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Extension and Compression of Grafted Polymer Layers in Strong Normal Flows

J.L. Harden (¹,2) and M.E. Cates (²)

(¹) Cavendish Laboratory, Cambridge University Madingley Road, Cambridge CB3 0HE, UK
(²) Department of Physics and Astronomy, University of Edinburgh, J.C. Maxwell Building, King’s Buildings, Mayfield Road, Edinburgh EH9 3JZ, UK

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Abstract. — We study the deformation of polymer brushes grafted to porous substrates in strong permeation flows normal to the grafting surface. Our model predicts a strong deformation regime for both compressive and extensive permeation flows of sufficiently high solvent flow rates. These regimes are characterized by non-linear scaling of brush thickness \( L \) with molecular weight \( N \) and solvent velocity \( V \) and by non-linear scaling of solvent velocity \( V \) with the pressure drop \( \Delta P \) across the brush. For the case of strong brush extension, \( L \sim N^{3}V^{-2} \), as in the case of isolated chains in uniform solvent flows, and \( V \sim \Delta P^{1/3} \); while for strong brush compression, \( L \sim N^{9/13}V^{-4/13} \) and \( V \sim \Delta P^{13/15} \).

1. Introduction

The properties of polymer brushes (polymers attached by one end to a surface at high grafting density) have been the subject of intensive study during the past two decades. The equilibrium properties of polymer brushes are now well established and there is substantial agreement between theoretical and experimental studies. Reviews of this work are given in references [1,2]. In recent years, studies have focused on the non-equilibrium properties of brushes and of adsorbed polymer layers in general. Of particular interest is the rheological behavior in response to applied perturbations, such as the frictional forces imparted by solvent flows in the neighborhood of grafted layers. The response of adsorbed and grafted polymer to flow has important technological implications for the rheology of colloidal dispersions stabilized by polymer layers, for the lubrication properties of polymer-coated interfaces, and for permeation flow through polymer-bearing porous media. The response of polymer brushes to both applied squeezing and shear flows has been studied both theoretically [3–6] and experimentally [7,8]. In the linear regime, in which solvent flow does not appreciably alter the brush structure, the principal effect of the brush is to exclude solvent flow from the region near the grafting surface. For strong flows, however, it has been suggested that the thickness of polymer brushes can increase in flow [6], leading to novel normal forces between brushes in shear flows. This point of view is supported by some experimental evidence [7,8], and is the basis for a recent proposal.
Fig. 1. — A sketch of the extended and compressed brush geometries. Figure 1a shows an extended brush in a solvent flow $V(x) = +V\hat{x}$, with $\xi(x) < \xi_0$ and $L > L_0$, where $\xi_0$ and $L_0$ are the equilibrium blob size and brush thickness in the absence of flow. Figure 1b shows an analogous compressed brush in a solvent flow $V(x) = -V\hat{x}$, with $\xi(x) < \xi_0$ and $L < L_0$.

to utilize polymers grafted to the walls of porous media to produce novel pressure-sensitive microvalves [9].

