Stretching of polymers in a random three-dimensional flow

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(March 30, 2022)

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 two orders of magnitude higher than in a laminar shear flow. The results indicate that the polymer molecules get strongly stretched by the random motion of the fluid.

PACS numbers: 83.10 Nn, 83.50 Ws

Behavior of flexible polymer molecules in a solution in various flows is one of the basic problems of polymer physics \cite{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 \cite{3}, optical \cite{9,10}, theoretical \cite{1}, and especially the most recent single molecule investigations \cite{11}, 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 directly indicate that polymer molecules can become strongly stretched in such a flow.

Three-dimensional flows with a random velocity field is 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 big size of the tank. The high \(Re\) flows are usually non-homogeneous in space even in statistical sense. Therefore, bulk optical measurements are difficult to interpret, and so are measurements of mechanical stresses, \(\sigma\), 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, \(\tau\), but also by the macroscopic motion of the fluid. The latter produces the Reynolds stress \(\rho < v_i v_j >\), where \(\rho\) is the fluid density, and \(\vec{v}\) is fluctuating part of the velocity \(\vec{V}\). Thus, we have a momentum balance equation for the average values of the stresses

\[
\sigma = \tau^s + \tau^p + \rho < v_i v_j >, \tag{1}
\]

where the right hand side is taken in the bulk of the fluid. That is, in order to calculate the average of \(\tau^p\), one needs to evaluate the average of \(\rho < v_i v_j >\) over the whole volume of the flow, which is rather difficult to carry out.

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 \cite{12}. It is an apparently turbulent flow that can arise in polymer solutions as a result of non-linear elastic effects at arbitrarily low \(Re\).

We carried out our experiments in a swirling flow between two parallel plates. 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 cup was mounted on top of a commercial rheometer (AR-1000 of TA-instruments) with a normal force transducer. The upper plate was attached to the shaft of the rheometer, which allowed precise control of its rotation velocity, \(\Omega\), and measurements of the torque, \(T\), and the average stress, \(\sigma\), applied to it. The sidewalls of the cup were made transparent which allowed measurements of the flow velocity in the horizontal plane by a laser Doppler velocimeter, LDV. In the first experiment, the radii of the upper plate and of 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 non-homogeneous even in a laminar flow. So, we defined the average applied shear rate as the ratio between \(\sigma\) in a laminar flow, and the fluid viscosity. It was \(\gamma_{av} = 2.78\Omega R/d\). The whole set-up was put into a transparent box, and temperature of fluid was stabilized to better than 0.05 °C by throughflow of air. We used 25 ppm solutions of high molecular weight polyacrylamide (\(M_w = 18,000,000\), Polyscience) in viscous sugar syrups. The syrups were made out of sucrose and sorbitol (corn sugar) in a proportion of 1 : 2, and 1% of NaCl was added to stabilize 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 polymer part
of the solution viscosity, \( \eta^p \equiv (\tau - \tau^s)/\dot{\gamma} \), was changing at \( \dot{\gamma}_{\text{av}} \), that we applied, in the range from 0.12\( \eta^p \) to 0.08\( \eta^p \), decreasing with the shear rate. At such low values of \( \eta^p/\eta^s \) effect of overlapping of separate polymer molecules is supposed to be minor.

When flexible polymers get stretched in a shear flow, they also get aligned along the flow direction. 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 \( (r, \phi, z) \) are cylindrical coordinates. This first normal stress difference results in a normal force, \( F_n \), which pushes the plates apart (the "hoop stress") \( \equiv \). So, \( N_1 \) can be evaluated from measurements of \( F_n \). For flexible polymer molecules, \( N_1 \) is connected with the polymer relaxation time, \( \lambda \), by \( N_1 = 2\eta^p\lambda\dot{\gamma}^2 \). For our solution we measured \( \lambda = 6.3 \times 10^{-4} \) s.

In the first experiment we evaluated dependence of the stress at the upper plate, \( \sigma \), and the normal force, \( F_n \), on the Weissenberg number, \( W_i = \lambda\dot{\gamma}_{\text{av}} \). (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.) Simultaneously, one velocity component was measured in the center of the set-up. Figure 1a, curve 1, shows \( \sigma \) divided by the stress, \( \sigma_{\text{lam}} \), measured in a laminar flow with the same applied shear rate, as a function of \( W_i \). It resembles very much Fig.2 from Ref.10. The flow at low \( W_i \) is laminar. At \( W_i \) of about 5 transition from the laminar flow to the elastic turbulence occurs. It manifests in growth of the flow resistance and in onset of fluctuations of the fluid velocity, Fig.1b. The amplitude of the velocity fluctuations increases with \( W_i \). The ratio \( \sigma/\sigma_{\text{lam}} \) increases with \( W_i \) as well, reaching a value of about 13 at \( W_i = 22 \). The Reynolds number, \( Re = \Omega Rd/\eta s \), is only 1.3 at the highest \( W_i \).

