

**Polymer stretching in laminar and random flows: Entropic characterization**Stefano Musacchio,<sup>1</sup> Victor Steinberg,<sup>2</sup> and Dario Vincenzi<sup>3</sup><sup>1</sup>*Dipartimento di Fisica and INFN, Università di Torino, Via P. Giuria 1, 10125 Torino, Italy*<sup>2</sup>*Department of Physics of Complex Systems, Weizmann Institute of Science, Rehovot 76100, Israel*<sup>3</sup>*Université Côte d'Azur, CNRS, LJAD, 06100 Nice, France*

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Polymers in nonuniform flows undergo strong deformation, which in the presence of persistent stretching can result in the coil-stretch transition. This phenomenon has been characterized by using the formalism of nonequilibrium statistical mechanics. In particular, the entropy of the polymer extension reaches a maximum at the transition. We extend the entropic characterization of the coil-stretch transition by studying the differential entropy of the polymer fractional extension in a set of laminar and random velocity fields that are benchmarks for the study of polymer stretching in flow. In the case of random velocity fields, a suitable description of the transition is obtained by considering the entropy of the logarithm of the extension instead of the entropy of the extension itself. Entropy emerges as an effective tool for capturing the coil-stretch transition and comparing its features in different flows.

DOI: [10.1103/PhysRevFluids.8.053301](https://doi.org/10.1103/PhysRevFluids.8.053301)**I. INTRODUCTION**

The configuration of a linear polymer in a moving fluid drastically changes from coiled to fully stretched when the Weissenberg number ( $Wi$ ), i.e., the product of the characteristic velocity gradient and the polymer relaxation time, exceeds a critical threshold. This phenomenon is known as the coil-stretch transition [1] and is observed in both laminar [2,3] and random flows [4–6], even though with partially different features in the two cases. In addition to the nature of the flow, the coil-stretch transition is influenced by whether the polymer is confined spatially or not [7], as well as by the solvent quality [8–10], the polymer concentration [11], and the occurrence of knots along the polymer [12]. Moreover, a coil-stretch transition has also been observed in ring polymers [13–15], entangled polymer melts [16–18], and elastic-sheets [19].

Characterizing the coil-stretch transition and accurately identifying the value of  $Wi$  at which it occurs is essential for predicting the viscoelastic properties of polymer solutions. For instance, phenomena such as turbulent drag reduction [20–22] and elastic turbulence [23–25] are observed only if the polymers get sufficiently stretched by the flow. In the case of linear polymers, several observables have been used to characterize the coil-stretch transition. A natural quantity is the steady-state distribution of polymer extensions [2–6], which changes dramatically near to the critical  $Wi$ : the mean increases rapidly, the coefficient of variation attains its maximum value, and the peak shifts from the equilibrium extension  $R_{eq}$  to the maximum length  $L$  (here  $R_{eq}$  is the polymer root mean square extension in the absence of flow). Another characterization considers the equilibration time of the statistics of polymer extension [26,27] or alternatively the autocorrelation time of the extension [28]. Near the coil-stretch transition these time scales are strongly amplified, and this causes a critical slowing down of the stretching dynamics.

The coil-stretch transition has also been studied using nonequilibrium thermodynamic concepts [29–35]. In particular, it has been shown that, in an extensional flow, the entropy of the polymer extension is maximum at the critical  $Wi$  [32]. This result has a clear interpretation in terms of

information, since the entropy quantifies the “randomness” of the extension within an ensemble of polymers. In the coiled and stretched states the information concerning the polymer elongation reaches a maximum because the distribution of polymer extensions is peaked around a single value ( $R_{\text{eq}}$  and  $L$ , respectively). These states are hence minima of entropy. Conversely, the broadening of the probability distribution of polymer elongations at the transition corresponds to a loss of information and therefore a maximum of entropy. Recently, Sultanov *et al.* [36] have extended this result to random flows by measuring the entropy of the extension of an ensemble of T4 DNA molecules of maximum length  $L = 71.7 \mu\text{m}$  and radius of gyration  $R_g = 1.5 \mu\text{m}$  in an elastic turbulence of von Kármán flow [23,37].

Here we pursue the entropic characterization of the coil-stretch transition by examining a set of analytical and numerical flows. The goal of our study is to show that since it concentrates information on the statistics of the extension in a single scalar quantity, entropy is as an effective tool for comparing polymer stretching in different flows.

