

Adsorbed polymers under flow. A stochastic dynamical system approach

Robert Armstrong and Myung S. Jhon

Citation: *The Journal of Chemical Physics* **83**, 2475 (1985); doi: 10.1063/1.449294

View online: <http://dx.doi.org/10.1063/1.449294>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/83/5?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Dynamics of collapsed polymers under the simultaneous influence of elongational and shear flows](#)

J. Chem. Phys. **135**, 014902 (2011); 10.1063/1.3606392

[Stochastic dynamics in polymer translocation](#)

AIP Conf. Proc. **965**, 181 (2007); 10.1063/1.2828731

[Dynamics of a Single Tethered Polymer under Shear Flow](#)

AIP Conf. Proc. **913**, 114 (2007); 10.1063/1.2746734

[Three-dimensional simulation of hexagonal phase of a specific polymer system under shear: The dynamic density functional approach](#)

J. Chem. Phys. **109**, 8751 (1998); 10.1063/1.477543

[Adsorbed polymer layers subjected to flow](#)

AIP Conf. Proc. **137**, 263 (1986); 10.1063/1.35512



Adsorbed polymers under flow. A stochastic dynamical system approach

Robert Armstrong

Sandia National Laboratories, Livermore, California 94550

Myung S. Jhon

Department of Chemical Engineering, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

(Received 14 August 1984; accepted 26 March 1985)

Recent experiments have shown that porous filters preadsorbed with polymer molecules exhibit an anomalously high pressure drop at high rates of flow. We have modeled the adsorbed polymers as dynamical systems and have found that the introduction of hydrodynamic interaction between molecules destabilizes at a high applied shear. As a direct result this instability will cause the molecules to unravel and stretch far into the cross section of the pore, and thus by inference, cause the observed anomalously high pressure drop. Although much of this paper is devoted to the stability characteristics of the deterministic system, Brownian motion is also considered, and an account of the statistics of the Brownian system when the deterministic system becomes unstable is given. The examples revealed in this paper are not of sufficient complexity to calculate with any accuracy the magnitude of this anomalous pressure drop. We simply present a procedure by which a large variety of more complex models could be undertaken and their ultimate effect clearly understood.

I. INTRODUCTION

Recently a great deal of attention has been drawn to the behavior of polymers adsorbed to the walls of pores in porous filters.¹⁻³ Particular attention has been paid to the response of such a system to an applied flow. This paper will present a theoretical approach that will account for some of the experimentally observed results.

The earliest experiments that dealt with this type of system were those of Gramain and Myard¹ (hereafter G&M). Their most notable result was that the flow resistance (or pressure drop) of the filter increased dramatically over a relatively small range of flow rates near some critical value of the flow rate. They surmised that this sudden increase in pressure drop, owing to its intensity, could only be accomplished by a sudden unravelling of the adsorbed polymer molecules extending themselves far into the cross section of the pore, and thus decreasing the "effective hydrodynamic radius of the pore." Different experimentalists,² however, have had difficulty replicating this result, and indeed have questioned its validity.

On the theoretical side, Dimarzio and Rubin³ (hereafter D&R) used a bead-spring model similar to that of Fig. 1. They employed a simple linear (Hookean) spring and neglected hydrodynamic interaction to find that under the influence of a simple shear and regardless of the nonhomogeneity imposed by a reflecting wall, the polymer would not extend at all into the cross section of the pore no matter what the magnitude of the applied shear. In fact, the amount of extension perpendicular to the wall was found to be no different than that of equilibrium. There is no *a priori* indication (due to symmetry, say) that this should be so. Presuming for the moment, that G&M have revealed a bona fide phenomenon, what is missing from D&R's model that would induce this effect? More beads and more springs would not correct the situation—this would only add more modes. Since the actual flow field is not a simple (homogeneous) shear but one that is more like a quadratic (Poiseuille-like)

flow, could the nonlinearity in the flow alone cause the observed behavior? Possibly. But more to the point of this paper: could the presence of hydrodynamic interactions between adsorbed polymers and the wall cause this precipitous increase in filter resistance around some critical flow rate? The answer, as we will find, is a qualified yes.

What we will do in this paper is lay out a framework whereby a believable explanation for these observations will be achieved. We will employ several variants of D&R's model as a vehicle to this end. The two major changes to their model will be the addition of hydrodynamic interaction, and using stochastic theory parlance: ignore the reflecting boundary at the wall. In addition, the preaveraging assumption will be made for these hydrodynamic interactions as a matter of computational convenience. As the physics of this phenomenon are, by degrees, revealed it will become clear that the effect, in essence, of the hydrodynamic interaction will be to destabilize the polymer molecule as a dynamical system, represented here by a bead-spring model. Intuitive-

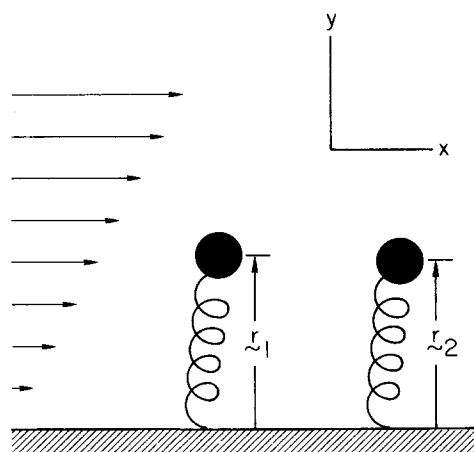


FIG. 1. This is a rendering of the two molecule model considered in Sec. III.

ly, if the dynamics of these bead-spring contraptions are unstable without the presence of a fully reflecting wall or Brownian motion, then the addition of these effects, which are—again intuitively—nonrestoring by nature, will do nothing to restabilize this system. It is this instability, induced by the presence of hydrodynamic interaction of adjacent molecules, that is at least one explanation of G&M's result. This is because approaching the critical flow rate can be interpreted as the approach of this instability, which manifests itself as a successive weakening of the (linear) spring, enabling the bead to visit regions successively further from the wall.

