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STATISTICAL, NONLINEAR, AND SOFT MATTER PHYSICS

Polymer Dynamics in Chaotic Flows with a Strong Shear Component[1]

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Abstract—We consider the dynamics of a polymer molecule injected into a chaotic flow with a strong mean shear component. The polymer experiences aperiodic tumbling in such flows. We consider a simplified model of the chaotic velocity field given by the superposition of a steady shear flow and a large-scale isotropic short-correlated random component. In the framework of this model, we present a detailed study of the statistical properties of single-polymer dynamics. We obtain the stationary probability distribution function of the polymer orientation, find the distribution of time periods between consequent events of tumbling, and find the tails of the polymer size distribution.

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1. INTRODUCTION

Hydrodynamics and rheology of dilute polymer solutions have recently attracted much theoretical and experimental attention. Adding a small amount of polymers to an ordinary liquid leads to radical changes in liquid properties. One of the most famous effects of this type is the phenomenon of drag reduction. The addition of a few parts per million (ppm) of long-chain polymer molecules produces a dramatic reduction in the friction drag. Although this effect was first observed in 1949 [1], there is still no rigorous theory explaining the phenomenon. A qualitative description was proposed in [2, 3], but no quantitative theory is available. Another spectacular phenomenon observed in dilute polymer solutions is the effect of elastic turbulence, discovered recently in [4, 5]. In this experiment, a chaotic fluid motion was observed in that system with a small Reynolds number, $\mathrm{Re} \ll 1$. Obviously, such behavior cannot be observed in Newtonian liquids, where the flow is laminar. Therefore, the chaotic flow is generated by elastic instabilities of the polymer solution. The dynamics of polymers and possible mechanisms explaining the chaotic state were studied in recent theoretical works [6–8]. It was proposed that elastic instabilities occur because of the back-reaction of dissolved polymers on the flow. It is therefore important to understand the dynamics of single polymers in external chaotic flows. The theoretical investigation of this problem has a long history. It was shown in the early 1970s [3, 9] that a polymer molecule in a random flow experiences a coil–stretch transition. In relatively weak flows, the molecule spends most of the time in the coiled state. However, when the Lyapunov exponent of the flow exceeds the inverse polymer relaxation time, the molecules become substantially elongated. With the development of novel optical methods, a number of high-quality experimental observations focusing on resolving dynamics of individual polymers (DNA molecules) placed into an inhomogeneous flow have been reported [10–13]. This has allowed direct observation of the coil–stretch transition [14].

Another important case corresponds to shearlike flows. The dynamics of polymer molecules in such flows have been extensively studied because of its importance in applications. For example, such a flow occurs whenever a polymer passes near a wall. Rheological properties of dilute polymer solutions are usually studied in shear geometries [15]. Direct observation of the polymer dynamics in a regular shear flow showed that the polymer experiences aperiodic tumblings [12]. This behavior is a combined effect of the shear flow and thermal fluctuations of a molecule. The statistical properties of such dynamics have been the subject of great attention both experimentally and theoretically [12, 13, 16–19].

The next important problem is the behavior of polymer molecules in flows where both the shear and chaotic flow components are important. Such flows occur in many experimental situations, such as drag reduction or elastic turbulence. Precisely this situation occurs when a chaotic or turbulent flow is generated on top of a shearlike velocity. The dynamics of polymers in such flows have much in common with the dynamics of polymers placed in statistically isotropic chaotic flows

[1] The text was submitted by the author in English.

or, conversely, in regular shear flows. However, there are some details that are unique to the discussed situation. A general qualitative analysis of such dynamics was presented in [20]. In that paper, the authors did not use any specific model of the turbulent flow but formulated some general predictions concerning this problem. In the present paper, we justify most of these predictions ab initio in some particular model flow and also present derivations of some general results, skipped in [20].

In the shear-flow geometry with a superimposed chaotic component, as in the case of isotropic random flows, the polymer experiences the coil–stretch transition. Below this transition, the polymer spends most of the time in the coiled state, and the effect of the flow results in algebraic tails of the probability distribution function (PDF) of the polymer size [6]. In the presence of a strong shear component, these tails become significantly broadened in comparison to isotropic flows without mean shear. More generally, it is shown that the Lyapunov exponent associated with the flow becomes parametrically large in the presence of mean shear. The effect of the Lyapunov exponent being increased by shear flow is rather surprising, because a simple shear flow cannot lead to exponential growth in polymer size. Therefore, such an increase is a combined effect of shear and chaotic components. This effect is discussed in detail in the last section of this article.

Above the coil–stretch transition, the polymer spends most of its time in a strongly elongated state. The thermal forces are then less important than the effect of velocity gradient, and the orientational dynamics is decoupled from the evolution of the polymer size [20]. In this case, the equation describing the polymer orientation dynamics formally coincides with the equation derived in [21] for thermal fluctuations of thin solid rods in a shear flow. The authors of [21] studied the stationary PDFs of the orientational angles of the solid rod direction vector. Although the statistical properties of thermal forces can be very different from the statistics of chaotic velocity gradients, most of the properties related to the stationary angular distribution remain the same. An interesting effect specific to the chaotic-flow problem is the nonuniversal algebraic tail of the PDF of the off-plane angle θ. This effect was briefly mentioned in [20] and is explained in detail in the present paper. Another extension of [21] presented in this paper is related to the statistics of tumbling time, i.e., the time between consequent flips of a polymer molecule. Obviously, this distribution cannot be expressed through the stationary distribution functions and requires additional analysis.

