Stretching of Polymers in a Random Three-Dimensional Flow

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Behavior of a dilute polymer solution in a random three-dimensional flow with an average shear is studied experimentally. Polymer contribution to the shear stress is found to be more than 2 orders of magnitude higher than in a laminar shear flow. The results indicate that the polymer molecules are strongly stretched by the random motion of the fluid.

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The behavior of flexible polymer molecules in a solution in various flows is one of the basic problems of polymer physics [1]. Flows that have been studied most extensively are simple shear and unilateral extension. Those flows are rather easy to create in the laboratory and the experimental data are most straightforward to interpret. As a result of many mechanical [1,2], optical [1,3,4], theoretical [5,6], and especially the most recent single molecule investigations [7,8], the major issues of polymer dynamics in these two types of flow seem to be resolved now. In contrast to it, there are virtually no experimental data on dynamics of polymer molecules in a generic case of a complex flow with a random velocity field. In this Letter we present results of our measurements of mechanical properties of a dilute polymer solution in a random three-dimensional (3D) flow. These results imply that polymer molecules can become strongly stretched in such a flow.

Stretching of polymer molecules manifests macroscopically as growth of optical anisotropy of the polymer solution and growth of the stress, τ^p, which is due to polymers [1]. By definition, $\tau^p = \tau - \tau^s$, where τ is the total stress in the solution, and τ^s is the stress in the same flow of a pure solvent.

Three-dimensional flows with a random velocity field are quite a general class of flows, which also includes turbulence. Such flows usually occur at high Reynolds number, Re, that implies large fluid velocity and a big tank size. The high Re flows are usually nonhomogeneous in space even in a statistical sense. Therefore, bulk optical measurements are difficult to interpret, and so are measurements of mechanical shear stresses, τ_w, at a wall of the flow system. In a random, high Re flow the momentum is transferred across the fluid not only by the molecular forces contributing to the stress, τ, but also by the macroscopic motion of the fluid. The latter produces the Reynolds stress $\rho\langle v_i v_j\rangle$, where ρ is the fluid density, and $\vec{v}$ is the fluctuating part of the velocity $\vec{V}$. The Reynolds stress in the fluid bulk may be of the same order as τ_w. Thus, to calculate an average of τ^p, one in general needs to evaluate the average of $\rho\langle v_i v_j\rangle$ over the whole volume of the flow, which is a rather difficult task.

A way to surmount the problem of the high Reynolds stress is to create a random flow with a low Reynolds number. Such a situation is realized in the case of the elastic turbulence, which we have reported recently [9]. It is an apparently turbulent flow that can arise in polymer solutions as a result of nonlinear elastic effects at arbitrarily low Re.

We carried out our experiments in a swirling flow between two parallel plates. The polymer solution was held in a stationary cylindrical cup with a flat bottom (lower plate). A coaxial rotating upper plate was just touching the surface of the fluid. The sidewalls of the cup were made transparent which allowed measurements of the flow velocity in the horizontal plane by a laser Doppler velocimeter. The cup was mounted on top of a commercial rheometer (AR-1000 of TA instruments) with a transducer for measuring the normal force, F_n, at the bottom of the cup. The whole setup was put into a transparent box, and the temperature of the fluid was stabilized to better than 0.05 °C by throughflow of air.

The upper plate was attached to the shaft of the rheometer, which allowed precise control of its rotation velocity, Ω, and measurements of the torque, T. The average shear stress at the upper plate, τ_w, was defined from the equation $T = \tau_w \int r\, dS$, that gave $\tau_w \equiv 3T/(2\pi R^3)$. (The integration was over the upper plate surface.) In the first experiment, the radii of the upper plate and the cup were $R = 30$ mm and $R_2 = 43.6$ mm, respectively, and the distance between the plates was $d = 30$ mm. Because of the big gap and short distance to the side wall, the shear rate profile was rather nonhomogeneous even in a laminar flow. In order to find the average shear rate near the upper plate, we measured the average stress, τ_w, as a function of Ω in a low Re flow of a Newtonian fluid with large viscosity, η_0. The applied shear rate, $\dot{\gamma}_{ap}$, was defined then as τ_w/η_0, and it was $\dot{\gamma}_{ap} = 2.78\Omega R/d$.