In this paper, we examine the behavior of grafted polymer in strong permeation flows. Such flows occur when polymers grafted to a permeable surface are subject to hydrodynamic pressure gradients normal to the polymer layer. We consider a brush consisting of monodisperse chains in good solvent conditions grafted at areal density $\sigma$ to a flat porous medium and subjected to a flow $\vec{V} = \pm V\vec{x}$ perpendicular to the grafting surface, as sketched in Figure 1. In the absence of flow, the brush will assume a parabolic density profile [10] with thickness scaling as $L_0 \sim N\xi_0^{-2/3}$, where $N$ is the degree of polymerization of the chains and $\xi_0 \sim \sigma^{-1/2}$ is the average separation between grafting points. At the level of scaling analysis, the equilibrium brush may be viewed as a step-function profile having uniform density from the grafting surface at $x = 0$ to $x = L_0$ [11, 12]. For weak flows, the brush profile will be only slightly perturbed from its equilibrium form. In this case, a permeation flow towards the wall will presumably compress the parabolic profile somewhat, making it more step-like; while a flow away from the wall will extend the tail of the profile. The precise behavior in this regime is somewhat delicate and to predict it would require a detailed self-consistent mean field (SCF) approach. For sufficiently strong flows, however, one expects more drastic modifications to the brush characteristics. Isolated grafted chains subjected to flow are predicted to stretch significantly and non-uniformly in strong flows [13]. We will show that this is also the case for polymer brushes in strong flows. The gross features of this behavior can be addressed through a scaling analysis. We have explored two approaches to this problem: i) a local approach involving the balance of chain tension with hydrodynamic drag, and ii) a global ("monoblock" [14]) approach in which one balances the total chain tension with the total hydrodynamic drag on a uniformly stretched or compressed chain. In either case, we represent the chains in the perturbed brush as strings of excluded-volume blobs, assume that all chain ends are at the outer edge of the brush, and write the free energy per chain as a sum of an elastic term $F_{el}$ involving the conformation of a deformed Gaussian string of blobs and an osmotic term $F_{im}$ involving interactions between blobs. In the local approach, the blob size is a function (to be determined) of the distance from
the grafting plane, while in the monoblock picture the effective blob size is taken as a constant which is fixed by the brush thickness $L$, the quantity to be determined. We find below that these two approaches give essentially equivalent results.

In Section 2, we consider “extensive” permeation flows, in which the fluid forces increase the thickness of the brush. We give local expressions for the chain free energies and obtain by force balance a differential equation for the local blob size $\xi(x)$. We then estimate the scaling of brush thickness and pressure drop with molecular weight and fluid permeation velocity. In Section 3, we give analogous calculations for the “compressive” case, in which the flow tends to flatten the layer. Section 4 contains a brief discussion.

2. Brush Extension

Following references [5] and [6], we picture the extended brush as consisting of chains of Pincus blobs [15], as shown in Figure 1a. Since the extension is due to the integrated hydrodynamic drag on each chain rather than a force applied to the chain ends, the hydrodynamic Pincus blob size is not constant, but is a function $\xi(x)$ of the distance $x$ from the grafting plane which we must determine. This situation is analogous to the model of single chain extension in strong solvent flows studied in reference [13], which was inspired by scaling theories of chain pull-out from polymer melts and quasi-rubbers [16]. In the strong extension regime, we generally have $\xi(x) < \xi_0$ (cf. Fig. 1a). This fact allows us to adapt several concepts from references [5,6] in constructing our model free energy. The elastic energy per chain is obtained by considering each chain as a Gaussian string of blobs, and may generally be written [10] as

$$F_{el} \simeq \frac{kT}{a^2} \int_0^L dx \left( \frac{dz}{dn} \right) \phi^\alpha$$  \hspace{1cm} (1)

where $a$ is the monomer size, $\phi$ is the volume fraction of monomers within the hydrodynamic blobs, and $\alpha$ is given in terms of the free chain swelling exponent $\nu \approx 3/5$ as $\alpha = (2\nu-1)/(3\nu-1) \approx 1/4$. The local chain stretching $dz/dn$ and the volume fraction $\phi$ are functions of $x$ which may be expressed in terms of the local blob size $\xi(x)$. Since bulk chain statistics prevail within the blobs, we have $\phi \sim (\xi/a)^{-4/3}$. The local chain stretching as a function of $\xi$ can be obtained by viewing a small section of chain containing $dn \ll N$ monomers as a linear string of Pincus blobs of length $dx \sim dn(\xi/a)^{-5/3}$. Hence, the local chain stretching $dx/dn$ is given by

$$\frac{dx}{dn} \sim \xi^{-2/3} a^{5/3}$$ \hspace{1cm} (2)

Rewriting equation (1) in terms of $\xi(x)$ gives the simple form

$$F_{el} \simeq kT \int_0^L \frac{dx}{\xi(x)}$$ \hspace{1cm} (3)

