Nonlinear elastic polymers in random flow

By M. MARTINS AFONSO¹ and D. VINCENZI^{2,3,4}

¹INFM-Dipartimento di Fisica, Università di Genova and INFN, Sezione di Genova, Via Dodecaneso 33, 16146 Genova, Italy

²Dipartimento di Fisica, Università di Genova, Via Dodecaneso 33, 16146 Genova, Italy

³Max-Planck-Institut für Dynamik und Selbstorganisation, Göttingen, Germany

⁴LASSP, Clark Hall, Cornell University, Ithaca, NY 14853, USA

(Received 17 January 2005 and in revised form 4 May 2005)

Polymer stretching in random smooth flows is investigated within the framework of the FENE dumbbell model. The advecting flow is Gaussian and short-correlated in time. The stationary probability density function of polymer extension is derived exactly. The characteristic time needed for the system to attain the stationary regime is computed as a function of the Weissenberg number and the maximum length of polymers. The transient relaxation to the stationary regime is predicted to be exceptionally slow in the proximity of the coil–stretch transition.

1. Introduction

The ability of polymers to considerably change the large-scale statistics of the advecting flow has important practical applications, drag reduction being one of the most relevant ones (see Gyr & Bewersdorff 1995). Polymers affect the dynamics of the advecting velocity field only if they are highly elongated. Understanding how a single polymer chain is stretched by a random flow is thus the first issue to address in the study of hydrodynamical properties of polymer solutions.

At equilibrium, the radial shape of coiled polymers is spherical due to their entropy. When placed in a non-homogeneous flow, polymers are deformed and stretched by the gradients of the velocity. The product of the longest relaxation time of polymers and the characteristic rate of deformation is called the Weissenberg number *Wi*. For small *Wi* the entropic force prevails and polymers are in the coiled state. When *Wi* exceeds a critical value the molecules become highly elongated and their extension increases sharply. This phenomenon is called coil–stretch transition and the critical Weissenberg number is known to be approximately one.

We investigate the statistics of polymer extension in the FENE (finite extensible nonlinear elastic) dumbbell model (see e.g. Bird *et al.* 1977, for a review). A polymer is described as two beads joined by an elastic spring. The elastic force diverges as the elongation of polymers attains its maximum value, R_m , and this gives a large-extension cutoff. Consequently the stationary regime exists however strong the velocity gradients are. Since attention is directed only to the dynamics of a single molecule, the feedback on the advecting flow is disregarded. To allow analytical progress, the random flow is chosen to have Batchelor–Kraichnan statistics. This means that the considered flow is Gaussian, white in time and linear in space. The Batchelor–Kraichnan model is a fullysolvable model for passive turbulent transport which can provide useful connections between theory and real behaviours (see Falkovich, Gawędzki & Vergassola 2001, for a review on the applications to scalar and magnetic fields). The results should be intended as a qualitative description of real polymer dynamics. We derive the complete form of the stationary probability density function (p.d.f.) of polymer extension and describe how the statistics of polymer stretching changes with increasing velocity gradients. Concerning the statistics at finite times, we compute the typical time needed for the system to reach the steady state and predict how it depends on the maximum length of polymers and the stretching by the flow. Our analysis shows that the coil– stretch transition of polymers is characterized by an anomalous dynamics in time.

The coil-stretch transition was predicted in 1974 for shear and hyperbolic flows (De Gennes 1974) and has been widely studied experimentally for such flows (Perkins, Smith & Chu 1997; Smith, Babcock & Chu 1999; Hur *et al.* 2002; Babcock *et al.* 2003). In contrast, the experimental study of polymer dynamics in random flows is a very recent achievement. This is due to the difficulty in generating a flow that is random at scales comparable with the size of polymers (about 100 μ m). This difficulty can be overcome thanks to the elastic turbulence discovered by Groisman & Steinberg (2000); the flow of a highly elastic polymer solution at low Reynolds numbers but large *Wi* has all the main properties of fully developed turbulence. Therefore, in solutions of sufficiently elastic polymers it is possible to excite turbulent motion in exceedingly small volumes. Exploiting elastic turbulence in polymer solutions, Gerashchenko, Chevallard & Steinberg (2005) thus investigated the stretching and the deformation of a single DNA molecule in a three-dimensional random flow.

