$ located at positions x_i and x_{i+1}, respectively, along a one-dimensional Rouse bead−spring model of a polymer chain which is threaded through an orifice in an otherwise impenetrable barrier.

References and Notes

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(14) Note that $\int\ldots\int dx^n\ W_n(x_1\ldots x_n\ldots x_N) \equiv \int\ldots\int dx_1\ldots dx_{n-1}dx_{n+1}\ldots dx_N\ W_n = \int\ldots\int\prod_{i=1}^{N-1} ds_i\ W_n(x_n,\{s_i\})$.
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MA9812938