We used 25 ppm solutions of high molecular weight polyacrylamide ($M_w = 18\,000\,000$, Polysciences) in viscous sugar syrups. The syrups were made of sucrose and sorbitol (corn sugar) in a proportion of 1:2, and 1% of NaCl was added to fix the ionic contents. In the first experiment the total sugar concentration was 76.3%, and the solvent viscosity at the temperature of the experiment, 18 °C, was $\eta^s = 1.36$ Pa s. The solution viscosity, $\eta(\dot{\gamma})$, was carefully measured in a narrow gap rheometric geometry. It decreased with $\dot{\gamma}$, changing at the shear rates applied in the experiment (see Fig. 1) from $1.12\eta^s$ to $1.08\eta^s$.

When flexible polymers get stretched in a shear flow, they also get aligned along the flow direction [1]. This leads to a difference in the normal stresses in the streamwise and transverse directions that, for a flow between two rotating plates, is $N_1 = \tau_{\phi\phi} - \tau_{zz}$. Here (r, ϕ, z) are cylindrical coordinates. This first normal stress difference results in the "hoop stress" and a normal force, $F_n \sim \bar{N}_1$, which pushes the plates apart [1]. So, average N_1 can be estimated from measurements of F_n. For flexible polymer molecules, N_1 is connected with the polymer relaxation time, λ, by $N_1 = 2\eta^p \lambda \dot{\gamma}^2$ [1], where $\eta^p \equiv \eta - \eta^s$. For our solution the relaxation time estimated from measurements of N_1 in a narrow gap cone-and-plate setup at $\dot{\gamma} = 1\ \mathrm{s}^{-1}$ was 6.3 s. (This $\dot{\gamma}$ corresponded to the elastic flow transition, Fig. 1).

In the first experiment we evaluated the dependence of the shear stress, τ_w, and the normal force, F_n, on the Weissenberg number, $\mathrm{Wi} = \lambda\dot{\gamma}_{ap}$. (The role of the Weissenberg number in the elastic turbulence is similar to the role of the Reynolds number in the usual turbulence in normal fluids [9].) Simultaneously, one velocity component was measured in the center of the setup. Figure 1a, curve 1, shows τ_w divided by the stress, τ_w^{lam}, in laminar flow with the same applied shear rate, as a function of Wi. [The stress, τ_w^{lam}, was defined as $\eta(\dot{\gamma}_{ap})\dot{\gamma}_{ap}$.] It resembles very much Fig. 2 in Ref. [9]. The flow at low Wi is laminar. At Wi of about 5, transition from the laminar flow to the elastic turbulence occurs. It manifests in the growth of the flow resistance and in the onset of fluctuations of the fluid velocity, (Fig. 1b). The amplitude of the velocity fluctuations increases with Wi. The ratio $\tau_w/\tau_w^{\mathrm{lam}}$ increases with Wi as well, reaching a value of about 13 at $\mathrm{Wi} = 22$. The Reynolds number, $\mathrm{Re} = \Omega R d\rho/\eta^s$, is only 1.3 at the highest Wi.