Theoretical studies concerning the coil-stretch transition in random flows have focused mainly on the Hookean dumbbell model (Chertkov 2000; Balkovsky, Fouxon & Lebedev 2000; Celani, Musacchio & Vincenzi 2005*a*). This model is suitable only for the coiled state (Wi < 1) since the linear force in principle allows infinite extensions and for large Wi polymers can become more and more elongated under the action of velocity gradients. For $Wi \ge 1$ a stationary p.d.f. of the extension no longer exists and this behaviour was conjectured to coincide with the coil-stretch transition. To overcome this oversimplification, the maximum length of polymers must be taken into account. One possibility is to replace the Hookean force by a nonlinear elastic force. Chertkov (2000) obtained the large-value tail of the stationary p.d.f. of the extension for a general anharmonic force; this approximate analysis was subsequently applied by Thiffeault (2003) to the FENE model. Here we exactly derive the complete statistics of polymer stretching within the context of the FENE dumbbell model at general Wi.

Concerning the statistics at finite times, preliminary results were obtained for the Hookean model by Celani *et al.* (2005*a*). There, the relaxation time to the stationary regime could be defined only in the coiled state. Celani *et al.* (2005*a*) thus derived the behaviour of the relaxation time for very small Wi and observed a divergence for Wi = 1; this suggested a critical behaviour close to the coil–stretch transition. We present the first prediction of the complete dependence of the transient relaxation time on Wi and R_m with the more realistic FENE model.

The rest of this paper is organized as follows. In §2 we introduce the model and present the main results. The stationary p.d.f. of the elongation and the transient relaxation time are computed in §3 and in §4 respectively. In §5 we discuss the relevance of our results for experiments and numerical simulations.

2. Coil-stretch transition

In elastic dumbbell models a polymer is described as two beads connected by a spring. The beads represent the ends of the molecule and their separation is a measure

of the extension. The beads experience: (a) a hydrodynamic drag force modelled by the Stokes law; (b) a Brownian force due to thermal fluctuations of the fluid; (c) an elastic force due to the spring connecting one bead to the other. We consider both two-dimensional and three-dimensional flows in the same way, the dimension of the flow being denoted by d. Since in physical applications the elongation of polymers is always smaller than the viscous scale of the flow, the dumbbell is assumed to move in a linear velocity field $\mathbf{v}(\mathbf{r}, t) = \mathbf{v}_0(t) + \mathbf{r} \cdot \nabla \mathbf{v}(t)$. Inertial effects and hydrodynamic interactions between the beads are neglected. Consequently, the separation vector between the beads, \mathbf{R} , evolves according to the stochastic differential equation (see Bird *et al.* 1977)

$$\mathrm{d}\boldsymbol{R} = (\boldsymbol{R} \cdot \nabla \boldsymbol{v}) \,\mathrm{d}t - \frac{\boldsymbol{F}(\boldsymbol{R})}{\tau} \,\mathrm{d}t + \sqrt{\frac{2R_0^2}{\tau}} \,\mathrm{d}W, \qquad (2.1)$$

where R_0 is the equilibrium length of the polymer, τ is its relaxation time in the absence of flow, and W is a *d*-dimensional Brownian motion which accounts for thermal noise. In the FENE dumbbell model, the elastic force F(R) takes the form $F(R) = R/(1-R^2/R_m^2)$, where R_m denotes the maximum extension of the molecule. In physical applications the ratio R_m/R_0 usually lies between 10 and 100 (Bird *et al.* 1977). The length of the vector **R** is a measure of the extension of the polymer.

Within the Kraichnan model v(x, t) is a statistically homogeneous Gaussian field with zero mean and second-order correlation (Kraichnan 1968):

$$\langle v_i(\boldsymbol{x},t)v_i(\boldsymbol{x}+\boldsymbol{r},t')\rangle = \boldsymbol{D}_{ii}(\boldsymbol{r})\delta(t-t').$$

In the so-called Batchelor regime the flow is assumed to be smooth in space. If we further impose incompressibility and statistical invariance with respect to reflections and rotations, the tensor $D_{ij}(r)$ must take the form (Monin & Yaglom 1975)

$$\boldsymbol{D}_{ij}(\boldsymbol{r}) = D_0 \delta_{ij} - D_1 [(d+1)\delta_{ij}r^2 - 2r_ir_j],$$

where D_0 represents the eddy diffusivity of the flow and D_1 determines the intensity of turbulent fluctuations. In random flows the Weissenberg number can be defined as $Wi = \lambda \tau$, where λ is the maximum Lyapunov exponent of the flow, that is the average logarithmic growth rate of nearby fluid particle separations. The maximum Lyapunov exponent of the Batchelor-Kraichnan flow has asymptotically a Gaussian p.d.f. with mean value $\lambda = D_1 d(d-1)$ and variance $\Delta = 2\lambda/d$ (Kraichnan 1974).