The statistical properties of real turbulent flows or flows observed in elastic turbulence experiments are not known in full detail. Furthermore, there exist no universal analytical tools for studying the problem in its full scale. To make any predictions regarding the polymer dynamics in such flows, one has to make some simplifications. In [20], the problem was studied under general assumptions regarding the velocity statistics. This allowed the authors to obtain some mostly qualitative predictions, which are universal (i.e., valid for a very wide range of systems) but lack precision. In this article, we follow another path by studying in detail a simplified, but reasonable model of chaotic flow. These rigorous results, derived ab initio, are certainly in full agreement with the general predictions in [20]. Recent computer simulations [17] also confirm and extend the results of the current paper.

In this paper, the external flow is modeled by the superposition of a constant shear component and a random component corresponding to a chaotic velocity field. We assume the random component to be relatively small. In the spirit of classical works [22, 23], we model the chaotic velocity part with a Gaussian delta-correlated stochastic field. Although such models are a great simplification of real flows, recent developments [24] showed that they can be successfully applied for analysis of advection in turbulent flows. As long as statistical properties of real flows are unknown, our approach is one possible way to model single polymers in chaotic flows. In the framework of this approach, we are able to derive most of the results analytically. The results in the present paper can form a basis for future studies of more complicated problems, such as the statistics of polymer conformation in chaotic flows.

We list the main results in this paper. First, we obtain an exact expression for the probability distribution of the polymer orientation vector. We show that the body of the angular distribution function is located in the region of small angles, which correspond to the polymer stretched in the shear direction. However, the tails of the PDF are algebraic, and hence the fluctuations of the polymer direction are anomalously strong. Second, we study the statistics of time periods between consequent events of polymer tumbling. We show that this PDF has an exponential tail at large tumbling times, and two different asymptotic regimes in the region of very small times. Finally, for polymers below the coil–stretch transition, we obtain the asymptotic form of the polymer size distribution function, which is also algebraic. We also show that the mean shear component leads to a significant broadening of the polymer size distribution in comparison to the pure chaotic flow. This effect is surprising at first sight, because the shear component itself does not lead to an exponential polymer growth, and cannot therefore lead to algebraic tails of the polymer size distribution.

The plan of this paper is as follows. We first detail the model that is used to study the polymer dynamics and discuss its underlying assumptions and its validity. In the next sections, we first analyze the stationary angular distribution of strongly elongated polymers, and then obtain the probability distributions of the tum-

bling time. In Section 4, we analyze the size distribution of the polymer molecules below the coil–stretch transition. The main results in this paper are listed in the Conclusions.

2. POLYMERS AND THE CHAOTIC-FLOW MODEL

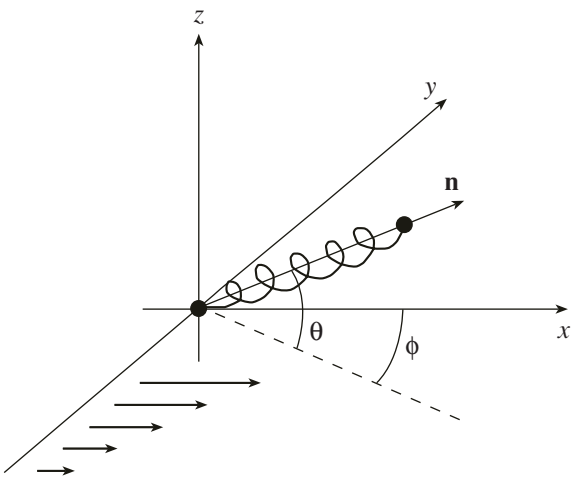
A polymer molecule injected into an external flow interacts with the fluid in two ways: it is advected as a whole, and the velocity gradient stretches and rotates it in different ways, thus affecting its internal dynamics. If we assume the shear flow to be stationary and spatially homogeneous, the advection of the polymer is not important. Furthermore, the inertial effects can be neglected for typical polymers, and we can assume that the monomers simply follow the Lagrangian trajectories of the velocity field. The effect of the flow can then be described in terms of the dynamic equation for the polymer end-to-end vector. We do not consider different conformations of a polymer here and instead use the simple dumb-bell model, where the end-to-end separation vector **R** satisfies the equation [25, 26]

$$\partial_t R_i = R_j \nabla_j v_i - \gamma(R) R_i + \zeta_i, \tag{1}$$

where the relaxation rate γ is a function of the absolute value R of **R** and the velocity gradient $\nabla_j v_i$ is taken at the molecule center of mass. The term ζ_i is the thermal Langevin force with the power κ. Real velocity fields are large-scale: their correlation length is much larger than the polymer length. Therefore, this field can be treated as smooth on the polymer size scale. This assumption justifies the linear approximation for the velocity field used in Eq. (1). We discuss two different situations. When the Lyapunov exponent associated with the velocity field is larger than the polymer relaxation rate, which corresponds to the state above the coil–stretch transition, the nonlinearity of the polymer becomes important, preventing an unbounded polymer stretching. In this case, the polymer length is much larger than in the coiled state, and thermal forces ζ_i can be neglected in comparison to the velocity gradient stretching. The polymer direction vector $\mathbf{n}_i = \mathbf{R}/R$ can then be introduced. Its dynamics are governed by the equation

$$\partial_t n_i = n_j(\delta_{ik} - n_i n_k)\nabla_j v_k. \tag{2}$$

We see that the direction evolution is completely decoupled from the dynamics of the polymer size R. In the state below the coil–stretch transition, the dynamics of the polymer are purely linear. Thermal forces cannot be neglected in this regime, and hence the orientation vector dynamics do not decouple from the evolution of the polymer size. We restrict our analysis in this case to the study of the polymer length distribution. For small enough polymer molecules, we can assume the relaxation $\gamma(R)$ to be constant, in which case Eq. (1) becomes linear and can be studied analytically in full detail.



