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(45) Some representative flow and retention diagrams are included here and the figures of the remaining systems are deposited as supplementary material.

Flows of Flexible Polymer Solutions in Pores

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ABSTRACT: We study the passage of flexible polymers in solution through pores (of diameter D smaller than the radius of gyration of the chains, R_F) driven by hydrodynamic flows through the pore (characterized by a current of the solvent, J_s). (1) For the case of slightly *conical* pores (first converging and then diverging) the chains are drawn in above a critical current J_c. For a dilute solution, $J_c \simeq J_{c_1}\epsilon$, where ϵ measures the angle of the cone and $J_{c_1} \simeq T/\eta_s$ depends only on the temperature T and the solvent viscosity η_s, but is independent of D and of the molecular weight (at large molecular weights). For a semidilute solution at the entrance of the pore, one finds three regimes depending upon the bulk concentration c_0, the minimal cross section, and the current's strength J_s: (α) a free flowing state of the SD solution throughout the pore, (β) a partially flowing state with a dilute region extending downstream from the minimal section, (γ) a clogged state where a dilute region is present both upstream and downstream. (2) For a capillary of *constant cross section* passing through a flat wall, the chains are subjected to an elongational flow at the entrance. Above a critical current $J_s = J_c'$, they are sufficiently stretched to enter the pore. For dilute solutions, $J_c' = J_{c_1}$. In semidilute solutions J_c' ought to vary as $C^{-15/4}$. We also discuss elongational effects at the entrance of macroscopic capillaries.

I. Introduction

Besides fundmental interest (polymers in one and two dimensions), the study of flexible polymer solutions trapped in porous media has important applications: in particular the extraction of oil from porous geological structures by injection of polymer solutions of high molecular weight. Practical situations always correspond to polymer solutions in good solvents: for this case, we have results concerning the partitioning and the dynamics of macromolecules confined in pores.[2] These two problems have been studied theoretically very recently by Daoud and de Gennes[5] (thermodynamic properties) and by Brochard and de Gennes[6] (diffusion and internal modes). In these studies the emphasis was placed on the behavior of chains in an immobile solvent. The corresponding experiments are rather difficult because of the small percentage of chains in pores of small diameter.

On the contrary, in all the experiments proposed here, one forces the polymer to penetrate into the pores by applying a solvent current J_s. We have considered two types of pores: (a) slightly conical pores (Figure 2), and (b) cylindrical pores with an entrance at which the flow is strongly convergent (Figure 8). In conical pores, the polymer is sucked in if the frictional force exerted by the solvent is sufficient to overcome the elastic forces resisting confinement. In pores of constant cross section, the process of penetration is due to the elongational shear which stretches the chain *before* its entrance. Case (a) is statistically realized by pores in porous media. Case (b) corresponds to commercially available structures (nucleopores in plexiglas have cylindrical geometries and diameters $D \gtrsim 150$ Å), or can be approximated by pores in leached glass[2] or with crystallographic structures such as zeolites ($D \gtrsim 20$ Å).

We assume that polymer adsorption on the solid surface is negligible. This can be achieved by treating the pores chemically.[2] We also restrict our attention to *flexible* uncharged polymers for which the statistical and dynamical properties in bulk solutions are now well described by scaling methods.[3,4]

Here also we use as a theoretical framework the techniques of scaling laws which are known to give good qualitative results, but all our results unfortunately lack exact numerical coefficients. In the first part, we review the equilibrium properties of confined chains for the two types of geometrics. In the second section we described the flow regimes of polymer solutions in conical pores (case a). In the third part, we study the effects of polymer accumulation and forced penetration at the entrance of cylindrical pores (case b).

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II. Static Properties

Before studying the effects of forced penetration by solvent flows, we shall review the equilibrium properties of confined polymers in immobile solutions.

What we need is to know the equilibrium concentration c of monomers inside conical and cylindrical pores in contact with a reservoir at concentration c_0. The concentration is obtained by the requirement that the monomer chemical potential be constant:

$$\mu(D) = \mu_0 \qquad \text{(II.1)}$$

where $\mu(D)$ and μ_0 are the chemical potential of monomers in the pore at diameter D and in the bulk, respectively. The chemical potential μ is calculated from the free energy F per cm^3:

$$\mu = \partial F/\partial c \qquad \text{(II.2)}$$

We shall derive in detail the chemical potential of confined solutions for which the results of ref 5 are incomplete and inexact.

Remark 1. It is also possible to determine c by the constancy of the chemical potential μ_s of the solvent related to the osmotic pressure of the solute by the relation

$$\mu_s = \mu_{s0}(P,T) - \pi v_s \qquad \text{(II.3)}$$

where v_s is the volume of the solvent molecules and μ_{s0} is the solvent chemical potential without solute molecules. The requirement μ_s = constant does not imply π = constant, contrary to what we first thought. Let $\Omega = N/c$ be the volume and $\mathcal{F}_N(\Omega,D) = \Omega F$ be the energy of one confined chain. We define the chemical potential of chains μ_p by the formula

$$\mu_p = N\frac{\partial F}{\partial C} = \mathcal{F}_N(\Omega,D) - \Omega\frac{\partial \mathcal{F}_N}{\partial \Omega}(\Omega,D)$$
$$= \mathcal{F}_N(\Omega,D) + \Omega\pi \qquad \text{(II.4)}$$

By differentiating eq II.4 we find the equilibrium equation

$$\mathrm{d}\mu_p = \frac{\partial \mathcal{F}_N}{\partial D}\,\mathrm{d}D + \Omega\,\mathrm{d}\pi = 0 \qquad \text{(II.5)}$$

Then, in a pore of variable cross section, an osmotic pressure gradient is necessary to equilibrate the force F_D' [$= -(1/\Omega)(\partial\mathcal{F}_N/\partial D)$] which tends to expel the chains.

Remark 2. Equations II.3 and II.5 also show that in conical pores one must have a variation of the hydrostatic pressure P to equilibrate the osmotic pressure gradient. The pressure P_i inside a cylindrical pore is less than the external pressure P_o.

