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ARTICLE

Piston Rotaxane Monolayers: Shear Swelling and Nanovalve Behavior

Ruud J. J. Boesten,*[†,‡] Edith M. Sevick,[§] and David R. M. Williams[†]

[†]*Research School of Physics and Engineering, The Australian National University, Canberra ACT 0200, Australia,* [‡]*Department of Applied Physics, Eindhoven University of Technology, Eindhoven, Netherlands, and* [§]*Research School of Chemistry, The Australian National University, Canberra ACT 0200, Australia*

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ABSTRACT: A piston-rotaxane is a rotaxane molecule where one of the free rings is attached to a rod-like polymer (the piston). We examine the behavior of a system of piston rotaxanes grafted by one end to a surface in the presence of a fluid flow. At a critical shear rate the rotaxane layer will extend perpendicular to the surface, i.e. the system undergoes shear-induced swelling. When the inside surface of a narrow tube is coated with these rotaxanes a nanovalve can be created which has a highly nonlinear flow-rate versus pressure curve. In particular a valve can be created which limits the maximum discharge over a wide range of pressures.

I. Introduction

In 1991, an experimental study was made of how polymer brushes behave under shear.[1] This study appeared to show that in some cases the brush layer would swell. This is unusual, in that one expects almost all systems to shrink under shear. There have been many studies since then on brush shearing but it still seems unclear exactly how the system behaves. Theoretically, the system is clearly very complex, combining both the many-body interactions between monomers and solvent and the dynamics of both the polymers and the fluid flow. What however is clear, is that if one could make a layer which swelled under shear the system would have interesting and potentially useful properties.[2] Here we study theoretically a system which should swell under shear. Our system, a piston rotaxane has the definite advantage that it is relatively simple since the polymers are rod-like, and can thus be analyzed much more readily than a flexible polymer brush.

In the past two decades there has been a rapid development in the field of rotaxanes.[3,4] The simplest form of these molecules is a rod-like molecule with one or more cyclodextrin rings threaded along its axle. They are free to move along the axis of the rod, but are prevented from sliding off the rod by stoppers on both ends. So far the theoretical research on rotaxane has focused on the slip-link behavior of the rings.[5−10] One of the most interesting aspects of rotaxanes is the ability of the rings to move along the axle. The rings have associated with them translational entropy and it would clearly be beneficial to control this entropy. One way of doing this has already been proposed.[11] This is to chemically attach a rod to one of the rings to form a piston rotaxane (see Figure 1). The motion of this piston then controls the position of the free ring and hence their entropy. In this paper we study a new type of rotaxane, a piston rotaxane, which swells under shear. A molecule very similar to the one proposed here has been synthesized by Brough et al.[12] The swelling property should enable the construction of a novel kind of nanovalve. These kind of valves have been studied in the polymer context previously.[2] More recently Adiga and Brenner[13] studied polypeptides with a pH dependent helix−coil transition for the same purpose.

The paper is arranged as follows. In section I, we look in detail at the rotaxane molecule and how we can describe its behavior with statistical mechanics. We focus on the case where a force is applied on the tip of the molecule. These results are used in section II to describe the piston rotaxane in a shear flow. Finally, in section III, the application of piston rotaxanes to create a pressure-sensitive valve is reviewed.

II. Piston Rotaxane in a Force Field

We first present a physical picture of rotaxane behavior under shear and then justify this picture by calculation. The essential physics can be understood by considering a single piston rotaxane chain as shown in Figure 1. The rotaxane is anchored on the surface by one end and the chemical bond with the surface means it prefers to point normal to the surface. Any tilting (shown as θ in the figure) implies a free energy penalty. The crucial observation here is that the rings in Figure 1 are free to move up and down the rod and the bottommost ring is connected to another rod (the piston). The entropy of the rings, which manifests itself as a force on the bottommost ring tends to drive the piston ring down toward the surface. Thus, in the absence of any external forces the molecule tends to stand normal to the surface with the piston ring close to the surface. Of course there are fluctuations about this state caused by Brownian motion, but the general picture is one of a short, upright molecule. The other essential thing to note about this molecule is that its length from base to tip can in principle vary. This is because the gas of free rings is compressible.