Schematic picture of the polymer orientation geometry.

It is important to discuss how the chaotic velocity component is modeled. The statistical properties of the velocity field observed in the elastic turbulence experiments are not well known from either the experimental or the theoretical standpoint. The simplest model of the velocity field studied in this paper consists of a strong stationary shear component and of a weak short-correlated chaotic component σ_{ij}. Under these assumptions, the velocity gradient matrix has the following statistical properties:

$$\nabla_j v_i = s\delta_{ix}\delta_{jy} + \sigma_{ij}, \tag{3}$$

$$\begin{aligned}&\langle \sigma_{ij}(t)\sigma_{kl}(t')\rangle \\ &= D\delta(t-t')(4\delta_{ik}\delta_{jl} - \delta_{il}\delta_{kj} - \delta_{ij}\delta_{kl}),\end{aligned} \tag{4}$$

where D is the "power" of the chaotic component and s is the shear rate. We assume that the shear flow gradients are in the xy plane. We also assume the shear component to be relatively strong, $s \gg D$. The exact form of correlation function (4) assumes the isotropy of the velocity component, but this assumption is not important, as we see in what follows, because for a strong shear component $s \gg D$, the polymer spends most of the time stretched in the x direction. Its angular dynamics are determined only by the y component of the chaotic velocity field.

To simplify the equations describing the polymer direction evolution, we parameterize the vector n by the angles as shown in the figure. Then Eq. (2) acquires the form

$$\partial_t \phi = -s\sin^2\phi + \xi_\phi, \tag{5}$$

$$\partial_t \theta = -s\sin\phi\cos\phi\sin\theta\cos\theta + \xi_\theta, \tag{6}$$

where ξ_ϕ and ξ_θ are zero-mean random variables related to the chaotic components of the velocity gradient. The

statistics of both ξ_ϕ and ξ_θ can be obtained from correlation function (4):

$$\langle \xi_\theta(t)\xi_\theta(t')\rangle = 4D\delta(t-t'), \quad (7)$$

$$\langle \xi_\phi(t)\xi_\phi(t')\rangle = \frac{4D}{\cos^2\theta}\delta(t-t'). \quad (8)$$

3. POLYMER DIRECTION STATISTICS

3.1. φ-Angle Distribution

In this section, we study the stationary distribution of polymer orientation angles. Equation (2) governing the dynamics of the polymer orientation vector formally coincides with the equation describing the dynamics of thin rigid rods. Some of the results described in this section can be found in [21]. Unlike polymer molecules, these thin rods have a fixed size and are driven solely by thermal forces. However, their dynamics are similar to the dynamics analyzed in this paper. In what follows, we first rederive the expression for the stationary ϕ-angle distribution and then present several new results, which have not been discussed in the literature to our knowledge. We first analyze the nontrivial contribution to the θ-angle distribution that comes from the stochastic dynamics and that can be observed in real experiments by inspecting the polymers in the stochastic region. This contribution also has an algebraic tail, but its exponent is nonuniversal and depends on the statistics of the random velocity field. For a Gaussian delta-correlated field, numerical analysis showed that this tail behaves as θ^{-3} [17] and therefore its contribution is subleading. Second, we study the statistical properties of the tumbling time. Obviously, the distribution of such quantities cannot be calculated from stationary angular distributions. But it can be easily measured experimentally [5, 18] or studied numerically [16, 17]. We obtain some rigorous results concerning the tumbling time distribution, which perfectly confirm the qualitative predictions in [20].

As noted above, the angular dynamics of stretched polymers are decoupled from the dynamics of the polymer length and can therefore be analyzed separately. There are two different terms in the right-hand side of Eq. (5) that contribute to the polymer orientation dynamics. In the limit $s \gg D$, the first term is relatively large, but the effect of the second term cannot be neglected, as we see in what follows. For the vanishing chaotic component ($D \longrightarrow 0$), the deterministic polymer dynamics can easily be analyzed: there are two semistable equilibrium states $\phi_{1,2} = 0, \pi$, with $\theta_{1,2} = 0$, and the polymer direction vector **n** asymptotically approaches one of these points depending on its initial orientation. However, as the angle between the polymer and the equilibrium directions becomes sufficiently small, the chaotic components ξ_k cannot be neglected and the polymer dynamics become stochastic. After some time, the chaotic component pushes the polymer into an unstable region, and the regular velocity rapidly (on times of the order of s^{-1}) transfers it to the opposite equilibrium direction. Due to the stochastic nature of the chaotic velocity component, random aperiodic tumbling of the polymer should be observed. This phenomenon was qualitatively analyzed in [20] for the general velocity statistics. In this paper, we focus on the situation where the chaotic flow is short-correlated, such that its characteristic correlation time τ_v is small compared with the time scale τ_t associated with the tumbling effect, which can be estimated as $\tau_t = (Ds^2)^{-1/3} \gg s^{-1}$. This time scale separation allows obtaining some explicit expressions for the stationary and dynamical statistics of the polymer orientation evolution.