## II. POLYMER MODEL AND FLOW CONFIGURATIONS

The polymer is modelled as a finitely extensible nonlinear elastic (FENE) dumbbell [38–40]. In the Appendix, we show that, for a bead-spring chain, the results only differ in minor quantitative details. The evolution equation for the polymer end-to-end vector  $\mathbf{R}$  is

$$\frac{d\mathbf{R}}{dt} = \boldsymbol{\kappa}(t) \cdot \mathbf{R} - f(R) \frac{\mathbf{R}}{2\tau} + \sqrt{\frac{R_0^2}{\tau}} \boldsymbol{\xi}(t), \quad (1)$$

where  $\kappa_{ij}(t) = \nabla_j u_i(t)$  is the velocity gradient at the center of mass of the polymer,  $\tau$  is the polymer longest relaxation time,  $R_0 = R_{\text{eq}}/\sqrt{3}$ ,  $f(R) = (1 - R^2/L^2)^{-1}$ , and  $\boldsymbol{\xi}(t)$  is three-dimensional white noise. Within this model, the radius of gyration is  $R_g = R_{\text{eq}}/2 = \frac{\sqrt{3}}{2}R_0$  and the extensibility parameter is defined as  $b = (L/R_0)^2$  [38]. The dumbbell model can in principle be refined to include effects such as hydrodynamic interactions or a conformation-dependent drag force [38,39]. Given that our work is focused on the entropic characterization of the coil-stretch transition, rather than on the properties of the dumbbell model itself, for the sake of simplicity we restrict to the basic version of the model, which in any case has proved useful for a qualitative, and sometimes even quantitative, understanding of the coil-stretch transition, in both steady [1–3,41] and random [21,42–44] flows.

Calculating the entropy requires obtaining the stationary probability density function (PDF) of the extension,  $P(R)$ , from Eq. (1), analytically or numerically. We shall consider the following set of model flows, which have been widely employed in the study of polymer stretching and are representative of more complex situations. For each of these flows, the main results on the statistics of the extension are recalled below.

### A. Extensional flow

The uniaxial extensional flow  $\mathbf{u} = \gamma(-x/2, -y/2, z)$  is the first configuration in which the coil-stretch transition has been predicted [1] and observed experimentally [2]. It consists of a direction of pure stretching and two directions of compression with magnitudes that ensure incompressibility. The Weissenberg number is defined as  $\text{Wi} = \gamma\tau$  and its critical value is  $\text{Wi}_{\text{cr}} = 1/2$ . If the rescaled end-to-end vector  $\boldsymbol{\rho} = \mathbf{R}/L$  is expressed in spherical coordinates as  $\boldsymbol{\rho} = \rho(\sin\theta \cos\phi, \sin\theta \sin\phi, \cos\theta)$ , then the stationary PDF of  $\boldsymbol{\rho}$  is

$$P(\boldsymbol{\rho}) \propto (1 - \rho^2)^{b/2} \exp\left\{\frac{b\text{Wi}}{2}\rho^2[3\cos^2(\theta) - 1]\right\}, \quad (2)$$

where  $b = (L/R_0)^2$  is the extensibility parameter [38]. An integration over the angular variables yields

$$P(\rho) = 2\pi \rho^2 \int_0^\pi P(\rho) \sin \theta d\theta \propto \rho e^{-\frac{bWi}{2}\rho^2} (1 - \rho^2)^{b/2} \operatorname{erf} \left( i \sqrt{\frac{3bWi}{2}} \rho \right), \quad (3)$$

where erf is the error function.

### B. Shear flow

In a linear shear flow  $\mathbf{u} = (\sigma y, 0, 0)$ , the coil-stretch transition is not observed [45]. Owing to thermal fluctuations, the dynamics of the polymer indeed consists of a sequence of tumbling events which in turn correspond to as many coiling and stretching events, so that persistent stretching is never realized [46–48]. Nevertheless, it will be instructive to study the entropy of polymer extension also in this configuration and compare its behavior with that observed in other flows. The Weissenberg number is  $Wi = \sigma \tau$ , and the PDF of  $\rho$  is now calculated numerically by means of Brownian Dynamics simulations of Eq. (1), where the nonlinearity of the elastic force is resolved by using Öttinger's rejection algorithm [49].

### C. Batchelor-Kraichnan (BK) flow

In random flows, it is convenient to define the Weissenberg number as  $Wi = \lambda \tau$ , where  $\lambda$  is the Lyapunov exponent of the flow, i.e., the average stretching rate of line elements. A general theory of the coil-stretch transition in random flows has been developed by Balkovsky *et al.* [43] for linear polymer elasticity (Oldroyd-B model) and by Chertkov [44] for nonlinear polymer elasticity (FENE model). For intermediate extensions  $1/\sqrt{b} \ll \rho \ll 1$ , the PDF of  $\rho$  behaves as  $\rho^{-1-\alpha}$  with  $\alpha$  decreasing as a function of  $Wi$  and crossing zero at  $Wi = 1/2$ . Therefore, in the limit  $L \rightarrow \infty$  the PDF of  $\rho$  is not normalizable if  $Wi \geq 1/2$ . This is interpreted as an indication that the coil-stretch transition also exists in random flows and the critical  $Wi$  is again  $Wi_{cr} = 1/2$ . For finite  $L$ , the measured slope may be affected by the nonlinearity of the elastic force, but the theory still implies an analogous strong modification of  $P(R)$  at  $Wi_c$  [44].

