Single polymer dynamics in elongational flow and the confluent Heun equation

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Abstract

We investigate the non-equilibrium dynamics of an isolated polymer in a stationary elongational flow. We compute the relaxation time to the steady-state configuration as a function of the Weissenberg number. A strong increase of the relaxation time is found around the coil–stretch transition, which is attributed to the large number of polymer configurations. The relaxation dynamics of the polymer is solved analytically in terms of a central two-point connection problem for the singly confluent Heun equation.

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1. Introduction

Dilute polymer solutions exhibit physical behaviours that distinguish them from ordinary Newtonian fluids. Even a small polymer concentration can considerably change the large-scale behaviour of the flow by enhancing viscosity and reducing the turbulent drag. A comprehensive understanding of hydrodynamical properties of polymer solutions is still lacking despite the large number of industrial applications (e.g. Sreenivasan and White (2000)). A starting point for the theoretical description of dilute polymer solutions is the dynamics of isolated polymer molecules. The knowledge of how a single molecule is deformed by the velocity gradient allows the development of constitutive models that in turn can be used to calculate the large scale flow. The stationary dynamics of a single, isolated polymer has received much attention to date (see Larson (2005), Shaqfeh (2005), for a review). In contrast, less is known about non-equilibrium dynamics of isolated polymers in flow. Since Rouse (1953) and Zimm's (1956) seminal works, experimental, numerical and theoretical studies focused on the internal relaxation dynamics of a polymer floating in a solvent under the influence of Brownian fluctuations. The two model situations considered were (a) a polymer suspended in solution and pulled at the ends (Quake *et al* 1997, Hatfield and Quake 1999); (b) a tethered polymer

submitted to a uniform flow and freely relaxing after cessation of the flow (Perkins *et al* 1994, Brochard-Wyart 1995, Manneville *et al* 1996, Rzehak and Zimmermann 2002). The above studies did not take into account the interaction between the polymer and an external flow. Hernández Cifre and García de la Torre (1999) note that Rouse and Zimm's theories may not provide the adequate time scale for coil–stretch processes in flow on the basis of Brownian dynamics simulations. Here, we investigate how an elongational flow influences polymer relaxation dynamics. We determine the time scale associated with polymer deformation *in the flow* and show a significant deviation from Rouse and Zimm's predictions in the vicinity of the coil–stretch transition. Our analysis is based on an eigenvalue problem for the confluent Heun equation, and constitutes a new physical application of this latter equation.

Polymer dynamics is extremely rich already in simple deterministic flows, such as elongational flows (Perkins *et al* 1997, Smith and Chu 1998), shear flows (Smith *et al* 1999, Celani *et al* 2005b, Puliafito and Turitsyn 2005, Gerashchenko and Steinberg 2006) or combinations of the two (Hur *et al* 2002, Babcock *et al* 2003). The velocity gradient of a non-uniform flow stretches the polymer, while entropic forces attempt to restore the polymer into the coiled equilibrium shape. In other words, the configuration of the polymer results from the counterbalance between the entropic forces and the hydrodynamic drag. Here we consider an elongational flow, which is defined by a constant velocity gradient λ. This flow is particularly effective in stretching polymers far from their equilibrium configuration. A transition to the stretched state of the polymer occurs as the velocity gradient exceeds the critical value $\lambda_c = 1/(2\tau)$, where τ is the time associated with the slowest relaxation mode of the polymer in thermal equilibrium with the surrounding medium. For $\lambda < \lambda_c$ polymers stay in the coiled equilibrium configuration; for $\lambda > \lambda_c$ they become fully extended. This phenomenon is known as the coil–stretch transition (de Gennes 1974). Rouse (1953) computed τ as a function of the number of monomers in the polymer assuming the polymer could be described as a beads-and-springs chain with Hookean interactions. Zimm (1956) refined Rouse's prediction by taking into account hydrodynamic interactions between segments of the chain.

The study of polymer dynamics has benefited from a class of mesoscopic models that are based on a coarse-grained treatment of the polymer molecule. One of the simplest is the elastic dumbbell model, which only takes into account the slowest oscillation mode of the molecule (Bird *et al* 1987). Notwithstanding this crude simplification, the dumbbell model captures the main aspects of polymer dynamics in elongational flows, such as the coil–stretch transition (Perkins *et al* 1997) and finite-time conformation hysteresis (Schroeder *et al* 2003, 2004). We examine how the probability density function (PDF) of the extension of a dumbbell-like molecule approaches its stationary form. We compute the typical time it takes for the initial PDF to attain its steady-state form and show that, in the proximity of the coil–stretch transition, this time is exceedingly long compared to τ. A similar behaviour is encountered in white-in-time isotropic random flows (Celani *et al* 2005a, Martins Afonso and Vincenzi 2005); however, for an elongational flow the amplification of the transient relaxation time is much stronger.