In the case where $D \ll s$, the polymer spends most of the time in the stochastic regime, close to the equilibrium point, and hence its orientation angles are small, $\theta, \phi \ll 1$ (we analyze only one equilibrium point, because of the symmetry $\mathbf{n} \longrightarrow -\mathbf{n}$). In this case, we can set $\theta = 0$ in correlation function (8). The dynamics of angle ϕ become decoupled from everything else, and we can write the corresponding Fokker–Planck equation

$$[\partial_t - s\partial_\phi \sin^2\phi - 2D\partial_\phi^2]P(t,\phi) = 0, \quad (9)$$

where P is the PDF of the ϕ angle, i.e., the function that represents the probability of finding the polymer in a state with the inplane angle equal to the value of ϕ. We use the usual normalization conditions for the PDF:

$$\int_0^\pi d\phi P = 1.$$

An important question that must be discussed here is the boundary conditions to be used for this equation. The equation is invariant under the transformations $\phi \longrightarrow \phi \pm \pi$. It is therefore natural to use the periodic boundary conditions $P(t, -\pi/2) = P(t, \pi/2)$. There then exists an asymptotic stationary solution $P_{st}(\phi)$ of Eq. (9). Obviously, all angles differing by an integer multiple of π are identical to each other in this solution. Another possibility is to use nonperiodic boundary conditions

$$\mathcal{P}(t,\infty) = \mathcal{P}(t,-\infty) = 0$$

with the normalization condition

$$\int_{-\infty}^{\infty} d\phi \mathcal{P} = 1.$$

In this case, the angles ϕ and $\phi + \pi k$ are not equivalent and the absolute value of the angle contains the information about the total number of polymer rotations. The main disadvantage of working with these boundary conditions is that there is no stationary solution of the Fokker–Planck equation, because the PDF is widening and drifting constantly. However, both

approaches lead to the same physical results, the two different PDFs being related by

$$P(t, \phi) = \sum_k \mathcal{P}(t, \phi + \pi k). \quad (10)$$

In this section, we work with the periodic boundary condition. To find the stationary PDF $P_{st}(\phi)$, we rewrite the Fokker–Planck equation as

$$\partial_\phi U^{-1}(\phi)\partial_\phi U(\phi) P_{st}(\phi) = 0, \quad (11)$$

$$U(\phi) = \exp\left[\frac{s}{4D}\phi - \frac{s}{8D}\sin 2\phi\right]. \quad (12)$$

Simple integration yields

$$P_{st}(\phi) = \frac{\omega}{D}\int_0^\pi d\varphi \exp\left\{-\frac{s}{4D}[\varphi - \sin\varphi\cos(\varphi - 2\phi)]\right\}, \quad (13)$$

where ω is the average rotation frequency of the polymer, which is determined from the normalization condition

$$\int_0^\pi P_{st}(\phi) d\phi = 1$$

and is given by

$$\omega = \frac{D\exp(\pi s/8D)}{\pi^2 I_{ix}(s/8D) I_{-ix}(s/8D)}, \quad (14)$$

where I_{ix} and I_{-ix} are the modified Bessel functions. For $s/D \gg 1$, the PDF is localized at small angles $\phi \sim (D/s)^{1/3} \ll 1$, and all expressions are significantly simplified:

$$\omega = \frac{(Ds^2)^{1/3}}{4\cdot 3^{1/6}\Gamma(7/6)\sqrt{\pi}}, \quad (15)$$

$$P_{st}(\phi) = \frac{\omega}{D}\int_0^\infty d\varphi \exp\left[-\frac{s}{8D}\varphi(\varphi - 2\phi)^2 - \frac{s\varphi^3}{24D}\right]. \quad (16)$$

We see that the PDF is asymmetric in ϕ, i.e., $P(-\phi) < P(\phi)$, which means that the polymer spends more time above the shear axis. In addition, the PDF has algebraic tails $P(\phi) \propto \phi^{-2}$, $(D/s)^{1/3} \ll \phi \ll 1$, which correspond to very large fluctuations of the angle:

$$\langle\phi\rangle = \left(\frac{D}{s}\right)^{1/3}\frac{\sqrt{\pi}3^{1/3}}{\Gamma(1/6)}, \quad (17)$$

$$P_{st}(\phi) \sim \frac{1}{16\cdot 3^{1/6}\Gamma(7/6)\sqrt{\pi}}\left(\frac{s}{D}\right)^{2/3}\frac{1}{\phi^2}, \quad (18)$$

where $\Gamma(z)$ is the gamma function and the last asymptotic formula is valid in the intermediate region $(D/s)^{1/3} \ll |\phi| \ll 1$. The asymptotic behavior $P_{st} \propto \phi^{-2}$ corresponds to a nonzero probability flux of the stationary solution. Physically, this means that there is some preferred direction of the polymer rotation, which is a manifestation of the tumbling effect described above. The positive value of the average angle ϕ shows that the polymer spends most of the time in the region $\phi > 0$, in agreement with the general analysis presented at the beginning of this section. It can be seen that the polymer spends most of the time in the region of small angles, and hence the only relevant velocity component is v_z. Therefore, the assumption of isotropic statistics of the chaotic velocity component is not significant for the qualitative results in this paper.

3.2. Tumbling Time Statistics

In this section, we calculate the PDF of the time intervals between consequent tumblings. Such a PDF can be directly measured experimentally. For this, it is natural to use the nonstationary PDF $\mathcal{P}(t, \phi)$. We define the tumbling process by a polymer direction "trajectory" starting at $\phi = \pi/2$ and reaching $\phi = -\pi/2$ at time T. In this case, the probability of finding the polymer inside this region is given by

$$p(t) = \int_{-\pi/2}^{\pi/2} \mathcal{P}(t, \phi) d\phi, \quad (19)$$

where the initial condition is $\mathcal{P}(t, \phi) = \delta(\phi - \pi/2 + 0)$, and hence $p(0) = 1$. The normalization condition for this PDF is $\int_{-\infty}^{\infty} d\phi\, \mathcal{P}(t, \phi) = 1$. We substitute $\mathcal{P}(t, \phi) = U^{1/2}(\phi)\Psi(t, \phi)$, where U is defined in Eq. (12). The evolution of Ψ is determined by the one-dimensional Schrödinger equation in imaginary time:

$$\partial_t \Psi = -\hat{H}\Psi, \quad (20)$$

$$\hat{H} = -2D\partial_\phi^2 + \frac{s^2}{8D}\sin^4\phi - s\sin\phi\cos\phi. \quad (21)$$