The BK flow has been used extensively in the analytical study of turbulent transport below the viscous-dissipation scale (see Ref. [50] and, for applications to polymer dynamics, Ref. [51] and references therein). The velocity gradient is an isotropic tensorial white noise with correlation  $\langle \kappa_{ij}(t) \kappa_{kl}(t') \rangle = \lambda \delta(t - t') (4\delta_{ik}\delta_{jl} - \delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk})/3$ , where  $i, j = 1, 2, 3$ . The properties of this stochastic flow allow an exact calculation of  $P(\rho)$  (see Refs. [44,52]):

$$P(\rho) = c \rho^2 \left( 1 + \frac{2bWi}{3} \rho^2 \right)^{-\beta} (1 - \rho^2)^\beta, \quad (4)$$

with  $Wi = \lambda \tau$ ,  $\beta^{-1} = 2(b^{-1} + 2Wi/3)$ , and

$$c^{-1} = \frac{\sqrt{\pi} \Gamma(\beta + 1)}{4\Gamma(5/2 + \beta)} {}_2F_1(3/2, \beta; 3/2 + \beta + 1; -2bWi/3). \quad (5)$$

Here  $\Gamma$  and  ${}_2F_1$  denote the Gamma and hypergeometric functions, respectively. In this case, the exponent of the power-law region of the PDF is  $\alpha = 2\beta - 3 \approx -3(1 - 1/2Wi)$  for  $b \gg 1$ .

### D. Isotropic turbulence

Although useful for a qualitative study of the coil-stretch transition, the BK flow is Gaussian and has zero correlation time. It therefore cannot capture all features of a fully turbulent flow. Thus, we also consider polymers in homogeneous isotropic turbulence. To this end, we use a database of Lagrangian trajectories from a direct numerical simulation (DNS) of the three-dimensional incompressible Navier-Stokes equations [53,54]. These were solved by means of a standard, fully

dealiased pseudospectral method on a cubic domain of size  $2\pi$  with  $512^3$  collocation points and periodic boundary conditions. The flow was driven to a stationary state by an external force that maintained a constant energy injection rate. The choice of the kinematic viscosity and the energy injection rate yielded a Taylor-microscale Reynolds number  $R_\lambda = 111$ . The velocity gradient  $\kappa(t)$  was calculated along a large number of fluid trajectories by using a bilinear interpolation algorithm. Here we use this database of time series of  $\kappa(t)$  to solve Eq. (1) for an ensemble of  $10^4$  polymers. Since attention is restricted to single polymer dynamics, the polymer feedback on the flow is disregarded. Equation (1) is again solved by using Öttinger's rejection algorithm [49]. The values of the parameters of the dumbbell model in the DNS are  $R_0 = 1$  and  $L = 18$ . The extensibility parameter is  $b = (L/R_0)^2 = 18^2$ . The effect of thermal noise on the position of the center of mass is disregarded, since thermal fluctuations are negligible compared to the fluctuations of the turbulent velocity field. The Weissenberg number is again defined in terms of the Lyapunov exponent. In the present simulation  $\lambda \approx 0.136\tau_K$ , where  $\tau_K$  is the Kolmogorov dissipation time scale, in accordance with previous estimates in isotropic turbulence [55,56]. Numerical simulations of isotropic turbulence [28,57] have shown that  $P(\rho)$  behaves as a power of  $\rho$  for  $1/\sqrt{b} \ll \rho \ll 1$ , as predicted by Balkovksy *et al.* [43].

### III. DIFFERENTIAL ENTROPY

Recent studies [32,36] have shown that the  $P(R)$  broadens at the transition from the coiled to the stretched state. The broadening of  $P(R)$  can be interpreted as a loss of information concerning the polymer elongation, which can be quantified in terms of the Shannon entropy. The results of Refs. [32,36] confirm that the Shannon entropy attains a maximum at the Weissenberg number corresponding to the transition.

The definition of the information entropy in the case of polymers requires some care, because the elongation  $R$  is a dimensioned and continuous variable. The extension of the discrete information entropy to a continuous random variable  $x \in \mathbb{R}$  has been originally proposed by Shannon, which introduced the concept of *differential* entropy:

$$S_x = - \int P(x) \log[P(x)] dx, \quad (6)$$

where  $P(x)$  is the steady-state probability density function of the variable  $x$ . Unlike the discrete entropy, the differential entropy has some drawbacks. It can be negative [because  $P(x)$  can assume values larger than 1], and it is not invariant under a change of variable. Considering a transformation  $y = g(x)$ , the corresponding entropies are related via  $S_y \leq S_x + \int P(x) \log \left| \frac{\partial g}{\partial x} \right| dx$ , where  $\left| \frac{\partial g}{\partial x} \right|$  is the Jacobian of the transformation  $g$  and the equality holds if the transform is a bijection. A further problem arises if  $x$  is a dimensioned variable, as in the case of the polymer elongation. In this case,  $P(x)$  has the dimension of  $[1/x]$  and therefore the definition of  $\log[P(x)]$  is inappropriate.