A. Chemical Potential. 1. Scaling Results for Bulk Solutions.[3] Let R_{F_3} be the Flory radius of one isolated chain:

$$R_{F_3} = aN^\nu \qquad \nu = 3/5 \qquad \text{(II.6)}$$

and c^* be the overlap concentration:

$$c^* = N/R_{F_3}{}^3 \qquad \text{(II.7)}$$

In the dilute regime "D" ($c < c^*$), one has an ideal solution and

$$\frac{F}{T} = \frac{c}{N}\log ca^3 + O(c^2) \qquad \text{(II.8)}$$

(see ref 13). In the semidilute regime "SD" ($c > c^*$), chains overlap and the excluded volume interactions are screened out in a length ξ

$$\xi = a(ca^3)^{-3/4} \qquad \text{(II.9)}$$

The chains can be represented by ideal chains of "blobs" of size ξ, each blob containing g monomers such as

$$g^\nu a = \xi \qquad \text{(II.10)}$$

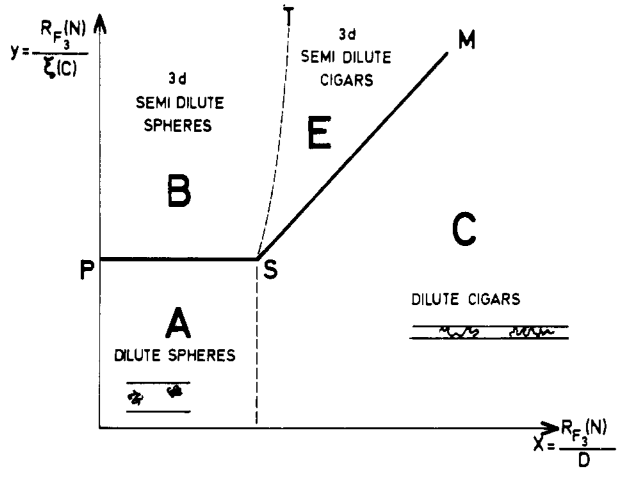

Figure 1. The four regimes of flexible polymer chains trapped in a tube (after Daoud and de Gennes[5]).

The size of one chain is then

$$R = (N/g)^{1/2}\xi \qquad \text{(II.11)}$$

The free energy is proportional to the density of blobs.

$$\frac{F}{T} = \frac{c}{g} = \frac{1}{\xi^3}\,(\sim c^{2.25}) \qquad \text{(II.12)}$$

2. Chains in a Tube. For $R_{F_3} > D$, the pore diameter, the chain is deformed into a long cigar of diameter D and length R_{F_1}. The chain can be conceived as a sequence of blobs each containing g_D monomers ($g_D{}^\nu a = D$) and each having a diameter D. R_{F_1} is then linear in N:

$$R_{F_1} = \frac{N}{g_D} \times D \qquad g_D{}^\nu a = D \qquad \text{(II.13)}$$

The free energy associated with the confinement is, for a chain:

$$\mathcal{F}_N/T = N/g_D \qquad \text{(II.14)}$$

As for bulk solution, it is essential to define a critical concentration of overlap c_1^*:

$$c_1^* = \frac{N}{R_{F_1}D^2} = \frac{g_D}{D^3} \qquad \text{(II.15)}$$

The different regimes of confined solutions described by Daoud and de Gennes[5] are represented in Figure 1.

(a) Dilute Regimes. Region A = analogous to bulk dilute solutions (see section A.1); region C = dilute solution of cigars. One must add to the free energy in eq II.8 a term due to confinement (II.14):

$$\frac{F}{T} = \frac{c}{N}\log ca^3 + \frac{c}{N}\frac{\mathcal{F}_N}{T} \qquad \text{(II.16)}$$

(b) "SD" Regimes. The semidilute regimes are represented by region B (semidilute spheres) and region E (semidilute cigars). For both regions, the local properties are identical to those of bulk SD solutions described in section A.1; the screening length ξ is given by eq II.9 and the dominant term of F is given by eq II.8. There are however two additional contributions:

(*i*) *Surface Effects.*[7] With our hypothesis of repulsive surface interactions, the monomer concentration is zero on the pore walls. Near the wall the concentration is reduced in a thickness ξ. Joanny and Leibler[7] have remarked that this monomer depletion must create a surface energy $(T/\xi^3)\xi = T/\xi^2$. It corresponds to a free energy change per cm^3 of the form:

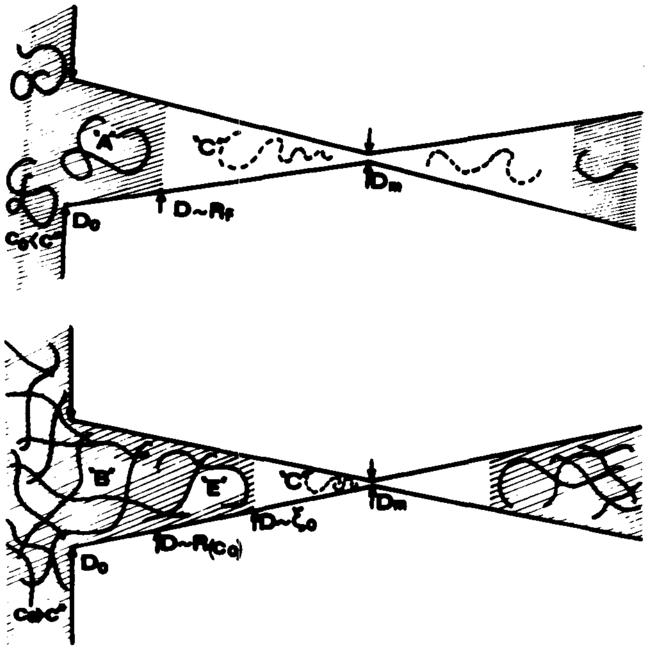

Figure 2. Partitioning of polymer solutions in conical pores. In hachured regions, the concentration of monomers is practically constant ($c \simeq c_0$) and zero otherwise: (a) for a dilute solution ($c_0 < c^*$), we have a sharp transition at $D \simeq R_F$ between dilute coils "A" and dilute cigars "C", beyond which $c(D)$ decreases exponentially; (b) for a semidilute solution ($c_0 > c^*$) we have a smooth transition from SD coils ("B") to SD cigars ("E") at $D \simeq R(c)$ and a sharp transition to a regime of dilute cigars ("C") at $D \sim \xi_0$.

$$F_s/T \simeq 1/\xi^2 D \qquad \text{(II.17)}$$

(*ii*) *Confinement Effects.* In region E, the overall shape of one coil is not a sphere of radius R (eq II.11) but is elongated. It leads to an energy change:

$$\frac{F_c}{T} = \frac{c}{N}\frac{R^2}{D^2} = \frac{1}{\xi D^2} \qquad \text{(II.18)}$$

This contribution is always smaller than the surface term F_s.