It is now possible to use the quantum mechanical analogy. The Hamiltonian $\hat{H}$ formally describes a particle in a periodic potential with period π. The general solution of this problem is given by

$$\Psi(t, \phi) = \sum_n \int dp \Psi_{np}(\phi)\Psi^*_{np}\left(\frac{\pi}{2}\right) \times \exp[-E_n(p)t], \quad (22)$$

where p is the particle quasimomentum and n is the Brillouin zone number. In this potential, the classical minima are separated by large barriers. For $s \gg D$, the tight-binding method can be used (see, e.g., [27]). Then the approximate relations

$$E_n(p) = \epsilon_n - \nu\cos(\pi p), \quad (23)$$

$$\Psi_{np}(\phi) = \sum_k \exp(i\pi kp)\psi_n(\phi - k\pi), \qquad (24)$$

where ψ_n and ϵ_n are the wave functions and energies, hold for the spectrum near classical minima (when the tunneling processes are neglected) and ν is an exponentially small bandwidth. Therefore, at large times, the leading asymptotic form of $p(t)$ is determined by the ground state energy ϵ_0:

$$p(t) \propto \exp(-\epsilon_0 t), \quad t \longrightarrow \infty. \qquad (25)$$

It is easy to verify that this energy is given by $\epsilon_0 = c(Ds^2)^{1/3}$, where c is a constant on the order of unity. Indeed, the classical minimum is situated in the region of small angles $|\phi| \ll 1$, and we can therefore use the Taylor expansion of trigonometric functions. After the substitution $\phi = (D/s)^{1/3}\eta$, we obtain the Hamiltonian

$$\hat{H} = (Ds^2)^{1/3}\left[-2\partial_\eta^2 + \frac{\eta^4}{8} - \eta\right]. \qquad (26)$$

The operator in square brackets contains no dimensionless parameters, and therefore its eigenvalues are on the order of unity. The body of the PDF is also located in the region of tumbling periods of the order of $T \sim (Ds^2)^{-1/3}$. The left tail of the tumbling time PDF, $T \ll (Ds^2)^{-1/3}$, is determined by rare trajectories, which turn the polymer through angle π at small times T. To find the optimal form of such trajectories, we use the functional integral representation of the transition probability:

$$p(T) \propto \int \mathcal{D}\phi \exp\left[-\frac{1}{8D}\int dt(\dot{\phi} + s\sin^2\phi)^2\right]. \qquad (27)$$

The integration is performed over trajectories with the boundary conditions $\phi(0) = \pi/2$, $\phi(T) = -\pi/2$. For small $T \ll (Ds^2)^{-1/3}$, the probability is determined by the action A on the optimal trajectory with exponential accuracy, $p(T) \propto \exp(-A)$.

Variation of the effective action leads to the following equation for the saddle-point trajectory:

$$\ddot{\phi} = s^2\sin^3\phi\cos\phi. \qquad (28)$$

This mechanical problem can easily be solved, yielding the following relation between the tumbling time and the effective particle energy:

$$T = \int_{-\pi/2}^{\pi/2} \frac{d\phi}{\sqrt{2E + s^2\sin^4\phi}} = \left[\frac{8}{E(2E+s^2)}\right]^{1/4} K\left(\frac{1}{2} - \sqrt{\frac{E}{4E+2s^2}}\right), \qquad (29)$$

where $K(x)$ is the elliptical integral of the first kind. The action is then evaluated as

$$A = \frac{ET}{4D} + \frac{s^2}{4D}\int d\phi \frac{\sin^4\phi}{\sqrt{2E + s^2\sin^4\phi}} = \frac{ET}{4D} + \frac{3\pi s^2}{32D\sqrt{2E}}{}_3F_2\left(\frac{1}{2}, \frac{5}{4}, \frac{7}{4}; \frac{3}{2}, 2; -\frac{s^2}{2E}\right), \qquad (30)$$

where we omit the constant term $2s\int\dot{\phi}\sin^2\phi dt = \pi s/8D$ because it is cancelled by the normalization constant. Because of the additional time scale s^{-1}, there are two different asymptotic branches of $p(t)$. For $sT \ll 1$, we have $s \ll \sqrt{2E}$ and $E = \pi^2/2T^2$. In this case,

$$A = \frac{\pi^2}{8DT}. \qquad (31)$$

In the other limit case, $s^{-1} \ll T \ll (Ds^2)^{-1/3}$, the energy is given by $E = 8K^4(1/2)/s^2T^4$ and the action is given by

$$A = \frac{2K^4(1/2)}{3Ds^2T^3}. \qquad (32)$$

The intermediate asymptotic form in (32) is determined by the dynamics in the region of small angles and is therefore a function of the product Ds^2T^3. The dynamics at these angles are determined mainly by the component v_y, and hence this asymptotic form is universal, in the sense that it is independent of the details of the chaotic velocity statistics. On the contrary, the asymptotic form (31) at small times does not depend on s at all, because such small times can be reached only due to very rare fluctuations of the chaotic velocity field. Therefore, this asymptotic form strongly depends on the assumption of isotropic velocity statistics and is not universal.