2.1. Stationary regime

The statistics of polymer elongation is described by the p.d.f. of the norm of \mathbf{R} averaged over velocity realizations $\dagger: \mathcal{P}(\mathbf{R}, t) = \int \langle P(\mathbf{R}, t) \rangle R^{d-1} d\Omega$, where $d\Omega$ denotes integration over angular variables. When the flow \mathbf{v} has Batchelor-Kraichnan statistics $\mathcal{P}(\mathbf{R}, t)$ obeys a one-dimensional Fokker-Planck equation with non-trivial drift and diffusion coefficients (see § 3). Under reflecting boundary conditions (the probability does not flow outside the domain of definition) the system reaches a steady state for all $Wi \ddagger$. The stationary p.d.f. of the elongation, $\mathcal{P}_{st}(R) = \lim_{t \to \infty} \mathcal{P}(R, t)$, has the form

 $[\]dagger$ Because of the statistical homogeneity of v, the average p.d.f. of the elongation does not depend on the point of application of the vector R.

[‡] This should be contrasted with the Hookean model where the stationary regime does not exist for $Wi \ge 1$ (see Chertkov 2000; Balkovsky *et al.* 2000; Thiffeault 2003; Celani *et al.* 2005*a*).



FIGURE 1. Stationary p.d.f. of polymer elongation for the three-dimensional FENE model at different Weissenberg numbers $Wi \ (R_m/R_0 = 50)$.



FIGURE 2. (a) Most probable rescaled elongation R_{\star}/R_m and average rescaled extension μ/R_m as functions of the Weissenberg number Wi (d=3, $R_m=50$, $R_0=1$). (b) First derivative of R_{\star}/R_m with respect to Wi.

(see § 3)

$$\mathscr{P}_{\rm st}(R) = N R^{d-1} \left(1 + \frac{Wi}{d} \frac{R^2}{R_0^2} \right)^{-h} \left(1 - \frac{R^2}{R_m^2} \right)^{h}, \qquad 0 \le R \le R_m, \tag{2.2}$$

where $h = [2(R_0^2/R_m^2 + Wi/d)]^{-1}$ and N is the normalization coefficient (see (3.5) below). The stationary p.d.f. is shown in figure 1 for different Wi. For small elongations compared to the equilibrium length, $\mathcal{P}_{st}(R)$ scales as R^{d-1} ; this result holds for a general elastic force since the left tail of \mathcal{P}_{st} comes from the events where the elastic force dominates and equation (2.1) reduces to a d-dimensional Langevin equation (for physically meaningful elastic interactions F(R) should scale as R for $R \to 0$). For intermediate extensions, $R_0 \ll R \ll R_m$, the stationary p.d.f. is proportional to the power law R^{d-1-2h} in accordance with the prediction of Balkovsky *et al.* (2000). For large elongations $\mathcal{P}_{st}(R)$ scales as $(R_m^2 - R^2)^h$ and vanishes for $R = R_m$. In practical applications, $R_0/R_m \ll 1$, the exponent h is approximatively d/(2Wi), as predicted by Thiffeault (2003). Obviously, when $R_m \to \infty$ and Wi < 1, $\mathcal{P}_{st}(R)$ tends to the stationary solution of the Hookean model (see Celani *et al.* 2005*a*).

The maximum of the p.d.f., R_{\star} , determines the fraction of polymers which are highly stretched. The graph of R_{\star} as a function of Wi is shown in figure 2(*a*). When Wi is smaller than one, R_{\star} is of the order of R_0 and most of polymers have the coiled equilibrium configuration. With increasing Wi the most probable elongation R_{\star} grows slowly



FIGURE 3. (a) Normalized root mean square σ/μ as a function of the Weissenberg number $Wi \ (d=3, R_m=50, R_0=1)$. (b) Skewness y vs Wi for the same values of the parameters.

until Wi exceeds d/(d-1). Then, a sharp transition occurs to a strongly elongated state. This can be appreciated from the behaviour of the first-order derivative of R_{\star} as a function of Wi (figure 2b). As Wi becomes very large, R_{\star} approaches R_m . The same analysis holds for the average extension μ , apart from the fact that it starts increasing for a smaller Wi and its limiting value is $\frac{3}{4}R_m$ (see figure 2). It is worth noticing that the coil-stretch transition becomes sharper and sharper with increasing R_m (not plotted).