The problem is solved within the framework of the Fokker–Planck equation for the PDF of the extension of the polymer. The computation of the transient relaxation time is recast as a central two-point connection problem (CTCP) for a singly confluent Heun equation. The Heun equation is the general Fuchsian differential equation with four regular singularities. Its singly confluent form, also known as the generalized spheroidal wave equation, results from the merging of two regular singularities into one irregular singularity of Poincaré rank 1 (see Slavyanov (1995) for a review). A CTCP is an eigenvalue problem for an ordinary differential equation where (a) at both endpoints of the interval of definition is located a

singularity of the equation; (b) the solutions are required to have a specified asymptotic behaviour while approaching the two singularities from inside. Contrary to the hypergeometric equation, an explicit formula for the CTCP is not known for the Heun family of equations. The eigenvalues can be determined only as solutions of transcendental equations involving continued fractions. Well-known applications of the confluent Heun equation are the electronic spectra of the hydrogen-molecule ion in the Born–Oppenheimer approximation (Jaffé 1933) and the Teukolsky equation describing small perturbations to the Kerr geometry in black hole theory (Leaver 1985). For a comprehensive introduction to physical applications of the Heun equations we refer the reader to the book by Slavyanov and Lay (2000).

The rest of this paper is organized as follows. The dumbbell model is introduced in section 2. The computation of the transient relaxation time and the related CTCP for the confluent Heun equation are presented in section 3. Section 4 is devoted to conclusions.

2. Elastic dumbbell model

When one is interested in the statistics of polymer extension the dynamics of a polymer molecule can be described, to a first approximation, in terms of its slowest oscillation mode. In this case, the molecule can be modelled as an elastic dumbbell, i.e. as two beads connected by a spring. The beads represent the ends of the molecule and the spring models entropic forces. The separation between the beads measures the extension of the polymer. When introduced into a non-uniform flow the molecule experiences collisions with fluid particles and becomes stretched under the action of the velocity gradient. In the simplest case, the drag force is assumed to be proportional to the velocity of the polymer relative to the fluid and thermal agitation is modelled by Brownian motion. In most applications the extension of the polymer remains smaller than the dissipative scale of the carrier flow, and therefore the velocity field can be assumed to be linear[4]. The separation vector of the ends of the polymer, $\boldsymbol{Q}$, is then a stochastic process evolving according to the three-dimensional stochastic ordinary differential equation[5] (e.g. Bird *et al* (1987))

$$\mathrm{d}\boldsymbol{Q} = \boldsymbol{Q} \cdot \nabla \boldsymbol{v}(s)\,\mathrm{d}s - f(Q)\,\frac{\boldsymbol{Q}}{2\tau}\,\mathrm{d}s + \sqrt{\frac{Q_0^2}{\tau}}\,\mathrm{d}\boldsymbol{B}(s),\qquad(1)$$

where $Q = |\boldsymbol{Q}|$, Q_0^2 is the equilibrium mean-square separation of the ends of the molecule, and $\boldsymbol{B}(s)$ denotes the three-dimensional standard Brownian motion. The function f determines the entropic force. We consider the finitely extensible nonlinear elastic (FENE) dumbbell model with

$$f(Q) = \frac{1}{1 - Q^2/L^2},\qquad 0 \leqslant Q < L,$$

where L is the maximum extension of the molecule. The force diverges as the molecular extension approaches L; thus the extension of the molecule will be finite and smaller than L. The FENE model is appropriate for synthetic polymers such as polyacrylamide and polyethyleneoxide; biological macromolecules such as DNA and polypeptides are better described by the worm-like chain model (e.g. Larson (2005)). In elongational-flow experiments, the flexibility parameter $b = L^2/Q_0^2$ usually ranges from 10^2 to 10^4 (Larson 2005, Shaqfeh 2005).

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[4] Davoudi and Schumacher (2006) recently investigated the situation where the extension of the polymer can reach the inertial range of turbulence.

[5] There is no Ito–Stratonovich ambiguity in this case because the coefficient of Brownian motion does not depend on $\boldsymbol{Q}$.