Now consider a slab of thickness $\xi(x)$ at distance $x$ from the grafting plane. When $\xi(x) < \xi_0$, the volume fraction of blobs in this slab is below the semi-dilute threshold, and hence the local interaction between chains may be approximated by a virial expansion in the blob density [5,6]. The local interaction energy per blob is of order $kT [\xi(x)/\xi_0]^2$ and the interaction energy per chain has the form

$$F_{int} \simeq kT \int_0^L \frac{dx}{\xi(x)} \frac{\xi(x)^2}{\xi_0^2} = kT \xi_0^2 \int_0^L dx \xi(x)$$ \hspace{1cm} (4)

Our estimate of the free energy per extended chain is given by the sum of the contributions from equations (3) and (4).
The local hydrodynamic Pincus blob size $\xi(x)$ is obtained by balancing the local chain tension with the hydrodynamic drag on a short section of chain, these are found as follows. Consider a section of chain between $x$ and $x + \Delta x$ in a solvent flow with velocity $V(x)\dot{\xi}$. For Zimm-Stokes blobs, the drag per blob scales as $\eta \xi(x)V(x)$, where $\eta$ is the solvent viscosity. There are of order $\Delta x/\xi(x)$ blobs in a section of length $\Delta x$. Hence the total hydrodynamic force on the section of chain is of order $f_h \sim \eta \xi(x)V(x)\Delta x/\xi(x) = \eta V(x)\Delta x$.

In mechanical equilibrium, $f_h$ is balanced by the differential tension $\Delta t$ on a section of chain of length $\Delta x$ at $x$: $\Delta t = (\partial t/\partial x)|_{x}\Delta x$. The chain tension $t(x)$ can be obtained from the variation of the local chain free energy with $x$ at fixed polymer arclength as follows. Consider an infinitesimal section of chain of length $dx$ containing $dn$ monomers. Equations (3) and (4) give the free energy of this section of chain as $dF = kT[\xi(x)^{-1} + \xi_0^{-2}\xi(x)]dx$. This expression may be written exclusively in terms of $dx$ and $dn$ by using the local chain stretching expression equation (2) to eliminate $\xi$ from $dF$. Subsequent variation of $dF$ with respect to $dx$ at fixed $dn$, and use again of equation (2), yields an effective local chain tension

$$t(x) = kT \left( t_1 \frac{1}{\xi(x)} - t_2 \frac{\xi(x)}{\xi_0^2} \right)$$

(5)

where $t_1$ and $t_2$ are positive constants of order unity. Since we have employed scaling relations to derive $t(x)$, the precise values of $t_1$ and $t_2$ are not meaningful. In the following we shall set $t_1 = t_2 = 1$. Equation (5) has a simple interpretation: the chain elasticity opposes chain stretching and hence gives a positive contribution to the tension, while osmotic pressure in the brush favors stretching and hence gives a negative contribution.

Balancing the local differential chain tension $\Delta t$ with the hydrodynamic drag $f_h$ on a section of chain of length $\Delta x$ gives a differential equation for $\xi(x)$ in terms of the solvent velocity $V(x)$. For the case of a spatially uniform velocity, $V(x) = V$ (appropriate for flow normal to an infinite planar porous layer), we obtain

$$\frac{1}{\xi(x)} - \frac{\xi(x)}{\xi_0^2} = \frac{\eta(L - x)V}{kT}$$

(6)

where, without loss of generality, we have written an integration constant in terms of the as yet unknown brush thickness $L$. Equation (6) can be solved analytically for $\xi(x)$ as

$$\xi(x) = \frac{\xi_0}{2} \left\{ \left(4 + \frac{\xi_0^2}{\xi_h^2}(L - x)^2\right)^{1/2} - \frac{\xi_0}{\xi_h^2}(L - x) \right\}$$

