Turbulent Dynamics of Polymer Solutions

E. Balkovsky,[1,2] A. Fouxon,[1] and V. Lebedev [1,3]

[1]*Physics Department, Weizmann Institute of Science, Rehovot 76100, Israel*
[2]*School of Mathematics, Institute for Advanced Study, Einstein Drive, Princeton, New Jersey 08540*
[3]*Landau Institute for Theoretical Physics, Moscow, Kosygina 2, 117940, Russia*
(Received 12 November 1999)

We study properties of dilute polymer solutions. The probability density function (PDF) of polymer end-to-end extensions R in turbulent flows is examined. We show that if the value of the Lyapunov exponent λ is smaller than the inverse molecular relaxation time $1/\tau$ then the PDF has a strong peak at the equilibrium size R_0 and a power tail at $R \gg R_0$. This confirms and extends the results of J.L. Lumley [Symp. Math. **9**, 315 (1972)]. There is no essential influence of polymers on the flow in this regime. At $\lambda\tau > 1$ the majority of molecules is stretched to the linear size $R_{op} \gg R_0$, which can be much smaller than the maximal length of the molecules due to their back reaction.

Dynamics of dilute polymer solutions is an important subject both from theoretical and practical points of view. Possible applications rely mainly on the fact that low concentrations of polymer molecules can lead to substantial changes in hydrodynamics. The most striking effect related to polymers is probably the so-called drag reduction in turbulent flows. A consistent explanation of this effect is a long-standing question [1]. One believes that the drag reduction is related to the effective increase of the viscosity due to the presence of polymers [2]. Here we address some aspects of this phenomenon.

An important underlying property of polymers is their flexibility [2–5]. At equilibrium, a polymer molecule coils up into a spongy ball with a radius R_0. For dilute solutions with concentrations n satisfying $nR_0^3 \ll 1$, the influence of equilibrium size molecules on hydrodynamic properties can be neglected. When placed in a flow, the molecule is deformed into an elongated structure of ellipsoidal form which can be characterized by its end-to-end extension R. Since the number N of monomers in a long-chain polymer molecule is large, R can be much larger than R_0. It explains why minute amounts of polymers can produce an essential effect. It was shown in [3] that in sufficiently intensive flows polymer molecules get strongly extended due to stretching. This is the key mechanism providing an essential back reaction of the polymer molecules on the flow.

Here we consider turbulent dynamics of polymer solutions. We assume that R is always much smaller than the viscous length of the turbulent flow r_v. Therefore, molecules can be treated as immersed into a spatially smooth external velocity field [4]. In this case the dynamics of polymer stretching is determined only by the gradients of the velocity. Since the gradients in turbulent flows are correlated at the viscous length, all the molecules inside regions with size of the order of r_v are subject to the same gradient, and therefore are stretched coherently.

As long as one can neglect the hydrodynamic interactions between molecules, the problem is reduced to dynamics of a single molecule.

We investigate the behavior of polymer molecules with the extensions R satisfying $R_0 \ll R \ll R_{max}$, where R_{max} is the maximal size of the polymer. Random walk arguments show that the entropy of such molecules is quadratic in R in this interval, which leads to Hooke's law (see, e.g., Ref. [6]). That is why one can expect a linear dynamics of the molecules. Even though hydrodynamic interactions of monomers make polymer's dynamics inherently nonlinear, the interactions can be neglected for elongated molecules. This expectation is confirmed by recent experiments with DNA molecules [7] where an exponential relaxation of a single molecule was observed. Numerics and theoretical arguments presented in Ref. [8] also show the linear character of the molecule dynamics for $R_0 \ll R \ll R_{max}$. In experiments [7] a number of the molecule eigenmodes have been seen. We will take into account only the mode which has the largest relaxation time τ, because the other modes are harder to get excited in turbulent flows.

A starting point of our theory is the dynamic equation for the vector $\boldsymbol{R}$ which can be defined, say, via the inertia tensor (per mass of a monomer) $R_\alpha R_\beta$ of the elongated molecule. Then $\boldsymbol{R}$ determines the orientation and the largest size of the molecule. We assume the following dynamic equation for the vector (cf. Refs. [2,5]):

$$\frac{d}{dt} R_\alpha = R_\beta \nabla_\beta v_\alpha - \frac{R_\alpha}{\tau}, \tag{1}$$

where τ is the relaxation time. The velocity gradient must be taken at the molecule position. The role of nonlinearity in the extended equation for $\boldsymbol{R}$ (and in the system of equations for N coupled beads) is examined in Ref. [9]. For our purposes this nonlinearity as well as the thermal noise is irrelevant (see the discussion below).