3.3. θ-Angle Distribution

It was shown in [20] that there are two contributions to the intermediate right tail of the θ-angle distribution, $(D/s)^{1/3} \ll \theta \ll 1$. The first comes from the deterministic regions where $\phi \sim 1$ and the angular dynamics are determined by the regular terms in Eqs. (5) and (6). The algebraic tail of the stationary PDF $P(\theta)$ is then proportional to θ^{-2} at $\theta \ll 1$. But there is also a nonuniversal algebraic part, which comes from the stochastic region of $\phi \sim (D/s)^{1/3}$ and is determined by statistical properties of the random velocity field. In this section, we analyze

this part and obtain a relation between the scaling exponent and the entropy function of the random velocity process. In the region $\theta \ll 1$, Eq. (6) can be easily solved:

$$\theta(t) = \int_0^\infty d\tau \times \exp\left(-\frac{s}{2}\int_{t-\tau}^{t} \sin 2\phi(t')dt'\right)\xi_\theta(t-\tau). \quad (33)$$

As we have seen, the random process $\phi(t)$ is stationary and independent of $\xi_\theta(t)$. This allows us to rewrite the expression for θ as

$$\theta = \int_0^\infty d\tau e^{-\varrho(\tau)}\xi_\theta(\tau), \quad (34)$$

$$\varrho(\tau) = \frac{s}{2}\int_0^\tau \sin 2\phi(t)dt. \quad (35)$$

To obtain the PDF $P(\theta)$, we first average over the noise ξ_θ:

$$P(\theta|\varrho) = \frac{1}{\sqrt{2\pi A}}\exp\left(-\frac{\theta^2}{2A}\right), \quad (36)$$

$$A = 4D\int_0^\infty d\tau \exp[-2\varrho(\tau)], \quad (37)$$

where $P(\theta|\varrho)$ is the PDF of θ for a fixed realization of the process $\varrho(t)$. Because of the positive average value $\langle\dot{\varrho}\rangle \sim (Ds^2)^{1/3}$, the dynamics are relaxational and the body of $P(\theta)$ is located in the region of small angles $\theta \sim (D/s)^{1/3} \ll 1$. The tails of the PDF are determined by large deviations of negative $\varrho(t)$. Assuming that the process $\varrho(t)$ reaches its most negative value at an instant τ^* such that $\varrho(\tau^*) = -\varrho^*$ and $\varrho^* \gg 1$, we can estimate the value of A with exponential accuracy as $A \sim (D/s)^{1/3}\exp(2\varrho^*)$.

The characteristic correlation time of $\varrho(t)$ is $\tau_c = (Ds^2)^{-1/3}$. Therefore, for large $\tau^* \gg \tau_c$, we can apply the results of the theory of large deviations [28], which predict the scaling for the tails of the ϱ^* PDF as

$$P(\varrho^*|\tau^*) = \exp\left[-\frac{\tau^*}{\tau_c}S\left(\frac{\varrho\tau_c}{\tau^*}\right)\right], \quad (38)$$

where $S(x)$ is the entropy function, which is one of the most important characteristic of the chaotic velocity. This function is nonuniversal and strongly depends on the statistical properties of velocity gradients. It is impossible to find the exact expression for this function analytically even in the framework of our model. Numerical computations of this entropy function were recently presented in [17].

We can now find the most probable time τ^* by maximizing the above probability with respect to τ^*. This leads to the expression $\tau^* = \tau_c\varrho^*/x^*$, where x^* is found from the equation

$$S(x^*) = x^*S'(x^*), \quad (39)$$

where S' is the derivative of $S(x)$ with respect to x. The entropy function is of the order of unity, and we can hence expect the same for x^*. The asymptotic form of the ϱ^* PDF is therefore given by

$$P(\varrho^*) \propto \exp[-\varrho^*S'(x^*)]. \quad (40)$$

After averaging Eq. (36) over ϱ^*, we obtain the asymptotic expression for the θ PDF:

$$P(\theta) \propto |\theta|^{-S'(x^*)}, \quad (D/s)^{1/3} \ll |\theta| \ll 1. \quad (41)$$

It follows that the tails are algebraic, as in the case of the angle ϕ, but the exponent is now nonuniversal and depends on the statistical properties of the velocity field. For the delta-correlated Gaussian process ξ_ϕ, this tail was found numerically in [17]. It was shown there that in the stochastic region $|\phi| \ll 1$, the θ-angle PDF behaves as $\theta^{-3.0}$. In our model, this contribution is small compared to the tail from the regular region θ^{-2}, but it can be expected that the situation may be different for some specific velocity statistics.

4. STATISTICS OF POLYMER ELONGATION

In this section, we study the polymer molecules placed in a relatively weak flow, where the Lyapunov exponent of the flow is smaller than the relaxation time of the polymer. In this case, the polymer spends most of the time in the coiled phase, and we can assume its relaxation force to be linear. Thermal noise can be neglected in this case, in contrast to the situation above the coil–stretch transition discussed in the previous sections. We study only the size distribution of the polymer for this situation. The tails of the polymer-size PDF can be examined similarly to the analysis in Section 3.3.

The formal solution of dynamic Eq. (1) in the case of a linear relaxation force is given by

$$R_i(t) = \int_0^\infty dt \exp[-\gamma(t-t')]W_{ij}(t,t')\zeta_j(t'), \quad (42)$$

$$W = T\exp\left[\int_{t'}^{t}\tilde{\sigma}(\tau)d\tau\right], \quad (43)$$

where $\tilde{\sigma}_{ij} = \nabla_j v_i$ is the velocity gradient matrix. To obtain the polymer elongation PDF, we first average over the thermal Langevin force $\xi_i(t)$:

$$P(\mathbf{R}|\tilde{\sigma}) \propto \exp\left[-\frac{1}{2}\mathbf{R}^T I^{-1}\mathbf{R}\right], \quad (44)$$

