Polymer Stretching by Turbulence

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The stretching of a polymer chain by a large-scale chaotic flow is considered. The steady state which emerges as a balance of the turbulent stretching and anharmonic resistance of the chain is quantitatively described, i.e., the dependency on the flow parameters (Lyapunov exponent statistics) and the chain characteristics (the number of beads and the interbead elastic potential) is made explicit.

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A great task is to develop a theory of turbulence for a dilute polymer solution which explains, particularly, polymer drag reduction, the so-called Toms' effect [1]. Although a very plausible qualitative theory of polymer's drag reduction, describing the bulk viscosity and the size of the viscous boundary layer increase, was given by Lumley [2,3], no quantitative theory of the phenomenon is available. It is also widely accepted that the enormous increase of the polymer contribution into the stress tensor (by a factor of 10 000 in a turbulent flow, e.g., [4], and up to 130 times in the recent experiment of Groisman and Steinberg on elastic turbulence at very low Reynolds number [5]) is associated with extreme polymer stretching [2,4] (there exists an alternative theory suggesting that the connection between the turbulent strain rates and the elongational viscosity is circumstantial [6]; see also a comprehensive discussion of the subject in [7]). Therefore, it seems logical to start a theoretical exploration of the whole problem of the polymer solution hydrodynamics from the description of a single polymer stretching.

In the present Letter I discuss a polymer chain placed in a statistically known random flow under the assumption that the back reaction of the polymer on the flow is negligible, i.e., the polymer is passive. Polymer stretching in laminar flows was extensively studied in the past, e.g., [4]. A recent experimental advance has come with the state-of-the-art capability to visualize a polymer (DNA molecule) and therefore to study its stretching directly [8,9]. A qualitative theory of polymer stretching by chaotic flow [3] has predicted the jump of the mean square polymer length at $O(1)$ value of the stretching-to-linear elasticity ratio. Based on the recent progress in the theory of the passive scalar advection by a large-scale flow [10–19], Balkovsky *et al.* [20] have developed the approach of [3] and have constructed a quantitative theory of the transition onset. In the present Letter I generalize the approach of [20]. Nonlinear, but still passive theory of polymer stretching above as well as below the aforementioned threshold is delivered. Of special note is the described dependence on the equilibrium polymer contour length.

Equilibrium and even extended-by-flow lengths of a polymer chain are typically much smaller than the Kolmogorov viscous scale. This allows one to model a velocity field (counted from a reference point, say, one of the polymer's end points) advecting the polymer by $u^\alpha(t;\rho) = \sigma^{\alpha\beta}(t)\rho^\beta$ (i.e., the velocity at all scales under consideration changes linearly with the separation). Here the statistics of the traceless $\hat{\sigma}$ (we consider incompressible flow) is assumed to be known. I will analyze a sequence of models moving steadily from (1), introduced in [20], through (6) to (16). Polymers will be modeled by a chain of beads [two beads in the cases of (1) and (6) and N beads for (16)] connected by elastic [harmonic for (1) and anharmonic for (6) and (16)] springs. Forces of friction acting on a bead, which occur as the bead is moving against the local flow, are equilibrated by elastic tension within the springs attached to the bead and by thermal forces. The goal is to describe statistics of the passive polymer(s) advected by $\mathbf{u}(t;r)$.

I start by elaborating on the features and defects of the two-bead-one-linear-spring model. The basic equation of motion for the interbead separation $\boldsymbol{\rho}$ is

$$\frac{d}{dt}\rho^\alpha - \sigma^{\alpha\beta}(t)\rho^\beta = -k\rho^\alpha + \xi^\alpha(t), \qquad (1)$$

where the friction force on the right-hand side of (1) is equated by elastic and thermal forces on the left-hand side. In (1) k is the ratio of the string linear tension to the friction coefficient; $\langle\xi(0)\xi(t)\rangle = 2\kappa\delta(t)$, and κ is the thermal (molecular) diffusion coefficient. The solution of (1) is given by

$$\boldsymbol{\rho}(t) = e^{-kt}\hat{W}(t)\left[\boldsymbol{\rho}(0) + \int_0^t e^{kt'}\hat{W}^{-1}(t')\boldsymbol{\xi}(t')\right], \qquad (2)$$