Conclusion. The chemical potential $\mu = \partial F/\partial c$ is respectively: in region A (dilute spheres)

$$\frac{\mu}{T} = \frac{1}{N}\log ca^3 \qquad \text{(II.19)}$$

in region C (dilute cigars)

$$\frac{\mu}{T} = \frac{1}{N}\log ca^3 + \frac{1}{g_D} \qquad \text{(II.20)}$$

in region E (semidilute cigars)

$$\frac{\mu}{T} = \frac{\partial}{\partial c}\left(\frac{k_1}{\xi^3} + \frac{k_2}{\xi^2 D} + \frac{k_3}{\xi D^2}\right) \qquad \text{(II.21)}$$

(see ref 14), and in region B (semidilute spheres)

$$\frac{\mu}{T} = \frac{\partial}{\partial c}\left(\frac{k_1}{\xi^3} + \frac{k_2}{\xi^2 D}\right) \qquad \text{(II.22)}$$

B. Polymer Partitioning Inside Pores. The determination of the monomer chemical potential (eq II.19 → 22) allows one to discuss the equilibrium between a pore (concentration $c(D)$) and a bulk solution (concentration c_0). We study only the general case of conical pores, because in a cylindrical pore the concentration is the same as in a conical pore for the same value of D.

1. Conical Pore in Equilibrium with a "D" Bulk Solution. In the bulk "D" solution, $\mu_0 = 1/N \log c_0a^3$. In the conical pore $\mu(D)$ is given by eq II.15 if $D > R_{F_3}$ and by eq II.12 if $D < R_{F_3}$. Setting $\mu_0 = \mu(D)$, we find a constant concentration $c = c_0$ for $D > R_{F_3}$ and an exponential decay when D becomes smaller than R_{F_3}:

$$\bar{c} \simeq e^{-N(a/D)^{5/3}} \qquad \text{(II.23)}$$

where $\bar{c} = c/c_0$. The monomer concentration profile is represented on Figure 2a. Qualitatively, we may say that the polymer solution does not penetrate the pore beyond $D = R_{F_3}$.

2. Conical Pore in Equilibrium with a "SD" Bulk Solution. In the reservoir, we may write $\mu_0 = {}^9\!/_4(k_1/c\xi_0{}^3)$. In the pore, as the cross section diminishes, one finds the regions B, E, and C of the diagram in Figure 1 where $\mu(D)$ is given by eq II.22, -21, -20, respectively (see Figure 2b). Setting $\mu(D) = \mu_0$ we arrive at an equilibrium condition of the form:

$$\bar{D} = \frac{5}{2}\frac{\bar{C}^{1/2}}{1 - \bar{C}^{5/4}} \qquad \text{(II.24)}$$

where $\bar{D} = D/\xi_0$ and $\bar{c} = c/c_0$. The validity of eq II.24 is limited by $\xi < D$, i.e., $\bar{D} > \bar{D}_1 \simeq 2$. For $D < D_1$, we enter into region C and the concentration decays exponentially according to eq II.23. The monomer concentration is represented on Figure 2b. The SD solution penetrates easily up to a diameter $D_1 \sim \xi_0$. At D_1, one has an abrupt change to a dilute regime beyond D_1 where the concentration decreases exponentially.

Conclusion. Dilute solutions can penetrate the pore only if the size of the pore is larger than the radius coil R_{F_3}. "SD" solutions can penetrate smaller pores up to diameter of the order of the bulk coherence length ξ_0, but are practically excluded as soon as D becomes less than ξ_0.

III. Flow Regimes of Polymer Solutions in Conical Pores

Flexible macromolecules resist confinement. On Figure 2b we show a sharp front located at $D = \xi_0$ beyond which the monomer concentration falls to zero exponentially. We study here the passage of macromolecules, driven by a flow of the solvent, through conical pores first converging from D_0 to D_m, then diverging from D_m to D_0. This situation is realized statistically in porous media. The flow exerts on the chains a frictional force which drags them into the pore. In steady state, we can derive the concentration c from the equilibrium between elastic and viscous forces.

The elastic restoring force can be obtained easily from the chemical potentials (eq II.19 → 22):

$$\phi_e = -c\frac{\partial \mu}{\partial x}(D,c) \qquad \text{(III.1)}$$

where $x = \epsilon D$ measures the position along the cone axis.

The frictional force is proportional to the relative velocity of the solvent v_s with respect to the polymer v_p:

$$\phi_v = cB^{-1}(v_s - v_p) \qquad \text{(III.2)}$$

B^{-1} is an effective monomer mobility which includes the hydrodynamic interactions between monomers in the presence of the pore walls. In a pore, as shown in ref 6, the backflow induced by the motion of a monomer is cut off at distances larger than the pore diameter D because on the boundary condition $v = 0$ at the wall. Superimposed on this "geometrical" screening there is a screening by surrounding monomers (discussed for bulk solutions in ref 4) with the same cutoff length D. Including these two effects, the values of B^{-1} are: $B^{-1} = \eta_s\,(\xi/g)$ (ref 4) for the semidilute regime (i.e., blobs are also uncorrelated units); for the dilute regime $B^{-1} = \eta_s\,(R_F/N)$ (ref 4) in region "A" and $B^{-1} = \eta_s(D/g_D)$ (ref 6) in region "C" of Figure 1. η_s is the solvent viscosity. In the following we shall use a mean value of ϕ_v on a cross section. We find then

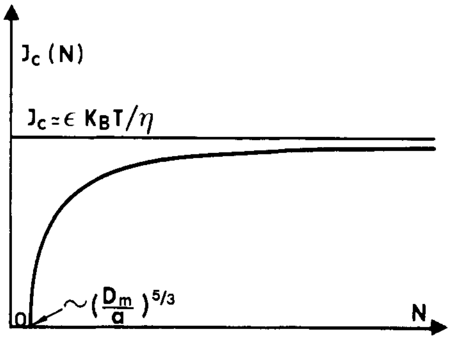

Figure 3. End effects: schematic variation of the critical solvent flow J_c to drive an isolated polymer chain through a conical pore as a function of N and D.

$$\phi_v = c\frac{B^{-1}}{D^2}\left(J_s - \frac{J_p}{ca^3}\right) = \frac{cB^{-1}}{D^2}J_s\left(1 - \frac{K}{\bar{c}}\right) \qquad \text{(III.3)}$$

where J_s and J_p are the currents of the solvent and the polymer. It is useful for the following to introduce the parameter $K = J_p/c_0J_sa^3$, which is independent of x. $K = 1$ corresponds to perfect draining ($v_s = v_p$, $c = c_0$). Equation III.3 is rigorously correct in the limit $\xi \ll D$ but is approximate for $\xi \sim D$ because of the variation of c in the cross section.