A secondary purpose of this paper is to provide an illustration that a complicated Fokker–Planck equation need not always be solved in order to learn something about a stochastic dynamical system, even when the stochastic driving force plays an important role. One of the reasons that Gaussian statistics have been preserved throughout is that the probabilistic effect of dynamical instabilities are particularly transparent. Finally, we would like to reiterate that what is presented here is a set of examples that is but one of many possible explanations for G&M's result. More importantly, the major finding here is that a method and a means towards many other such models is given.

II. THE ELEMENTS OF HYDRODYNAMIC INTERACTION

In this section we will consider a model similar to D&R's but without a boundary at the wall. Here, for simplicity, a perturbation to the deformation will take the place of a true Oseen interaction. The purpose is not to produce the most physically realistic model but to acquaint the reader with the intuition necessary to appreciate the more complicated mathematical structure of the models that follow.

This simple model will take the form of just one bead connected through a single spring to the wall—a wall that does not impede the bead in any way other than providing a base for the spring connection (similar to D&R). The dynamics of this system can be written down in the form of a stochastic differential equation:

$$\dot{\mathbf{p}} = \mathbf{K} \cdot \mathbf{p} - h(\mathbf{p} - \mathbf{p}_0) + \Phi(t). \quad (2.1)$$

Here, \mathbf{p} is the position vector of the bead and the velocity gradient (\mathbf{K}) has the following form:

$$\mathbf{K} = \nabla \mathbf{v} = \begin{pmatrix} \epsilon' & \epsilon'' + \dot{\gamma} \\ \epsilon & -\epsilon' \end{pmatrix} \quad \text{note: } \text{tr}(\mathbf{K}) = \nabla \cdot \mathbf{v} = 0$$

with ϵ' , ϵ'' , ϵ as a homogeneous perturbation to the velocity field that has a shear rate $\dot{\gamma}$ applied parallel to the wall. h is roughly twice the unadsorbed time scale of the molecule and is a direct result of the presence of the linear restoring spring force. $\Phi(t)$ is the Brownian force random, presumed to be only a function of time. \mathbf{p}_0 is the zero point size of the molecule—i.e., if the Brownian motion and flow field are both turned off, the size of the bead-spring molecule (i.e., the distance between the bead and the wall) is exactly \mathbf{p}_0 . In many applications, this \mathbf{p}_0 is taken to be identically zero especially in unbounded homogeneous situations where the time scale and not the absolute size of the polymer is of importance. Here in this highly nonhomogeneous case, it would seem to be more appropriate to have some size to the molecule not dictated solely by Brownian motion. In this case, the Brownian forces have the net effect of causing the molecule to fluctuate from its zero point size.

ian forces have the net effect of causing the molecule to fluctuate from its zero point size.

In the final analysis, this zero point size provides a mechanistic advantage in that it prevents the bead from straying below the wall too often; at least it can be constructed as such for equilibrium. This means that we can define the mean $\langle \mathbf{p} \rangle$ at equilibrium ($\langle \mathbf{p} \rangle = \mathbf{p}_0$) to be one or two rms fluctuations from the wall. Note also that if we conjecture that this hydrodynamic perturbation ϵ , ϵ' , ϵ'' comes from other molecules adsorbed upstream or downstream from the molecule at hand, then we would hardly expect these perturbations to be altogether homogeneous as supposed here. This serves to emphasize that this example is merely an artifice concocted to introduce the reader to the scaling philosophy and the technology of linear operators that will become the foundation of more physically realistic but more mathematically enigmatic examples to follow.

Equation (2.1) can be rewritten into a more customary form:

$$\dot{\tilde{\mathbf{p}}} = \Lambda \cdot \tilde{\mathbf{p}} + \mathbf{M} \cdot \mathbf{p}_0 + \Phi(t), \quad (2.2)$$

where $\tilde{\mathbf{p}} = \mathbf{p} - \mathbf{p}_0$ and the operators can be inferred from Eq. (2.1). To a very good approximation:

$$\Lambda = \begin{pmatrix} -h & \dot{\gamma} \\ \epsilon & -h \end{pmatrix}; \quad \mathbf{M} = \begin{pmatrix} \epsilon' & \dot{\gamma} \\ \epsilon & -\epsilon' \end{pmatrix}$$

when all ϵ , ϵ' , ϵ'' are much smaller than $\dot{\gamma}$ and h . Executing the usual⁴ assumptions about the stochastic process, an equation for the first and second moments of $\tilde{\mathbf{p}}$ can be obtained from Eq. (2.2):

$$\langle \dot{\tilde{\mathbf{p}}} \rangle = \Lambda \cdot \langle \tilde{\mathbf{p}} \rangle + \mathbf{M} \cdot \mathbf{p}_0$$

and when $\langle \dot{\tilde{\mathbf{p}}} \rangle = 0$ (steady state):

$$\langle \tilde{\mathbf{p}} \rangle = -\Lambda^{-1} \cdot \mathbf{M} \cdot \mathbf{p}_0, \quad (2.3)$$

$$\dot{\Xi} = \Lambda \cdot \Xi + \Xi \cdot \Lambda^\dagger + \sigma \mathbf{I} \quad (2.4)$$