We now apply a constant horizontal force to the free end of the piston, to say, the left. This force tends to drag the free end of the piston to the left. This motion is possible by two different mechanisms. First the molecule can remain of fixed length and merely tilt. Second, provided it has tilted slightly, it can also increase its length. Both of these scenarios are encouraged by the horizontal shearing force. However, tilting is opposed by the surface molecular potential which tends to keep the rod normal to the surface, and extension is opposed by the pressure of the free rings, which favors a molecule as short as possible. The minimum free energy configuration will tell us how far the molecule tilts for a given force and also how much it extends. It turns out (as shown by detailed calculation below) that the molecule first tilts with zero extension, and then at a critical force it begins to extend. Physically tilting must come first since extension gives zero benefit if there is no tilt. Once tilting has occurred extension is not immediately favored because of the pressure of the free rings.

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*To whom correspondence should be addressed. E-mail: r.j.j.boesten@student.tue.nl.

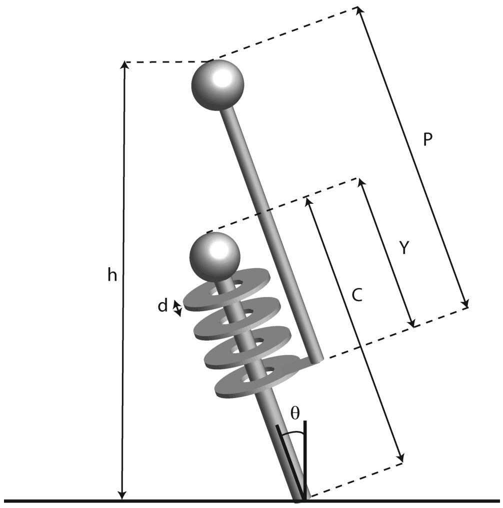

Figure 1. An overview of a piston rotaxane molecule. The rotaxane with n rings and length C is grafted to the surface. The rigid linealr polymer with length P is connected to the bottom rotaxane ring. The whole molecule has the freedom to tilt.

This sudden onset of extension is in itself interesting. However of much greater interest is the distance of the free tip of the piston from the surface, shown as h (Figure 1). For a perfectly rigid rod this distance would always decrease with increasing shear force, i.e., the rod would simply tilt over and a layer of such rods would always decrease in height when sheared. Our system is however not a rod and can extend along its length. It turns out that this extension, can, in many situations, lead to h increasing with increasing force. A layer of such rods will swell in the direction normal to the surface under shear. In other words, a horizontal force leads to a vertical extension. This is a very unusual behavior since almost all materials shrink under shear. It is this swelling which we now demonstrate by detailed calculation, and which forms the basis for most of the remainder of the paper.

The rotaxane we study (Figure 1) consists of two stiff linear polymers of which the one grafted to the surface has length C and $n+1$ rings. The second polymer of length P is connected to the cyclodextrin ring closest to the surface. The angle between the axis of the rotaxane and the normal to the plane is called θ. The molecule acts like a piston due to the translational entropy of the rings, hence the name piston rotaxane. The distance between the ring connected to the rigid polymer and the tip of the piston roxane molecule is called Y. The total length of the molecule is $l = P + C - Y$. Without any external forces acting on the molecule, the ring will be at its zero force equilibrium position $Y_{f=0}$, which depends on the number of rings and the width of the rings d.

The length of the molecule (l) has both an upper and a lower limit. Without any forces working on the molecule the length attains its minimum: $\lambda = P + C - Y_{f=0}$. Geometrical constraints create an upper limit for the length of the piston $\lambda = P + C - (n + {}^1\!/_2)d$. We call the ratio of these two lengths $\lambda/\Lambda = \tau$, with $1 \geq \tau \geq {}^1\!/_2$.

Now we discuss the behavior of the piston rotaxane in a constant force field. We assume that the force f on the rotaxane is applied parallel to the surface at the tip. The free energy F of this system has three contributions: the potential energy associated with the angle of the rotaxane, the potential energy associated with the applied force and the translational entropy of the free rings:

$$F = -\frac{\alpha k_B T}{2}\cos^2(\theta) - f\sin(\theta)(P+C-Y) - k_B T n \ln(Y-(n+1/2)d) \qquad (1)$$

where T is the temperature, k_B the Boltzmann constant, and α a dimensionless constant. The system in equilibrium will occupy its free energy minimum configuration. Minimizing the free energy over the two independent variables Y and θ gives us the behavior of the piston rotaxane as a function of the applied force. Minimizing 1 with respect to Y gives:

$$Y = \begin{cases} Y_{f=0}, & f < f_j \\ (n+1/2)d + \dfrac{k_B T n}{f\sin(\theta)}, & f > f_j \end{cases} \qquad (2)$$

For $f < f_j$ (f_j to be discussed later) the molecule acts as a rigid rod, while for $f > f_j$ the free energy minimum yields an extended rotaxane.