with $\hat{W}(t)$ as the time-ordered exponential $T\exp[\int_0^t dt' \times \hat{\sigma}(t')]$. The temporal evolution of $\hat{W}$ is described by two Lyapunov exponents at times greater than the inverse of the exponents, while all other ("angular") degrees of freedom are frozen [18]. Respectively, $\mathrm{tr}[\hat{W}\hat{W}^+]$ grows as $\exp[2\lambda t]$ and one gets the following estimation for the length of the polymer, $\rho^2(t) \sim \max\{1, \exp[2(\lambda - k)t]\}\kappa/|\lambda - k|$. Here the long-time statistics of the leading Lyapunov exponent (according to a matrix version of the large deviation theory [19]) is described by the weight

$$d\lambda \exp[-tS(\lambda)]. \qquad (3)$$

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The entropy function $S(\lambda)$ is concave with a zero minimum at $\lambda = \bar{\lambda}$. At the largest times, the moments of ρ are governed by a saddle point value, $\lambda = \lambda_n$, $S'(\lambda_n) = n$,

$$\frac{\langle \rho(t)^n \rangle}{\kappa^{n/2}} \sim \max\left\{\frac{1}{|\bar{\lambda} - k|^{n/2}}, \frac{e^{t[-nk + n\lambda_n - S(\lambda_n)]}}{|\lambda_n - k|^{n/2}}\right\}. \quad (4)$$

This result shows, particularly, that only the lowest moments (and only if $k > \bar{\lambda}$) are steady. However small the $\bar{\lambda}$ (in comparison with k) may be, it cannot prevent the higher moments from an asymptotic in time growth, the steady probability distribution function (PDF) of ρ decays algebraically [20] with a large-ρ-cutoff growing in time. The threshold for the nth moment convergence is given by

$$S'(\lambda_n) = n, \qquad k_n = \lambda_n - S(\lambda_n)/n. \quad (5)$$

k_n as a function of n has a minimum, $\bar{\lambda}$, at $n = 0$. The $n = 2$ value of the threshold is associated with the convergence of the dilute polymer solution contribution into the overall strain rate, and therefore can be identified as the onset of the drag reduction [20]. The dependence of the onset value on the number of elements in a long polymer chain (i.e., on square equilibrium radius of gyration of the polymer) will be discussed later in the Letter. A problem, however, is that the linear theory does not allow one to describe statistics of polymer (and, particularly, to find the steady length of the stretched polymer) above the drag reduction onset.

Accounting for the elastic elasticity solves the latter problem. The anharmonic generalization of (1) to consider is

$$\frac{d}{dt}\rho^\alpha - \sigma^{\alpha\beta}(t)\rho^\beta = -\partial_\rho^\alpha U(\rho) + \xi^\alpha(t), \quad (6)$$

where $U(\rho)$ is an arbitrary bounded potential. Isotropy dictates that the distribution function of ρ^α should depend on the polymer length only. For the dynamically relevant times, $t \gg 1/\bar{\lambda}$, the problem reduces to a study of (6) projected on the major stretching direction. First, consider the case of the Gaussian entropy function, $S(\lambda) = (\lambda - \bar{\lambda})^2/2\Delta$, for which the reduction from the stochastic differential equation (6) to the Fokker-Planck equation for the distribution function of the separation ρ, $\mathcal{P}$, is especially simple

$$\left\{\partial_t + \frac{\Delta}{2}\partial_\rho\rho\partial_\rho\rho - \bar{\lambda}\partial_\rho\rho + 2\kappa\partial_\rho^2 + \partial_\rho U'(\rho)\right\}\mathcal{P} = 0. \quad (7)$$

The stationary solution of (7) is

$$\mathcal{P}(\rho) = C\rho^{-1}\exp\left[-\int_0^\rho dr' \frac{U'(r') - \bar{\lambda}r'}{2\kappa + \Delta r'^2/2}\right], \quad (8)$$

where C is the normalization coefficient. One observes that when the molecular diffusivity is small it enters only as an ultraviolet cutoff, $r_d = \sqrt{\kappa/\Delta}$ in the large-scale ($\rho \gg r_d$) behavior. In the forthcoming calculations the diffusion will be considered small. We will not be counting for effect of diffusion explicitly and yet introducing the r_d cutoff if appropriate. The general case of a non-Gaussian entropy function does not lead to a simple differential equation for the PDF. However, it may always be described by the path integral

$$\mathcal{P}(r) = \int^{\rho(0)=r} \mathcal{D}\lambda(t)\,\mathcal{D}\rho(t)\,\mathcal{D}p(t) \times \exp\left[-\int_{-\infty}^0 \mathcal{L}\,dt\right], \quad (9)$$

$$\mathcal{L} \equiv -p[\dot{\rho} - \lambda\rho + U'(\rho)] + S(\lambda). \quad (10)$$