The FENE model (1) neglects hydrodynamic interactions between the segments of the polymer. Inclusion of hydrodynamic interactions makes the coil–stretch transition sharper, but do not change the transition qualitatively (e.g. Wiest *et al* (1989), Hernández Cifre and García de la Torre (1998, 1999)). Furthermore, the dumbbell model without hydrodynamic interactions accurately reproduces the extension–strain curve observed in experiments (Perkins *et al* 1997). The accuracy of the model can be ascribed to the cancellation between the effect of the distribution of drag forces along the chain and the effect of the increase in effective drag coefficient with polymer extension (Larson *et al* 1997). Neglecting hydrodynamic interactions has the benefits of providing analytical results.

3. Relaxation dynamics

A steady planar elongational flow is characterized by one direction of stretch, one direction of compression and one neutral direction. The velocity gradient is constant along the directions of both the extensional and compressional axes: $\nabla_j v_i = \lambda(\delta_{i1}\delta_{j1} - \delta_{i2}\delta_{j2})$, $\lambda > 0$. When a polymer is immersed in that flow the first component of the separation vector rapidly becomes much greater than the other components: $Q_1 \gg Q_2$ and $Q_1 \gg Q_3$. The extension of the molecule, therefore, is approximatively $Q \simeq Q_1$, and $f(Q)$ can be replaced by $f(Q_1)$.[6] According to this approximation, the first component of (1) gives a one-dimensional stochastic differential equation for the extension of the dumbbell:

$$\mathrm{d}Q = \lambda Q \, \mathrm{d}s - f(Q) \frac{Q}{2\tau} \, \mathrm{d}s + \sqrt{\frac{Q_0^2}{\tau}} \, \mathrm{d}B(s), \tag{2}$$

where $B(s)$ is the one-dimensional Brownian motion. For the sake of notational simplicity, we introduce the rescaled separation vector $\boldsymbol{q} = \boldsymbol{Q}/L$. The PDF of $q = |\boldsymbol{q}|$, $\psi(q;t)$ with $q \in [0, 1]$, satisfies the one-dimensional Fokker–Planck equation associated with (2) (e.g. Stratonovich (1963))

$$\partial_t \psi = \mathscr{L}\psi,$$

$$\mathscr{L}\psi := -\frac{\partial}{\partial q}\left[\left(Wi - \frac{\hat{f}(q)}{2}\right)q\psi\right] + \frac{1}{2b}\frac{\partial^2\psi}{\partial q^2}, \tag{3}$$

where $t = s/\tau$, $\hat{f}(q) = f(Lq)$ and $Wi = \lambda\tau$. The dimensionless number Wi is known as the Weissenberg number and measures the level of polymer stretching. For $Wi < 1/2$ polymers are in the coiled state; for $Wi > 1/2$ polymers are fully extended. The critical value $Wi_c = \lambda_c\tau = 1/2$ marks the coil–stretch transition in elongational flows (de Gennes 1974). Strictly speaking, the approximation leading to (2) and (3) holds true when the polymer is sufficiently stretched, i.e. only for $Wi \gtrsim Wi_c$. Equation (3), indeed, does not yield a good approximation of $\psi(q;t)$ at low Wi. However, as we shall see at the end of this section, it is appropriate to investigate polymer relaxation dynamics in terms of (2) and (3) also below the coil–stretch transition.

The Fokker–Planck equation (3) is solved with reflecting boundary conditions, that is the probability current

$$j(q;t) = Wi\, q\psi(q;t) - \frac{\hat{f}(q)}{2}q\psi(q;t) - \frac{1}{2b}\left.\frac{\partial\psi}{\partial q}\right|_{q,t}$$

is assumed to vanish at the endpoints of the interval of definition: $j(0;t) = j(1;t) = 0 \,\forall\, t > 0$

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[6] The above approximation holds true for a steady uniaxial extensional flow as well: $\nabla_j v_i = \lambda(\delta_{i1}\delta_{j1} - \delta_{i2}\delta_{j2}/2 - \delta_{i3}\delta_{j3}/2)$. Therefore, the results henceforth presented are unchanged for this flow.

(Stratonovich 1963). Under these conditions, the stationary distribution of the extension, $\psi_0(q) = \lim_{t \to \infty} \psi(q; t)$, can be derived by simple integration (Bird *et al* 1987):

$$\psi_0(q) = N \, \mathrm{e}^{bWiq^2}(1 - q^2)^{\frac{b}{2}}, \qquad 0 \leqslant q \leqslant 1, \tag{4}$$

where

$$N = 2\Gamma((b+3)/2)/[\sqrt{\pi}\,\Gamma(b/2+1) \times {}_1F_1(1/2; (b+3)/2; bWi)]$$

and Γ and ${}_1F_1$ denote the Euler Gamma function and the confluent hypergeometric function, respectively (e.g. Erdélyi *et al* (1953)). Large extensions become more and more probable with increasing Wi in accordance with experiments (Perkins *et al* 1997). Note however that, at low Wi, equation (4) does not constitute a good description of the PDF of small extensions due to the approximation behind (3).