To get rid of inessential degrees of freedom responsible for the orientation of the molecule we write $\boldsymbol{R} = R\boldsymbol{n}$ passing to the absolute value R of the vector $\boldsymbol{R}$. Then we obtain from Eq. (1) (cf. [10])

$$\frac{d\rho}{dt} = \zeta - \frac{1}{\tau}, \qquad \frac{dn_\alpha}{dt} = n_\beta \nabla_\beta v_\alpha - \zeta n_\alpha, \quad (2)$$

$$R = R_0 \exp(\rho), \qquad \zeta = n_\alpha n_\beta \nabla_\beta v_\alpha. \quad (3)$$

We see that the evolution of ρ is determined by the scalar function ζ which is a functional of the velocity field.

For turbulent flows where the velocity randomly varies in time one should use a statistical approach. A natural first step is to take the polymers being passively embedded into the fluid, disregarding their back reaction on the flow. We will demonstrate that there is a wide region of applicability of this approximation. Neglecting the back reaction we can treat the velocity dynamics as independent of polymers. Then ζ, defined by Eq. (3), is independent of ρ. We will not specify the velocity statistics. Irrespective of its character one can use the large deviation theory (see, e.g., Ref. [11] devoted to different aspects of Lagrangian dynamics in turbulent flows). The scheme presented below is valid for any random flow. Integrating Eq. (2) we get

$$\rho(t) = \rho_0 + z - \frac{t}{\tau}, \qquad z = \int_0^t dt' \, \zeta(t'), \quad (4)$$

where ρ_0 is the value of ρ at $t = 0$. One should keep in mind that the expression (4) for ρ is correct if one can neglect the presence of the boundaries R_0 and R_{max} where Eq. (1) is violated.

The integral z in Eq. (4) possesses some universal properties for times much larger than the correlation time τ_ζ of the random process ζ. For turbulent flows τ_ζ can be estimated as the characteristic time of the Lagrangian motion on the viscous scale, which coincides with the characteristic inverse strain on this scale. For $t \gg \tau_\zeta$ the variable z can be considered as a sum of a large number of independent variables. Then in order to establish the statistics of z for fluctuations near its mean value one can use the central limit theorem. If we are interested in large deviations from the mean, a more general formulation is needed (see, e.g., [12,13]). Namely, the PDF of z can be written as the homogeneous function

$$\mathcal{G}(t, z) \approx \frac{1}{\sqrt{2\pi\Delta t}} \exp\left[-tS\left(\frac{z - \lambda t}{t} \right) \right], \quad (5)$$

$$\lambda = \langle \zeta \rangle, \qquad \Delta = \int dt' \left(\langle \zeta(t)\zeta(t') \rangle - \lambda^2 \right). \quad (6)$$

"The entropy density" S is a functional of the velocity statistics. It is impossible to calculate S without knowing the statistics explicitly. Fortunately, only general properties of S (such as positivity and convexity) are needed for us. The central limit theorem is reproduced by Eq. (5) if to consider a vicinity of the entropy maximum where

$S(x) \approx x^2/(2\Delta)$. The constant λ defined in (6) is the principal Lyapunov exponent of the turbulent flow, which is the average logarithmic rate of growth of the distance between two initially close Lagrangian trajectories.

As follows from Eq. (4), $\mathcal{G}(t, z)$ determines the conditional probability that $\rho(t)$ has the value $\rho_0 + z - t/\tau$ provided $\rho(0) = \rho_0$. Therefore one can write the equation

$$\mathcal{P}(t, \rho) = \int d\rho_0 \, \mathcal{G}(t, \rho - \rho_0 + t/\tau)\mathcal{P}(0, \rho_0) \quad (7)$$

for the PDF $\mathcal{P}(t, \rho)$. In the stationary case $\mathcal{P}$ is t independent and Eq. (7) can be treated as a relation determining the PDF. Writing $\mathcal{P}$ as the Laplace integral $\mathcal{P}(\rho) = \int d\alpha \exp(-\alpha\rho)\tilde{\mathcal{P}}(\alpha)$ we observe that the convolution in Eq. (7) becomes a product and the equation can be easily resolved. The value of $\tilde{\mathcal{P}}(\alpha)$ is nonzero if

$$\int \frac{dx}{\sqrt{2\pi\Delta t}} \exp\left[\alpha x - tS\left(\frac{x}{t} + \frac{1}{\tau} - \lambda \right) \right] = 1. \quad (8)$$

Apart from the trivial solution $\alpha = 0$ this equation defines α uniquely.