The effective action in (9) is as large as the time of evolution in the strong flow is. Therefore, the semiclassical saddle-point approximation should work. The saddle system of equations, supplied by the final condition (at the observation time) $\rho(0) = r$, is

$$\begin{cases} \dot{\rho}_{\rm sp} - \lambda_{\rm sp}\rho_{\rm sp} + U'(\rho_{\rm sp}) = 0, \\ -\dot{p}_{\rm sp} - \lambda_{\rm sp}p_{\rm sp} + p_{\rm sp}U''(\rho_{\rm sp}) = 0, \\ p_{\rm sp}\rho_{\rm sp} + S'(\lambda_{\rm sp}) = 0. \end{cases} \quad (11)$$

Notice also that this system of equations is consistent with the conservation of energy

$$E = -p_{\rm sp}[-\lambda_{\rm sp}\rho_{\rm sp} + U'(\rho_{\rm sp})] + S(\lambda_{\rm sp}) = \text{const.} \quad (12)$$

Because one is looking for finite action during an infinite time (beginning at $t = -\infty$) evolution, the choice $E = 0$ is mandatory. The saddle point PDF is given by

$$\mathcal{P}_{\rm sp}(r) \sim \exp\left[-\int_0^r \frac{d\rho_{\rm sp}}{\rho_{\rm sp}} S'(\lambda_{\rm sp})\right], \quad (13)$$

with $\lambda_{\rm sp}$ and $\rho_{\rm sp}$ related to each other locally through $U'(\rho_{\rm sp})/\rho_{\rm sp} = \lambda_{\rm sp} - S(\lambda_{\rm sp})/S'(\lambda_{\rm sp})$. For the Gaussian $S(\lambda)$, one derives $\dot{\rho}_{{\rm sp};G} + \bar{\lambda}\rho_{{\rm sp};G} - U'(\rho_{{\rm sp};G}) = 0$ and

$$\mathcal{P}_{{\rm sp};G}(r) \sim \exp\left[-\frac{2}{\Delta}\int_{r_d}^r \frac{dr'}{r'^2}[U'(r') - \bar{\lambda}r']\right]. \quad (14)$$

Comparing the semiclassical expression (14) with the exact one (8), one concludes that the algebraic $1/r$ factor is gained through the fluctuations calculated on the top of the saddle solution. [Notice also, that the saddle-point solution becomes exact after changing to log $\ln(r/r_d)$ variables.] To find the steady length of the polymer, one should also perform an additional variation of the effective action in (14) with respect to r. The result is given by the time-independent solution of (11)

$$\bar{\lambda}\rho_{st} = U'(\rho_{st}). \quad (15)$$

The last equation is valid for an arbitrary form of $S(\lambda)$.

Consider now the case of a long polymer modeled by N anharmonic springs connected in a chain

$$\frac{d}{dt}\rho_i^\alpha = \sigma^{\alpha\beta}\rho_i^\beta - [\partial^\alpha U(\boldsymbol{\rho}_{i;i-1}) + \partial^\alpha U(\boldsymbol{\rho}_{i;i+1})] + \xi_i^\alpha, \quad (16)$$

with $\boldsymbol{\rho}_{i;k} \equiv \boldsymbol{\rho}_i - \boldsymbol{\rho}_k$, and the boundary condition, $\boldsymbol{\rho}_{1;0} = \boldsymbol{\rho}_{N+1;N} = 0$, imposed at the fictitious end points of the polymer, added for convenience. As the strong flow regime when the chain is extremely stretched (so that anharmonicity becomes more important while off-linear conformations of the polymer are less relevant) one can (1) take into account only linear (straight-line) conformations of the polymer; (2) neglect diffusion; and (3) replace the projected (on the major stretching direction) $\hat{\sigma}$ by the leading Lyapunov exponent. The continuous version of the scalar projection of (16) (to be considered for $N \gg 1$, the major case of interest) is

$$\frac{d}{dt}\rho_n = \lambda(t)\rho_n + \partial_n U'(\partial_n \boldsymbol{\rho}), \tag{17}$$