As we showed elsewhere, the flow of a polymer solution at high \( W_i \) (above the transition) bears all features of developed turbulence. The flow velocity changes randomly in space and in time, and the fluid motion is excited in a broad range of spatial and temporal scales. The subject of the current study is 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, origin of forces driving a flow is not directly relevant to the problem of polymer stretching. Extension of polymers can only depend on local properties of the flow velocity field along the trajectory of the fluid element, which contains the polymer molecules.

In spite of turbulent character of the fluid motion at high \( W_i \), the Reynolds stresses were so small, that the corresponding term in Eq.(1) could be totally neglected. So, at \( W_i=22 \) characteristic amplitude of the velocity fluctuations, \( \langle \dot{V}_{\text{rms}} \rangle \), measured in different points was about 0.7 mm/s (see Fig.1b for \( \dot{V}_{\text{rms}} \) in the center). Thus, the Reynolds stress could be estimated as \( \rho\dot{V}_{\text{rms}}^2 = 7 \times 10^{-4} \) Pa, while the stress \( \sigma \) was 91 Pa. Eq. (1) is written in a general form valid for momentum transfer in the direction perpendicular to a wall. In our case we have circular symmetry. So, it is torque, \( T \), at the upper plate, which is measured, and it is angular momentum, which is transferred from the plate through the liquid to the stationary cup. The average flux of angular momentum due to the solvent stress, \( \tau^s \), is defined by \( \eta^s\dot{r}^2(\partial \omega/\partial r) \) and \( \eta^p(\partial \omega/\partial \phi) \), where \( \dot{\omega} \equiv \dot{\omega}/r \) is local average angular velocity of the fluid. The turbulent flow changes the distribution of \( \dot{\omega} \) compared to the laminar case, leading to larger gradients of \( \dot{\omega} \) near the upper plate. Nevertheless, the boundary conditions on \( \omega \) at the surfaces of the upper plate and of the cup remain the same. So, for our estimates we take the volume average of the flux of the angular momentum due to solvent to be the same as in the laminar flow. Then the whole increment in \( T \) and \( \sigma \) should be solely due to growth of average \( \tau^p \) in the fluid bulk. Taking contribution of the solvent stresses to \( \sigma \) to be the same as in the laminar flow, we get for the contribution of the polymer stresses to \( \sigma \) the curve 2 in Fig.1a. This curve gives the ratio of the average shear stresses due to polymers in the turbulent and the laminar flows, \( \tau^p/\tau^p_{\text{lam}} \). This ratio reaches a value of 170, which is an evidence of strong stretching of the polymers in the turbulent flow.

Dependencies of average \( N_1 \) on \( W_i \) measured in the elastic turbulent flow and in a laminar flow are shown in Fig.1c. One can learn that \( N_1 \) in the turbulent flow becomes about an order of magnitude higher than in the laminar flow with the same \( \dot{\gamma}_{\text{av}} \). This is another 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 decay with their characteristic relaxation time, \( \lambda \). 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 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%, that gave \( \eta^s \) of about 7.2 Pa-s and \( \lambda \) of about 30 sec at the temperature of the experiment, 15 °C. The size of the set-up was reduced by a factor of 2, \( R = 15 \) mm, \( R_2 = 21.8 \) mm, \( d = 15 \) mm. In this small set-up the dependence of \( \sigma \) on \( W_i \) for the polymer solution from the first experiment was the same as in Fig.1a (see also Ref.10). The characteristic torques were 8 times smaller, however, that enabled a sharp stop of the upper plate.

Rotation of the upper plate was started abruptly at angular velocity \( \Omega = 0.07 \) s\(^{-1} \) corresponding to \( W_i \approx 6 \) and \( Re \approx 3 \times 10^{-3} \). The rotation continued for a while, and then, at a time moment taken as zero, \( \Omega \) was abruptly stopped.
brought to zero. In the first run, curve 1 in Fig.2b, the
time of the rotation was short, about 115 seconds. It was
just enough for the polymers to get properly stretched by
the primary shear and for the polymer stress to reach its
value of the torque due to polymers in the laminar flow,

\[T_{lam}^p = 0.85 \mu Nm.\]

In the second run the time of rotation, about 4500 sec,
was long enough for the transition to developed elastic
turbulence to complete. The torque reached its satu-
rated value, \(T = 82.5 \mu Nm\), corresponding to applied
\(Wi\). From Fig.2a one can see that the fluid velocity was
fluctuating during the time, that the torque increased.