One would expect the piston to extend even for small forces, it has been shown[11] that the extension for this regime is: $Y \sim Y_0[1 - fY_0(k_BT)^{-1}n^{-1}]$, which turns out to be negligible. The reason we do not see an extension is that we calculate an average force for a fixed position of the ring, rather than the average position under an applied force.

For small forces $f < f_j$ the height of the rotaxane tip above the surface is:

$$h_1 = \lambda\cos(\theta) = \lambda\sqrt{1-\sin^2(\theta)} = \lambda\sqrt{1-\left(\frac{f\lambda}{\alpha k_B T}\right)^2} \qquad (3)$$

It is convenient to use dimensionless parameters with the maximum length of the piston Λ as the unit of length and $\alpha k_B T$ as the unit of energy, with $\delta = h/\Lambda$ and $\beta = f\Lambda/(\alpha k_B T)$. The dimensionless height (eq 3) can then be recast as

$$\delta_1 = \tau\sqrt{1-\tau^2\beta^2} \qquad (4)$$

For a large force $f > f_j$, the piston rotaxane will start extending $l > \lambda$. Just as in the previous case, we can substitute the length in the free energy (eq 1) and minimize the free energy over the angle θ. This will give us the height which minimizes the free energy:

$$\delta_2 = l\cos(\theta) = \left(1 - \frac{2\sigma}{\beta^2\left(1+\sqrt{1-\frac{4\sigma}{\beta^2}}\right)}\right)\sqrt{1-\frac{\beta^2}{4}\left(1+\sqrt{1-4\frac{\sigma}{\beta^2}}\right)^2} \qquad (5)$$

with $\sigma = n/\alpha$, the piston strength ratio. This determines whether the piston rotaxane extends easily. By looking at eq 1, we can see that for an extending piston the entropy of the rings decreases and a free energy penalty has to be paid. This has to be compensated for by the free energy gain resulting from the tip moving in the direction of the field. For a weak piston, $\sigma \ll 1$, the free energy penalty associated with the entropy of the rings is small compared to the free energy gain associated with the force potential, so it will extend for a relatively small force and it will extend to almost its maximum length. For a strong piston in contrary, $\sigma > 1/\tau - 1$, the piston does not extend at all.

Now we consider when the transition from eq 4 to eq 5 occurs, or when does the piston start extending? Equating the latter two expressions for the height gives for the dimensionless force: $\beta_j = \sigma^{1/2}(\tau(1-\tau))^{-1/2}$. The angle θ for both configurations is the same: $\theta_1(\beta_j) = \theta_2(\beta_j)$, so the length of the piston rotaxane must be equal too. Because the free energy of the system for a given force f depends only on the length of the piston rotaxane and the angle

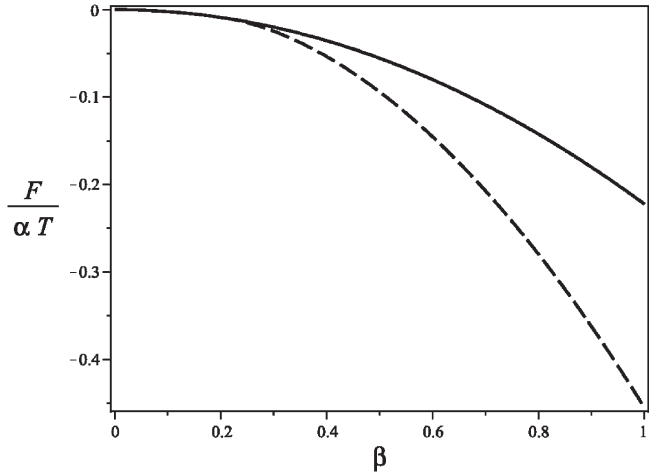

Figure 2. Free energy versus the dimensionless force for the rigid rod (—) and the piston rotaxane (· · ·) in a constant force field.