with $\Xi = \langle \tilde{\mathbf{p}} \tilde{\mathbf{p}} \rangle - \langle \tilde{\mathbf{p}} \rangle \otimes \langle \tilde{\mathbf{p}} \rangle$ the second cumulant. The principal axes of Ξ can be regarded as the “size” of the molecule deviating from its mean value. Here, σ arises from the usual white noise assumption and relates the statistical information of the Brownian force process. Because the model has been constructed so that the wall presents no additional boundary condition and since all of the contributions to the equation of motion are linear, the statistics are, not surprisingly, Gaussian. In this paper it will not be necessary to consider the full time dependent case of Eq. (2.4) in order to see the effect we are looking for. Though the consideration of time dependence does not incur any additional mathematical hardship, it is inessential to our purpose. The solution to Eq. (2.4) with all time derivatives vanishing gives the statistics we seek, in particular the probability density of $\tilde{\mathbf{p}}$ is given by

$$P(\tilde{\mathbf{p}}) = \left(\frac{\det \Xi^{-1}}{2\pi} \right) \exp \left[-\frac{1}{2} (\tilde{\mathbf{p}} - \langle \tilde{\mathbf{p}} \rangle) \otimes (\tilde{\mathbf{p}} - \langle \tilde{\mathbf{p}} \rangle) : \Xi^{-1} \right] \quad (2.5)$$

and assuming $\epsilon/h \ll 1$ as was the original intent:

$$\Xi = \frac{\sigma}{4h \left(1 - \frac{\epsilon\dot{\gamma}}{h^2}\right)} \begin{bmatrix} 2 + \frac{\dot{\gamma}^2}{h^2} - \frac{\epsilon\dot{\gamma}}{h^2} & \frac{\dot{\gamma}}{h} \\ \frac{\dot{\gamma}}{h} & 2 - \frac{\epsilon\dot{\gamma}}{h^2} \end{bmatrix}. \quad (2.6)$$

Note that if $\epsilon\dot{\gamma}/h^2 \sim 1$ (i.e., a fairly high shear rate is applied) the cumulant and hence the second moment can become arbitrarily large. In fact, analysis of the spectrum and metric of Ξ reveals that the molecule is elongating into the pore.

So it seems that, at least under this naive model, we can get extension of the molecule into the cross section of the pore, presumably in concurrence with G&M's experimental result. But physically what is going on? We know that in reality the polymer molecule will not have any dimension that can become infinite. It occurs in this simple example because the hydrodynamic perturbation manifests itself as a linear contribution. This has the effect of destabilizing the linear model chosen here to represent a polymer molecule. In the language of linear algebra, the addition of a hydrodynamic perturbation, ϵ (which is presumed positive) causes Λ to cease being negative definite.

Identifying this transition to instability is the major purpose of this work. It will become important as we proceed to more complicated systems to be able to identify this transition from the dynamical system characterized by Λ rather than going through the whole statistical workup as was done in this section. The eigenvalues of the deterministic dynamical system characterized by Λ are

$$\{\lambda(\Lambda)\} = -h + \sqrt{\epsilon\dot{\gamma}}, \quad -h - \sqrt{\epsilon\dot{\gamma}}. \quad (2.7)$$

This shows that when the dynamical system ceases to be stable (i.e., $\gamma\epsilon/h^2 \sim 1$) the same dynamical system, while under the influence of Brownian motion, yields statistical observables that reflect this instability by exhibiting a singularity. Note that this scaling approach is fundamentally different from a well known similar transition caused by strong pure-extensional flow.⁵ The scaling concept we adapted in this paper is philosophically similar to the mathematical logic of singular perturbation theory often used in fluid mechanics.^{6,7}

The fact that the wall has not been considered to be a fully reflecting boundary here may be a source of some consternation to those who follow theoretical developments on this topic closely. It should be clear though, that such a reflecting wall would serve only as a boundary condition in, say, the Fokker-Planck version of this problem. This condition contributes nothing, however, to the underlying mechanics of the system. The addition of both Brownian forces and a new reflecting barrier confer no new restoring forces and therefore alters nothing related to its stability.⁸ This fact applies to any dynamical system that might suit one's fancy and not just to the case we are considering here. This is the key idea to keep in mind as things progress to more physical but far more complicated models. For this example, and for the rest of this paper, we shall continue to ignore the effect of the impermeability of the wall as a major complication inessential to our objective. This can be justified, however, by noting that the probability of finding the bead below the wall is very small and thus events that might otherwise occur to

prevent the bead from doing so would add commensurately little to any statistical observable of the system.

III. TWO COADSORBED POLYMER MOLECULES

The motivation for this section is to lend credence to the reasoning of the previous section by proceeding to a more believable model: two polymer molecules interacting through the viscous media with an applied shear flow. In the previous section we were able to adjust the amount of hydrodynamic perturbation directly. Here we will seek to do the same thing, only in this case the strength of the hydrodynamic interaction may be adjusted by changing the distance between the two molecules. Again the bead spring model will be used just as in the previous section except that now there will be two of them (see Fig. 1):

$$\begin{pmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \end{pmatrix} = \begin{pmatrix} K - h \mathbf{1} & -h\zeta \mathbf{\Omega} \\ -h\zeta \mathbf{\Omega} & K - h \mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{r}_1 - \mathbf{r}_1^0 \\ \mathbf{r}_2 - \mathbf{r}_2^0 \end{pmatrix} + \begin{pmatrix} K & 0 \\ 0 & K \end{pmatrix} \begin{pmatrix} \mathbf{r}_1^0 \\ \mathbf{r}_2^0 \end{pmatrix} + \begin{pmatrix} \mathbf{1} & \zeta \mathbf{\Omega} \\ \zeta \mathbf{\Omega} & \mathbf{1} \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}. \quad (3.1)$$