The time behaviour of the system depends on the form of the spectrum of the operator $\mathscr{L}$ with reflecting boundary conditions:

$$\mathscr{L}\psi_\mu = -\mu\psi_\mu, \tag{5}$$

$$j_\mu(0) = j_\mu(1) = 0, \tag{6}$$

where j_μ denotes the probability current associated with the eigenfunction ψ_μ. Under conditions (6), $\mathscr{L}$ is non-positive defined and symmetric with respect to the scalar product with weighting function $1/\psi_0$. Its eigenvalues μ are therefore real and non-negative, $\mu = 0$ being associated with the long-time solution ψ_0 (Stratonovich 1963). If $\mathscr{L}$ has a countable spectrum $\{0, \mu_1, \mu_2, \ldots\}$ with $\mu_i < \mu_{i+1}$, then $T_{\mathrm{rel}} = \tau/\mu_1$ is the characteristic time needed for $\psi(q; t)$ to attain its long-time form $\psi_0(q)$ when the initial condition $\psi(q; 0)$ is taken far from equilibrium (Schenzle and Brand 1979). We note that while τ is the relaxation time of the polymer *in the absence of flow*, T_{rel} characterizes polymer relaxation dynamics *in the flow*.

To compute T_{rel}, we need to solve the eigenvalue problem (5), (6). By making the substitutions $z = q^2$, $\psi_\mu(z) = (1 - z)^{\frac{b}{2}} w_\mu(z)$, we can rewrite (5) in the form

$$w_\mu'' + \left(\beta + \frac{\gamma}{z} + \frac{\delta}{z - 1}\right) w_\mu' + \frac{\alpha\beta z - \nu}{z(z - 1)} w_\mu = 0, \tag{7}$$

where $w_\mu' := \mathrm{d}w_\mu/\mathrm{d}z$, $\gamma = 1/2$, $\delta = b/2$, $\alpha = (1 + b - \mu/Wi)/2$, $\beta = -bWi$ and $\nu = b(\mu - Wi)/2$. The above equation is a singly confluent Heun equation in the non-symmetrical canonical form (Decarreau *et al* 1978a, 1978b, Slavyanov 1995)[7].

Equation (7) has two regular singularities at $z = 0$ and $z = 1$ and an irregular singularity of Poincaré rank 1 at $z = \infty$. The characteristic exponents at $z = 0$ are 0 and $1 - \gamma$; at $z = 1$, they are 0 and $1 - \delta$. We neglect the case of b integer and odd since it does not have physical relevance. Consequently, there are no logarithmic solutions and, for $|z| < 1$, $w_\mu(z)$ can be written as $w_\mu(z) = a_0\varphi_0(z) + d_0 z^{1/2}\chi_0(z)$ with a_0, d_0 complex constants and φ_0, χ_0 analytic functions of z (equivalently of q^2) such that $\varphi_0(0) \neq 0$ and $\chi_0(0) \neq 0$. Similarly, for $|z - 1| < 1$, $w_\mu(z)$ takes the form $w_\mu(z) = a_1\varphi_1(z - 1) + d_1(1 - z)^{1-b/2}\chi_1(z - 1)$ with a_1, d_1 complex constants and φ_1, χ_1 analytic functions of z such that $\varphi_1(0) \neq 0$ and $\chi_1(0) \neq 0$.

It is easily seen that boundary conditions (6) can be matched only by those solutions of (7) that belong to the exponent 0 both in $z = 0$ and $z = 1$ (that is both d_0 and d_1 have to be zero)[8]. The eigenvalue problem defined by (5) and (6) is therefore mapped into a CTCP on $[0, 1]$

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[7] The worm-like chain model, $\hat{f}(q) = 2/3 - 1/(6q) + 1/[6q(1-q)^2]$, would lead to a second-order linear differential equation with two irregular singularities of Poincaré rank 1 and 3, respectively. The FENE model in a δ-correlated random flow can be solved in terms of a general Heun equation (Martins Afonso and Vincenzi 2005).