Jaynes proposed to fix these issues by introducing the concept of *relative* entropy in terms of the limiting density of discrete points [58]. The relative entropy is defined as the negative Kullback-Leibler divergence [59] from the distribution  $P$  to the reference invariant measure  $M$ :

$$H_x = -D_{\text{KL}}(P||M) = - \int P(x) \log \left[ \frac{P(x)}{M(x)} \right] dx. \quad (7)$$

An alternative approach consists in nondimensionalizing the argument of the logarithm with a characteristic scale  $\Delta$  homogeneous to  $x$ :

$$S_x^\Delta = - \int P(x) \log[P(x)\Delta] dx. \quad (8)$$

The modified entropy  $S_x^\Delta$  is related to the Shannon differential entropy via  $S_x^\Delta = S_x - \log \Delta$ . Recalling that  $P(x)\Delta = P(x/\Delta)$ , the modified entropy is equivalent to the differential entropy of the dimensionless quantity  $x/\Delta$ , that is,  $S_x^\Delta = S_{x/\Delta}$ .

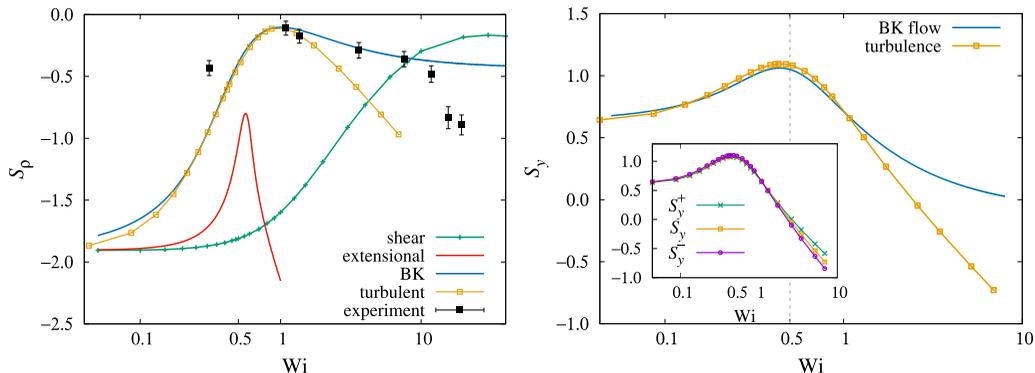


FIG. 1. Left: Entropy of  $\rho$  vs  $Wi$  for different flows. In all cases (except for the experimental data) the extensibility parameter is set to  $b = 18^2$ . The experimental data have been translated vertically by  $\Delta S_\rho = 0.33$ , which corresponds to a fit to a dumbbell with  $b \approx 30^2$ . Right: Entropy of  $y = \ln \rho$  for the BK and turbulent flows and for the same parameters as in the left panel. The inset shows  $S_y$  together with the entropies  $S_y^-$  and  $S_y^+$  associated with the PDFs of  $y$  conditional on  $Q < 0$  and  $Q > 0$ , respectively.

For the specific case of the polymer end-to-end distance  $R$ , we propose here to use the differential entropy of the rescaled polymer elongation  $\rho = |\mathbf{R}|/L$ , defined as

$$S_\rho = - \int_0^1 P(\rho) \ln[P(\rho)] d\rho. \quad (9)$$

Here and in the following we use the natural logarithm in the definition of the entropy. The variable  $\rho$  assumes values in the interval  $(0,1)$  and its PDF is normalized as follows:  $\int_0^1 P(\rho) d\rho = 1$ . The differential entropy (9) is equivalent to the relative entropy (7) with respect to the uniform measure  $M(\rho) = 1$ . As a consequence, the entropy  $S_\rho$  assumes only negative or null values. The maximum value  $S_\rho = 0$  is attained for a uniform distribution  $P(\rho) = 1$ , which corresponds to the maximum uncertainty of the polymer elongation. The differential entropy (9) is also equivalent to the modified entropy (8) of  $R$  with characteristic scale  $L$ :  $S_\rho = S_R^L = - \int P(R) \ln[P(R)L] dR$ . The relation  $S_\rho = S_R^L = S_R - \ln L$  shows that a change of the maximum elongation  $L$  corresponds to a shift of the entropy. In the next Section we will discuss how this property can be exploited to determine the parameter  $L$  of the dumbbell model which best fits the experimental data. For the cases of random or turbulent flows, we will also show that the coil-stretch transition is better described in terms of the differential entropy of the dimensionless quantity  $y = \ln \rho$ . The entropies of  $y$  and  $\rho$  are related via  $S_y = S_\rho - \mathbb{E}[\ln(\rho)]$ . Finally, we note that in the case of a dumbbell in potential flows, the differential entropy  $S_R = S_\rho + \ln L$  coincides with the thermodynamic entropy in Ref. [32].