A. Passage of One Isolated Chain. The passage of one isolated chain has already been studied in ref 6. A solvent current J_s gives rise to a frictional force η_sv_sD per blob of the confined chain supposed immobile (according to eq III.2), and the sum of the N/g_D blobs of the confined chain leads to

$$\phi_v = \frac{N}{g_D}\eta_sv_sD \qquad \text{(III.4)}$$

The elastic restoring force per chain is derived from the confinement energy $\mathcal{F}_N$ (eq II.14)

$$\phi_e = -\frac{d}{dx}\left(\frac{NT}{g_D}\right) \simeq \frac{\epsilon NT}{g_DD} \qquad \text{(III.5)}$$

where $\epsilon = x/D$ measures the angle of the cone. The equilibrium between ϕ_e and ϕ_v can be realized only if J_s reaches a critical value J_c:

$$J_c = \epsilon T/\eta_s \qquad \text{(III.6)}$$

If $J_s < J_c$, the frictional force is too weak to drag the macromolecule into the pore. If $J_s > J_c$, the macromolecule can pass through the pore. Contrary to what is expected intuitively, J_c is independent of both the size of the macromolecule (N) and the minimal diameter of the pore (D_m), both forces being proportional to N/D.

Remark 1. This cancellation disappears if one includes end effect, as discussed briefly here. The two blobs at the ends of the chain have a larger contribution to the viscous force and a smaller contribution to the confinement energy. To include these corrections, we correct the number of blobs N/g_D in eq II.14 and III.4 by positive constants α' and α ranging about unity:

$$\frac{\mathcal{F}_N'}{T} = \frac{N}{g_D} - \alpha' \qquad \text{(II.14a)}$$

$$\phi_v' = \left(\frac{N}{g_D} + \alpha\right)\eta_s\frac{J_s}{D} \qquad \text{(III.4a)}$$

We find for the critical current

$$J_c(N) = \frac{\epsilon T}{\eta}\left(1 - \alpha\frac{g_m}{N}\right) \qquad \text{(III.7)}$$

with $g_m = (D_m/a)^{5/3}$. As shown on Figure 3, $J_c(N)$ increases as N increases and D_m decreases. This correction becomes negligible in the limit of large N values. In all that follows, we shall consider only the limit of large N.

Remark 2. The fact that J_c is independent of N (in the limit of large N) is a characteristic property of confined systems (because chains behave as "Rouse" chains of units D[6]) whatever the geometry of the pore. For a wedge, ϕ_e and ϕ_v obey eq III.4 and III.5 but now $J_s = v_sDL$, where D is the decreasing thickness and L the constant width of the slit. This leads to $J_c = \epsilon(T/\eta)(L/D_m)$, which depends upon geometrical parameters but not upon the molecular index N.

B. Dilute Solutions. At both ends of the converging diverging pore, we impose the same concentration $c = c_0$ with $c_0 < c^*$. Then, in an immobile solvent, a sharp front ($D \sim R_{F_3}$) separates the bulk dilute solution from a dilute solution of cigars where C is exponentially decreasing. When a flow J_s of the solvent is applied, one has two effects: (1) the concentration profile is modified, and (2) a certain fraction of the polymer is carried away by the current, leading to a polymer flow J_p. This new equilibrium is defined by the equality between (1) the friction force (eq III.3) written in the "D" confined regime where $B^{-1} = \eta_sD/g_D$:

$$\phi_v = \frac{c\eta_sJ_s}{Dg_D}\left(1 - \frac{K}{\bar{c}}\right) \qquad \text{(III.8)}$$

with K adjusted to satisfy boundaries conditions, and (2) the elastic restoring force calculated from eq II.19

$$\phi_e = -c\frac{\partial\mu}{\partial x} = \sigma\left(\frac{\epsilon cT}{g_DD} - \frac{\epsilon T}{N}\frac{dc}{dD}\right) \qquad \text{(III.9)}$$

with $\sigma = +1$ in the converging part and $\sigma = -1$ in the diverging part. We are led to the equilibrium equation:

$$\frac{d\bar{c}}{dD} = \frac{N}{g_DD}(\sigma\bar{J}_s - 1)(\bar{c}_l - \bar{c}) \qquad \text{(III.10)}$$

expressed in terms of the reduced variables $\bar{J}_s = J_s/J_c$, $\bar{c} = c/c_0$, and where $\bar{c}_l = [\sigma\bar{J}_s/(\sigma\bar{J}_s - 1)]K$. This equation can easily be integrated

$$\bar{c} - \bar{c}_l = (1 - \bar{c}_l)\exp\left((\sigma\bar{J}_s - 1)\frac{N}{g_D}\right) \qquad \text{(III.11)}$$

which defines c as a function of D in the two parts of the pore ($\sigma = +1$ and $\sigma = -1$). The requirement that these two expressions join at $D = D_m$ fixes the value of K:

$$K = \frac{e^{(\bar{J}_s-1)N/g_{D_m}} - e^{-(\bar{J}_s+1)N/g_{D_m}}}{[\bar{J}_s/(\bar{J}_s + 1)](1 - e^{-(J_s+1)N/g_{D_m}}) - [\bar{J}_s/(\bar{J}_s - 1)](1 - e^{(\bar{J}_s-1)N/g_{D_m}})} \qquad \text{(III.12)}$$

One has to distinguish two cases:

$$\bar{J}_s < 1 \qquad K \simeq \frac{1 - \bar{J}_s^{\,2}}{2\bar{J}_s}e^{-(1-\bar{J}_s)N/g_{D_m}} \ll 1$$

and

$$\bar{J}_s > 1 \qquad K \simeq \frac{\bar{J}_s - 1}{\bar{J}_s} \simeq 1$$

which correspond to two different regimes: (α) below the critical current ($J_s < J_c$) the polymer is practically clogged ($J_p \simeq 0$), and (β) above the critical current ($J_s > J_c$) the polymer flows freely ($J_p \simeq c_0a^3J_s$). The transition between these two regimes ($\bar{J}_s = 1, K \simeq g_{D_m}/N$) is very sharp (especially if D_m is small and N is large). The two regimes are illustrated on Figure 4: for $\bar{J}_s = 0.5$, the front at $D \sim R_{F_3}$ between the "dilute" and the "confined dilute" regime is simply displaced and $K \simeq 0$ (no flow of polymers). For $\bar{J}_s = 2$, one finds a flow of polymer ($K = 0.5$) and a penetration of the "dilute" solution inside the pore ($c \simeq c_0$) up to D_m. At D_m, $\bar{c}$ decreases abruptly from 1 to $\bar{c}_m = (\bar{J}_s - 1)/(\bar{J}_s + 1)$. Note that in a large region of the diverging capillary, the polymer flows faster than the solvent ($\bar{c} < K \rightarrow v_p > v_s$).