The normalized r.m.s. value of the extension, σ/μ , $\sigma^2 = \int (R - \mu)^2 \mathscr{P}_{st}(R) dR$, is represented in figure 3(*a*). It increases at low *Wi* until it reaches a maximum value; then σ is compensated by the sharp increase in μ and at large *Wi* the rescaled r.m.s. eventually relaxes to the constant value $1/\sqrt{15}$.

The skewness $y = \left[\int (R - \mu)^3 \mathscr{P}_{st}(R) dR\right] / \sigma^3$ is positive for small Wi and becomes negative at large Wi (figure 3b), corresponding to the qualitative behaviour of the stationary p.d.f. (figure 1). The maximum of skewness in the neighbourhood of the coilstretch transition can be easily understood as follows. At low Wi the p.d.f. is peaked at R_0 and the skewness is positive. With increasing Wi the right tail starts increasing, but μ is still of the order of R_0 : the skewness, therefore, increases and achieves is maximum value. Beyond the coil-stretch transition μ starts moving towards the maximum extension and the skewness decreases until it becomes negative at large Wi, that is when the p.d.f. has a long left tail. The limiting value of y for $Wi \rightarrow \infty$ is $-\frac{2}{3}\sqrt{5/3}$.

2.2. Relaxation to the stationary regime

We now turn to the time dependence of the p.d.f. of the elongation. Starting from an initial condition peaked at R_0 , the system relaxes to the stationary regime described by (2.2). The time needed to reach the stationary regime, T, is the solution of a transcendental equation which involves continued fractions (see §4).

For small Weissenberg numbers, $0 \le Wi \le d/(d+4)$, the transient relaxation time *T* behaves according to the prediction of the linear model (Celani *et al.* 2005*a*):

$$T/\tau = \frac{1}{2} [1 - Wi(d+2)/d]^{-1}$$
(2.3)

independently of R_m (see inset in figure 4).

In the proximity of the coil-stretch transition T displays a maximum as a function of Wi. The relaxation is exceptionally slow in this range of Wi because the stationary regime results from the competition between the coiled state and the highly stretched state. The position and the value of the maximum relaxation time T_{max} depend on the cutoff R_m (figure 4b). As the maximum allowed extension of polymers increases, T_{max} is closer and closer to Wi = 1 and grows; at large R_m the FENE model should



FIGURE 4. (a) Rescaled time of relaxation to the stationary regime, T/τ , as a function of the Weissenberg number Wi for three different values of R_m/R_0 (d = 3). The inset shows the linear-model approximation given by equation (2.3) (dashed line) for $R_m/R_0 = 50$: the agreement is good up to $d/(d+4) \simeq 0.4$. (b) Dependence of the maximum rescaled relaxation time T_{max}/τ on the maximum relative extension of polymers R_m/R_0 .

indeed match the Hookean model, where T diverges as Wi tends to one (Celani *et al.* 2005*a*).

For very large Weissenberg numbers the stretching time is small compared to τ and the molecules are expected to rapidly reach the highly stretched configuration. Hence, T vanishes as Wi tends to infinity. A numerical fit shows that T scales as Wi^{-1} at large Wi.

In the next sections we explicitly derive (2.2) and the equation for T.

3. Fokker–Planck equation

For a fixed realization of the velocity field the p.d.f. of the end-to-end vector, $P(\mathbf{R}, t)$, satisfies the Fokker–Planck equation associated with (2.1) (see e.g. Risken 1989):

$$\partial_t P + \operatorname{div}_{\boldsymbol{R}}\left[\left(\boldsymbol{R} \cdot \nabla \boldsymbol{v} - \frac{\boldsymbol{F}(\boldsymbol{R})}{\tau}\right) P\right] = \frac{R_0^2}{\tau} \nabla_{\boldsymbol{R}}^2 P.$$
 (3.1)