#### IV. RESULTS

The differential entropy of the rescaled polymer length is now used to characterize and compare the coil-stretch transition in the flows introduced in Sec. II.  $S_\rho$  is plotted in Fig. 1 (left panel) as a function of  $Wi$ ; in all cases (except for the experimental data) the extensibility parameter is set to a representative value of  $b = 18^2$ .

In the extensional flow,  $S_\rho$  displays a narrow maximum at  $Wi$  near critical, i.e., the coil-stretch transition is marked by a strong amplification of the entropy of  $\rho$ . This behavior reflects the fact that, at both small and large  $Wi$ , the PDF of  $\rho$  is dominated by a peak (near to either  $1/\sqrt{b}$  or 1), whereas only in a narrow range of  $Wi$  around  $Wi_{cr}$  the PDF has a broader shape. A large variety of polymer configurations is thus observed at the coil-stretch transition, as can be appreciated by direct inspection of the time series of  $\rho$  [27,60].

In the shear flow,  $S_\rho$  starts growing in an appreciable way only when  $Wi$  is significantly greater than  $Wi_{cr}$ . However, it eventually reaches values higher than for the extensional flow. This is consistent with the distributions of the extensions that have been observed in experiments [45,46] and numerical simulations [61,62]. The aforementioned tumbling events indeed entail continuous recoiling and restretching of the polymer. Therefore, fairly large  $Wi$  are required to stretch polymers appreciably, and since the tumbling frequency increases with  $Wi$  [46–48], the distribution of the extensions becomes broader and broader as  $Wi$  grows. A pronounced maximum at extensions comparable to  $L$  only forms for  $Wi$  as large as 200 [62], and only then is  $S_\rho$  expected to start decreasing.

Coming to the random case,  $S_\rho$  displays a maximum for both the BK flow and isotropic turbulence. At small and moderate  $Wi$ , the two curves are remarkably close despite the idealization of the BK flow. It has indeed been shown in Ref. [63] that the shape of  $P(R)$  and the exponent of the power-law intermediate region [ $P(R) \sim R^{-1-\alpha}$  for  $R_0 \ll R \ll L$ ] are largely insensitive to the correlation time of the flow up to correlation times of the order of  $\lambda^{-1}$ . At large  $Wi$ , the behavior differs:  $S_\rho$  saturates in the BK flow, whereas it decreases in isotropic turbulence. The reason for this is that if the flow is turbulent and  $Wi$  is sufficiently large,  $P(R)$  displays a power-law intermediate region together with peak near to  $L$  [28]. The development of this sharp peak causes the reduction of  $S_\rho$  at increasing  $Wi$ . In contrast, such a peak is absent in the BK flow, because a time-decorrelated velocity field is less effective in stretching polymers up to their maximum length [52].

Figure 1 (left panel) also shows a qualitative comparison with the experimental data of Sultanov *et al.* [36]. This comparison requires some caveats. First of all, the experimental points have been translated vertically, which corresponds to using the extensibility parameter  $b$  of the dumbbell model as fitting parameter [2,41]. Indeed, the entropy  $S_\rho$  defined from the PDF of the rescaled elongation  $\rho = R/L$  can be expressed in terms of the entropy of  $P(R/R_0)$  as  $S_\rho = S_{R/R_0} - \ln(b)/2$ , where  $S_{R/R_0} = \int P(R/R_0) \ln(P(R/R_0)) d(R/R_0)$ , therefore a vertical translation of the entropy is equivalent to a change of  $b$ . In particular, the observation that  $S_\rho^{(dumb)} \simeq S_\rho^{(exp.)} + \Delta S_\rho$  corresponds to fitting the experimental data with a dumbbell with equivalent extensibility  $b^{(fit)} = b^{(exp.)} [\exp(-\Delta S_\rho)]^2$ . Thanks to this simple relation, the comparison of the entropy curves provides a useful tool for determining the parameter  $b$  of the dumbbell model which fits the experimental data. A precise, quantitative comparison between the experiment and the theory is not possible because the Weissenberg number was defined in a different way in the two cases. However, the analysis shows that the experimental data are qualitatively compatible with the entropy of a dumbbell in a random flow with extensibility parameter  $b \approx 30^2$ . The latter estimate is obtained from the entropy shift  $\Delta S_\rho = 0.33$ . The corresponding value of the ratio  $(L/R_g)^{(fit)} \approx 34.5$  is not far from the experimental value  $(L/R_g)^{(exp.)} = 47.8$ .