Since $t \gg \tau_\zeta$, one can use the saddle-point approximation in calculating the integral (8). It gives the condition

$$\alpha = S'(\beta + 1/\tau - \lambda), \quad (9)$$

where β is the saddle-point value of the ratio $(\rho - \rho_0)/t$. Equating the integral in the left-hand side of Eq. (8) (calculated in the same approximation) to unity we get the equation for β

$$S\left(\beta - \lambda + \frac{1}{\tau} \right) - \beta S'\left(\beta - \lambda + \frac{1}{\tau} \right) = 0. \quad (10)$$

It is important that β is independent of t and ρ. Solving Eq. (10) and substituting the result into Eq. (9) we find the exponent α. The trivial solution $\beta = \lambda - 1/\tau$ of Eq. (10), corresponding to $\alpha = 0$, should be discarded.

We conclude that a single component $\tilde{\mathcal{P}}(\alpha)$ is nonzero and therefore $\mathcal{P}(\rho) \propto \exp(-\alpha\rho)$. Recalculating this distribution of ρ into that of R we obtain the power tail of the PDF of the molecule size R

$$\mathcal{P}(R) \sim R_0^\alpha R^{-\alpha - 1}. \quad (11)$$

For positive α the normalization integral $\int dR \, \mathcal{P}(R)$ is determined by small R, which means that the majority of molecules has nearly equilibrium size. On the contrary, the normalization integral diverges at large R if $\alpha < 0$. Then the majority of molecules is strongly stretched.

Another way to obtain the result (11) is to consider the typical fluctuation making the largest contribution into the tail of the PDF. Starting from a nearly equilibrium shape, that is from $\rho_0 \sim 1$, the velocity stretches the molecule up to $\rho \gg 1$. The contribution of fluctuations with stretching period t is equal to $\mathcal{G}(t, \rho + t/\tau)$. It has a sharp maximum at time t_* determined from $d\mathcal{G}(t, \rho + t/\tau)/dt = 0$. This condition gives $t_* = \rho/\beta$. The probability density is thus dominated by fluctuations with stretching period

t_*. It is proportional to $\mathcal{G}(t_*, \rho + t_*/\tau)$ which reproduces Eq. (11) with α given by Eq. (9). Note that the characteristic value of the velocity gradient for the relevant fluctuations is given by $\zeta \sim \rho/t_* + 1/\tau$ and is of the order $1/\tau$.

Let us establish the dependence of α on the control parameter, which is the strength of velocity fluctuations at the viscous length measured by the Lyapunov exponent λ. As λ tends to zero, the function $S(x)$ contracts to $x = 0$ and therefore α tends to infinity, which implies strong suppression of the tail. It is quite natural since in a weak flow the molecules are only weakly stretched. Note that even for intense flows the Lyapunov exponent λ is suppressed in the regions where the rotation rate dominates the strain rate. As λ increases, the exponent α decreases and at a certain level of fluctuations approaches zero. If λ is close to $1/\tau$ then one can use the quadratic approximation for S which leads to the law

$$\beta = \frac{1}{\tau} - \lambda, \qquad \alpha = \frac{2}{\Delta}\left(\frac{1}{\tau} - \lambda\right). \qquad (12)$$

We see that α changes its sign at $\lambda = 1/\tau$. Thus the majority of molecules becomes stretched when $\lambda > 1/\tau$. This can be interpreted as the criterion for the coil-stretch transition in turbulent flows discussed in [2,3,14].

We can use Eq. (7) only if ρ and ρ_0 belong to the asymptotic region between zero and $\rho_{\max}$, where Eq. (1) is valid. The saddle-point approximation used above gives $\rho_0 = \rho - \beta t$. Thus the above scheme works only if $t < t_* = \rho/\beta$ (here we assume $\beta > 0$, i.e., $\alpha > 0$). Then the polymer molecules spend most of the time fluctuating near the equilibrium shape, occasionally getting stretched by strain fluctuations which overcome the elastic reaction. The fluctuations leading to a given R have the duration $t_* \approx \rho/\beta$. Since β tends to zero when $\lambda \to 1/\tau$ one should observe a critical behavior $t_* \propto |\lambda - 1/\tau|^{-1}$ in accordance with Eq. (12). We see that in the vicinity of $\lambda = 1/\tau$ the time t_* is much larger than τ_ζ which justifies our scheme. Similar considerations are valid for $\alpha < 0$.

One can generalize the scheme taking into account a number of molecular eigenmodes. Since the critical value of λ is determined by the inverse relaxation time, then in the vicinity of the critical value corresponding to the principal mode, the other modes are at most weakly excited. However, they can be important at larger λ.