In this case, K is the undisturbed velocity gradient, different from the preceding section:

$$K = \begin{pmatrix} 0 & \dot{\gamma} \\ 0 & 0 \end{pmatrix}.$$

The subscripts 1 and 2 refer to the particular molecule in question and, in particular, \mathbf{r}_1^0 and \mathbf{r}_2^0 refer to their respective dynamical equilibria, *sans* flow. Also as is customary⁹ in these cases, $h\zeta \mathbf{\Omega}$ is a "preaveraged" Oseen tensor (T) which in the light of the previous section, begs the notation

$$\langle T \rangle = [h\zeta \mathbf{\Omega}] = \begin{pmatrix} \tilde{\epsilon}' & \tilde{\epsilon} \\ \tilde{\epsilon} & \tilde{\epsilon}'' \end{pmatrix}. \quad (3.2)$$

With an eye toward producing a scaling criterion similar to that of Sec. II, note for now that these epsilons scale as the inverse of some average separation distance of the beads which, presumably, makes all of these coefficients small. For reasons similar to those of Sec. II it is essential that this preaveraged Oseen tensor be small but nonzero. Arranging Eq. (3.1) into a notation that is somewhat more compact:

$$\dot{\mathbf{r}} = \mathbf{L}_4 \cdot (\mathbf{r} - \mathbf{r}^0) + \mathbf{M}_4 \cdot \mathbf{r}^0 + \mathbf{N}_4 \cdot \Phi, \quad (3.3)$$

where \mathbf{L}_4 , \mathbf{M}_4 , and \mathbf{N}_4 can be inferred directly from Eq. (3.1). In an analogy to the scaling limits already established previously, consider the situation where: $\tilde{\epsilon}$, $\tilde{\epsilon}'$, $\tilde{\epsilon}'' \sim \tau$, and $\dot{\gamma}\tilde{\epsilon}/h^2 \sim 1$ ($\dot{\gamma} \sim 1/\tau$) with $\tau \rightarrow 0$. In this limit then, the four eigenvalues of \mathbf{L} become

$$\lambda + h = \pm \sqrt{\dot{\gamma}\tilde{\epsilon}}, \quad \pm i\sqrt{\dot{\gamma}\tilde{\epsilon}}. \quad (3.4)$$

This shows that whatever happens the underlying dynamical system at $\dot{\gamma}\tilde{\epsilon}/h^2 \sim 1$ will not be stable and hence, after an accounting of Brownian motion and wall effects are taken, any observable statistic will cease to have meaning (diverge).

Something must be said at this point about the expected size of $\tilde{\epsilon}$: can we reasonably expect that $\tilde{\epsilon}\dot{\gamma}/h^2 \sim 1$ in G&M's experiments? Recognizing that $\tilde{\epsilon}$ arises from the xy (off diagonal) component of the preaveraged Oseen tensor, scrutiny of this component unaveraged should give a reasonable idea of the order of magnitude of its approximation, $\tilde{\epsilon}$.

Simple order-of-magnitude reasoning yields

$$\frac{\tilde{\epsilon}}{h}, \frac{\tilde{\epsilon}'}{h}, \frac{\tilde{\epsilon}''}{h} \sim \frac{a}{r} \sim \frac{a}{d}.$$

This means that the hydrodynamic perturbation scales with the ratio of the internal size (bead diameter, a) to the external size (molecular diameter, d). This ratio is, by definition, less than one and probably, in this one bead model, greater than a tenth. So we can peg $\tilde{\epsilon}$ at around 0.1 to 0.5. This seems to support the previously unsubstantiated posit that $\dot{\gamma}\tilde{\epsilon}/h^2 \sim 1$ is experimentally attainable, since $\dot{\gamma}/h$ has been observed to be in the range¹⁰ of 3 to 5 at the onset of this precipitous increase in pressure drop.

Due to the simplicity of the one bead model, estimating these quantities often strains the imagination. This serves though, to reaffirm the original intent here—we are only after a qualitative description of what might be going on. Rather drastic improvements would have to be made before any measure of quantitative realism could rightly be expected.

The scenario of G&M's experiments then, should unfold something like this: The molecules are adsorbed with their geometry dictating a certain amount of hydrodynamic interaction, gauged at $\tilde{\epsilon} = 0.1$ –0.5. Starting at equilibrium the applied shear rate is increased steadily until $\dot{\gamma}\tilde{\epsilon}/h^2 \sim 1$ is approached whereat the polymers suddenly extend themselves away from the wall and far into the pore causing a large increase in the pressure drop across the filter. To illustrate precisely how the polymer, modeled by beads and springs, behaves as this limit is approached a set of equations for the statistics of this system (at its stationary state) can be derived:

$$\langle \mathbf{r} \rangle = -\mathbf{L}_4^{-1} \cdot \mathbf{M}_4 \cdot \mathbf{r}^0,$$

$$\mathbf{L}_4 \cdot (\langle \mathbf{r}\mathbf{r} \rangle - \langle \mathbf{r} \rangle \otimes \langle \mathbf{r} \rangle) + (\langle \mathbf{r}\mathbf{r} \rangle - \langle \mathbf{r} \rangle \otimes \langle \mathbf{r} \rangle) \cdot \mathbf{L}_4^\dagger + \sigma \mathbf{1} = \mathbf{0}. \quad (3.5)$$