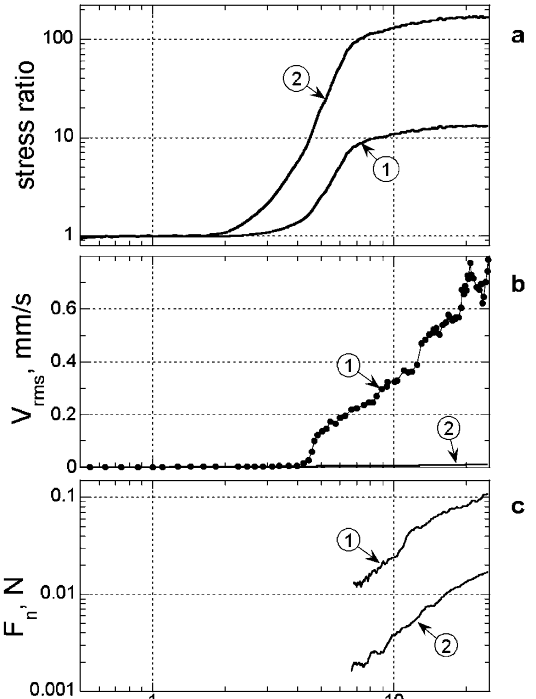

FIG. 1. Dependence of different parameters of flow on Wi. Wi was raised by 9%, 2.4%, and 7%/min in the ranges [0.35, 2.1], [2.1, 8.7], and [8.7, 25], respectively. (a) The ratio of the total stresses, $\tau_w/\tau_w^{\mathrm{lam}}$, curve 1. The ratio of the polymer contribution to the stress, $\tau^p/\tau^p_{\mathrm{lam}}$, curve 2. (b) V_{rms} in the center of the setup, curve 1. Large fluctuations of velocity at high Wi are due to the short time of averaging. Instrumental noise level in a laminar flow is shown for comparison, curve 2. (c) Normal force, F_n, in the turbulent flow, curve 1, and in a laminar flow between the same plates with a narrow gap, curve 2.

As we showed elsewhere [9], the flow of a polymer solution at high Wi (above the transition) bears all of the features of developed turbulence. The flow velocity changes randomly in space and time, and the fluid motion is excited in a broad range of spatial and temporal scales. The subject of the current paper is the stretching of the polymer molecules in this random 3D flow. The elastic turbulence itself is driven by the polymer stresses, which are generated by the stretched polymer molecules. However, the origin of forces driving a flow is not directly relevant to the problem of polymer stretching. Extension of polymers can depend only on local properties of the flow velocity field along the trajectory of the fluid element, which contains the polymer molecules.

In spite of the turbulent character of the fluid motion at high Wi, the Reynolds stresses were so small that their contribution to the total shear stress could be totally neglected. So, at $\mathrm{Wi} = 22$ the rms of the velocity fluctuations, V_{rms}, measured in different points, was always below 1 mm/s (see Fig. 1b for V_{rms} in the center). Thus, the Reynolds stresses could be estimated from above as $2\rho V_{\mathrm{rms}}^2 = 2.8 \times 10^{-3}$ Pa, while the stress τ_w was 91 Pa.

The turbulent flow causes significant perturbation of the field of the average flow velocity, $\bar{V}$, and of the average viscous stresses, $\tau_{ij}^s = \eta^s(\frac{\partial \bar{V}_i}{\partial x_j} + \frac{\partial \bar{V}_j}{\partial x_i})$. However, the viscous stresses are linear in $\bar{V}$, and conditions on $\bar{V}$ at solid boundaries of the system are identical in turbulent flow and in laminar shear flow with the same Ω. Therefore, in the first approximation, τ^s averaged over the fluid volume should be the same as in the laminar flow.

Then the whole increment in T and τ_w should be solely due to the growth of the average τ^p. Taking the contribution of the solvent stresses to τ_w to be the same as in the laminar flow, we get, for the contribution of the polymer stresses to τ_w, the curve 2 in Fig. 1a. This curve gives an estimate for the ratio of the average shear stresses due to polymers in the turbulent and laminar flows, $\tau^p/\tau^p_{\mathrm{lam}}$. This ratio reaches a value of 170, which is evidence of strong stretching of the polymers in the turbulent flow.

Dependencies of F_n on Wi measured in the elastic turbulent flow and in a laminar flow are shown in Fig. 1c. One can learn that F_n in the turbulent flow becomes about an order of magnitude higher than in the laminar flow with the same $\dot{\gamma}_{ap}$. This is an indication of the growth of N_1 and other evidence of stretching of the polymers by the random 3D fluid motion.

A specific feature of the elastic stresses is that they do not turn to zero immediately after the fluid motion stops, but rather they decay with their characteristic relaxation time, λ [1]. That is how they can be clearly distinguished from the viscous stresses, which decay instantaneously. So, a way to independently examine the origin of stresses applied to the upper plate is to stop its rotation and to measure the decay of the stresses. This was the objective of our second experiment (Fig. 2). It required a higher polymer relaxation time. Therefore, the concentration of sugars was increased to 80.3%, which gave η^s of about 7.2 Pa s and λ of about 30 s at the temperature of the experiment, 15 °C. The size of the setup was reduced by a factor of 2, $R = 15$ mm, $R_2 = 21.8$ mm, and $d = 15$ mm. In this small setup the dependence of τ_w on Wi for the polymer solution from the first experiment was the same as in Fig. 1a (see also Ref. [9]). The characteristic torques were 8 times smaller, however, which enabled a sharp stop of the upper plate.