The rest of the paper is devoted to the discussion of the back influence of the polymers on the flow. A consistent investigation should be based on the complete system of equations coupling turbulence with polymers. One of these equations is the modified Navier-Stokes equation

$$(\partial_t + \boldsymbol{v}\nabla)v_\alpha = -\nabla_\alpha p + \nu\nabla^2 v_\alpha + \nabla_\beta \Pi_{\alpha\beta}, \quad (13)$$

where $\Pi_{\alpha\beta}$ is the polymer contribution to the stress tensor. Equation (13) should be supplemented with the equation describing dynamics of $\Pi_{\alpha\beta}$. In the considered case, $\Pi_{\alpha\beta}$ can be defined as a sum of stresses of polymer molecules in a volume divided by the mass of the fluid inside the

volume [15]. We are interested in the situation when the molecules are strongly elongated. Then due to Hooke's law the stress of such a molecule is proportional to $R_\alpha R_\beta$. Next, taking the volume smaller than the viscous length we deal with coherently elongated molecules. Therefore the stress tensor can be written as

$$\Pi_{\alpha\beta} = \Pi_0 \exp(2\rho)n_\alpha n_\beta, \qquad (14)$$

where n_α is a unit vector, $\Pi_0 \exp(2\rho)$ is the principal eigenvalue of $\Pi_{\alpha\beta}$, and the elongated molecules correspond to $\rho > 0$. Then from Eq. (1) we get the same Eqs. (2) for ρ and $\boldsymbol{n}$, where d/dt should be understood as the material derivative $\partial_t + \boldsymbol{v}\nabla$. Thus the velocity $\boldsymbol{v}$ is now coupled to ρ and $\boldsymbol{n}$ via Eqs. (13) and (14). Note that the constant Π_0 in Eq. (14) is proportional to the concentration of the polymer molecules.

Let us consider the PDF of R not assuming that the flow is unperturbed by the polymers. We start from the case $\lambda\tau < 1$. One recovers Eq. (11) if the back influence is small, i.e., $\Pi \ll \nu\nabla v$ for the relevant fluctuations characterized by $\nabla v \sim 1/\tau$. Since $\Pi \propto R^2$, the polymer contribution in the stress tensor grows with R and the inequality $\Pi \ll \nu\nabla v$ is violated for the molecules with $R \gtrsim R_{\text{back}}$. The value of R_{back} can be found from the estimate $\nu/\tau \sim \Pi_0 R_{\text{back}}^2/R_0^2$. For $R \gtrsim R_{\text{back}}$ the back reaction switches on and suppresses the velocity fluctuation. Hence, the probability of fluctuations producing $R > R_{\text{back}}$ is small and therefore at $R \gtrsim R_{\text{back}}$ the PDF decays much faster than prescribed by Eq. (11).

Now we study the case $\lambda > 1/\tau$. For $R \ll R_{\text{back}}$ the polymer stress tensor is small and as explained above velocity is decoupled from the elastic degrees of freedom. Since stretching is stronger than the elastic force, R grows for any typical velocity realization. On the other hand, at $R \gtrsim R_{\text{back}}$ the polymer stress influences the velocity, suppressing it strongly for sufficiently large R. This leads to a decrease in R. Therefore, the majority of molecules has sizes near an optimal size $R_{\text{op}} > R_{\text{back}}$. The PDF is an increasing function of R at $R < R_{\text{op}}$ and decays fast at $R > R_{\text{op}}$. In this state velocity gradients can be estimated as $1/\tau$ [16]. This can be proven, e.g., by averaging Eq. (2). It means that the Lyapunov exponent of the solution is smaller than that of the solvent at the same energy input. The energy dissipation is related mainly to the polymer stress tensor and hence R_{op} grows as the input of energy increases [16]. The effective viscosity defined as the proportionality coefficient between Π and ∇v, also grows. Note that there exists an interval where $R_{\text{op}} \ll R_{\text{max}}$. This contradicts the widely accepted view that at some level of turbulent fluctuations there is a sharp transition between the state where most of the molecules have $R \sim R_0$ and the state where all the molecules are stretched up to R_{max}.

We conclude that for $\alpha > 0$ (i.e., $\lambda < 1/\tau$) the end-to-end extensions of the majority of molecules are of the order of the equilibrium size R_0, and there is no

essential contribution to the stress tensor. For $\alpha < 0$ (i.e., $\lambda > 1/\tau$) extensions of most of the molecules are of the order of $R_{op} \gg R_0$. Then the polymer stress tensor Π is estimated as $\Pi_0 R_{op}^2 / R_0^2$. Its value can be much larger than the viscous contribution $\nu\lambda$ [16].