Let us now come back to the comparison between the entropy curves in the random flows and the extensional flow. In both cases, the maximum of  $S_\rho$  is an indication of an increased randomness of the polymer configuration in the transitional regime. However, there are some important differences in the behavior of  $S_\rho$  observed in random flows with respect to that of the extensional flow. First, for a comparable value of  $Wi$  the entropy is always greater in random flows. This is because in random flows  $P(\rho)$  has a power-law intermediate region and is therefore broader. Second, the maximum of  $S_\rho$  is much wider, since in random flows the transition from the coiled to the stretched state is much less sharp [4]. Third, the maximum of  $S_\rho$  is located at a value of  $Wi$  larger than  $Wi_{cr} = 1/2$ . To understand this latter point, it is necessary to examine the power-law behavior of  $P(\rho)$ .

As mentioned earlier, in random flows  $P(\rho)$  displays a power-law in the intermediate region  $1/\sqrt{b} \ll \rho \ll 1$  which scales as  $P(\rho) \sim \rho^{-1-\alpha}$ , where the exponent  $\alpha$  turns from positive to negative at  $Wi_{cr}$ . Therefore, at the transition  $P(\rho) \sim \rho^{-1}$ . Given that  $\alpha$  decreases monotonically with  $Wi$ , it is rather at  $Wi > Wi_{cr}$  that  $P(\rho) \sim \rho^0$  and the PDF of  $\rho$  is the broadest [28,52]. Since  $S_\rho$  is a measure of the randomness of  $\rho$ , it is therefore natural that in random flows  $S_\rho$  reaches its maximum value at  $Wi > Wi_{cr}$ . This fact explains the behavior of  $S_\rho$ . However, it also raises the

issue of an apparent discrepancy between the critical  $Wi$  for the coil-stretch transition and the value of  $Wi$  at which  $S_\rho$  is maximum. How to reconcile these two different thresholds?

The time-dependent PDF  $P(\rho, t)$  satisfies the diffusion equation

$$\frac{\partial P}{\partial T} = -\frac{\partial}{\partial \rho_i} \{[\kappa_{ij}(t)\rho_j - f(L\rho)\rho_i]P\} + \frac{1}{b} \Delta_\rho P, \quad (10)$$

where time has been rescaled as  $T = t/2\tau$  [38,49]. In a statistically isotropic flow and after the initial transient, the PDF of the rescaled extension can be assumed to depend only on the polymer length and not on the polymer orientation (this is true at any time if the initial PDF of  $\rho$  is independent of the polymer orientation). It is therefore convenient to move to spherical coordinates (see Ref. [64] for the transformation of the diffusion equation under a change of variables) and drop the derivatives with respect to the angular variables. This turns the relaxation and Laplacian terms into  $\partial_\rho[\rho f(L\rho)P]$  and  $b^{-1}\partial_\rho\rho^2\partial_\rho(P/\rho^2)$ , respectively. The flow term can be modelled *à la* Richardson, i.e., by describing the stretching effect on the polymer as a diffusion with  $\rho$ -dependent eddy diffusivity [65]. For a smooth random flow (recall that even in turbulent flows polymers generally lie in the dissipation range, where the velocity field is smooth), the eddy diffusivity must be proportional to  $\rho^2$  [50]. In summary, moving to spherical coordinates, assuming that the solution of Eq. (10) only depends on  $\rho$ , and modeling the flow term via an eddy diffusivity proportional to  $\rho^2$  yields the following equation for  $P(\rho, t)$ :

$$\frac{\partial P}{\partial T} = \frac{\partial}{\partial \rho} [\rho f(L\rho)P] + \frac{\partial}{\partial \rho} \rho^2 \mathcal{K}(\rho) \frac{\partial P}{\partial \rho \rho^2}, \quad (11)$$

with  $\mathcal{K}(\rho) = K\rho^2 + b^{-1}$ . The coefficient  $K$  depends on the Reynolds and Weissenberg numbers in a way that is specific to the particular random flow. However, its explicit expression is not needed for the discussion below.