To obtain an equation for $\mathscr{P}(R, t)$, we average the above equation over the velocity realizations and integrate the result over angular variables. The terms of the type $\langle v_i P \rangle$ in general do not lead to a closed form for the mean p.d.f. and a closed equation cannot be deduced from (3.1). The Gaussianity and the δ -correlation in time of the Batchelor-Kraichnan model provide an exact closure. Exploiting the Novikov-Furutsu formula (see e.g. Klyatskin, Woyczynski & Gurarie 1996), we obtain: $\langle (\nabla_i v_j) P \rangle = -C_{ijk\ell} \partial_{R_\ell} [R_k \langle P \rangle]$ with $C_{ijk\ell} = D_1 [(d+1) \delta_{ik} \delta_{j\ell} - \delta_{ij} \delta_{k\ell} - \delta_{i\ell} \delta_{jk}]$. We can thus derive from (3.1) a one-dimensional Fokker-Planck equation for $\mathscr{P}(R, t)$:

$$\partial_s \mathscr{P}(R,s) = -\partial_R [A(R)\mathscr{P}(R,s)] + \partial_R^2 [B(R)\mathscr{P}(R,s)], \qquad (3.2)$$

where the time has been rescaled with τ , $s = t/\tau$, and the drift and diffusion coefficients have the form

$$A(R) = \frac{(d+1)}{d} Wi R - F(R) + (d-1) \frac{R_0^2}{R} \quad \text{and} \quad B(R) = \frac{Wi}{d} R^2 + R_0^2.$$
(3.3)

The coefficients A and B are time independent due to the stationarity of the advecting flow. If R_0 is set to zero, then equation (3.2) reduces to the approximate equation for the large-value tail of the p.d.f. derived by Chertkov (2000).

To solve (3.2) we impose reflecting boundary conditions, that is the probability current associated with the solution, $J(R, s) = A(R)\mathscr{P}(R, s) - \partial_R [B(R)\mathscr{P}(R, s)]$, vanishes in R = 0 and $R = R_m$ for all $s \ge 0$. This means that there is no flow of probability through the boundaries of the domain. Under these conditions the stationary p.d.f. of the elongation takes the form (Risken 1989)

$$\mathscr{P}_{\rm st}(R) = \frac{C}{B(R)} \exp\left[\int_{R_1}^R A(x)/B(x)\,\mathrm{d}x\right] \tag{3.4}$$

where the constant C and the lower integration limit R_1 are fixed by the normalization condition. The above formula holds for a general elastic force of the form F(R) = f(R)R. Placing the force of the FENE model into (3.4), we thus obtain (2.2) with

$$N = \frac{2\Gamma(d/2 + h + 1)}{R_m^d \Gamma(d/2)\Gamma(h+1)_2 F_1(d/2, h; d/2 + h + 1; -Wi R_m^2/dR_0^2)}.$$
(3.5)

The function ${}_{2}F_{1}$ in the normalization coefficient denotes the hypergeometric function.

4. Relaxation time

The time-dependent solution of equation (3.2) can be obtained by separation of variables (Risken 1989). In other words, $\mathcal{P}(R, s)$ can be sought in the form

$$\mathscr{P}(R,s) = \mathscr{P}_{st}(R) + \sum_{k=1}^{\infty} c_k \,\mathrm{e}^{-\mu_k s} \,p_k(R) \tag{4.1}$$

where the coefficients c_k are fixed by the initial condition $\mathcal{P}(R, 0)$, and μ_k , $p_k(R)$ are respectively the eigenvalues and the eigenfunctions of the ordinary differential equation

$$\frac{d^2}{dR^2}[B(R)p_k(R)] - \frac{d}{dR}[A(R)p_k(R)] + \mu_k p_k(R) = 0.$$
(4.2)

The above equation should be solved with reflecting boundary conditions: $J_k(0) = \lim_{R \to R_m} J_k(R) = 0$, J_k being the probability current associated with the eigenfunction p_k . It can be shown that the eigenvalues μ_k are real and non-negative, $\mathscr{P}_{st}(R)$ belonging to the eigenvalue $\mu_0 = 0$ (Risken 1989). As we will see, the eigenvalues form a countable set and may be arranged in ascending order: $0 < \mu_1 < \mu_2 < \ldots$ The reciprocal of μ_1 , therefore, is the time of relaxation to the stationary regime rescaled by τ .