[8] We leave aside the case $b = 2$ since it does not have physical relevance.

for the confluent Heun equation (7). To compute the eigenvalues μ, we adapt the procedure exploited by Svartholm (1939) and Erdélyi (1942, 1944) to (7) (see also Slavyanov (1995), Slavyanov and Lay (2000)). We then expand w_μ in series of Jacobi polynomials having the required characteristic exponent at $z = 0$ and $z = 1$:

$$w_\mu(z) = \sum_{n=0}^{\infty} c_n(\mu) u_n(z), \tag{8}$$

with

$$u_n(z) = {}_2F_1(-n, \omega + n; \gamma; z) = (-1)^n \frac{n!\sqrt{\pi}}{\Gamma(n+\gamma)} P_n^{(\omega-\gamma,\gamma-1)}(2z-1)$$

and $\omega = \gamma + \delta - 1$. The function ${}_2F_1$ denotes the Gauss hypergeometric function; $P_n^{(\omega-\gamma,\gamma-1)}$ are the Jacobi polynomials of parameters $\omega - \gamma$ and $\gamma - 1$ and degree n (e.g. Erdélyi *et al* (1953)). The conditions for the convergence of (8) will determine the spectrum of $\mathscr{L}$.

By defining the operators

$$\mathscr{D}_1 w_\mu := z(z-1)\left[w_\mu'' + \left(\frac{\gamma}{z} + \frac{\delta}{z-1}\right) w_\mu'\right],$$
$$\mathscr{D}_2 w_\mu := -z(z-1) w_\mu',$$

we can rewrite (7) in the form

$$\mathscr{D}_1 w_\mu + \varepsilon \mathscr{D}_2 w_\mu + (\rho z + \sigma) w_\mu = 0, \tag{9}$$

where $\varepsilon = bWi$, $\rho = b[\mu - (1+b)Wi]/2$, $\sigma = b(Wi - \mu)/2$. The polynomials u_n satisfy the differential relations (Erdélyi *et al* 1953)

$$\mathscr{D}_1 u_n = n(\omega + n) u_n \tag{10}$$

and

$$\mathscr{D}_2 u_n = \widetilde{A}_n u_{n+1} + \widetilde{B}_n u_n + \widetilde{C}_n u_{n-1}, \tag{11}$$

with

$$\widetilde{A}_n = \frac{n(n+\omega)(n+\gamma)}{(2n+\omega)(2n+\omega+1)}, \qquad \widetilde{B}_n = \frac{n(n+\omega)(\delta-\gamma)}{(2n+\omega-1)(2n+\omega+1)},$$
$$\widetilde{C}_n = -\frac{n(n+\omega)(n+\delta-1)}{(2n+\omega)(2n+\omega-1)}.$$

In addition, the following recurrence relation holds (Erdélyi *et al* 1953):

$$z u_n = \widehat{A}_n u_{n+1} + \widehat{B}_n u_n + \widehat{C}_n u_{n-1}, \tag{12}$$

with coefficients

$$\widehat{A}_n = -\frac{(n+\gamma)(n+\omega)}{(2n+\omega)(2n+\omega+1)}, \qquad \widehat{B}_n = \frac{2n(n+\omega) + \gamma(\omega-1)}{(2n+\omega-1)(2n+\omega+1)},$$
$$\widehat{C}_n = -\frac{n(n+\delta-1)}{(2n+\omega-1)(2n+\omega)}.$$

Inserting expansion (8) in (9) and exploiting relations (10), (11), (12) yield the following three-term recurrence relation for $c_n(\mu)$:

$$g_{-1} c_0 = 0 \tag{13}$$

$$g_0 c_1 + h_0 c_0 = 0 \tag{14}$$

$$g_n c_{n+1} + h_n c_n + k_n c_{n-1} = 0 \qquad \text{for} \quad n \geqslant 2, \tag{15}$$

where the coefficients

$$g_n = \varepsilon \widetilde{C}_{n+1} + \rho \widehat{C}_{n+1}, \qquad h_n = n(\omega + n) + \varepsilon \widetilde{B}_n + \rho \widehat{B}_n + \sigma,$$
$$k_n = \varepsilon \widetilde{A}_{n-1} + \rho \widehat{A}_{n-1}$$

depend on μ through ρ and σ. The asymptotic behaviour of h_n/g_n and k_n/g_n is given by

$$\frac{h_n}{g_n} \sim -\frac{4n}{\varepsilon} \qquad \text{and} \qquad \frac{k_n}{g_n} \sim -1 \qquad (n \to \infty). \tag{16}$$