The above analysis implies that $R_{back} \ll R_{max}$ since at $R \sim R_{max}$ one must consider nonlinear corrections to Hooke's law and hence to Eq. (1). The condition $R_{back} \ll R_{max}$ is realized for sufficiently high concentrations of polymers. Then the fluid displays non-Newtonian properties. When most of the molecules are stretched up to R_{max} but the back reaction is not switched on, one has a Newtonian fluid whose properties do not differ significantly from the properties of the solvent. This is the case for very dilute solutions where $\Pi \ll \nu\nabla\upsilon$.

Since a turbulent flow is multiscale, the real picture is more complicated. We have shown that the main characteristics of the flow that determine the behavior of polymer molecules is the Lyapunov exponent λ, which is defined at the viscous scale. Hence, the dynamics of a molecule is sensitive to the fluid motion at the viscous scale whereas the velocity varies over a wide interval of scales. Therefore the Lyapunov exponent varies in time and space over scales from the inertial interval. We thus have an "intermittent picture": In the regions where $\lambda < 1/\tau$ one deals with a Newtonian fluid with the viscosity ν of the solvent, whereas in the regions where $\lambda > 1/\tau$ the polymers are strongly stretched and the effective viscosity can be much larger than ν.

As the Reynolds number Re increases, the relative volume of the regions with $\lambda > 1/\tau$ increases and the averaged (over space) viscosity grows. The average value of R_{op} also grows. After it has reached the value of the order R_{max}, the back influence cannot grow anymore. It means that the effective viscosity first grows and then decreases back to the solvent value ν. Note that the effective viscosity varies smoothly without onset. As a consequence, the drag reduction also varies smoothly with Re, having a maximum at some intermediate value. Experiments seem to confirm our picture (see, e.g., [17]).

To avoid misunderstanding let us stress that we consider conventional turbulent flows which have the inertial interval of scales. In the inertial interval the polymer back reaction is small compared to the nonlinear term in Eq. (13). In principle, in some region of parameters the back reaction can be stronger than this nonlinearity everywhere and the properties of the fluid are drastically different [18]. This case requires a separate analysis.

[1] R. B. Bird, C. F. Curtiss, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids* (John Wiley, New York, 1987).

[2] J. L. Lumley, J. Polym. Sci. Macromol. Rev. **7**, 263 (1973).

[3] J. L. Lumley, Symp. Math. **9**, 315 (1972).

[4] J. L. Lumley, Annu. Rev. Fluid Mech. **1**, 367 (1969).

[5] E. J. Hinch, Phys. Fluids **20**, S22 (1977).

[6] C. Kittel, *Elementary Statistical Physics* (John Wiley, New York, 1967).

[7] S. R. Quake, H. Babcock, and S. Chu, Nature (London) **388**, 151 (1997); T. T. Perkins, S. R. Quake, D. E. Smith, and S. Chu, Science **264**, 822 (1994).

[8] J. W. Hatfield and S. R. Quake, Phys. Rev. Lett. **82**, 3548 (1999).

[9] M. Chertkov, preceding Letter, Phys. Rev. Lett. **84**, 4761 (2000).

[10] M. Chertkov, G. Falkovich, I. Kolokolov, and V. Lebedev, Phys. Rev. E **51**, 5609 (1995).

[11] E. Balkovsky and A. Fouxon, Phys. Rev. E **60**, 4164 (1999); M. Chertkov, G. Falkovich, I. Kolokolov, and M. Vergassola, Phys. Rev. Lett. **83**, 4065 (1999).

[12] U. Frish, *Turbulence: The Legacy of A. N. Kolmogorov* (Cambridge University Press, New York, 1995), Ch. 8.

[13] O. E. Lanford, *Entropy and Equilibrium States in Classical Mechanics,* in Statistical Mechanics and Mathematical Problems (Springer, Berlin, 1973).

[14] P. G. de Gennes, J. Chem. Phys. **60**, 5030 (1974).

[15] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon Press, New York, 1987), Ch. 2.

[16] E. Balkovsky, A. Fouxon, and V. Lebedev (to be published).

[17] A. Gyr and H.-W. Bewersdorf, *Drag Reduction in Turbulent Flows by Additives* (Kluwer, London, 1995).

[18] A. Groismann and V. Steinberg, Europhys. Lett. **43**, 165 (1998); Nature (London) (to be published).