Equation (4.2) is a second-order linear differential equation with four regular singularities in the complex plane. By a change of dependent and independent variables $z = (R/R_m)^2$, $p_k(z) = z^{(d-1)/2} (1-z)^h w_k(z)$, this equation can be transformed into a standard Heun equation for the function $w_k(z)$ (see Ronveaux 1995, for a review):

$$\frac{\mathrm{d}^2 w_k}{\mathrm{d}z^2} + \left(\frac{\gamma}{z} + \frac{\delta}{z-1} + \frac{\epsilon}{z-a}\right) \frac{\mathrm{d}w_k}{\mathrm{d}z} + \frac{\alpha\beta z - q}{z(z-1)(z-a)} w_k = 0, \tag{4.3}$$

where

$$a = -\frac{d}{Wi} \frac{R_0^2}{R_m^2}, \qquad \qquad q = \frac{d}{2} \left(h + \frac{\mu_k}{2Wi} \right),$$

$$\alpha = h + \frac{d}{4} - \frac{1}{4} \sqrt{d\left(d - \frac{4\mu_k}{Wi}\right)}, \qquad \qquad \beta = h + \frac{d}{4} + \frac{1}{4} \sqrt{d\left(d - \frac{4\mu_k}{Wi}\right)},$$

$$\gamma = d/2, \qquad \delta = h, \qquad \epsilon = 1 + h,$$

with $h = [2(R_0^2/R_m^2 + Wi/d)]^{-1}$. Reflecting boundary conditions for p_k map into the following limiting conditions for w_k :

$$\lim_{z \to 0} z^{\gamma - 1} w_k(z) = 0 \quad \text{and} \quad \lim_{z \to 1} (1 - z)^{\delta - 1} w_k(z) = 0.$$
(4.4)

The Heun equation is the general Fuchsian equation with four singularities. In the standard form (4.3) the singular points are 0, 1, a, ∞ . Let z_0 be a generic singularity of (4.3). From the theory of Fuchsian equations, the local behaviour of $w_k(z)$ near z_0 is specified by the characteristic exponents ρ_1 , ρ_2 associated with z_0 (see e.g. Whittaker & Watson 1996). If $\rho_1 - \rho_2$ is not integer, in a neighbourhood of z_0 which excludes the nearest other singularity, $w_k(z)$ can be written in the form $b_1(z-z_0)^{\rho_1}\varphi(z-z_0) + b_2(z-z_0)^{\rho_2}\psi(z-z_0)$, where b_1 , b_2 are constant and φ , ψ are analytic functions such that $\varphi(z_0) \neq 0$, $\psi(z_0) \neq 0$. If $\rho_1 - \rho_2$ is integer and $\rho_1 \ge \rho_2$, the function ψ can be no longer analytic in z_0 and involve the function $\log(z-z_0)$.

The singularity z = 0 has characteristic exponents 0 and $1 - \gamma$; the singularity z = 1 has characteristic exponents 0 and $1 - \delta$. In physical applications we can exclude the situation where δ is integer. On the contrary, $1 - \gamma$ is zero when d = 2.

Consider first the case d = 3, where there are not logarithmic singularities in z = 0. To fulfil conditions (4.4), w_k must be simultaneously a local solution about z = 0 and z = 1, in both cases belonging to the exponent 0. Such a solution is called a Heun function of class I relative to the points 0 and 1, and exists only for a countable set of values of q and hence of μ_k (see Ronveaux 1995). The condition for the aforementioned Heun function to exist leads to a transcendental equation for the eigenvalues μ_k (Erdélyi 1944):

$$L_0 - \frac{M_0 K_1}{L_1 - \frac{M_1 K_2}{L_2 - \dots}} = 0, (4.5)$$

where

$$\begin{split} K_{i} &= \frac{(i+\alpha-1)(i+\beta-1)(i+\gamma-1)(i+\omega-1)}{(2i+\omega-1)(2i+\omega-2)}, \\ L_{i} &= q+ai(i+\omega) - \frac{\epsilon i(i+\omega)(\gamma-\delta) + [i(i+\omega)+\alpha\beta][2i(i+\omega)+\gamma(\omega-1)]}{(2i+\omega-1)(2i+\omega+1)}, \\ M_{i} &= \frac{(i+1)(i+\omega-\alpha+1)(i+\omega-\beta+1)(i+\delta)}{(2i+\omega+1)(2i+\omega+2)}, \end{split}$$

with $\omega = \gamma + \delta - 1$. The rescaled relaxation time T/τ is then the reciprocal of the lowest non-zero solution of (4.5). In the case d = 2 the conclusions are unchanged since the solution involving a logarithm in the neighbourhood of z = 0 should be discarded.