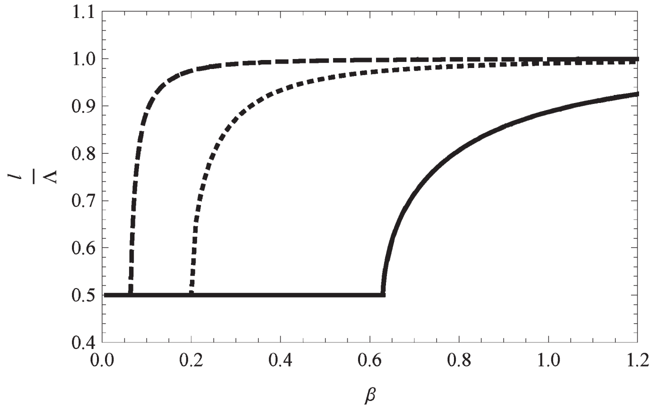

Figure 3. Dimensionless length versus the dimensionless force for $\sigma = 0.1$ (solid), $\sigma = 0.01$ (dotted) and $\sigma = 0.001$ (dashed).

θ, $F = F(\theta, l = P + C - Y)$, we can conclude that the continuous transition from a non extended piston rotaxane to an extended configuration occurs at a dimensionless force $\beta = \beta_j$. So, for $\beta < \beta_j$, the molecule will act as a rigid rod and eq 4 is valid. For $\beta > \beta_j$, the free energy of the piston rotaxane is lower than the free energy of a rigid rod (Figure 2). We conclude that for this range eq 5 is valid.

Figure 3 shows the length of the rotaxane for several values of σ. For small dimensionless forces the piston rotaxane attains its minimum length λ. It rapidly increases at $\beta = \beta_j$ to almost its maximum length Λ. The piston strength ratio σ determines β_j and the rate of extension. Figure 4 shows the behavior of the piston rotaxane for a range of forces. For $\beta < \beta_j$, the length of the piston rotaxane is $Y_{f=0}$, and it slowly tilts in the direction of the field. For $\beta > \beta_j$, the piston extends, which results in an increase of the height. It keeps tilting in the direction of the field, and finally for high forces ($\beta > \beta_0 = (1 + 4\sigma)^{1/2}$), it is parallel to the plate.

In summary, we have shown that for small lateral forces the piston rotaxane acts as a rigid rod and merely tilts. At a critical force the rotaxane begins to extend along its length, and this can lead to swelling in the direction normal to the force, as shown in Figure 4.

III. Shear Flow over Many Grafted Rotaxanes

In the previous section, we showed that a single rotaxane can extend under a constant force. Here we examine how a layer of many rotaxanes behaves under an applied fluid shear flow. A 2D slit is constructed by two infinite plates H apart with a velocity difference V (Figure 5). The medium between the plates is a liquid with viscosity η, and we assume a low Reynolds number ($Re < 1000$) so that the fluid behaves in a laminar way. The assembly of piston rotaxanes is grafted to the lower plate only. The molecules do not interact with each other in any way and we expect them all to behave similarly so that we can model it as a bulk layer.

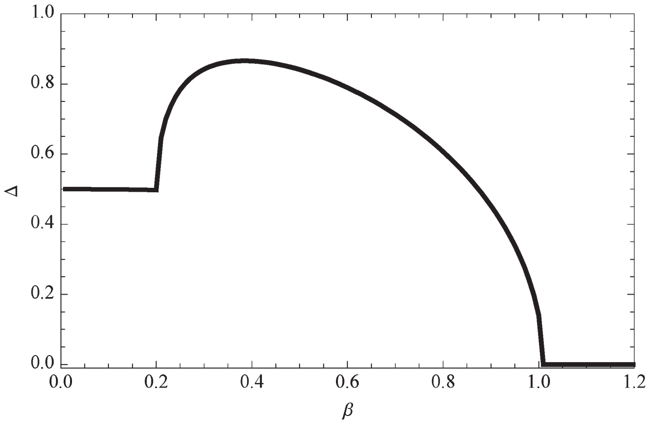

Figure 4. Dimensionless height $\Delta = h/\Lambda$ versus the dimensionless force for $\tau = {}^{1}/_{3}$ and $\sigma = 0.01$. The height slowly decreases for $\beta < \beta_j = 0.2$. For $0.2 < \beta < 0.6$, it extends to almost its maximal length; for $\beta > 0.6$, it acts like a rigid rod again with length Λ until for $\beta > 1.02$ the piston rotaxane lies flat on the surface of the plane.