(7)

where $\xi_h = (kT/\eta V)^{1/2}$ is the characteristic hydrodynamic blob size introduced in reference [13]. (Note that in the absence of flow, Eqs. (6) and (7) give $\xi(x) = \xi_0$, the correct blob size for the unperturbed Alexander-de Gennes brush). The solid lines in Figure 2 show sample profiles $\xi(x)$ vs. $x$ for $\xi_h/\xi_0 = 0.5, 1.0$, and $2.0$. For low $V$ [large $\xi_h$], $\xi$ is weakly dependent on $x$ (increasing roughly linearly with $x$); while for high $V$ [small $\xi_h$], $\xi(x) \sim 1/(L - x)$. The continuum expression for $\xi(x)$ given in equation (7) is valid until the final blob in the extended chain is reached. This occurs at $x \simeq L - \xi_{\text{max}}$, where $\xi_{\text{max}}$ is the size of this last blob. Setting $\xi(L - \xi_{\text{max}})$ to $\xi_{\text{max}}$ in equation (7) one obtains

$$\xi_{\text{max}} \simeq (\xi_h^{-2} + \xi_0^{-2})^{-1/2}$$

(8)

As one would expect, $\xi_{\text{max}} \simeq \xi_0$ for weak flows. For strong flows, in which chains in a brush behave as isolated chains, $\xi_{\text{max}} \simeq \xi_h$, the maximum blob size reported in reference [13].
Given \( \xi(x) \), we may determine the brush thickness \( L(N, V) \) by demanding that a stretched chain of length \( L \) has \( N \) monomers. In principle, one may do this by explicitly evaluating the conservation relation

\[
N \simeq \int_0^L \frac{dx}{\xi} \left( \frac{\xi}{a} \right)^{5/3}
\]

(9)

However, such an integration must be done numerically for \( \xi(x) \) given by equation (7). There is an alternative way to estimate \( L(N, V) \) analytically which gives equivalent results. This bypasses the calculation of \( \xi(x) \) altogether, by utilizing the “monoblock picture” introduced in reference [14]. The approach amounts to viewing the chain as a uniformly extended string of hydrodynamic Pincus blobs of effective blob size \( \xi_{mb} \leq \xi_0 \). In this picture, \( \xi_{mb} \) is related to \( L \) by \( L \sim N\xi_{mb}^{-2/3}a^{5/3} \). One then obtains \( L \) by balancing the global chain tension \( \partial F/\partial L \) with the total hydrodynamic drag on the chain. In the monoblock case, \( F = F_{el} + F_{int} \) from equations (3) and (4) may be written explicitly in terms of \( L \) as

\[
F \simeq kT\left( \frac{L}{R_F} + \frac{R_F}{\xi_0^{4/5}L^{1/5}} \right)^{5/2}
\]

(10)

where \( R_F = N^{3/5}a \) is the Flory radius of an isolated chain. The total hydrodynamic drag on the chain is roughly the product of the drag on a blob of size \( \xi_{mb} \) and the total number \( L/\xi_{mb} \) of such blobs per chain: \( f_{tot} \sim \eta V \xi_{mb}(L/\xi_{mb}) = \eta VL \). Balancing the drag on a chain with the global chain tension \( \partial F/\partial L \) gives

\[
l^3 - l^{5/2}n_b^{3/2}V \frac{V}{V_0} - n_b^3 = 0
\]

(11)

where \( n_b = N(a/\xi_0)^{5/3} \) is the number of blobs in the unperturbed brush, \( l = L/\xi_0, V_0 = kT/(\eta\xi_0^2) \), and where all numerical coefficients have been set to unity. The characteristic velocity scale \( V_0 \) is that for which an isolated chain of size \( \xi_0 \) becomes significantly perturbed by the flow. Analysis of equation (11) then indicates that \( V_* = V_0/n_b \) is the characteristic solvent velocity separating the weak and strong deformation regimes for a brush composed of \( n_b \) blobs. For \( V \ll V_* \), equation (11) gives \( L \sim N \); while for \( V \gg V_* \), it gives \( l \sim n_b^2(V/V_0)^2 \) or \( L \sim N^3V^2 \). The latter result may also be found directly from the local picture, equations (7) and (9), in the strong deformation limit. The maximum chain extension, however, is \( L_{max} = Na \). This implies that equation (11) is only valid for \( V < V_{max} \approx [3/2 + (\xi_0/a)^{1/3}]V_* \). Thus, there is a finite window of velocities, \( V_* < V < V_{max} \), for which the brush is stretched, but not fully so, and our calculation applies.