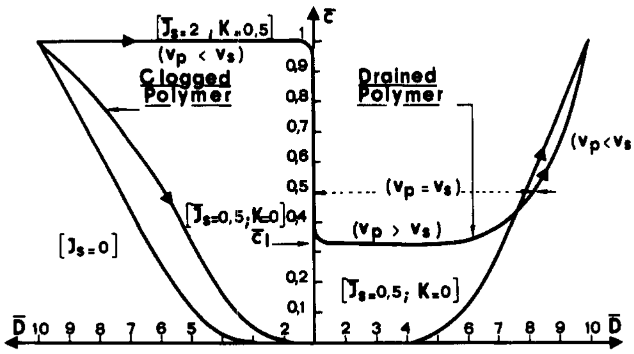

Figure 4. Flows of dilute solutions in converging diverging conical pores: we have represented the monomers concentration profile $\overline{C}(\overline{D})$, in immobile solvent ($J_s = 0$), above and below the single chain critical flow ($J_s = 2$ and $J_s = 0.5$, respectively) in reduced units ($\bar{c} = c/c_0$, $\overline{D} = 10D/R_{F_3}$, $\bar{J}_s = J_s/J_c$).

Remark 1. We have implicitly assumed when using eq III.9 that molecules travelling along the tube are in their equilibrium state. We must verify that the transit time θ_t is longer than the relaxation time $\tau_\parallel$ of confined chains. $\tau_\parallel$ is calculated in ref 6

$$\tau_\parallel \simeq \tau_z\left(\frac{R_{F_3}}{D}\right)^{1/3}$$

where $\tau_z = \eta_s R_{F_3}{}^3/T$ is the relaxation time of a free chain.[4] The transit time θ_t of molecules in the dilute confined region is

$$\theta_t = \int_{R_F}^{D_m}\frac{dx}{v_p} > \int_{R_F}^{D_m}\frac{dx}{v_s} \simeq \frac{\tau_z}{\epsilon^2\bar{J}}$$

The condition $\theta_t \gg \tau_\parallel$ is then always satisfied; with $\bar{J} \simeq 1$, we find $\epsilon \ll (D/R_{F_3})^{1/6} \sim 1$.

Remark 2. We have also neglected the possible stretching of molecules due to the elongational shear in a conical pore $S = J_s\epsilon/D^3$. As explained in the last section, this effect is negligible if $S\tau_\parallel < 1$, i.e., $\epsilon < 10^{-1}$ with $R_F/D \sim 10$. The threshold J_c' associated with this stretching process is much higher than J_c ($J_c' \sim J_c/\epsilon^2$) and is thus unimportant.

C. Semidilute Solutions. We take now $c_0 > c^*$, i.e., the pore in contact with a SD solution. In immobile solvent, a front located at $D \sim \xi_0$ separates the SD solution from a dilute solution of "cigars" extremely poor in polymer (Figure 2b)). A flow of the solvent J_s modifies the monomer concentration profile and may induce a flow J_p of polymer.

The elastic force ϕ_e is now deduced from eq II.21.

$$\phi_e = \sigma\left\{\frac{3}{2}\epsilon\frac{k_2}{\xi^2D^2} - \frac{3}{4}\epsilon\frac{dc}{dD}\left(\frac{15}{4}\frac{k_1}{c\xi^3} + \frac{k_2}{c\xi^2D}\right)\right\} \quad \text{(III.13)}$$

The frictional force in the SD regime is, according to eq III.3, with $B^{-1} = \eta_s\xi/g$:

$$\phi_v = \frac{c}{gD^2}6\pi\eta_s\xi J_s\left(1 - \frac{K}{c}\right) \quad \text{(III.14)}$$

This leads to the first order differential equation for c written in reduced variables

$$\frac{d\bar{c}}{d\overline{D}} = \frac{2(\sigma\bar{J}_s - 1)(\bar{c}_l - \bar{c})}{\overline{D}(1 + \bar{c}^{3/4}\overline{D})} \quad \text{(III.15)}$$

(a) Case $J_p = 0$. It is interesting to study first the concentration profile by assuming that the polymer is clogged ($J_p = 0$). This can be achieved by a constriction in the middle part of the pore which allows only a flow of the solvent. By setting $X = D/\xi$ and $K = 0$, eq III.15 reduces to

$$\frac{dD}{D} = \frac{X + 1}{X(X + A)}dX \quad \text{(III.16)}$$

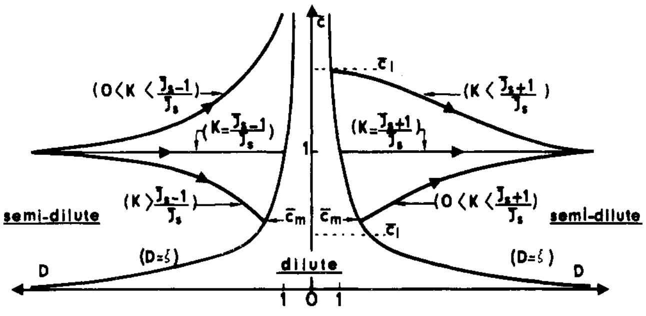

Figure 5. Schematic representation of the monomer concentration profile $\overline{C}(\overline{D})$ for semidilute solution in conical pores for different values of the relative polymer flow parameter K.

with $A = (5 - 3\sigma\bar{J}_s)/2$. The integration is straightforward:

$$\frac{D}{D_0} = \left(\frac{X}{\overline{D}_0}\right)^{1/A}\left(\frac{X + A}{\overline{D}_0 + A}\right)^{(A-1)/1} \quad \text{(III.17)}$$

The front where the SD ends corresponds to $\xi = D$ ($X = 1$). We define by D_l and D_l' the positions of the fronts: In the converging part one finds that $D_l(J_s)$ decreases as J_s increases up to $D_l = 0$ for $J_s = 7/3$ ($A \leqslant -1$). Above $\bar{J}_s = 7/3$, the front disappears; the solution remains semidilute up to D_m, whatever the value of D_m. The curve $D_l(J_s)$ is represented on Figure 6 by the line BB′. In the diverging part, the front D_l' is driven away monotonically. There is no particular value of J_s. Between the two fronts (D_l,D_l'), the solution is "confined dilute" (Figure 7c; curve $J_s = 0.5$, $K = 0$).