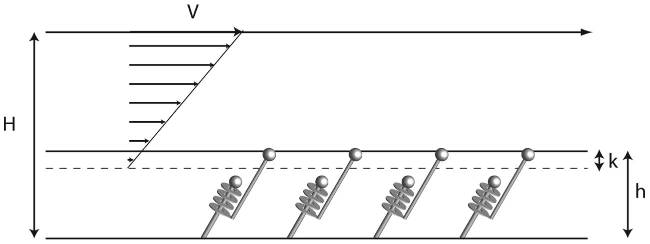

Figure 5. Shear flow slit geometry. The velocity difference V between the two infinite plates, of which one is grafted with piston rotaxane, results in a shear flow. The flow penetrates the rotaxane layer for a small distance k, and the two plates are H apart.

The rotaxane layer can be considered as a porous medium, and the flow through it can be modeled by the Brinkman equation.[14] This is analytically solvable but the solution is lengthy. In this case, it results in a shear flow in the gap between the porous medium, the rotaxane layer, and the plate. The velocity would decrease exponentially in the rotaxane layer. Here we use a simpler approach, we assume that the flow penetrates the bulk for a small distance k. This layer is held constant at about 5−10% of the maximum length of the piston rotaxane. It does not depend on the height of the brush or the length of the piston rotaxane. Sevick and Williams[2] showed that for a similar configuration the flow through the porous medium is negligible as long as the gap is bigger than the penetration depth ($H - h > k$). The Navier−Stokes equation for this problem is

$$\frac{\mathrm{d}^2 v(y)}{\mathrm{d}y^2} = 0 \qquad (6)$$

with the boundary conditions $v(H) = V$ and $v(h - k) = 0$, this results in a shear flow

$$v(y) = \begin{cases} 0, & y \leq h - k \\ \dfrac{y - h + k}{H - h + k} V, & y > h - k \end{cases} \qquad (7)$$

with y the height relative to the lower plane. The force a steady state flow exerts on a object depends on the velocity of the fluid,

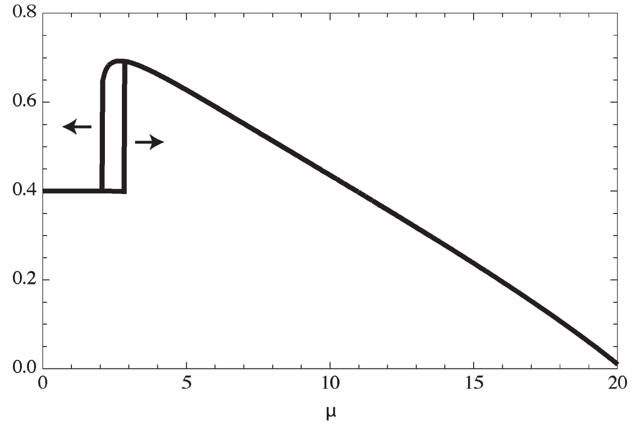

Figure 6. Height Δ versus the velocity μ for $\kappa = 0.015$, $\tau = 0.5$, $\gamma = 0.8$, and $\sigma = 0.01$. The jump from the nonextended to the extended configuration depends on the starting conditions. Thus resulting in hysteresis which is denoted with arrows for increasing (→) and decreasing (←) velocity.

the viscosity and the shape of the object. For example for a sphere with radius r in a flow with constant velocity V the drag force is: $f = 6\pi r\eta V$ along the direction of the fluid velocity.[14] The fluid will exert a force on the top part (k) of the molecule assembly. The fluid velocity is varying along this length so the force becomes an integral along the length of the top part of the molecule. The major part of the force will be exerted on the tip. The integral can thus be approximated by a force acting on the tip in the form: $f = S\eta v(h)$ in which S is a constant which incorporates the relation of the tip geometry. Combining this with eq 7 gives for the force

$$f = \eta S \frac{\lambda}{H + \lambda - h} V \tag{8}$$

This can be restated in dimensionless parameters for which we now use H as the new unit length: $\Delta = 1 + \kappa - \mu/\beta'$. With $\Delta = h/H$, $\gamma = \Lambda/H$, $\kappa = k/H$, $\beta' = fH/(\alpha T)$ and $\mu = \eta SVH/(\alpha T)$. The latter is the dimensionless velocity of the upper plate. Solving this simultaneously with eqs 4 and 5 gives the height versus dimensionless speed as displayed in Figure 6.