In practice, the flux of liquid through a porous layer is controlled by an externally applied pressure drop. Hence, it is desirable to relate our expressions for the thickness of the extended brush \( L(N, V) \) to the pressure drop \( \Delta P \) across the brush necessary to maintain this extension [18]. This procedure will give us the pressure-velocity relation of the extended brush system. Consider a patch of brush between \( x \) and \( x + \Delta x \) of cross sectional area \( A \) under the influence of a uniform solvent flow with velocity \( \dot{V} \). In general there will be a pressure gradient \( \nabla P(x) \) in the brush due to the hydrodynamic drag of solvent against the extended polymer chains. Recall that the frictional drag force on a section of chain of length \( \Delta x \) is \( f_h \simeq \eta V \Delta x \). Since there are \( \sigma \simeq 1/\xi_0^2 \) chains per unit area, the total drag force on the slab of solvent between \( x \) and \( x + \Delta x \) scales as \( f_{tot} \simeq -\eta V \Delta x A/\xi_0^2 \). In steady state, this is balanced by the contribution from the external pressure, \( \nabla P(x) \Delta A \), and we recover Brinkman’s equation with a spatially independent permeability coefficient, \( \nabla P(x) = -\eta V/\xi_0^2 \). Since \( V \) is constant
in our case, the solution is simply \( P(x) = P_s + \Delta P(1 - x/L) \), where \( P_s \) is the pressure in the free solvent, and where the pressure drop \( \Delta P \) across the extended brush is given by

\[
\Delta P = \eta V L / \xi_0^2
\]

Using the monoblock result, equation (11), for \( l = L/\xi_0 \), we may obtain an implicit expression for \( V \) as a function of \( \Delta P \). For the case of a strongly extended brush in good solvent, in which \( L \sim N^3 \), one finds

\[
V \sim V_\ast \left( \frac{\Delta P}{P_\ast} \right)^{1/3} \text{ for } V_\ast \ll V < V_{\text{max}}
\]

where \( P_\ast = kT/\xi_0^3 \). (The same result can be recovered from the local picture.) The lower curve in Figure 3 is a plot of \( V(\Delta P) \) obtained using the numerical solution for \( L(N, V) \) from equation (11). For \( P \ll P_\ast, V \sim \Delta P \), while for \( P \gg P_\ast \), equation (13) holds. Hence, we may interpret \( P_\ast \) as the characteristic pressure drop needed to induce strong chain extension. For reasonable values of the parameters (say \( T \approx 300^\circ \text{K}, \eta \approx 10^{-2} \text{ Poise}, a \approx 10 \text{ Å}, n_b = 10, \) and \( \xi_0 \approx 100 \text{ – } 1000 \text{ Å} \)), we have \( P_\ast \approx 0.05 \text{–} 50 \text{ N/m}^2 \), and \( V_\ast \approx 5 \times 10^{-5} \text{ – } 5 \times 10^{-3} \text{ m/sec} \). These \( P_\ast \) values correspond to gravity pressure heads of order microns to millimeters in height.

3. Brush Compression

We now consider the situation in which a brush is compressed by a solvent flow \(-V \hat{x}\) towards the porous grafting surface. In this case, the brush is composed of close-packed layers of hydrodynamic blobs with \( \xi(x) \leq \xi_0 \), as sketched in Figure 1b. The elastic free energy per chain is again given by equation (1) but with a modified expression for the local chain stretching \( d \hat{x}/d \hat{n} \). (We assume that despite the compression, chains remain extended compared to \( R_F \).)