(b) General Case ($J_p \neq 0$). The differential eq III.15 has to be integrated numerically. However, before giving numerical results, it is possible to estimate qualitatively the behavior from the sign of dc/dD as a function of K. The discussion is illustrated schematically on Figure 5. In the converging part, c decreases in the flow direction if $K > (\bar{J}_s - 1)/\bar{J}_s$ and increases if $K < (\bar{J}_s - 1)/\bar{J}_s$. In the diverging part, c increases from $\bar{c}_m$ to 1 if $K < (\bar{J}_s + 1)/\bar{J}_s$ and decreases otherwise. To assume continuity at the boundary $D = D_m$, one must have $(\bar{J}_s - 1)/\bar{J}_s < K < (\bar{J}_s + 1)/\bar{J}_s$ and $\bar{c}_m$ is necessarily smaller than 1.

It is possible to define the domain of K more accurately by expressing the continuity condition for c:

$$\int_{D_0}^{D_m}\left(\frac{dc}{dD}(\sigma = +1) - \frac{dc}{dD}(\sigma = -1)\right)dD \sim \int_{\overline{D}_0}^{\overline{D}_m}\frac{(\bar{c} - K)\,d\overline{D}}{\overline{D}(1 + \bar{c}^{3/4}\overline{D})} = 0 \quad \text{(III.18)}$$

which can be satisfied only if $\bar{c}_m < K < 1$. This implies that there always exists an intermediate region around D_m where the polymer flows faster than the solvent ($c < K$, $v_p > v_s$). One notices also on Figure 5 that the solution is SD in the whole pore if $\overline{D}_m > 1$. If $\overline{D}_m < 1$, one must necessarily cross the limiting curve $D = \xi$ between the "SD" and "D" regimes and one must have an intermediate "dilute confined" solution in the center of the pore. In this region, the results of the last section hold and one expects a clogged situation for $\bar{J}_s < 1$ and a flow of polymer for $\bar{J}_s > 1$. We have then the three possible regimes for a SD solution, which are represented on Figure 7: (α) if $\overline{D}_m > 1$, the solution is SD in the whole pore and the polymer flows with the solvent; (β) if $\overline{D}_m < 1$, $\bar{J}_s > 1$, one has a dilute intermediate region and a flow of polymer ($K \simeq (\bar{J}_s - 1)/\bar{J}_s$); and ($\gamma$) if $\overline{D}_m < 1$, $\bar{J}_s < 1$ the pore is clogged ($J_p \simeq 0$) with an intermediate dilute solution.

To specify in more detail these flows regimes, we have resolved numerically eq III.15 in the converging part ($\sigma = +1$) and in the diverging part ($\sigma = -1$) as a function of the parameter K with a fixed value $c = c_0$ at both ends ($D = D_0$) of

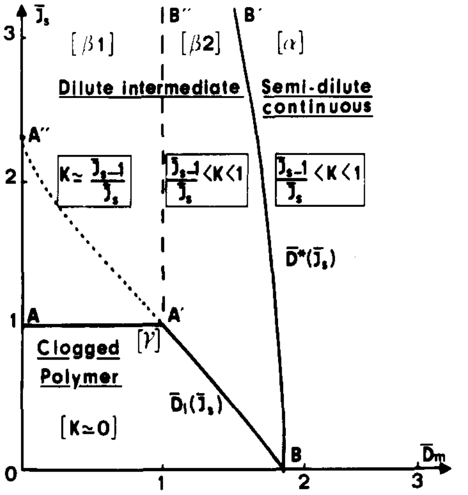

Figure 6. Diagram representing the three flow regimes of semidilute solutions in conical pores as a function of $\bar{J}_s = J_s/J_c$ and $\bar{D}_m = D_m/\xi_0$.

the pore. For a pair of values (J_s, D_m), one calculates the profiles of the concentration $(c_0, c_{m_1}(K))$ in the converging part and $(c_{m_2}(K), c_0)$ in the diverging part and one determines K (i.e., J_p) by the condition $c_{m_1} = c_{m_2}$. Then one must distinguish among the three announced cases corresponding to the three regimes in the diagram of Figure 6.

(α) *Continuous SD Solution.* For $D_m > D_1^*(J_s)$ (domain α), we have a flow of the SD solution in the whole pore: $K \simeq 1$ and K is an increasing function of J_s and D_m (Figure 7α and Figure 8a).

(β) *Partially Clogged Regime.* In the domain AA'BB' (AA' is a segment of the line $J_s = 1$, A'B' is a part of the curve $D_1(J_s)$ for $K = 0$) we have a front between "SD" and "D" solution defined by (D_1, C_1) in the converging part and (D_2, C_2) in the diverging part. In this region, eq III.15 is replaced by eq III.11. One finds in most of this domain ($D_m < 1$) that $K \simeq (J_s - 1)/\bar{J}_s$ and $D_1 \simeq D_m$. This leads, as for the case of dilute solution, to a sharp variation of the concentration at D_m (Figures 7β and 8c). Lastly, for $\bar{D}_m > 1$, the profile of the concentration is no longer flat in the converging part; the front D_1 moves away from D_m and K is of the order one (Figure 8b).

(γ) *Clogged State.* In the domain AA'B, the solution is dilute in an intermediate region and the polymer does not flow ($K \simeq 0$) (Figures 7γ and 8c). The current of polymer one has a smooth crossover through A'B but a very sharp increase through AA'.

Remark. In the case of a conical pore with a sudden constriction the domain for the clogged state is expanded (limited by the dotted line A'A'' instead of AA').

Conclusion. The existence of a dilute intermediate region for constricted pores ($D_m < \xi_0$) confers to "SD" solution flows behavior similar to "D" solutions (i.e., for $\bar{J}_s < 1$, $K \simeq 0$ and exponential decrease of c; for $\bar{J}_s > 1$, $K \simeq (\bar{J}_s - 1)/\bar{J}_s$ and almost constant concentration in the convergent part, with a fast decrease of c at D_m).

Remark. We have not included the stretching of the molecules due to the elongational shear $S = \epsilon J_s/d^3$ as soon as $ST_r > 1$, where T_r is the reptation time[4] which increases rapidly with $c(T_r \simeq \tau_z(c/c^*)^{3/2})$. We estimate briefly the contribution δF_a of the stretching to the free energy per cm^3 (a detailed discussion of elongational effects is given in the next section).