The set of equations may have more than one solution for the height for certain μ. While slowly increasing the dimensionless speed of the plate $\mu = \mu_0$ to $\mu = \mu_0 + \mathrm{d}\mu$, we expect the piston rotaxane to occupy the state closest to its previous state at $\mu = \mu_0$. Vice versa for decreasing speed. In this way hysteresis occurs for increasing or decreasing speeds as can be seen in Figure 6. For increasing μ starting with $\mu = 0$ the height decreases slightly and then suddenly makes a jump in which the piston extends instantenously.Finally it decreases again until the rotaxane lies flat on the surface of the plane. For decreasing μ it follows almost the same curve except for the jump which occurs at a lower velocity. Notice that our assumption for a constant penetration layer means that the results in which the layer is almost flat $\Delta \sim \kappa$ should be treated with care. Changing the piston strength ratio σ and our estimate of the penetration depth results in qualitatively similar solutions.

Thus, a monolayer of piston rotaxanes in a shear flow acts in much the same way as a single rotaxane with an applied force; i.e., for a certain range of shear speeds, the height of the layer can increase. The only slight complication is that there is sometimes more than one solution and so hysterisis in the height is possible.

IV. Valve Operation

In this section, we study the system displayed in Figure 7. It consists of two plates $W = 2H$ apart of length L and width Z with piston rotaxane grafted on *both* plates. The pressure drop over L is P, and once again we assume that the flow penetrates the rotaxane layers over a length k. Effectively the flow through this slit is the same as the flow between two plates $W - 2h$ apart. Solving the Navier–Stokes equation for this problem:

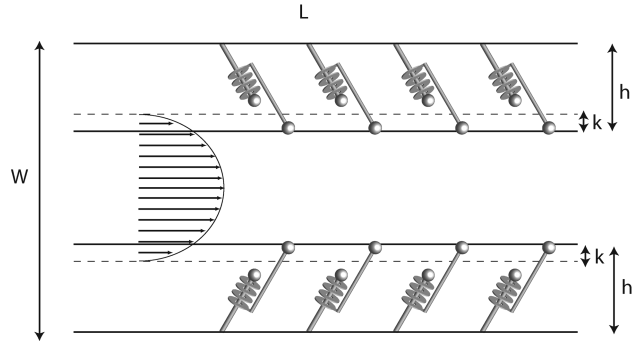

Figure 7. 2D slit geometry. Two infinite plates W apart are both grafted with piston rotaxane. The pressure drop P over the length L results in a parabolic velocity profile.

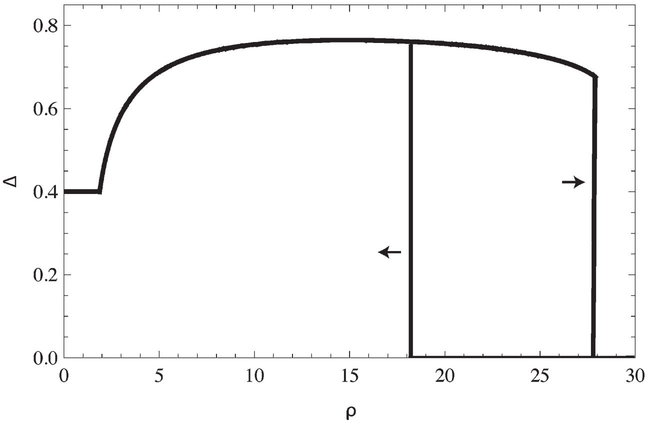

Figure 8. Dimensionless height Δ versus the dimensionless pressure ρ for $\kappa = 0.015$, $\tau = 0.5$, $\gamma = 0.8$, and $\sigma = 0.01$. For $\rho < 3$, the piston rotaxane acts as a rigid rod with length λ. For $\rho > 3$, it starts extending. The jump to and from the configuration that the piston rotaxan lies flat on the surface depends on the starting conditions.