According to the Perron–Kreuser theorem (e.g. Gautschi (1967), Wimp (1984)), (16) implies that the recurrence relation (15) has two linearly independent solutions $\left(c_n^+\right)_n$ and $(c_n^-)_n$ such that

$$\frac{c_{n+1}^+}{c_n^+} \sim \frac{4n}{\varepsilon} \qquad \text{and} \qquad \frac{c_{n+1}^-}{c_n^-} \sim -\frac{\varepsilon}{4n} \qquad (n \to \infty). \tag{17}$$

The above sequences have the property $\lim_{n\to\infty} c_n^- / c_n^+ = 0$; hence $(c_n^-)_n$ is what is called a minimal solution of (15). Every other solution non-proportional to $(c_n^-)_n$ is asymptotically proportional to $\left(c_n^+\right)_n$, and therefore diverges with increasing n. Therefore, we can already say that (8) can converge only if the sequence $(c_n)_n$ is a minimal solution of (15).

The second limit in (17) implies that $\lim_{n\to\infty} \sqrt[n]{|c_n^-|} = 0$. This condition ensures that, if the coefficients c_n form a minimal solution of (15), then expansion (8) converges absolutely to an analytic function in the whole complex plane (Szegö 1939, p 252).

Nonetheless, it is also required that $c_n = 0$ for $n < 0$, that is the sequence $(c_n)_n$ is subject to initial conditions (13) and (14). Equation (13) is trivially satisfied since $g_{-1} = 0$, and so does (14) for $\mu = 0$. (This is in accordance with the fact that ψ_0 exists for all Wi and b.) However, for $\mu \neq 0$, equation (14) fixes the ratio $c_1/c_0 = -(b+3)/2$. This latter requirement is not satisfied by whatever μ and therefore selects the spectrum of $\mathscr{L}$.

To summarize, the spectrum of $\mathscr{L}$ is the set of those μ such that $(c_n(\mu))_{n\geqslant 0}$ is a minimal solution of (15) satisfying $c_1(\mu)/c_0(\mu) = -(b+3)/2$. From Pincherle's theorem (e.g. Gautschi (1967), p 31), this conclusion is equivalent to stating that the eigenvalues μ are the solutions of

$$\cfrac{k_1/g_1}{h_1/g_1 - \cfrac{k_2/g_2}{h_2/g_2 - \cfrac{k_3/g_3}{h_3/g_3 - \cdots}}} = \frac{b+3}{2}.$$

The latter represents a transcendental equation for the relaxation spectrum associated with the Fokker–Planck equation (3). The reciprocal of the smallest nonzero solution is T_{rel}/τ.

We calculated T_{rel} numerically by means of the modified Miller algorithm (Wimp 1984, pp 82–85). The behaviour of T_{rel} as a function of Wi is reported in figure 1. For very small Wi the influence of the external flow is negligible and T_{rel} is approximately equal to τ. With increasing Wi the ratio T_{rel}/τ starts growing as $1/(1 - 2Wi)$. This behaviour can be deduced by replacing the spring force with a Hookean force, $\hat{f}(q) = 1$, and computing the relaxation of the moments of q. For a fixed b, the rescaled relaxation time reaches a sharp maximum T_{max} in the neighbourhood of the coil–stretch transition ($Wi_c = 1/2$); the value of T_{max} increases linearly with $\sqrt{b}$ (figure 2). With increasing b, T_{rel} attains its maximum value T_{max} closer and closer to Wi_c and the width of the peak decreases (figure 2). For large Wi the relaxation time is fixed by the time scale of the flow λ^{-1}, and therefore T_{rel}/τ decreases as Wi^{-1}.