supplemented by $\partial_n \boldsymbol{\rho}(0) = \partial_n \boldsymbol{\rho}(N) = 0$. The saddle-point method explained above in detail for the single-spring model is also valid (it is even enhanced as N appears to be an additional saddle parameter) for analyzing the following system of equations:

$$\begin{cases} \dot{\rho}_{\rm sp} - \lambda_{\rm sp}\rho_{\rm sp} + \partial_n U'(\partial_n \boldsymbol{\rho}_{\rm sp}) = 0, \\ -\dot{p}_{\rm sp} - \lambda_{\rm sp} p_{\rm sp} + \partial_n^2 p_{\rm sp} U''(\partial_n \boldsymbol{\rho}_{\rm sp}) = 0, \\ \int_0^N p_{\rm sp}\rho_{\rm sp}\, dn + S'(\lambda_{\rm sp}) = 0. \end{cases} \tag{18}$$

The zero energy condition, consistent with (18), is $\int_0^N dn\, p_{\rm sp}[-\lambda_{\rm sp}\rho_{\rm sp} + \partial_n U'(\partial_n \rho_{\rm sp})] = S(\lambda_{\rm sp})$. The saddle-point system of equations supplied by the final condition $\rho_n(t = 0) = r(n)$ has a unique solution. The functional PDF is given by $\mathcal{P}\{r(n)\} \sim \exp[\int_{-\infty}^0 p_{\rm sp}\dot{\rho}_{\rm sp}\, dt]$. If, however, one is interested in the PDF of the final point (polymer length) only, variation with respect to all the $r(n)$ except the end of the polymer, $r(N)$, should be taken. A very symmetric solution of the enhanced saddle-point system is available. The hint is that not only the global energy vanishes but also the energy density (for each and every value of n) does. This leads to

$$\lambda_{\rm sp} - \frac{\partial_n U'(\partial_n \rho_{\rm sp})}{\rho_{\rm sp}} = \frac{S(\lambda_{\rm sp})}{S'(\lambda_{\rm sp})} = \frac{\dot{\rho}_{\rm sp}}{\rho_{\rm sp}}. \tag{19}$$

The first equation in (19) can be integrated

$$n + (N - 2n)\theta\left(\frac{N}{2} - n\right) = \frac{\int_0^\tau \frac{U''(x)\,dx}{\sqrt{2\int_x^{\tau_*} yU''(y)\,dy}}}{\sqrt{\lambda_{\rm sp} - \frac{S(\lambda_{\rm sp})}{S'(\lambda_{\rm sp})}}},$$

where $\tau \equiv \partial_n \rho_{\rm sp}$, and $\theta(x)$ is the step function. Therefore, the maximal tension on the string $\tau_*(t)$ and the length of the polymer, $\rho_*(t) = \rho_{\rm sp}(t; N)$, are related to each other through

$$N\sqrt{\lambda_{\rm sp} - \frac{S(\lambda_{\rm sp})}{S'(\lambda_{\rm sp})}} = \sqrt{2}\int_0^{\tau_*} \frac{U''(x)\,dx}{\sqrt{\int_x^{\tau_*} yU''(y)\,dy}}, \tag{20}$$

$$\frac{\rho_*^2}{4}\left[\lambda_{\rm sp} - \frac{S(\lambda_{\rm sp})}{S'(\lambda_{\rm sp})}\right] = \int_0^{\tau_*} xU''(x)\,dx. \tag{21}$$

Finally, according to the second part of (19), applied to $n = N$, the dynamics of all the time-dependent fields $(\lambda_{\rm sp}(t),\ \rho_*(t),\ \tau_*(t))$ is unambiguously fixed by $d\ln[\rho_*(t)]/dt = S(\lambda_{\rm sp})/S'(\lambda_{\rm sp})$, $\rho_*(0) = R$. The probability to observing a polymer of length R is given by (13) with $\rho_{\rm sp}$ replaced by ρ_*, ρ_*, and $\lambda_{\rm sp}$ related to each other through (20) and (21). The PDF has a pronounced maximum at some value, R_*, which is the steady state polymer length. R_* is described by (20) and (21) taken at $\lambda_{\rm sp} \to \bar{\lambda}$ (then $\rho_* \to R_*$).