$$\frac{\mathrm{d}^2 v(y)}{\mathrm{d}y^2} = \frac{P'}{\eta} \tag{9}$$

with $P' = P/L$ results in a parabolic, Poiseuille flow: $v(y) = P'/\eta(y^2 - (H - h - k)^2)$. y is the height, measured from the symmetry plane between the two plates. We can use this to find a relation between height, force and pressure drop: $\Delta = 1 + \kappa - \beta'/(\rho\kappa)$ with the dimensionless pressure $\rho = P'SH/(\alpha T)$. Solving this together with eqs 4 and 5 along the same lines as in the previous section we end up with a height profile as shown in (Figure 8). Again because of multiple solutions for this set of equations we see hysteretic behavior for increasing and decreasing pressure.

For a valve it is interesting to look not just at the height of the piston rotaxane layer, but also to look at the volumetric rate or discharge (the amount of fluid flowing through the system for a given pressure drop per unit time):

$$Q(h) = P' \frac{Z(W - 2h + 2k)^3}{12\eta} \tag{10}$$

which for convenience can be expressed in dimensionless form: $q = Q(\Delta)/Q(h = 0, \rho = 1) = \rho(1 - (h + k)/H)^3$. Thus the discharge is highly sensitive to the height of the piston rotaxane layer. Figure 9 displays the discharge versus the dimensionless pressure ρ.

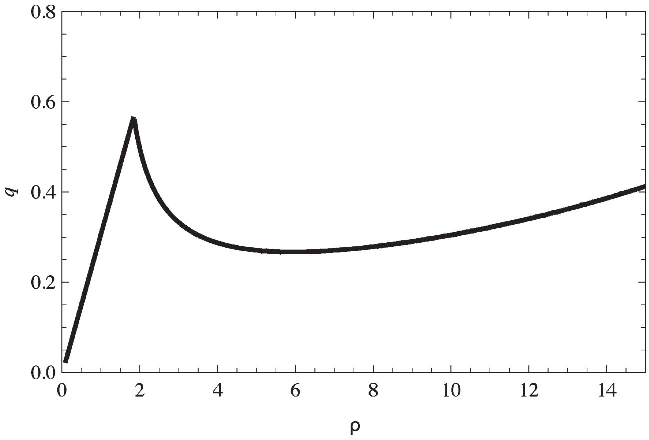

Figure 9. Dimensionless discharge q versus the dimensionless pressure ρ for the 2D slit configuration with $\kappa = 0.015$, $\tau = 0.5$, $\gamma = 0.8$, and $\sigma = 0.01$. After an initial linear increase, the discharge suddenly drops when the piston starts extending.

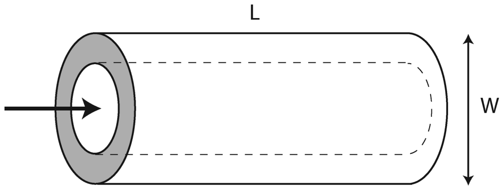

Figure 10. Cylindrical valve geometry. A tube of length L and diameter $W = 2H$ with piston rotaxane grafted on the inside (gray area). The pressure drop P over the length L results in a flow through the tube.

The final system we study is a cylindrical valve of length L (Figure 10). The inside of the tube is grafted with piston rotaxane with the flow penetrating a length k into the rotaxane layer. The pressure drop over the tube is P and the diameter of the tube is $W=2H$. By Solving the Navier–Stokes equation for cylindrical coordinates gives a radial profile which on its turn results in a dimensionless discharge:

$$q = \frac{Q(\Delta)}{Q(\Delta = 0, \rho = 1)} = \rho(1 - \Delta + \kappa)^4 \tag{11}$$

The discharge depends on an even higher degree on the height of the piston rotaxane layer and the estimate for the penetration depth than for a 2D valve.

Along the same lines as in the previous section we can derive the force exerted on the tip of the rotaxane

$$f(h) = \eta SP' 4\eta(H^2 - (H - h + k)^2) \tag{12}$$

We use this to calculate the height of the piston rotaxane layer and the discharge. The height and corresponding discharges are displayed in Figure 11.

The most promising results are obtained for small $\sigma \ll 1$. At first the discharge increases linearly with velocity to a local maximum after which it drops rapdily. For $\sigma = 0.001$ it drops to ~5% of its local maximum value (Figure 12). Finally it will increase again. Notice that the behavior is very similar to that for bulk piston rotaxane in a shear flow.