The computation of T_{rel} shows that, near the coil–stretch transition, the typical time scale involved in polymer relaxation dynamics is strongly different from τ. The time associated with the fundamental oscillation mode is not representative of polymer temporal dynamics
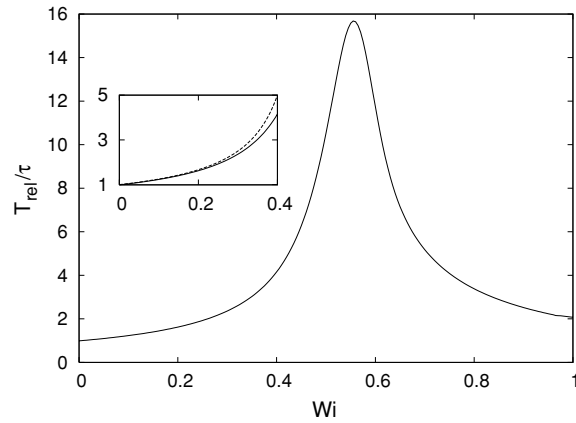
Figure 1. Rescaled relaxation time T_{rel}/τ as a function of the Weissenberg number Wi for $b = 600.25$; the inset shows the comparison with the small Wi behaviour $1/(1 - 2Wi)$ (dashed line).
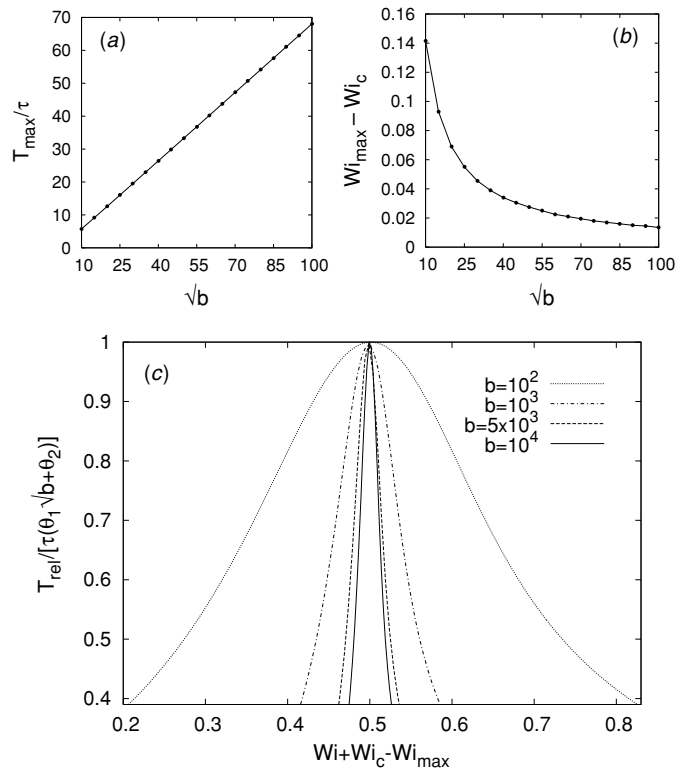
Figure 2. (a) Maximum rescaled relaxation time T_{max}/τ versus the square root of the flexibility parameter $b = L^2/Q_0^2$: T_{max}/τ increases as $\theta_1\sqrt{b} + \theta_2$ with $\theta_1 \approx 0.69$ and $\theta_2 \approx -1.18$; (b) behaviour of Wi_{max} as a function of $\sqrt{b}$, where Wi_{max} is the Weissenberg number at which the relaxation time attains its maximum value T_{max}; (c) relaxation time versus Wi for different b, rescaled to make the maximum values coincide.
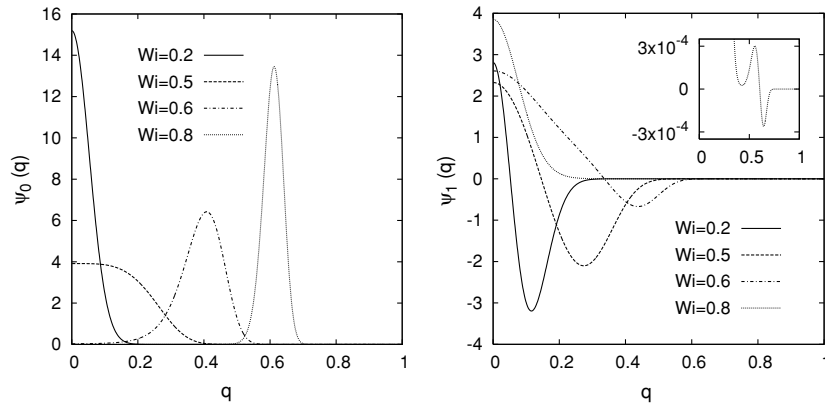
Figure 3. Stationary PDF of the extension and eigenfunction of the Fokker–Planck operator $\mathscr{L}$ associated with the smallest nonzero eigenvalue μ_1. The eigenfunctions have been computed numerically by means of the iteration-variation method (Morse and Feshbach 1953).

in flow. These results confirm the behaviour encountered in isotropic δ-correlated Gaussian flows (Celani *et al* 2005a, Martins Afonso and Vincenzi 2005), but here the enhancement of T_{rel} is stronger since the elongational flow is more efficient in deforming polymers.