If D_c is the diameter at which S reaches its critical value T_r^{-1}, i.e.,

$$\frac{D_c}{R_F} = \left(\epsilon^2 \bar{J}_s \left(\frac{c}{c^*}\right)^{3/2}\right)^{1/3} \qquad \text{(III.19)}$$

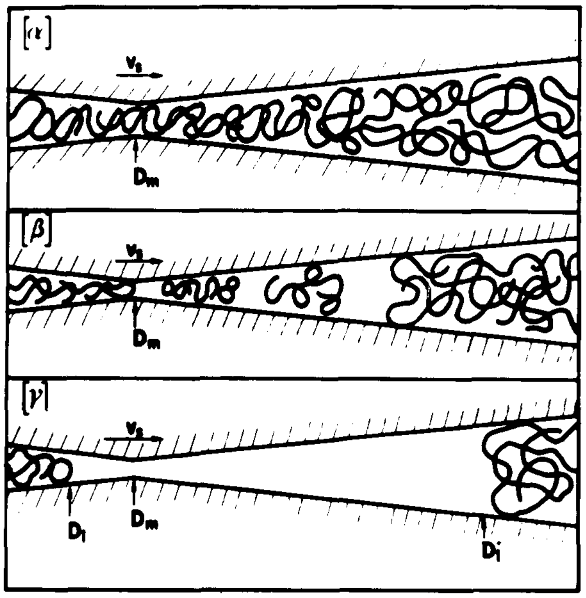

Figure 7. Illustration of the three regimes α, β, γ defined in Figure 6.

the length R_a of the molecules at diameter D for a affine deformation is

$$R_a(D) = (D_c/D)^2 R(D_c) \qquad \text{(III.20)}$$

Because chains are ideal in the semidilute regime, the deformation free energy δF_a is simply:

$$\delta F_a(D) = \frac{CT}{N} \frac{R_a^2(D)}{R_3^2(c)} \qquad \text{(III.21)}$$

To measure the importance of this effect, we can compare δF_a to the confinement free energy $\delta F_c = (cT/N)(R_\parallel^2(D)/R_3^2(c))$, where $R_\parallel(D)$ is the length of semidilute cigars at diameter D:

$$\frac{\delta F_a}{\delta F_c} \simeq \frac{R_a^2}{R_\parallel^2} \simeq \left(\frac{D_c}{R_F}\right)^4 \frac{R_{F_3}{}^4}{D^2 R_3^2(c)} \simeq \bar{J}_s{}^{4/3} \epsilon^{8/3} \left(\frac{c}{c^*}\right)^{17/8} \left(\frac{R_F}{D_m}\right)^2$$

by using eq III.19–20 and the scaling result $R_3(c) = R_{F_3}(c^*/c)^{1/8}$ with $R_F/D_m \simeq 5$, $c/c^* \simeq 10$, we find $\delta F_a/\delta F_c < 1$ if $\epsilon < 1/20$. Because the confinement energy is itself a small contribution to the free energy, the possible stretching of the molecules in the elongational shear leads only to small corrections in the flow behavior of SD solutions.

IV. Flow-Through Cylindrical Pores

In an immobile solvent, as shown in section II, a flexible macromolecule practically does not penetrate into a cylindrical pore if the diameter D is less than the size R_{F_3} of the coil (or the size ξ of the blobs in SD solutions). An accurate measure of critical permeation size of dextran fractions on glass of narrow pore size distribution agrees with this result.[8]

However, the molecules can be driven into the pore by a flow of the solvent: at the entrance of the pore, the chains are subjected to an elongational flow and for large enough currents, the chains are sufficiently stretched to enter into the pore. We study here the passage of dilute and semidilute solutions through a capillary of constant circular cross section of diameter D passing through a flat wall (Figure 9).

At the entrance of the pore, the flow of the solvent is convergent. The velocity can be written simply as a function of the distance r from the mouth in a region not too close to the wall (where v has to be zero) and not too close to the entrance (where flow lines align parallel to the pore axis, at $r < D$):

$$v_s = J_s/r^2 \qquad \text{(IV.1)}$$

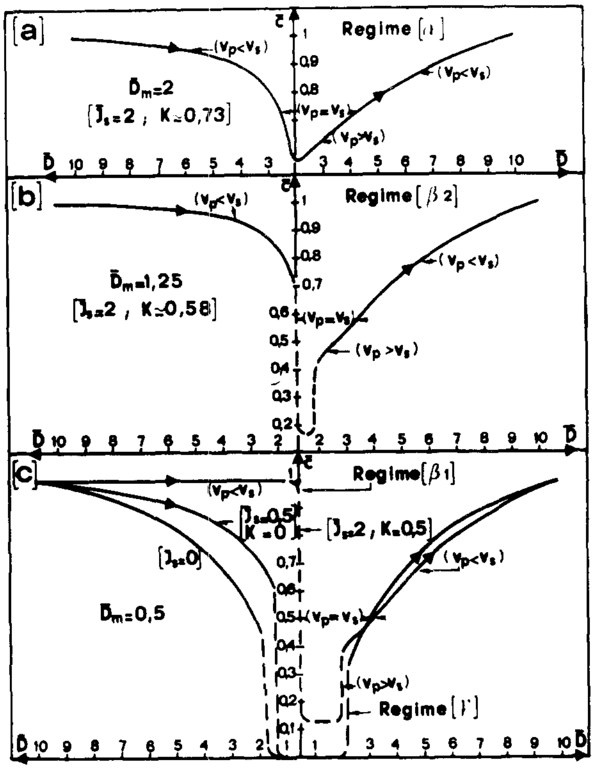

Figure 8. Flows of semidilute solutions in conical pores: the curves $C(D)$ for different values of $\bar{J}_s$, $\bar{D}_m$ characterize the different regimes of Figure 6.

It leads to an elongational shear

$$s = -\frac{\mathrm{d}v_s}{\mathrm{d}r} \simeq \frac{J_s}{r^3} \tag{IV.2}$$

A. Dilute Solutions. An isolated molecule subjected to an elongational flow S is slightly deformed if S is less than a critical value S_c; on the contrary, the molecule follows perfectly the deformation imposed by the solvent if $S > S_c$;[9] this type of deformation is called affine,[10] which amounts to saying that the molecule is deformed in the same way as a fluid element. The critical value S_c is of the order of the Zimm relaxation frequency of the polymer chain[11]

$$S_c = \tau_z^{-1} = T/\eta_s R_F^3 \tag{IV.3}$$

If r_c is the distance at which $S = S_c$, the chain is stretched and its transversal radius for an affine deformation is $R_\perp = R_{F3}\cdot(r/r_c)$ at a distance $r < r_c$ from the pore. The entrance condition $R_\perp$ $(r = D) = D$ leads to $r_c = R_{F3}$. From eq IV.2 and IV.3 we find the critical value J_c' of J_s for the chain to enter into the pore:

$$J_c' = T/\eta_s \tag{IV.4}$$

The critical current to force the passage of the chain is much larger for a cylindrical pore than for a conical pore ($J_c = \epsilon J_c'$, where ϵ measures the cone angle).

It is remarkable that J_c', as J_c, be independent on both the molecular size and the capillary diameter. However, as shown now, this property is less universal for J_c' than for J_c and depends upon the pore geometry.