An important mechanistic note should now be made. \mathbf{L}_4 can be decomposed into two important constituent quantities: its eigenvalues and the metric associated with them. Since \mathbf{L}_4 has no nilpotent component, it is in terms of these that the second cumulant and mean can be expressed

$$\mathbf{G} = \frac{h}{\sigma \left(4 + \left(\frac{\dot{\gamma}}{h} \right)^2 \right)} \begin{pmatrix} 8 \left(1 - \left(\frac{\tilde{\epsilon}}{h} \right)^2 - \frac{1}{2} \left(\frac{\tilde{\epsilon}\dot{\gamma}}{h^2} \right)^2 \right) & -4 \left(1 + \left(\frac{\tilde{\epsilon}}{h} \right)^2 \right) \frac{\dot{\gamma}}{h} \\ -4 \left(1 + \left(\frac{\tilde{\epsilon}}{h} \right)^2 \right) \frac{\dot{\gamma}}{h} & 8 \left(1 + \frac{1}{2} \frac{\dot{\gamma}^2}{h^2} - \frac{\tilde{\epsilon}^2}{h^2} \right) \end{pmatrix}, \quad (3.8)$$

$$\langle \mathbf{r}_1 \rangle \langle \mathbf{r}_1^0 \rangle = \frac{1}{1 - \left(\frac{\tilde{\epsilon}\dot{\gamma}}{h^2} \right)^2 - 2 \left(\frac{\tilde{\epsilon}}{h} \right)^2 + \left(\frac{\tilde{\epsilon}}{h} \right)^4} \begin{pmatrix} \frac{\tilde{\epsilon}\dot{\gamma}^2}{h^3} y_2^0 + \left(\frac{\dot{\gamma}}{h} - \frac{\tilde{\epsilon}^2\dot{\gamma}}{h^3} \right) y_1^0 \\ \left(\frac{\tilde{\epsilon}\dot{\gamma}}{h^2} - \frac{\tilde{\epsilon}^3\dot{\gamma}}{h^4} \right) y_2^0 + \frac{\tilde{\epsilon}^2\dot{\gamma}^2}{h^4} y_1^0 \end{pmatrix}. \quad (3.9)$$

Here the scaling limit has been anticipated by ignoring contributions from $\tilde{\epsilon}'$ and $\tilde{\epsilon}''$ for the reasons stated in the preceding two paragraphs. Note that although \mathbf{G} is the same for both P_1 and P_2 , the averages $\langle \mathbf{r}_1 \rangle$ and $\langle \mathbf{r}_2 \rangle$ are not the same since \mathbf{r}_1^0 and \mathbf{r}_2^0 are different.

$$\langle \mathbf{r} \rangle = - \left\{ \sum_i 1/\lambda_i \mathbf{e}^i \otimes \mathbf{e}_i \right\} \cdot \mathbf{M}_4 \cdot \mathbf{r}^0 \quad (3.6)$$

$$\langle \mathbf{r}\mathbf{r} \rangle - \langle \mathbf{r} \rangle \otimes \langle \mathbf{r} \rangle = - \left\{ \sum_{ij} \frac{a}{\lambda_i + \lambda_j} g^{ij} \mathbf{e}_i \otimes \mathbf{e}_j \right\},$$

where λ_i is the eigenvalue corresponding to the right and left eigenvectors \mathbf{e}_i and \mathbf{e}^i , respectively ($g^{ij} = \mathbf{e}^i \cdot \mathbf{e}^j$). The above confirms that if the system ceases to be stable (one of the eigenvalues has zero real part) then the statistics determined by interactions between this dynamical system and Brownian motion will exhibit a singularity. Luckily it turns out that both the spectrum and metric associated with \mathbf{L}_4 are order τ^2 or higher in all contributions involving $\tilde{\epsilon}'$ or $\tilde{\epsilon}''$ so that, in the scaling limit already discussed, these quantities can be ignored, thus easing an already formidable task.

To further the purpose of illustration, it would be useful to find the probability of the conformation of just one of these molecules without regard to the conformation of the other—in other words with the conformation of the other averaged out. In the full four dimensional construction we have currently, all of the cross correlations are intact which, for the sake of a comparison with Sec. II, will greatly inhibit interpretation of the results. These cross correlations can be averaged out via a prescription that appears in many books on the subject¹¹:

$$P_1(\mathbf{r}_1) = \int d^2 \mathbf{r}_2 \text{ (total probability),}$$

$$P_2(\mathbf{r}_2) = \int d^2 \mathbf{r}_1 \text{ (total probability).}$$

What results is a two-dimensional Gaussian probability for both molecules that have identical cumulants:

$$P_1(\mathbf{r}_1) = \left(\frac{\det(\mathbf{G})}{2\pi} \right) \exp \left[-\frac{1}{2} (\mathbf{r}_1 - \langle \mathbf{r}_1 \rangle) \otimes (\mathbf{r}_1 - \langle \mathbf{r}_1 \rangle) : \mathbf{G} \right], \quad (3.7)$$

$$P_2(\mathbf{r}_2) = \left(\frac{\det(\mathbf{G})}{2\pi} \right) \exp \left[-\frac{1}{2} (\mathbf{r}_2 - \langle \mathbf{r}_2 \rangle) \otimes (\mathbf{r}_2 - \langle \mathbf{r}_2 \rangle) : \mathbf{G} \right],$$

where \mathbf{G} is the same for both upstream and downstream molecules:

Figure 2 replicates Eqs. (3.8) and (3.9) graphically for varying amounts of hydrodynamic interaction as a contour within which the bead remains 90% of the time. This case has been chosen so that the upstream molecule's equilibrium distance from the wall is somewhat larger than that of the