As a result of the turbulent fluid motion, the slowly re-
xisting part of the torque increased by almost two orders
of magnitude. One can learn from the inset that the re-
xisting torque can be reasonably extrapolated to 72.5
\(\mu Nm\) at \(t = +0\). Thus, the immediately relaxing part
of the torque is again due to the solvent shear stresses,
\(T^s \approx 10 \mu Nm\), and the results of these relaxational mea-
surements are quite consistent with the suggestion, that
the whole increment in the torque is due to the polymers
in the laminar flow, 

\[T_{lam}^p = \frac{10}{5} \mu Nm.\]

Further, the PDF in Fig.3 has pronounced exponential
tails, so that flow events with large rate of extension oc-
cur 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 kind of polymer stretching should occur
in the usual, high \(Re\), turbulent flows, when the velocity
gradients are sufficiently large compared to \(\lambda\).

Dynamics of a polymer molecule in a random 3D flow
were first considered by Lumley [1], and have been re-
vised recently [2,3]. It is suggested that the flow is al-
ways homogeneous on the scale of a polymer molecule, so
that 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 structure properties of the flow at larger scales
are not important for the issue of the polymer stretching.
It only depends on statistics of the tensor of rate of de-
formation, \(\kappa\), which varies randomly in time and space.
If the flow is truly 3D, \(\kappa\) always has an eigenvalue with a
positive real part, so that there is a direction along which
pure extension occurs [4]. The direction and the rate of
extension change randomly as a fluid element is rotat-
ing in the flow and moving along its trajectory. Neverthe-
less, if \(\kappa\) remains correlated within finite time intervals,
the overall statistical result of such random motion will
be exponential divergence of two closely spaced material
points. In a turbulent flow an estimate for the correlation
time of \(\kappa\) is given by the inverse of the velocity gradients
themselves. Then the average Lyapunov exponent, \(a\),
for divergence of two material points is given by the rms
of longitudinal velocity gradients with a prefactor of order
unity. Thus, in the statistical sense, a random 3D flow acts
as an extensional flow with \(\partial V_x/\partial x = a\), where the
direction, \(x\), of the maximal extension of a fluid element
is changing randomly in time and space [1,2]. In such a
flow polymer molecules should become vastly stretched,
if the condition \(a \lambda > 1/2\) is fulfilled [1,2]. In fact,
strong polymer stretching in a turbulent flow is expected
to occur even at smaller average \(a\) [2].

A probability distribution function (PDF) of a longitu-
dinal velocity gradient, \(\partial V_x/\partial x\), for \(Wi = 12\) in the
big set-up (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, relax-
ation of polymer molecules is a complex process, which
involves a whole range of times. We measured relaxation
of \(\tau^p\) in our polymer solution after a sudden stop of a
stationary shear flow with \(Wi = 6\). The apparent re-
ximation time, defined as \((\partial ln(\tau^p)/\partial t)^{-1}\), increased from
3 s to 40 s as the stress was decaying (see also Fig.2b).
Further, the PDF in Fig.3 has pronounced exponential
tails, so that flow events with large rate of extension oc-
cur 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 kind of polymer stretching should occur
in the usual, high \(Re\), turbulent flows, when the velocity
gradients are sufficiently large compared to \(\lambda\).

We gratefully acknowledge E. Balkovsky, G. Falkovich,
A. Fouxon and V. Lebedev for numerous helpful dis-
cussions. The work was partially supported by the Minerva
Center for Nonlinear Physics of Complex Systems and by
a Research Grant from the Henri Gutwirth Fund.
FIG. 1. Dependence of different parameters of flow on \( W_i \). \( W_i \) was raised by 9%/min, 2.4%/min 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, \( \sigma/\sigma_{lam} \), curve 1. The ratio of the polymer contribution to the stress, \( \tau_p/\tau_{lam} \), curve 2. b) \( V_{rms} \) in the center of the set-up, curve 1. Instrumental noise level in a laminar flow is shown for comparison, curve 2. c) Average first normal stress difference, \( N_1 \), in the turbulent flow, curve 1, and in a laminar flow between two plates, curve 2.

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 the curve 2 below. b) The torque applied to the upper plate. Inset: curve 2 in a vicinity of \( t = 0 \).

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. \( V_{\phi} \) was measured at \( z = 3.75 \) mm from the upper plate, at \( r = 15 \) mm, with time intervals \( \Delta t = 0.44 \) sec. The differences between the consecutive velocity readings were divided by \( \Delta t \) and by \( \bar{V}_{\phi} = 2.93 \) mm/s. The thin line is a Gaussian fit.