Consider a slab of blobs of area \( \xi_0^2 \) between \( x \) and \( x + dx \) containing \( d \hat{n} \) monomers. Since the density of grafted chains is \( \sigma \approx 1/\xi_0^2 \), we have \( d \hat{n}(\xi/a)^{-5/3} \xi_0^2 dx \). Thus our estimate of the local chain stretching is

\[
\frac{d \hat{x}}{d \hat{n}} \approx \xi_0^{-2} \xi_0^{2/3} a^{5/3}
\]

and the elastic free energy per chain has the form

\[
F_{el} \approx \frac{kT}{\xi_0^2} \int_0^L dx \xi(x)
\]

For the interaction energy per chain, we simply count \( kT \) per blob for close packed blobs, giving

\[
F_{int} \approx kT \xi_0^2 \int_0^L dx \xi(x)^{-3}
\]

Our estimate of the total free energy per chain is given by the sum of equations (15) and (16). (Note that these differ strongly from Eqs. (3) and (4) for the case of brush extension).

As in the case of extension, the local hydrodynamic Pincus blob size \( \xi(x) \) is obtained by balancing the local differential chain tension \( \Delta t \) with the hydrodynamic drag on a short section of chain between \( x \) and \( x + \Delta x \). For a solvent flow with velocity \(-V \hat{x}\), the hydrodynamic force is of order \( f_h \approx -\eta V \Delta x \). The chain tension \( t(x) \), obtained as before from the variation of the local chain free energy with \( x \) at fixed arclength, now has the form

\[
t(x) = kT \left( \frac{\xi(x)^2}{\xi_0^2} - \frac{\xi_0^2}{\xi(x)^3} \right)
\]
where \( \bar{t}_1 \) and \( \bar{t}_2 \) are again positive numerical coefficients of order unity. In the following we shall set \( \bar{t}_1 = \bar{t}_2 = 1 \). Balancing the differential chain tension \( \Delta t = (\partial t/\partial x)_{\alpha} \Delta x \) with the hydrodynamic drag on a section of chain of length \( \Delta x \), we obtain [c.f., Eq.(6)]

\[
\xi(x)^4 + \frac{\xi_0^2(L-x)}{\xi_h^2} \xi(x)^3 = \xi_0^4
\]

The solution for \( \xi(x) \) is the real positive root of equation (18); this is easily found but cumbersome, so we do not reproduce it here. The dashed lines in Figure 2 show plots of the solution for \( \xi_h/\xi_0 = 0.5, 1.0, \) and \( 2.0 \). For high \( V \) [small \( \xi_h \)], equation (18) gives \( \xi(x) \sim 1/(L-x)^{1/3} \); while for low \( V \) [large \( \xi_h \)], \( \xi(x) \) is a weak (roughly linear) function of \( x \). As before, the final blob of a compressed chain occurs at \( x \simeq L - \xi_{\text{max}} \), where \( \xi_{\text{max}} \) is the size of this last blob. Using equation (18), one then obtains the maximum blob size

\[
\xi_{\text{max}} \simeq \xi_0 \xi_h^{1/2} \left( \xi_h^2 + \xi_0^2 \right)^{-1/4}
\]

We may determine the brush thickness \( L(N,V) \) by demanding that a chain compressed in a tube of length \( L \) and area \( \xi_0^2 \) has \( N \) monomers [c.f., Eq. (9)]

\[
N \simeq \int_0^L \frac{dx}{\xi} \left( \frac{\xi_0}{\xi} \right)^2 \left( \frac{\xi}{a} \right)^{5/3}
\]

As in the case of extension, however, it is simplest to estimate \( L(N,V) \) within the monoblock approximation by treating the chains as being composed of uniformly compressed blobs of effective size \( \xi_{\text{mb}} \). As before, the relation between \( \xi_{\text{mb}} \) and \( L \) is obtained from the local stretching factor \( dx/dn \) in equation (14), giving \( L \simeq N \xi_0^{-2} \xi_{\text{mb}}^{4/3} a^{5/3} \). The total free energy per
chain from equations (15) and (16) may then be written as

\[ F \simeq kT \left( \frac{R_p^3}{L\xi_0^2} + \frac{L^{1/5}}{R_p\xi_0^{2/5}} \right)^{5/4} \]