Equation (11) can be recast as a Fokker-Planck equation with drift coefficient  $D_1(\rho) = 4K\rho - \rho f(L\rho) + 2/b\rho$  and diffusion coefficient  $D_2(\rho) = K\rho^2 + b^{-1}$ . The associated Itô stochastic equation is

$$\dot{\rho} = D_1(\rho) + \sqrt{2D_2(\rho)} \eta(t), \quad (12)$$

where  $\eta(t)$  is white noise. Note that, for the BK flow, Eqs. (11) and (12) hold exactly with  $K = 2Wi/3$  [44,52]. One important property of Eq. (12) is that the amplitude of the noise depends on  $\rho$ . This follows from the fact that if the flow is random, the velocity gradient in Eq. (1) plays the role of a multiplicative noise. However, to be able to use  $Wi$  as a control parameter for the coil-stretch transition, it is desirable to move to a representation where the amplitude of the noise is independent of the stochastic variable, i.e., a stochastic equation with additive noise only. This is achieved by considering a transformation of variable of the form [64]:

$$y \propto \int \frac{d\rho}{\sqrt{D_2(\rho)}} = \frac{1}{\sqrt{K}} \ln[K\rho + \sqrt{K(K\rho^2 + b^{-1})}] + \text{const.} \quad (13)$$

Around the coil-stretch transition, the coefficient  $K$  is  $O(1)$ . For  $\rho \gg 1/\sqrt{b}$  Eq. (13) thus gives

$$y \sim \ln \rho. \quad (14)$$

Now note that the PDF of  $y$  is related to that of  $\rho$  via the relationship  $P(y) \propto \rho P(\rho)$ . Therefore, according to the theory of Balkovsky *et al.* [43], at  $Wi = Wi_{cr}$  the power-law region of  $P(y)$  is flat and the entropy of  $y$ ,

$$S_y = - \int P(y) \ln[P(y)] dy, \quad (15)$$

is expected to reach its maximum value. This suggests that, for random flows, it may be more appropriate to characterize the coil-stretch transition by measuring the entropy of  $y$  rather than that

of  $\rho$ . (The logarithm of the polymer extension has also been used in other contexts, for instance to improve accuracy in numerical simulations of constitutive models of polymer solutions [66,67] or to develop a geometric decomposition of the conformation tensor  $\mathbf{C} = \langle \boldsymbol{\rho} \otimes \boldsymbol{\rho} \rangle_{\xi}$  that guarantees the positive definiteness of both its mean and fluctuating components [68].)

Figure 1 (right panel) shows  $S_y$  versus  $Wi$  for the BK flow and isotropic turbulence. The experimental data have not been included because calculating  $P(y)$  from  $P(\rho)$  would require a higher resolution of the small extensions than that available in the experiment [recall that  $P(y) \sim \rho P(\rho)$ ]. As expected,  $S_y$  is maximum at  $Wi = Wi_{cr}$ , which confirms that in random flows  $S_y$  provides a convenient characterization of the coil-stretch transition. The differences between the BK flow and isotropic turbulence that have been discussed earlier obviously also manifest themselves in the behavior of  $S_y$ .

Previous studies have investigated the correlation between the polymer extension and the local flow topology [28,69,70]. In a three-dimensional turbulent flow, the sign of the second invariant of the velocity gradient,  $Q = -\text{tr}(\nabla \mathbf{u})^2/2$ , discriminates between the regions of the flow that are dominated by strain ( $Q < 0$ ) and those that are dominated by vorticity ( $Q > 0$ ) [71]. To determine the dependence of entropy on the local flow topology, we consider the conditional probabilities  $P^-(y) = P(y|Q < 0)$  and  $P^+(y) = P(y|Q > 0)$  and the associated entropies  $S_y^-$  and  $S_y^+$ , respectively. These are shown in the inset of Fig. 1 (right panel) as a function of the Weissenberg number.  $S_y^-$  is obviously greater than  $S_y^+$  at large  $Wi$ , but the difference between the two entropies is not big. This is consistent with the fact that the extension of a polymer depends on its stretching history and not only on the instantaneous velocity gradient.

## V. SUMMARY AND CONCLUSIONS

In a nonuniform flow, polymers can be highly deformed by the local velocity gradients. However, the statistics of the deformation and the way it varies with  $Wi$  depend very sensitively on the properties of the flow. In particular, substantial differences are observed between laminar and random velocity fields. An entropic characterization of the coil-stretch transition was proposed by Latinwo *et al.* [32] for an extensional flow. This characterization has been recently extended to random flows by Sultanov *et al.* [36]. We have further developed this approach by examining a set of flows that have been regarded as benchmarks for the study of polymer stretching, in both the laminar and the random case. This study confirms that the dependence of entropy on  $Wi$  provides a useful characterization of the change in the statistics of polymer extension that occurs near the coil-stretch transition. Moreover, it allows a quantitative comparison between flows with different stretching properties. This characterization is particularly relevant to practical situations where limited statistics is available. Entropy is indeed less sensitive to statistical fluctuations than quantities, such as the slope of  $P(\rho)$  or the correlation time of  $\rho(t)$ , which have been used previously to describe the coil-stretch transition.