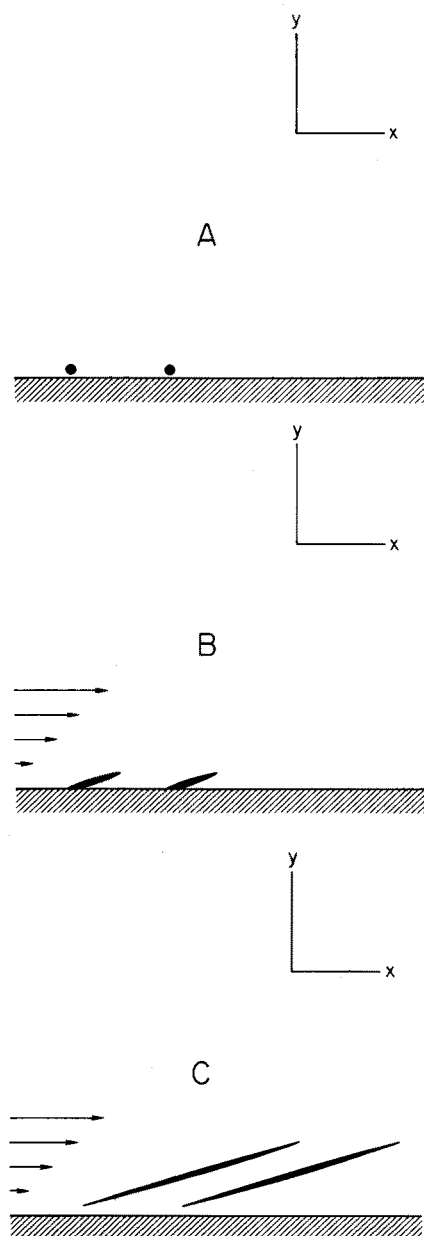


FIG. 2. These are the actual probability contours calculated from the results of Sec. III. These contours are constructed such that the bead will remain within the blackened ellipses 90% of the time. In (a) the equilibrium contour is given for reference. In (b) a simple shear flow is applied without any hydrodynamic interaction between the beads ($\dot{\gamma}/h = 3$). Finally in (c), hydrodynamic interaction is "turned on" ($\dot{\gamma}/h = 3$ and $\epsilon\dot{\gamma}/h^2 = 0.8$).

downstream molecule. This circumstance causes $\bar{\epsilon}$ to be negative with the result that both the means ($\langle \mathbf{r}_1 \rangle$ and $\langle \mathbf{r}_2 \rangle$) and the deviations (G for both) become large and extend into the pore. Other configurations will produce other results; some of which may even cause the expectation to be close to or even below the wall. This event would therefore not do as an illustration. Even so, the conjectures that we draw from any one of these possibilities will apply to all for the reason that in every case the deviation itself becomes large. Although the bead is not allowed to stray below the wall it can wander as far as it pleases above it and as the deviation (G) becomes larger (along some axis) it will do so with increasing regularity. In this sense the presence of a reflecting wall will only enhance the tendency for the polymer molecule to extend

itself far into the cross section of the pore and thus produce an anomalously high pressure drop.

The case of Fig. 2 though, would be little altered by the presence of such a boundary—the contour shows that the bead comes into contact with the wall only rarely, and rarer still as the transition to instability is approached. One would naturally assume that if there is little opportunity for the bead to come in contact with the wall then the inclusion of such a boundary condition in an admittedly more realistic model would have little effect. The important thing to remember here is that the addition of a wall will contribute nothing to affect the stability of this two molecule system and that in every situation imaginable the molecules will extend themselves away from the wall. It is exactly this inference that we will draw heavily upon in the next section in order to handle a vastly more complicated but substantially more realistic situation: an arbitrarily large number of hydrodynamically interacting adsorbed polymers. In real systems just two molecules interacting alone must be relatively rare, rather we should expect a large number of mutually interacting molecules and that the case of Fig. 1 is but one representative of many possibilities.

IV. THE GENERAL CASE OF COADSORBED POLYMERS

This section will present a model with an arbitrary number of beads connected through springs to a wall, which of course interact hydrodynamically—but only with their nearest neighbors. Here again we will be looking for small off-diagonal (xy) contributions that may couple with the possibly very large applied shear, which may, in a fashion not unlike that of the previous sections, produce an instability. The equations of the last section are easily generalized to this case:

$$\begin{aligned} \langle \hat{\mathbf{f}} \rangle &= -\mathbf{L}_{2n}^{-1} \cdot \mathbf{M}_{2n} \cdot \hat{\mathbf{f}}^0, \\ \mathbf{L}_{2n} \cdot (\langle \hat{\mathbf{f}} \hat{\mathbf{f}} \rangle - \langle \hat{\mathbf{f}} \rangle \otimes \langle \hat{\mathbf{f}} \rangle) + (\langle \hat{\mathbf{f}} \hat{\mathbf{f}} \rangle - \langle \hat{\mathbf{f}} \rangle \otimes \langle \hat{\mathbf{f}} \rangle) \cdot \mathbf{L}_{2n}^\dagger + \sigma \mathbf{1} &= 0 \end{aligned} \quad (4.1)$$

here

$$\mathbf{L}_{2n} = h\zeta \begin{bmatrix} \mathbf{H} & -\Omega_1 & & & \\ -\Omega_1 & \mathbf{H} & -\Omega_2 & & \\ & -\Omega_2 & \mathbf{H} & -\Omega_3 & \\ & & & \ddots & \\ & & & -\Omega_{n-1} & \mathbf{H} \end{bmatrix},$$

where $\mathbf{H} = 1/h\zeta \mathbf{K} - 1/\zeta \mathbf{1}$ and \mathbf{K} is the same as it was in Sec. III. Now $\hat{\mathbf{f}}$ is a $2 \times n$ dimensional vector and Ω_m describes the preaveraged or preevaluated Oseen interactions between the m th and $m-1$ st beads. These hydrodynamic interactions can be further broken down into

$$h\zeta [\Omega_m] = \begin{pmatrix} \bar{\epsilon}'_m & \bar{\epsilon}_m \\ \bar{\epsilon}_m & \bar{\epsilon}''_m \end{pmatrix}. \quad (4.2)$$