We solved (4.5) numerically: the continued fraction was computed by the modified Lentz method and the first non-zero solution was evaluated by the root false position method (see e.g. Press *et al.* 1993).

5. Summary and discussion

The goal of the paper was to investigate polymer stretching in a turbulent flow within the context of a fully solvable model. The statistical features of the Batchelor–Kraichnan flow allow us to derive the complete form of the stationary p.d.f. of polymer elongation for a general elastic force. When specializing to finitely extensible polymers

106

we recover the main properties of polymer dynamics in real turbulent flows and compute the time of relaxation to the stationary regime.

It should be noted that the velocity field we consider is statistically isotropic. Together with the δ -correlation in time, this is a key assumption in order to derive a fully analytical solution of the problem. In the experimental setup of Gerashchenko *et al.* (2004) the elastic turbulent flow is superimposed on a mean shear flow. The long-time statistics of polymer extension in the presence of a mean shear has been recently considered by Chertkov *et al.* (2005); Celani, Puliafito & Turitsyn (2005b); Puliafito & Turitsyn (2005).

The main result of our study is the behaviour of the time of relaxation to the steady state as a function of Wi. At low Wi the transient relaxation time is an increasing function of Wi, it is maximum close to the coil-stretch transition, and eventually tends to zero with increasing Wi. Knowing the dependence of the transient time on Wi is relevant both for numerical simulations and experiments. For example, in the former case, the time required for uncorrelated polymer chains that are suddenly exposed to the same flow to correlate is (implicitly) related to the sharpness of stress gradients one can expect in the flow. Hence, the prediction of the transient time in our study is useful to estimate the required grid spacing to fully resolve those gradients (L. Collins 2005, private communication). In the latter case, the fact that the transient relaxation time is especially long just below the coil-stretch transition implies that within such range of Wi experimental measures are more sensitive to statistical fluctuations.

Experiments concerning the transient relaxation to the stationary regime can investigate the time dependence of the conditional p.d.f. $\mathcal{P}(R, t|R_0, 0)$, which corresponds to the initial condition peaked at the equilibrium size: $\mathcal{P}(R, 0|R_0, 0) = \delta(R - R_0)$. Such an initial condition can be fixed experimentally as follows (A. Celani 2005, private communication). The p.d.f. of the extension is constructed by following the motion of different polymer molecules and collecting R(t) for each molecule: one should then start counting time only when the length of the corresponding polymer is approximatively R_0 . This is equivalent to selecting the initial state where all molecules have the equilibrium extension, $R(0) = R_0$.

The transient relaxation time can be measured directly from the time behaviour of the conditional moments of the extension: $\overline{R^n}(t) = \int R^n \mathscr{P}(R, t|R_0, 0) dR$, where *n* is a positive integer. The conditional p.d.f. can indeed be expanded as in (4.1) and the order of series and integral can be interchanged in the definition of $\overline{R^n}$ due to the integrability of $R^n p_k(R)$ and the uniform convergence of series (4.1) (see e.g. Smirnov 1984). Therefore, all the moments of the extension converge to their stationary value with the same rate as the p.d.f. of the extension.

To conclude, we believe that the results obtained for the nonlinear dumbbell model are relevant for the comprehension of polymer dynamics in turbulent flows at any Weissenberg number. Moreover, we hope that our study may stimulate new experiments directed to investigate the transient relaxation to the stationary regime.

We are deeply grateful to E. Bodenschatz, A. Celani, and L. Collins for very useful suggestions. We wish to thank C. M. Casciola, M. Chertkov, J. Davoudi, E. De Angelis, B. Eckhardt, A. Mazzino, S. Musacchio, J. Schumacher, and V. Steinberg for illuminating discussions. This research has been supported in part by the European Union under contract No. HPRN-CT-2000-00162, by the French-German program PAI "Procope" 07574NM, and by the Italian Ministry of Education, University and Research under contract Cofin. 2003 (prot. 020302002038).