The algebraic system of Eqs. (20) and (21), with the result substituted in the $\rho_* \to \rho_{\rm sp}$ version of (13), solves unambiguously the problem of finding the probability for the N-chain polymer characterized by the interbead interaction $U(x)$ to be stretched to the length R in the flow described by $S(\lambda)$. For the Gaussian entropy function $S(\lambda)$ and the algebraic potential $U(x) = qx^{2+\alpha}$ one derives

$$\mathcal{P}(R) \sim \left(\frac{R}{r_d}\right)^{2\bar{\lambda}/\Delta} \exp\left[-\frac{2\bar{\lambda}}{(2+\alpha)\Delta}\left(\frac{R}{R_*}\right)^{2+\alpha}\right], \tag{22}$$

$$R_* = \frac{2[\bar{\lambda}/q]^{1/\alpha}}{(1+\alpha)^{1/\alpha}}\left(\frac{\Gamma[\frac{4+3\alpha}{4+2\alpha}]}{\Gamma[\frac{1+\alpha}{2+\alpha}]\sqrt{2\pi}}N\right)^{1+2/\alpha}. \tag{23}$$

Notice also that (23) holds for an arbitrary form of $S(\lambda)$. For the linear harmonic chain, $U = kx^2$, and the Gaussian entropy function, one gets $\Delta\ln[P(R)]/(2\ln[R/r_d]) = \bar{\lambda} - \pi^2 k/N^2$; i.e., for N greater than $\pi\sqrt{\bar{\lambda}/k}$ the pure harmonic consideration has no sense as the resulting PDF is not normalizable. In other words, a transition to the nonlinear regime is taking place at a very small $(\pi^2 k/N^2)$ value of $\bar{\lambda}$.

Knowledge of $P(R)$ allows one to calculate any correlation functions of R. I will briefly discuss two examples of interest. First of all, as was already mentioned above, the kinetic theory estimate for the polymer contribution into strain tensor is proportional to $\langle R^2\rangle \equiv \int R^2 P(R)\,dR$ [20]. Therefore, (20), (21), and (13) applied to the case of a complex potential $U(x) = kx^2 + qx^{2+\alpha}$ will describe the "first order phase transition" (jump of the $\langle R^2\rangle$ value) from the linear theory estimate, $\sim r_d^2$, valid at $\bar{\lambda} + 2\Delta < \pi^2 k/N^2$, up to $\sim R_*^2$, correspondent to the nonlinear case. The second example explains how to recalculate the probability, $P_{\rm deg}$, of the polymer to degrade (to break in two pieces) under the action of turbulence. Indeed, assume that the polymer string breaks if the maximal (along the polymer) tension exceeds the critical value, τ_c. Then, $P_{\rm deg}$ is given by the integration of $P(R)$ from R_c up to ∞, where R_c solves the system (20) and (21) with ρ_* and τ_* replaced by R_c and τ_c, respectively.

Let me briefly mention other passive problems of interest which remained beyond the scope of the present Letter. First of all, it is known that in the case of fully developed turbulence, the degenerate (or very close to degenerate) sheetlike flow configurations (associated with the so-called Vieillefosse tail of the velocity gradient PDF) can

be favored, especially in the viscous range [21]. Polymer stretching in the degenerate case requires a separate investigation accounting for off-straight-line but planar conformations of the polymer. Notice also that turbulent stretching of a flexible but inextensible polymer [4] (the one which is considered to be a good model of B-DNA [22]) is yet another problem which requires an accurate account for the off-straight-line conformations. Second, excluded volume effect along with hydrodynamic self-interaction of the polymer, known to be of great importance in the equilibrium theory [23,24], may also play a significant role in the random flow case. Third, compressibility of the flow (responsible for the sign change of $\bar{\lambda}$ [25]) may cause new effects interesting enough to study (the saddle-point approach will not work if $\bar{\lambda}$ is negative). Finally, steady statistics of comblike, starlike, and randomly branched polymers, dendrimers, or polymeric membranes, placed in a chaotic flow, can also be studied within the passive approach demonstrated above for the linear polymer.

If concentration of polymer solution is small enough, the passive approach developed above is valid. However, the elastic contribution into the strain tensor grows with the concentration. Once the elastic contribution into the stress tensor becomes of the order of the kinetic one the problem cannot be treated as passive. The steady length of the polymer may still be much smaller than the viscous scale. The scale separation, in principle, allows one to generalize the passive approach of the present work and to describe various chaotic effects of the non-Newtonian hydrodynamics (see [26] for an attempt to proceed in the active direction).

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