Using what should be a familiar argument by now, let us say for each m : $\epsilon_m, \epsilon'_m, \epsilon''_m \sim \tau$ and $\dot{\gamma} \sim 1/\tau$ so that τ is the familiar scaling parameter and the limit we seek is $\tau \rightarrow 0$. Note that $\bar{\epsilon}_m \dot{\gamma}/h^2 \sim 1$ for each m .

Here it will only be possible to pursue the stability of the system computationally we can only afford to look at the

spectrum of L_{2n} . The statistics of this unwieldy system will remain unknown to us. By now, though, it should be clear that if the dynamical system *sans* Brownian motion and wall effects becomes unstable, the polymers will have a high probability of being found deeply extended into the cross section of the pore—even when these effects are included. So in the end it is only the spectrum of L_{2n} that we desire anyway. In the Appendix the details for deriving the general characteristic polynomial of L_{2n} is given. This can be solved in the scaling limit for the eigenvalues

$$(\lambda + h)^4 = 4S^2 \cos^2 \theta, \quad (4.3)$$

where θ is any (real valued) angle that satisfies

$$\sin((n+1)\theta) = 0,$$

where n is the number of molecules adsorbed and S^2 is an average of $(\epsilon_m \dot{\gamma})^2$ over the index m . So for large n (a large number of mutually interacting molecules) the transition to instability is dictated by

$$\sqrt{\frac{2S}{h^2}} \sim 1 \quad (4.4)$$

and since S can be considered to be some net contribution of the form

$$S = \bar{\epsilon} \dot{\gamma}, \quad (4.5)$$

it is evident that this transition is not significantly different from the previous cases.

V. CONCLUSION

Clearly other generalizations of this model come to mind. One could, for example, chain these beads one to another, attaching the last to the wall. The result would be a model with gross features not unlike the model considered here. Although on the mathematical front the algorithm for dealing with such a construct would be unchanged, the physical interpretation of a single many bead molecule and many single bead molecules are far apart. The transition to instability of the former is related to the *intramolecular* structure (presumably the spacing between neighboring beads in the chain) while the stability of the latter is governed by the *intermolecular* structure (primarily the distance separating adjacent molecules). This, of course, poses a question that can only be answered in the arena of experiment (could the surface coverage on the interior pore surface be varied at will?).

The purpose of this work has been twofold: To propose one possible mechanism for G&M's result and to re-emphasize that dynamical systems are largely dominated by their deterministic analog. Much can be said about their behavior without resorting to the somewhat dangerous and certainly more complicated Fokker-Planck formalism.

The underlying posit of this paper has been that this observed anomalous increase in the pressure drop noticed by G&M was due to the extension of the molecule away from the wall and into the cross section of the pore. In order to calculate precisely this pressure drop close to the transition (to instability), one would have to calculate an averaged kinetic energy dissipation resulting from the molecule protruding further into the pore. Since the theory presented here is based on scaling and order-of-magnitude reasoning, it

would seem imprudent to do this here. It suffices to simply state that this energy dissipation will become large—indeed infinite, as the transition criterion $\bar{\epsilon} \dot{\gamma} / h^2 \sim 1$ is approached.

This fact that virtually every observable of interest becomes undefined or infinite at the transition might bear some discussion. Real polymer molecules cannot be expected to stretch infinitely or yield infinite energy dissipation as has been suggested here. These singularities are an unfortunate artifact of using a linear model. The “spring” binding real polymer molecules to the wall would be expected to tighten disproportionately as it is stretched further and further from the wall. Clearly this must happen or bonds will be broken or the molecule will be desorbed bodily—circumstances which apparently do not occur in practice. What would happen if we used the same model but with a nonlinear add on to the spring as $\bar{\epsilon} \dot{\gamma} / h^2 \sim 1$ was approached and exceeded? The deterministic dynamical system (no Brownian motion) would bifurcate and evolve to a new stable state. In this new state, the molecule would be stretched a great deal, but not infinitely much. When the transition criterion is well exceeded and the new state is firmly gained, Brownian motion would cause only minor perturbations away from this new equilibrium. By and large the properties of the molecule will be dictated by the characteristics of the new equilibrium state. Though easy to manage, linear models are troublesome in that they can only exhibit either one (stable) solution, or none at all. The transition from stability to instability in a linear system augurs the existence of a new stable fixed point in a more realistic nonlinear system.

It cannot be overemphasized that whether this transition is identified as bifurcation or an instability, the presence of a reflecting boundary (wall) or a stochastic forcing function (Brownian motion) cannot alter the transition nor where it takes place. Walls and Brownian forces are not dynamically restoring by their very nature.

G&M¹ have deduced from their data that this transition correlates best not with $\dot{\gamma}$ as might be supposed, but with the maximum velocity at the center of the pore. The models presented here though, could never produce such a result since only a single wall with a homogeneous shear was considered. As the size of the pore is increased relative to the size of the molecule though, the transition can *only* depend on the wall shear $\dot{\gamma}$. This is because the polymer cannot be affected by a parameter—in this case, the velocity along the pore center line—that occurs on a length scale the molecule itself cannot probe. Given this, and assuming that the G&M correlation is correct, a far more complicated model should be considered: one involving two walls, or a quadratic velocity profile (assuming a cylindrical pore) or both. It seems reasonable that this modified model of D&R is adequate for a first cut at the underlying mechanism of the problem, while fervently hoping that this mechanism is not fundamentally altered as further complexities are added.