$$I = \kappa\int_0^\infty dt' W^T(t')W(t)e^{-2\gamma t}, \quad (45)$$

where $W(t) = W(t, 0)$ and $P(\mathbf{R}|\tilde{\sigma})$ stands for the PDF with a fixed realization of the process $\tilde{\sigma}(t)$. At large enough times $t \gg \tau_c$, the eigenvalues of the matrix W^TW become widely separated and the absolute value of the end-to-end vector $\mathbf{R}$ is determined by the largest eigenvalue I_1:

$$P(R|\tilde{\sigma}) \propto \exp\left(-\frac{R^2}{2I_1}\right). \quad (46)$$

It can be easily shown (see, e.g., [29]) that for large times, when the eigenvalues λ_i of the matrix W^TW are widely separated ($\lambda_1 \gg \lambda_2 \gg \lambda_3$), the dynamics of the largest eigenvalue $\lambda_1 = \exp(2\rho)$ are described by the equation

$$\dot{\rho} = \frac{s}{2}\cos^2\theta\sin 2\phi + 6D + \xi_p, \quad (47)$$

$$\langle \xi_\rho(t)\xi_\rho(t')\rangle = 2D\delta(t-t'), \quad (48)$$

where ξ_ρ is obtained from the chaotic velocity correlation function (4). The eigenvalue I_1 is then given by the expression

$$I_1 = \kappa\int_0^\infty dt \exp[2\rho(t) - 2\gamma t]. \quad (49)$$

As in the previous section, $\rho(t)$ is an integral of the stationary random process with the correlation time of the order of $\tau_c = (Ds^2)^{-1/3}$, and large deviations of I_1 are determined by large deviations of $\rho(t)$. Assuming that integral (49) is determined by one saddle point τ^*, we can estimate it as $I_1 \propto \exp(2\rho^* - 2\gamma\tau^*)$, where $\rho^* = \rho(\tau^*)$. The asymptotic behavior of the ρ^* PDF for a fixed value of τ^* is given by

$$P(\rho^*|\tau^*) \propto \exp\left[-\frac{\tau^*}{\tau_c}S_\rho\left(\frac{\rho^*\tau_c}{\tau^*}\right)\right], \quad (50)$$

where $S_\rho(x)$ is an entropy function corresponding to the process $\rho(\tau)$.

Exactly as in the previous section, we find the optimum value $\tau^* = \tau_c\rho^*/x$. The coefficient x satisfies the equation

$$S_\rho(x) - xS'_\rho(x) + \gamma\tau_c S'_\rho(x). \quad (51)$$

In the linear region below the coil–stretch transition, we have $\gamma\tau_c > 1$. The tail of the PDF is algebraic, as in case of the θ angle, $P(R) \propto R^{-1-\alpha}$, and the value of a can be determined for large values of $\gamma\tau_c \gg 1$. Large deviations of R are determined by the region where thermal Langevin forces can be neglected and Eq. (47) can be used.

We are interested in the asymptotic behavior of the polymer size moments

$$M_q(t) = \langle R^q(t)\rangle \propto \exp(A_q t).$$

The value of α is then determined from the equation $A_\alpha = 0$. Integrating over the function ξ_ρ, we can rewrite M_q as

$$M_q = \exp(Dq^2t - \gamma qt)\int d\phi Z_q(\phi, t), \quad (52)$$

$$Z_q = \langle \exp[q\rho(t)]\delta(\phi - \phi(t))\rangle, \quad (53)$$

where the angular brackets denote averaging over the process $\phi(t)$. The function Z_q satisfies the equation

$$\partial_t Z_q = \left[2D\partial_\phi^2 + s\partial_\phi\sin^2\phi + \frac{qs}{2}\sin 2\phi\right]Z_q. \quad (54)$$

The only difference from Fokker–Planck equation (9) is in the last term. We follow the same procedure as in Section 2.2. Substituting $Z_q = U(\phi)\Psi(t, \phi)$, we obtain the imaginary-time Schrödinger equation

$$\partial_t\Psi = -\hat{H}_q\Psi, \quad (55)$$

$$\hat{H}_q = -2D\partial_\phi^2 + \frac{s^2}{8D}\sin^4\phi + (q-1)s\sin\phi\cos\phi. \quad (56)$$

This equation cannot be explicitly solved in the case $q \sim 1$, but the solution can be easily found for $q \gg 1$.

In this case, the leading exponential asymptotic behavior at large times is given by $Z_q(t) \propto \exp[-\epsilon(q)t]$, where $\epsilon(q)$ is the ground-state energy. For $q \gg 1$, the main contribution to $\epsilon(q)$ is equal to the value of the classical minimum of the potential. After some simple algebra, we obtain

$$\epsilon(q) \sim -3\cdot 2^{-5/3}(q^4Ds^2)^{1/3}, \quad 1 \ll q \ll s/D, \quad (57)$$

$$\epsilon(q) \sim qs/2, \quad q \gg s/D. \quad (58)$$

Finally, we have

$$A(q) = Dq^2 - \gamma q - \epsilon(q), \quad (59)$$

and the critical value a depends on the dimensionless parameter γ/s:

$$\alpha = \begin{cases} \dfrac{81}{32}\dfrac{\gamma^3}{Ds^2}, & \gamma \ll s \\ \dfrac{\gamma}{D}, & \gamma \gg s. \end{cases} \quad (60)$$

The last expression coincides with the value of the exponent for a purely isotropic chaotic velocity, because for $\gamma \gg s$, large polymer-size fluctuations are determined by rare fluctuations of the chaotic component, when the flow has a strong elongation component with the Lyapunov exponent $\lambda > \gamma$ for a long time. On the other hand, the top line in (60) shows that in the case $\gamma \ll s$, the shear component can significantly broaden the tails of the polymer-size PDF compared to the chaotic flow without mean shear. This fact is nontrivial because the regular shear component itself cannot lead to an exponential polymer elongation and a nontrivial exponent comes from the combined effect of the chaotic and regular components.