In Brownian dynamics simulations and experiments the relaxation time of $\psi(q;t)$ can be measured from the decay of the moments of the extension to their steady-state value. To observe T_{rel}, one has to make sure that the initial condition $\psi(q;0)$ is not orthogonal to the first eigenfunction of $\mathscr{L}$, that is $\psi_1(q)$ in (5), with respect to the scalar product with weighting function $\psi_0(q)$. Figure 3 shows the shape of $\psi_1(q)$ for different *Wi*. An initial PDF concentrated either at a coiled or a stretched extension $\bar{q}$ (formally $\psi(q;0) = \delta(q - \bar{q})$) has projection onto $\psi_1(q)$ equal to $\psi_1(\bar{q})/\psi_0(\bar{q})$ by construction (e.g. Stratonovich (1963)). The initial condition with all the polymers having the same extension $\bar{q}$ is therefore not orthogonal to $\psi_1(q)$ if $\psi_1(\bar{q}) \neq 0$; all the moments will thus tend to their stationary value with a typical time scale T_{rel}.

We now show that it is accurate to compute T_{rel} by means of (3) also for $Wi < Wi_c$. At low *Wi*, the entropic force can be modelled as a Hookean force, i.e. $f(Q) = 1$ in (1). The vector equation (1) therefore reduces to a set of three decoupled stochastic differential equations for Q_1, Q_2, Q_3. Hence we have $\Psi(\boldsymbol{q};t) = \psi^{(1)}(q_1;t)\psi^{(2)}(q_2;t)\psi^{(3)}(q_3;t)$, where $\Psi(\boldsymbol{q};t)$ is the PDF of the vector $\boldsymbol{q}$ and $\psi^{(i)}(q_i;t)$ is the PDF of the *i*th component of $\boldsymbol{q}$. The relaxation time of $\Psi(\boldsymbol{q};t)$ is thus the longest of the relaxation times of $\psi^{(1)}(q_1;t)$, $\psi^{(2)}(q_2;t)$ and $\psi^{(3)}(q_3;t)$ given that all $\psi^{(i)}(q_i;t)$ have a non-trivial long-time limit. It is easy to check that at low *Wi* the relaxation time of $\psi^{(1)}(q_1;t)$ is $T_{\mathrm{rel}}^{(1)} = \tau/(1 - 2Wi)$, while $T_{\mathrm{rel}}^{(2)} = \tau/(1 + 2Wi)$ and $T_{\mathrm{rel}}^{(3)} = \tau$ (with obvious notation). The function $\Psi(\boldsymbol{q};t)$ therefore has the same relaxation time as $\psi^{(1)}(q_1;t)$. Now we note that $\psi(q;t)$ and $\Psi(\boldsymbol{q};t)$ have the same long-time behaviour since $\psi(q;t) = q^2 \int_0^\pi \int_0^{2\pi} \Psi(\boldsymbol{q}(q,\vartheta,\phi);t) \sin\vartheta \, \mathrm{d}\vartheta \, \mathrm{d}\phi$. We thus come to the following conclusion: the relaxation times of $\psi(q;t)$ and $\psi^{(1)}(q_1;t)$ coincide at low *Wi* and $\psi^{(1)}(q_1;t)$ satisfies (3). This fact explains why (3) yields an accurate computation of T_{rel} also below the coil–stretch transition.

4. Summary and conclusions

We have investigated the relaxation dynamics of an isolated polymer in an external flow. Previous studies focused on the relaxation of a polymer in a solvent driven only by Brownian

motion. Those studies determined the time τ associated with the slowest oscillation mode of the molecule in the absence of external flow. We have considered an elongational flow and derived a transcendental equation for the relaxation spectrum associated with the time evolution of the PDF of polymer extension. The problem of computing this spectrum has been recast as a central two-point connection problem for a confluent Heun equation. The Heun equation results from the separation of the time variable in the Fokker–Planck equation for the PDF of the extension.

Our analysis shows that an external elongational flow strongly influences polymer relaxation dynamics. The longest relaxation time associated with the evolution of the PDF of the extension provides an estimation of the time scale of polymer deformation. Near the coil–stretch transition, this time is significantly greater than τ (already one order of magnitude greater for short molecules). The physical reason is the large number of polymer configurations close to the coil–stretch transition. At intermediate Weissenberg numbers polymer conformation results from a critical competition between the entropic force and the velocity gradient. Therefore, around the transition, coiled and stretched polymer coexist in the flow, and this makes the relaxation to the equilibrium PDF particularly long. It is worth noting that the amplification of the relaxation time is stronger when hydrodynamic interactions are taken into account; this behaviour is intimately related to the finite-time conformation hysteresis observed in elongational flows (Celani *et al* 2006).

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