Finally it should be reiterated that the models entertained here are but one realization among a manifold of possibilities, though it is this one that the authors find most plausible. Regardless of which combination of beads, springs, walls, and hydrodynamic interactions one might wish to consider, the method outlined here is quite valid and

is probably more facile, while preserving more of the physical understanding, than the corresponding Fokker–Planck representation.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation under Grant CBT-8204509.

APPENDIX: THE DETAILS CONCERNING EQUATIONS (4.3) AND (4.4)

For simplicity consider a linear operator of the form

$$L_{2n} = \begin{bmatrix} A & \epsilon_1 & & & \\ \epsilon_1 & A & \epsilon_2 & 0 & \\ & \epsilon_2 & A & \epsilon_3 & \\ & & & \ddots & \\ 0 & & & \epsilon_{n-1} & A \end{bmatrix}. \quad (A1)$$

Here:

$$A = \begin{pmatrix} -h & \dot{\gamma} \\ 0 & -h \end{pmatrix} \text{ and } \epsilon_n = \begin{pmatrix} \epsilon'_n & \epsilon_n \\ \epsilon_n & \epsilon''_n \end{pmatrix}$$

and for the moment assume that

$$\epsilon_1 = \epsilon_2 = \dots = \epsilon_{n-1} = \epsilon = \begin{pmatrix} \epsilon' & \epsilon \\ \epsilon & \epsilon'' \end{pmatrix}.$$

Now the equation for the eigenvalues and eigenvectors of L_{2n} becomes

$$(L_{2n} - \lambda \mathbf{1}) \mathbf{X} = 0$$

or

$$\begin{aligned} \epsilon X_0 + AX_1 + \epsilon X_2 &= \lambda X_1, \\ \epsilon X_1 + AX_2 + \epsilon X_3 &= \lambda X_2, \\ &\vdots \\ \epsilon X_{n-1} + AX_n + \epsilon X_{n+1} &= \lambda X_n, \end{aligned} \quad (A2)$$

where X_0 and X_{n+1} have been added to take advantage of the apparent symmetry with the provision that $X_0 = X_{n+1} = 0$. Let us now take a guess at the form of each of these X_m 's:

$$X_m = \sin(m\theta)\alpha,$$

where α is a constant vector and θ is any solution of

$$\sin((n+1)\theta) = 0.$$

Substituting this guess into Eq. (A2) the determining equation for the eigenvalues is found to be

$$2\epsilon \cos \theta + A - \lambda \mathbf{1} = 0. \quad (A3)$$

Of course the only way Eq. (A3) can hold is if the determinate of the left-hand side vanishes and this occurs under the condition

$$(h + \lambda)^4 = 4(\epsilon\dot{\gamma})^2 \cos^2 \theta \quad (A4)$$

when we take the scaling limit $\epsilon\dot{\gamma}/h^2 \rightarrow 1$ while $\epsilon', \epsilon'', \epsilon \rightarrow 0$ in the usual fashion.

Now $\epsilon'_m, \epsilon''_m, \epsilon_m$ are not likely to be the same for each pair of adsorbed molecules. It can be shown by a more complicated analysis that only terms quadratic in $(\epsilon_m \dot{\gamma})^2$ will survive the above scaling limit and if we assume that $\langle (\epsilon_m \dot{\gamma})^2 \rangle_m = S^2$ and that $\langle (\epsilon_m \dot{\gamma})^2 (\epsilon_n \dot{\gamma})^2 \rangle_{m,n} = \langle (\epsilon_m \dot{\gamma})^2 \rangle_m \langle (\epsilon_n \dot{\gamma})^2 \rangle_n = S^4$, i.e., they are uncorrelated. The eigenvalues calculated from the characteristic polynomial averaged over m takes on a form similar to Eq. (A4):

$$(h + \lambda)^4 = 4S^2 \cos^2 \theta \quad (A5)$$

from which the eigenvalues are easily calculated:

$$\lambda = -h \pm \sqrt{2S} |\cos \theta|, \quad -h \pm i\sqrt{2S} |\cos \theta|.$$

¹Ph. Gramain and Ph. Myard, *Macromolecules* **14**, 180 (1981).

²Y. Cohen and A. B. Metzner, *Macromolecules* **15**, 1425 (1982).

³E. A. Dimarzio and R. J. Rubin, *J. Polymer Sci.* **16**, 457 (1978).

⁴V. I. Klyatskin and V. I. Tartarskii, *Sov. Phys. Usp.* **16**, 494 (1974).

⁵A. Keller, *Polymer* **24**, 1081 (1983).

⁶M. M. Denn, *Process Fluid Mechanics* (Prentice-Hall, Englewood Cliffs, 1980), p. 237.

⁷L. A. Segal, *SIAM Rev.* **14**, 547 (1972).

⁸N. G. Van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1983).

⁹“Customary” was the very word used in this eminent review: R. B. Bird, O. Hassager, R. C. Armstrong, and C. F. Curtiss, *Dynamics of Polymeric Liquids* (Wiley, New York, 1977), Vol. II.

¹⁰Ph. Gramain and Ph. Myard, *J. Colloid Interface Sci.* **84**, 114 (1981).

¹¹S. Karlin and H. M. Taylor, *A Second Course in Stochastic Processes* (Academic, New York, 1981).