5. CONCLUSIONS

We have studied the statistical properties of the dynamics of a single polymer molecule in a chaotic flow with mean shear. In the framework of the velocity flow model consisting of a stationary shear part and a delta-correlated chaotic part, and the dumb-bell model of a polymer molecule, we have obtained several analytically rigorous results. First, for strongly elongated polymers, the stationary angular distribution was discussed in detail. We obtained an explicit expression for a ϕ-angle probability distribution. The asymptotic behavior of this function formally coincides with the results obtained for solid rods [21]. Second, we analyzed the previously unreported contribution to the algebraic tail of the θ-angle PDF. In contrast to the universal tail coming from the regular region, which was analyzed in [20, 21], this tail is determined by the polymer dynamics in the stochastic region. In contrast to the θ-angle PDF, this asymptotic form is not universal and depends on the statistical properties of the chaotic velocity component. Next, we discussed the probability distribution of the tumbling time, i.e., the time between consequent polymer flips. We have shown that the characteristic time is of the same order as the inverse Lyapunov exponent associated with the flow. However, the fluctuations of the tumbling time are rather strong. The asymptotic tail corresponding to the large-time periods between flips has a universal exponential form, while the tail corresponding to quick flips has a far more complicated structure, which is in general sensitive to the velocity field statistics. We have also discussed the size distribution of linear polymers placed in a strong shear flow with a chaotic component. We have shown that the existence of the strong shear component results in significant broadening of the size distribution compared to the isotropic case considered in [6]. This effect is rather nontrivial in our opinion, because the shear component itself cannot lead to an exponential elongation of the polymer and the distribution broadening is the combined effect of the chaotic and regular velocity components. Finally, we mention that all the results in this paper were obtained under the assumption of an isotropic and short-correlated chaotic velocity flow. As was discussed throughout the paper, the first assumption is irrelevant for most of the results, but the effect of the finite correlation time requires a more sophisticated analysis. Comparison of our results with the more general results in [20] shows that the delta-correlated model reflects most of the qualitative features of the problem. Furthermore, all rigorous results obtained in its framework are in agreement with general predictions in [20].

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REFERENCES

1. B. A. Toms, in *Proceedings of the International Congress of Rheology, Holland, 1948* (North-Holland, Amsterdam, 1949), p. II-135.
2. J. L. Lumley, Annu. Rev. Fluid Mech. **1**, 367 (1969); J. Polym. Sci., Part D: Macromol. Rev. **7**, 263 (1973).
3. J. L. Lumley, Symp. Math. **9**, 315 (1972).
4. A. Groisman and V. Steinberg, Nature **405**, 53 (2000); Phys. Rev. Lett. **86**, 934 (2001).
5. A. Groisman and V. Steinberg, New J. Phys. **6**, 29 (2004).
6. E. Balkovsky, A. Fouxon, and V. Lebedev, Phys. Rev. Lett. **84**, 4765 (2000); Phys. Rev. E **64**, 056301 (2001).
7. M. Chertkov, Phys. Rev. Lett. **84**, 4761 (2000).
8. A. Fouxon and V. Lebedev, Phys. Fluids **15**, 2060 (2003).
9. P. G. de Gennes, J. Chem. Phys. **60**, 5030 (1974).
10. T. T. Perkins, D. E. Smith, and S. Chu, Science **276**, 2016 (1997).
11. D. E. Smith and S. Chu, Science **281**, 1335 (1998).
12. D. E. Smith, H. P. Babcock, and S. Chu, Science **283**, 1724 (1999).
13. J. S. Hur, E. Shaqfeh, H. P. Babcock, et al., J. Rheol. **45**, 421 (2001).
14. S. Gerashchenko, C. Chevallard, and V. Steinberg, Europhys. Lett. **71**, 221 (2005).
15. R. G. Larson, *The Structure and Rheology of Complex Fluids* (Oxford Univ. Press, Oxford, 1999).
16. A. Celani, A. Puliafito, and K. Turitsyn, Europhys. Lett. **70**, 439 (2005).
17. A. Puliafito and K. Turitsyn, Physica D (Amsterdam) **211**, 9 (2005).
18. R. E. Teixeira, H. P. Babcock, E. Shaqfeh, and S. Chu, Macromolecules **38**, 581 (2005).

19. J. S. Hur, E. Shaqfeh, and R. G. Larson, J. Rheol. **44**, 713 (2000).
20. M. Chertkov, I. Kolokolov, V. Lebedev, and K. Turitsyn, J. Fluid Mech. **531**, 251 (2005).
21. E. J. Hinch and L. G. Leal, J. Fluid Mech. **52**, 683 (1972).
22. G. K. Batchelor, J. Fluid Mech. **5**, 113 (1959).
23. R. H. Kraichnan, Phys. Fluids **10**, 1417 (1967); J. Fluid Mech. **47**, 525 (1971); J. Fluid Mech. **67**, 155 (1975).
24. G. Falkovich, C. Gawedzky, and M. Vergassola, Rev. Mod. Phys. **73**, 913 (2001).
25. E. J. Hinch, Phys. Fluids **20**, S22 (1977).
26. R. B. Bird, C. F. Curtiss, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids* (Wiley, New York, 1987).
27. A. A. Abrikosov, *Fundamentals of the Theory of Metals* (Nauka, Moscow, 1987; North-Holland, Amsterdam, 1988).
28. R. Ellis, *Entropy, Large Deviations, and Statistical Mechanics* (Springer, Berlin, 1985).
29. E. Balkovsky and A. Fouxon, Phys. Rev. E **60**, 4164 (1999).