Remark. Case of a slit of constant thickness (D). For a slit, the longitudinal shear at distance r is

$$S = J_s/r^2 \tag{IV.5}$$

where J_s is the flow through the pore per unit length. The condition $R_\perp = D$ for entrance into the pore leads to $J_c'/R_F = T/\eta_s R_F^3$, i.e.

$$J_c' = \frac{T}{\eta_s R_F} \sim N^{-3/5} \tag{IV.6}$$

J_c' for a slit depends upon N, whereas the critical currents for conical pores are always independent of N whatever the exact geometry of the cross section.

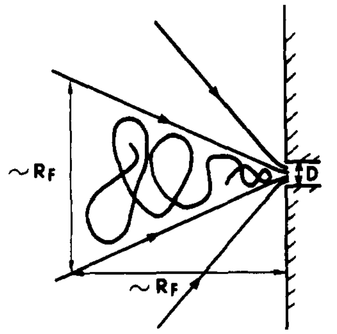

Figure 9. Elongational stretching of a polymer chain at the entrance of a cylindrical pore.

B. Semidilute Solution. In SD solutions, chains form a transient network and ξ measures the size of the mesh. The reorganization characteristic time of the network is the reptation time T_r to disentangle one chain from the others, calculated in ref 4:

$$T_r = \frac{\eta_s R_F^3}{T}\left(\frac{c}{c*}\right)^{3/2} \sim \tau_z\left(\frac{c}{c*}\right)^{3/2} \tag{IV.7}$$

In the elongational shear S (eq IV.2), the deformation of the network is affine if $S > S_c = 1/T_r$. The mesh length of the network is elongated in the flow direction ($\xi_\parallel \simeq \xi(r_c/r)^2$) and shortened in the perpendicular direction ($\xi_\perp \simeq r/r_c$).

1. Microscopic Capillary. For a microscopic capillary, we are led then to the following conjecture: the entrance condition for a semidilute solution to penetrate into the capillary is $\xi_\perp = D$, i.e., $r_c \simeq \xi$. Physically, this means that blobs are allowed to enter in the capillary as soon as their lateral cross section is geometrically small enough. It leads to the equation for J_c'

$$\frac{J_c'}{\xi^3} = \frac{T}{\eta_s R_F^3}\left(\frac{c*}{c}\right)^{3/2} \tag{IV.8}$$

Using the scaling law $\xi = R_F(c*/c)^{3/4}$, we find

$$J_c'(c > c*) = \frac{T}{\eta_s}\left(\frac{c*}{c}\right)^{15/4} \tag{IV.9}$$

We have a strong dependence of J_c' upon c in the SD regime and the critical currents are much smaller.

2. Macroscopic Capillary. At the entrance of a macroscopic capillary ($D \sim 1$ mm), the polymer solution flows freely, but we have a large region where the polymer chains are stretched by the elongational shear. We evaluate the size r_e of this region.

The affine deformation starts at a distance r_e from the entrance defined by $ST_r \simeq 1$, i.e.

$$J/r_e^3 \simeq 1/T_r \tag{IV.10}$$

As a function of the pressure gradient ∇P to induce a flow J in the capillary:

$$\nabla P = P/L = \eta_s J/D^4 \tag{IV.11}$$

where L is the length of the capillary and r_e is given by

$$\frac{r_e}{D} = \left(\frac{D}{L}\frac{P}{T}R_F^3\left(\frac{c}{c*}\right)^{3/2}\right)^{1/3} \tag{IV.12}$$

with $L = 1$ cm, $D = 1$ mm, $P = 1$ atm, $R_F = 200$ Å, we find $r_e/D \simeq 10$, i.e., $r_e \simeq 1$ cm. A large birefringent region should appear at the entrance of the capillary.

In fact, secondary flows take place at the entrance of the capillary[11] due to the non-Newtonian character of polymer solutions, which lead to a reduction of the elongational shear. It will be better to perform this experiment by aspirating the polymer solution with the capillary in contact with a free surface, then secondary flows do not appear.

It is very easy to visualize the stretched birefringent region between crossed polarizers. This very simple experiment can lead to a direct measure of the reptation time T_r of semidilute polymer solutions.

V. Concluding Remarks and Best Possible Experiments

Let us summarize the principal results of this study: (1) Dilute solutions have a sharp behavior. The molecules can cross through pores of diameter less than R_F only above a critical value of the current of solvent. In a weakly conical pore of initial diameter larger than R_F, they are progressively drained by the solvent if $J_s > \epsilon T/\eta_s$. At the entrance of a cylindrical pore of diameter less than R_F, the molecules are sufficiently stretched by the elongational shear if $J_s > T/\eta_s$. Although these two forms of J_s agree at large ϵ, it must be pointed out that the detailed processes are rather different: in the weakly conical pores, our description does not correspond to an affine deformation of each chain.

(2) Semidilute solutions have a behavior similar to dilute solutions to penetrate into pores of diameter less than ξ_0, which have an abrupt entrance (cylindrical pores), but the threshold is much smaller and concentration dependent $J_c'^{\text{“SD”}} = J_c'^{\text{“D”}}(c^*/c)^{15/4}$. In pores of cross section slowly decreasing, the polymer starts to flow if J_s is larger than the threshold $J_c = \epsilon T/\eta_s$ (the same as for dilute solution). Below this value, the polymer is clogged if the minimal cross section is smaller than ξ_0 and flows freely otherwise.

Some of the experiments proposed in the present paper can be realized by using different kinds of porous media, which are now commercially available: nucleopores[12] (cylindrical pores in polycarbonate of diameter larger than 150 Å) and millipores (irregular network of cellulose ester of minimal size 250 Å). In leached glass, one can obtain pores of diameter as small as 20 Å. Conical pores are statistically realized in porous rocks. It would also be possible to construct well defined, conical pores by using a glass slab with a varying chemical composition, bombarded by charged particles and then attacked chemically.

The main experiments which we propose follow: (1) Critical threshold and measurements of the polymer flow. A porous wall separates two reservoirs; one measures the critical gradient pressure necessary to drain the polymer chains across the wall. One can think of two different situations: (a) the second reservoir is empty and one determines the pressure gradient at which the polymer appears, (b) the two reservoirs have initially the same concentration, but we mark polymers of reservoir 1 by a fluoresent tracer and measure the concentration of marked chains in reservoir 2. (2) Stretching of polymer chains at the entrance of macroscopic (or microscopic) pores by optical birefringence. This should lead to a simple measure of the reptation time of entangled chains in semidilute solutions. (3) Measurement of the free energy of confinment of individual chains through the passive diffusion between two reservoirs at different concentrations of polymers.

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