Rotation of the upper plate was started abruptly at angular velocity $\Omega = 0.07\ \mathrm{s}^{-1}$ corresponding to Wi ≈ 6 and Re $\approx 3 \times 10^{-3}$. The rotation continued for a while, and then, at a time moment taken as zero, Ω was abruptly brought to zero. In the first run, curve 1 in Fig. 2b, the time of the rotation was short, about 115 s. By this time τ_w just reached the value, τ_w^{lam}, measured in laminar flow with the same applied shear rate. Therefore, the average stretching of the polymers was equal to their equilibrium stretching in a stationary flow with the same shear rate. So, by the time the rotation was stopped at $t = 0$, the major part of torque was due to the solvent, $T^s \approx 10\ \mu$N m, and it relaxed almost immediately. (Characteristic viscous diffusion time is very small, $d^2\rho/\eta^s = 0.04$ s.) This torque value, 10 μN m, was also measured just after rotation started and polymers had not had time to get stretched yet. Extrapolation of curve 1 in Fig. 2b to $t = +0$ gives the value of the torque due to polymers in the laminar flow, $T^p_{\mathrm{lam}} = 0.85\ \mu$N m.

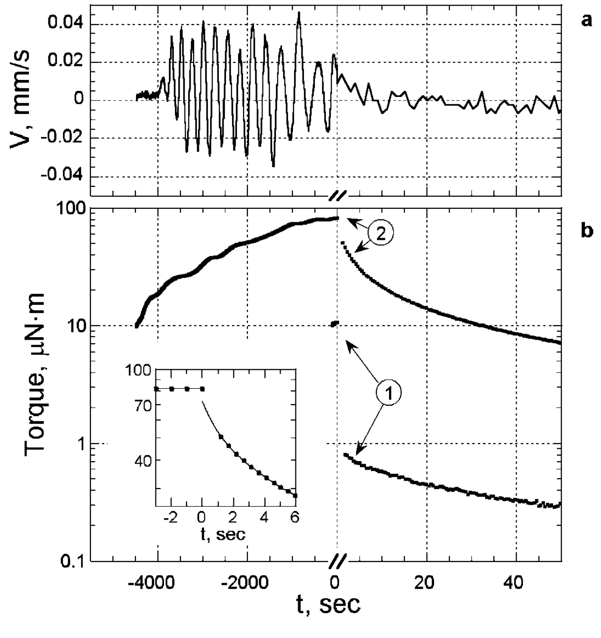

FIG. 2. Dependence of different parameters of flow on time, t. The time axis is compressed by a factor of 100 for $t < 0$. (a) Flow velocity in the center corresponding to curve 2 below. (b) The torque applied to the upper plate. Inset: curve 2 in the vicinity of $t = 0$.

In the second run the time of rotation, about 4500 s, was long enough for the transition to develop elastic turbulence to complete. The torque reached its saturated value, $T = 82.5\ \mu$N m, corresponding to applied Wi. From Fig. 2a, one can see that the fluid velocity starts to fluctuate during the time the torque increases. Those transient fluctuations finally develop into the elastic turbulent flow [9]. As a result of the irregular 3D motion of the fluid, the slowly relaxing part of the torque increases by almost 2 orders of magnitude. One can learn from the inset that the relaxing torque can be reasonably extrapolated to 72.5 μN m at $t = +0$. Thus, the immediately relaxing part of the torque is again due to the solvent shear stresses, $T^s \approx 10\ \mu$N m, and the results of these relaxational measurements are quite consistent with the suggestion that the whole increment in the torque is due to the growth of the polymer contribution. If inertial effects were important, they would obviously lead to torques of the opposite sign. The polymer torque $T^p = 72.5\ \mu$N m at $t = 0$ means on average increase of τ^p by 85 times compared with the laminar flow.

Our measurements show that as a result of a secondary random 3D flow, superimposed on the primary applied shear, the polymer contribution to shear stress, $\tau^p_{z\phi}$, can become as much as 170 times larger. If linear elasticity of the polymer molecules is assumed, the stress is related to the polymer extension via $\tau^p_{z\phi} \sim \langle R_z R_\phi \rangle$, where $\vec{R}$ is the vector connecting the ends of a polymer chain [1]. Then the factor of an additional extension of the polymer molecules due to the random 3D flow is about 13. In fact, measurements of the stress in the turbulent regime can be viewed as a mechanical test, where shear is applied to a polymer solution, which flows turbulently with zero average shear rate. Then, one can say that the polymer contribution to viscosity, defined as $\eta^p = \tau^p/\dot{\gamma}_{ap}$, increases by more than 2 orders of magnitude because of the turbulent flow. In theories of polymer dynamics, η^p is usually connected with an effective volume occupied by the polymer chains [1]. Thus, our experimental results suggest that the effective volume can significantly increase, and polymer molecules can get strongly stretched in a random 3D flow with zero averages.