(21)

where \( R_p = N^{3/5}a \). Balancing the total drag on a chain, \( f_{\text{tot}} \sim -\eta VL \), with the global chain tension \( \partial F/\partial L \) gives an implicit equation for \( \ell = L/\xi_0 \)

\[ \ell^{13/4} + \ell^3 n_b^{-3/4} \frac{V_0}{V} - \frac{n_b^{9/4} V_0}{V} = 0 \]

(22)

where we have set the unknown numerical coefficients to unity. For weak flows, \( V \ll V_* \), equation (22) gives \( L \sim N \); while for strong flows, \( V \gg V_* \), it yields a somewhat compressed state with \( L \sim N^{9/13}V^{-4/13} \). Here, \( V_* = V_0/n_b \) is the characteristic velocity defined above for brush extension in flow. There may also be a maximum velocity scale \( [19] \) which differs in origin from the extensional case.

We now analyse the pressure-velocity relation of the compressed brush system. Consider a patch of brush of cross sectional area \( A \) between \( x \) and \( x + \Delta x \) under the influence of a uniform solvent flow with velocity \(-V\hat{x}\). As before, the frictional drag force on a section of chain of length \( \Delta x \) has magnitude \( \eta V \Delta x \). However, there are now \( 1/\xi(x)^2 \) blobs per unit area, i.e., each chain of blobs cuts a plane at height \( x \) on average \([\xi_0/\xi(x)]^2 \) times. Hence the total drag force on the slab of solvent at \( x \) scales as \( f_{\text{tot}} \simeq -\eta V \Delta x A/\xi(x)^2 \). In steady state, this is balanced by the contribution from the external pressure, \( \nabla P(x) \Delta x A \), giving us Brinkman's equation with a spatially dependent permeability coefficient, \( \nabla P(x) = -\eta V/\xi(x)^2 \) \([21]\). The pressure drop across the compressed brush for a constant \( V \) is then given by

\[ \Delta P = \eta V \int_0^L dx \xi(x)^{-2} \]

(23)

In the limit of strong flows, we may estimate \( \Delta P \) from equation (23) by using \( \xi(x) \) from the solution of equation (18) and \( L = \ell \xi_0 \) from the asymptotic solution of equation (20). This procedure yields

\[ V \sim V_* \left( \frac{\Delta P}{P_0} \right)^{13/15} \quad \text{for} \quad V \gg V_* \]

(24)

This result for \( V(\Delta P) \) also may be obtained from the monoblock picture, as follows. Replacing \( \xi(x) \) by \( \xi_{mb} \) in equation (23) gives \( \Delta P = \eta V L/\xi_{mb}^2 \). Then, using equation (22) for the monoblock estimate of \( L \) and the relation between \( L \) and \( \xi_{mb} \) given above equation (21), we obtain an implicit expression for \( V \) as a function of \( \Delta P \) whose asymptote is equation (24). The upper curve in Figure 3 is a plot of \( V(\Delta P) \) obtained from the monoblock estimate. It shows that equation (24) holds for \( P \gg P_* \), while \( V \sim \Delta P \) for \( P \ll P_* \), as in the case of extension. Figure 3 demonstrates the inequivalence of the extensive and compressive permeation flows in the non-linear regime: in good solvent conditions \( V \sim \Delta P^{1/3} \) for strong extension, while \( V \sim \Delta P^{13/15} \) for strong compression.