REFERENCES

- BABCOCK, H. P., TEIXEIRA, R. E., HUR, J. S., SHAQFEH, E. S. & CHU, S. 2003 Visualization of molecular fluctuations near the critical point of the coil-stretch transition in polymer elongation. *Macromolecules* 36, 4544–4548.
- BALKOVSKY, E., FOUXON, A. & LEBEDEV, V. 2000 Turbulent dynamics of polymer solutions. *Phys. Rev. Lett.* **84**, 4765–4768.
- BIRD, R. B., HASSAGER, O., ARMSTRONG, R. C. & CURTISS, C. F. 1977 Dynamics of Polymeric Liquids, Kinetic Theory, vol. II. Wiley.
- CELANI, A., MUSACCHIO, S. & VINCENZI, D. 2005*a* Polymer transport in random flow. J. Statist. Phys. **118**, 531–554.
- CELANI, A., PULIAFITO, A. & TURITSYN, K. 2005b Polymers in linear shear flow: a numerical study. *Europhys. Lett.* **70**, 464–470.
- CHERTKOV, M. 2000 Polymer stretching by turbulence. Phys. Rev. Lett. 84, 4761-4764.
- CHERTKOV, M., KOLOKOLOV, I., LEBEDEV, V. & TURITSYN, K. 2005 Statistics of polymer extension in a random flow with mean shear. J. Fluid Mech. 531, 251–260.
- DE GENNES, P. G. 1974 Coil-stretch transition of dilute flexible polymer under ultra-high velocity gradients. J. Chem. Phys. 60, 5030-5042.
- ERDÉLYI, A. 1944 Certain expansions of solutions of the Heun equation. Q. J. Maths (Oxford Series) 15, 62–69.
- FALKOVICH, G., GAWĘDZKI, K. & VERGASSOLA, M. 2001 Particles and fields in fluid turbulence. Rev. Mod. Phys. 73, 913–975.
- GERASHCHENKO, S., CHEVALLARD, C. & STEINBERG, V. 2005 Single polymer dynamics: coil-stretch transition in a random flow. *Europhys. Lett.* **71**, 221–227.
- GROISMAN, A. & STEINBERG, V. 2000 Elastic turbulence in a polymer solution flow. *Nature* 405, 53–55.
- GYR, A. & BEWERSDORFF, H. W. 1995 Drag Reduction of Turbulent Flows by Additives. Kluwer.
- HUR, J. S., SHAQFEH, E. S., BABCOCK, H. P. & CHU, S. 2002 Dynamics and configurational fluctuations of single DNA molecules in linear mixed flows. *Phys. Rev.* E **66**, 011915.
- KLYATSKIN, V. I., WOYCZYNSKI, W. A. & GURARIE, D. 1996 Short-time correlation approximations for diffusing tracers in random velocity fields: A functional approach. In *Stochastic Modeling in Physical Oceanography* (ed. R. J. Ader). Progress in Probability, pp. 221–270, Birkhauser.
- KRAICHNAN, R. H. 1968 Small-scale structure of a scalar field convected by turbulence. *Phys. Fluids* **11**, 945–963.
- KRAICHNAN, R. H. 1974 Convection of a passive scalar by a quasi-uniform random straining field. *J. Fluid Mech.* 64, 737–762.
- MONIN, A. A. & YAGLOM, A. M. 1975 Statistical Fluid Mechanics. MIT Press.
- PERKINS, T. T., SMITH, D. E. & CHU, S. 1997 Single polymer dynamics in an elongational flow. Science 276, 2016–2021.
- PRESS, W. H., FLANNERY, B. P., TEUKOLSKY, S. A. & VETTERLING, W. T. 1993 Numerical Recipes. Cambridge University Press.
- PULIAFITO, A. & TURITSYN, K. 2005 Single polymer dynamics in shear flow. Physica D (in press).
- RISKEN, H. 1989 The Fokker-Planck Equation, Methods of Solution and Applications (ed. H. Haken). Springer Series in Synergetics, Springer.
- RONVEAUX, A. (Ed.) 1995 Heun's Differential Equations. Oxford University Press.
- SMIRNOV, V. 1984 Cours de Mathématiques Supérieures, Vol. IV, 2nd part. MIR.
- SMITH, D. E., BABCOCK, H. P. & CHU, S. 1999 Single-Polymer Dynamics in Steady Shear Flow. Science 283, 1724–1727.
- THIFFEAULT, J.-L. 2003 Finite extension of polymers in turbulent flow. Phys. Lett. A 308, 445-450.
- TURITSYN, K. S. 2005 Polymer dynamics in chaotic flows with strong shear component. *Phys. Rev.* E (submitted).
- WHITTAKER, E. T. & WATSON, G. N. 1996 A Course of Modern Analysis, 4th edn. Cambridge University Press.