In this section, we have shown that the shear swelling of a rotaxane layer can give rise to nonlinear discharge versus pressure drop behavior and hence allow us to create a novel kind of nanovalve. This kind of system was suggested previously in the more complicated context of grafted polymer layers.[2]

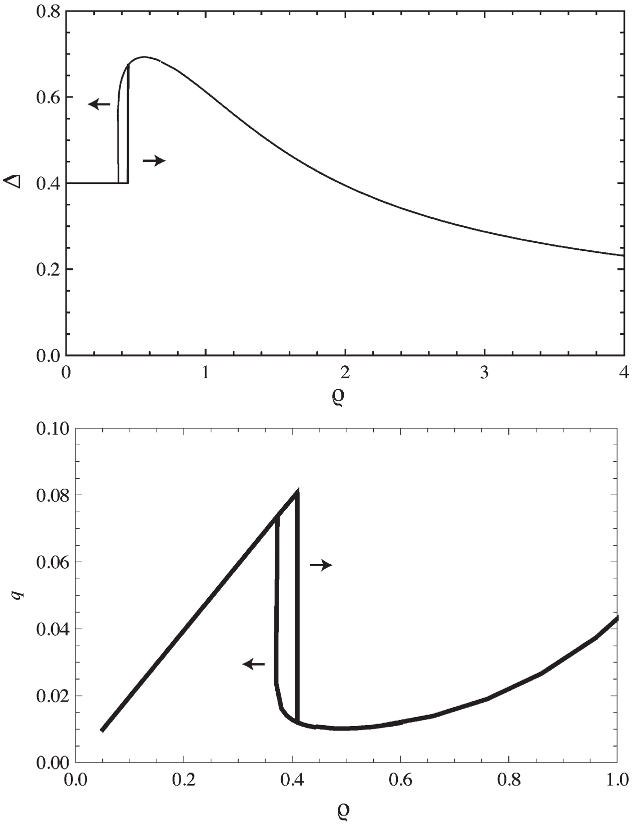

Figure 11. Dimensionless height Δ and discharge q versus the dimensionless pressure ρ for $\sigma = 0.01$. An initial steep rise in the discharge is followed by a sudden drop when the piston starts extending. Finally it starts increasing again. Note the differences between the scales of the horizontal axes.

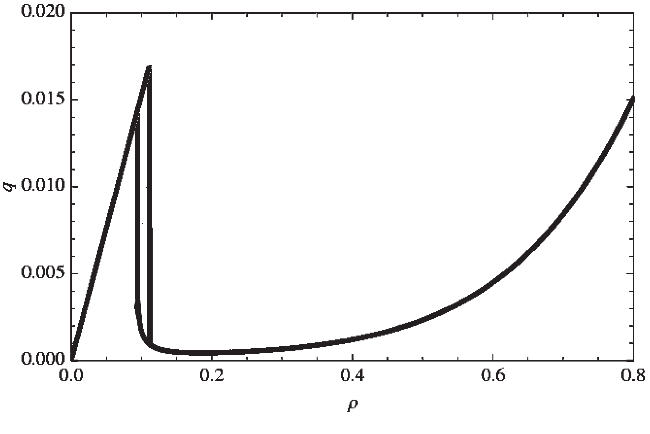

Figure 12. Dimensionless discharge versus the dimensionless pressure for $\kappa = 0.08$, $\sigma = 0.001$, $\gamma = 0.9$, and $\tau = 0.5$.

V. Conclusion

The piston rotaxane length depends on the applied force in a nonlinear way, which in some cases can lead to the swelling under shear of a rotaxane layer. This is a novel effect, which has previously been claimed for ordinary flexible polymer layers, although the physics in that situation is much less clear-cut. This swelling implies nonlinear behavior for the discharge as a function of the pressure drop in a valve system. The results for both the 2D valve and the cylindrical valve are promising. They limit the discharge for a wide region of pressures to a maximum value. For this reason they have possible applications in filtration systems, controlled drug release, ink jet printers and systems of medical and biological importance. An advantage of the system studied here is that it can be analyzed exactly, in contrast to most flexible polymer dependent systems.

Calculation of the zero force equilibrium position Y_0 of the piston ring and the height equation of the piston rotaxane in a constant force field.

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