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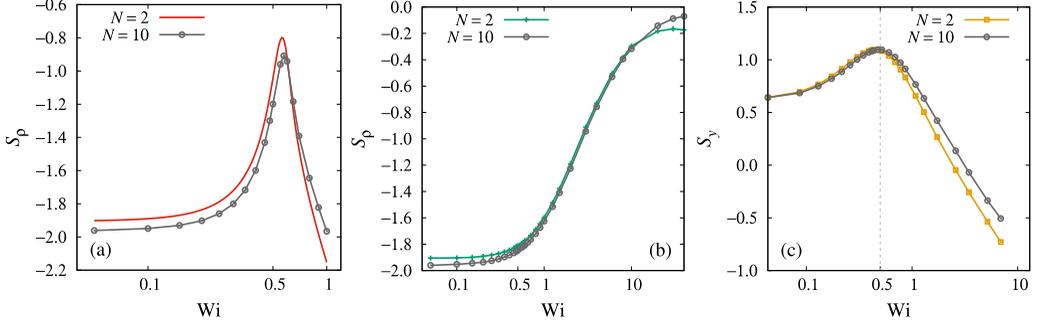


FIG. 2. Entropy of the fractional end-to-end separation as a function of  $Wi$  for a dumbbell and a chain with  $N = 10$  in (a) a uniaxial extensional flow, (b) a linear shear flow, and (c) isotropic turbulence.

### APPENDIX

Consider a chain with  $N$  beads and  $N - 1$  springs. If the position of the  $i$ th bead is denoted as  $\mathbf{x}_i$ , the connectors  $\mathbf{Q}_i = \mathbf{x}_{i+1} - \mathbf{x}_i$  ( $i = 1, \dots, N - 1$ ) satisfy

$$\begin{aligned} \dot{\mathbf{Q}}_1 &= \kappa(t) \cdot \mathbf{Q}_1 - \frac{1}{4\tau} (2f_1 \mathbf{Q}_1 - f_2 \mathbf{Q}_2) + \frac{Q_{\text{eq}}^c}{\sqrt{6\tau}} [\xi_2(t) - \xi_1(t)], \\ \dot{\mathbf{Q}}_i &= \kappa(t) \cdot \mathbf{Q}_i - \frac{1}{4\tau} (2f_i \mathbf{Q}_i - f_{i+1} \mathbf{Q}_{i+1} - f_{i-1} \mathbf{Q}_{i-1}) + \frac{Q_{\text{eq}}^c}{\sqrt{6\tau}} [\xi_{i+1}(t) - \xi_i(t)], \\ &\quad (i = 2, \dots, N - 2) \\ \dot{\mathbf{Q}}_{N-1} &= \kappa(t) \cdot \mathbf{Q}_{N-1} - \frac{1}{4\tau} (2f_{N-1} \mathbf{Q}_{N-1} - f_{N-2} \mathbf{Q}_{N-2}) + \frac{Q_{\text{eq}}^c}{\sqrt{6\tau}} [\xi_N(t) - \xi_{N-1}(t)], \end{aligned} \quad (\text{A1})$$

where  $\tau^c$  and  $Q_{\text{eq}}^c$  are the relaxation time and equilibrium length of the springs, respectively, and  $\xi_i(t)$  are independent three-dimensional white noises. The coefficients

$$f_i = \frac{1}{1 - (Q_i/Q_{\text{max}}^c)^2} \quad (\text{A2})$$

describe the nonlinear elasticity of the springs and fix the maximum length of each of them to  $Q_{\text{max}}^c$ . Therefore the maximum length of the chain is  $L^c = Q_{\text{max}}^c(N - 1)$ .

Equations (A1) have been solved by means of the Euler-Maruyama method supplemented with Öttinger's rejection algorithm, which rejects those time steps for which there exists at least one index  $i$  such that  $|\mathbf{Q}_i| > Q_{\text{max}}^c (1 - \sqrt{dt/10\tau})^{1/2}$  [49]. We have checked that the fraction of rejected time steps was negligible for all  $Wi$  and for all flows considered here.

The end-to-end separation vector of the chain is  $\mathbf{R} = \sum_{i=1}^{N-1} \mathbf{Q}_i$ . To compare the results for a dumbbell ( $N = 2$ ) with those for a multi-bead chain ( $N > 2$ ), we have used the mapping proposed in Ref. [72]. This mapping assumes that the statistics of the end-to-end separation of a  $N$ -bead chain is equivalent to that of a dumbbell with parameters:

$$\tau = \frac{N(N+1)\tau^c}{6}, \quad R_{\text{eq}} = Q_{\text{eq}}^c, \quad L = Q_{\text{max}}^c \sqrt{N-1} = L^c / \sqrt{N-1}. \quad (\text{A3})$$

In Fig. 2, we plot the entropy of the rescaled end-to-end separation  $\rho = R/L^c$  as a function of  $Wi$  for the uniaxial extensional flow, the linear shear flow, and isotropic turbulence. The curves for the dumbbell model shown in Fig. 1(a) are compared with those for an equivalent chain with  $N = 10$  beads. Only small quantitative differences are observed between the results for  $N = 2$  and  $N = 10$ .

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