Dynamics of a polymer molecule in a random 3D flow were first considered by Lumley [10], and have been revised recently [11,12]. It is suggested that the flow is always homogeneous on the scale of a polymer molecule, so that the velocity field in some vicinity of a molecule with the center at $\vec{r}_0$ is given by $\vec{V} = \vec{V}(\vec{r}_0) + \kappa \cdot (\vec{r} - \vec{r}_0)$. Possible complex structural properties of the flow at larger scales are not important for the issue of the polymer stretching. It depends only on statistics of the tensor of the rate of deformation, κ, which varies randomly in time and space. If the flow is truly 3D, κ always has an eigenvalue with a positive real part, so that there is a direction along which pure extension occurs [3,10]. The direction and the rate of this purely extensional flow change randomly as a fluid element rotates in the flow and moves along its trajectory. Nevertheless, if κ remains correlated within finite time intervals, the overall statistical result of such random motion will be that the maximal linear dimension, X, of a small fluid element will on average increase in time exponentially fast, $d(\ln X)/dt = a$ [10–12]. In a turbulent flow, where an estimate for the correlation time of κ is given by the inverse of the velocity gradients themselves, the average Lyapunov exponent, a, is given by the rms of longitudinal velocity gradients with a prefactor of order unity [10]. The direction $\hat{x}$ along which X is measured will fluctuate quickly in the laboratory frame because of the fluid element rotation. However, stretching of polymer molecules along $\hat{x}$ inside this fluid element should be similar to their stretching in a *stationary* extensional flow with $\partial V_x/\partial x = a$ [10]. In particular, the polymer molecules should become vastly stretched, if the condition $a > 1/(2\lambda)$ is fulfilled [6,7,10,11]. Recent calculations show that strong polymer stretching in a chaotic flow is expected to occur even at average a smaller than $1/(2\lambda)$ [11].

A probability distribution function (PDF) of a longitudinal velocity gradient, $\partial V_\phi/(r\partial\phi)$, for Wi = 12 in the big setup (first experiment) is shown in Fig. 3. The rms of the distribution is 0.043 s^{-1}, which gives a reasonable value of 0.25, when multiplied by $\lambda = 6.3$ s. In fact, relaxation of polymer molecules is a complex process, which involves a whole range of times. We measured relaxation of τ^p in our polymer solution after a sudden stop of a stationary shear flow with Wi = 6. The apparent relaxation time, defined as $[-\partial \ln(\tau^p)/\partial t]^{-1}$, increased from 3 to 40 s as the stress decayed (see also Fig. 2b). Further, the PDF in Fig. 3 has pronounced exponential tails, so that flow events with large rate of extension occurs rather often. Therefore, we can conclude that the observed significant stretching of the polymers is quite consistent with the theoretical predictions. We believe that a similar type of polymer stretching should occur in the usual, high Re, turbulent flows, when the velocity gradients are sufficiently large compared to λ.

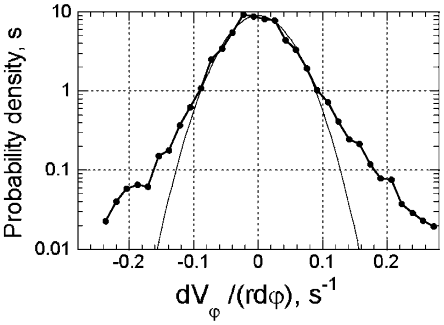

FIG. 3. PDF for the longitudinal velocity gradients, $\partial V_\phi/(r\partial\phi)$, estimated according to the Taylor hypothesis, with smoothing over about 1.3 mm. V_ϕ was measured at $z = 3.75$ mm from the upper plate, at $r = 15$ mm, with time intervals $\Delta t = 0.44$ s. The differences between the consecutive velocity readings were divided by Δt and by $\bar{V}_\phi = 2.93$ mm/s. The thin line is a Gaussian fit.

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