4. Discussion

We have presented a model for the deformation of grafted polymer layers in solvent flows. This model is essentially a synthesis of models for the deformation of polymer brushes under strong uniform tension \([5,6]\) and for the deformation of individual polymer chains in solvent...
flows [13]. For sufficiently high velocity flows normal to a porous grafting surface our model predicts strong brush deformation. This deformation is especially strong for extensive flows; in this case the brush thickness scales with molecular weight and solvent velocity as \( L \sim N^3 V^2 \) for \( V_* \ll V < V_{\text{max}} \). This scaling law was also obtained for isolated chains in flow by Brochard [13]. For compressive permeation flows the deformation is weaker, with \( L \sim N^{9/13} V^{-4/13} \) at high \( V \). As a result of strong brush deformation, our model predicts non-linear relations between the velocity \( V \) of solvent permeating a brush and the pressure drop \( \Delta P \) across a brush. Furthermore, the \( V-\Delta P \) relation is different for extended and compressed brushes (cf. Fig. 3), with \( V \sim \Delta P^{1/3} \) for strong extension and \( V \sim \Delta P^{13/15} \) for strong compression. Note that at high flow rates the system is more permeable under compression, mainly because the permeability in extension is compromised by the expansion of the brush. Thus there is in principle the possibility that densely grafted polymer brushes on porous substrates could function as rectifying microvalves [9].

The systems we have described could be realized by grafting polymer chains to thin, rigid, porous substrates such as Vycor glass, Nucleopore filters and aerogel materials. Our predictions for brush thickness \( L \) as a function of solvent permeation rate or pressure gradient could in principle be checked for such systems by performing neutron reflectivity measurements under flow conditions using deuterated chains and/or solvent [22]. Another possible system of interest is a hybrid bilayer membrane composed of short and long chain amphiphilic molecules. Bilayer membranes, especially those of biological origin, often contain micropores and are quite permeable to water [23]. Furthermore, liposomes incorporating grafted polymers have been reported [24]. If such liposomes are subjected to even modest osmotic pressure differences between their inside and outside environments, the resulting water currents produced may be sufficient to significantly deform their grafted polymer coats.

The calculations of brush deformation under strong permeation flows presented here are rather idealized and have certain inherent limitations. Firstly, we have not discussed solvent flow within the porous support which, unless very thin, may dominate the pressure drop...
$\Delta P_{\text{tot}}$ [20]. Furthermore, the brush structure and solvent flow profile in the proximal region near the grafting surface could be much more complex than that predicted by our idealized model, particularly for very porous substrates. We also note that in the case of compressive flows, aspiration of chains into the porous material may occur for sufficiently strong pressure drop [17,20]. Within our own approach, the scaling results for extension are also limited by finite extensibility effects arising at $V \sim V_{\text{max}}$. Furthermore, rather than a full SCF treatment of excluded volume effects, we have assumed that all chains behave alike (this reduces to the Alexander-de Gennes picture in the static limit). Within this framework, we have found (perhaps surprisingly) that the monoblock description compares well with a more detailed local approach. However, this might not apply for a parabolic brush in which not all chains behave alike.

The calculations that we have made for polymer brushes in normal permeation flows also serve as a paradigm for the response of interfacial polymer layers in more complicated solvent flow profiles. Future reports [20] will address the problems of polymer brushes in strong shear flows, and of adsorbed homopolymers in strong permeation and shear flows, the latter complementing recent studies of the linear regime in the homopolymer case [25,26].

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References

[18] In practice, one cannot control the pressure drop across the brush directly. Rather, one controls the total pressure drop $\Delta P_{\text{tot}} = \Delta P_n + \Delta P$, where $\Delta P_n$ is the pressure drop across the porous support material and $\Delta P$ is the pressure drop across the extended brush [20]. We ignore this complication here.
Once $\xi$ at the grafting surface, $x = 0$, is of order the effective pore size of the substrate, chain aspiration into the porous medium should occur $[17,20]$. Thus, there is a maximum solvent velocity beyond which the discussion above is incomplete. Furthermore, we have also assumed that chains in the compressed state remain somewhat stretched, this breaks down at $L \approx R_F$, corresponding to a additional limiting velocity $V_{\text{max}} \sim V_s n_b^{13/10} [20]$.


