Chaotic flow and efficient mixing in microchannel with a polymer solution.

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Microscopic flows are almost universally linear, laminar and stationary because Reynolds number, $Re$, is usually very small. That impedes mixing in micro-fluidic devices, which sometimes limits their performance. Here we show that truly chaotic flow can be generated in a smooth micro-channel of a uniform width at arbitrarily low $Re$, if a small amount of flexible polymers is added to the working liquid. The chaotic flow regime is characterized by randomly fluctuating three-dimensional velocity field and significant growth of the flow resistance. Although the size of the polymer molecules extended in the flow may become comparable with the micro-channel width, the flow behavior is fully compatible with that in a table-top channel in the regime of elastic turbulence. The chaotic flow leads to quite efficient mixing, which is almost diffusion independent. For macromolecules, mixing time in this microscopic flow can be three to four orders of magnitude shorter than due to molecular diffusion.

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\section{I. INTRODUCTION.}

Flows of liquids in microscopic channels have been attracting increasing interest recently due to fast development of microfluidics and soft lithography [1,2]. The microfluidic devices, which are becoming increasingly advanced and reliable, allow dramatic reduction of amounts of reagents required for fine chemistry and biochemistry [3], well controlled manipulation and sophisticated experiments on individual cells [4–6] and macromolecules [7]. The microscopic flows are almost universally laminar, with linear dependence of the flow rate on the driving force. They also usually remain steady as long as the driving force does not change. All of that has to do with low to moderate values of the Reynolds number, $Re = V d \rho/\eta$, which is a general measure of non-linear inertial effects in the flow and of likelihood to find it being chaotic or turbulent [8]. Here $V$ is the flow velocity, $d$ is the diameter of the channel, and $\rho$ and $\eta$ are the density and the viscosity of the fluid, respectively. When $d$ is reduced, the flow velocity needed to reach a given high $Re$, which is required to generate chaotic or turbulent flow, increases as $d^{-1}$. The driving pressure per unit length scales like $\Delta P/\Delta L \sim \eta V/d^2$ giving $\Delta P \sim \Delta L/d^3$ at a given $Re$ in the channel. Therefore, if the channel proportions are preserved, $\Delta P$ grows quadratically with $d^{-1}$ and when the channels are only a few tens of microns wide, achieving sufficiently high $Re$ requires impractically high driving pressures.

The laminar character of microscopic flows has multiple practical advantages including possibility of precise control of flow velocity, chemical concentration profiles [4–6], and targeted delivery of chemicals and particles [5]. On the other hand, the laminar flows have an inherent problem of inefficient mass transfer in directions perpendicular to the main flow, which occurs due to molecular diffusion only. Diffusion time, $d^2/D$, across a typical micro-channel with a width of 100 $\mu$m is on the order of 100 s even for moderate size proteins, such as bovine serum albumin with a diffusion coefficient of $D \approx 3 \cdot 10^{-7}$ cm$^2$/s in water [9].

A few techniques have been proposed to generate stirring by a three-dimensional flow in order to increase the rate of mixing in the micro-channels. They include application of time dependent external forces [10,11] and raising $Re$ to moderately high values in curvilinear three-dimensional channels [12,13]. An ingenious method of mixing has been suggested recently, which involves special ”herring-bone” patterning of a micro-channel wall to generate fluid motion perpendicular to the main flow direction in the linear, low $Re$ regime [14]. The fluid elements are continuously stretched and folded in the flow as they advance along the channel. That separates closely spaced fluid particles and brings distant particles together, dramatically reducing the characteristic length scales and diffusion time and increasing the rate of homogenization of the mixture. The flow was stationary in the laboratory frame, however. Therefore, the concentration profiles of the fluorescent dye used as a tracer were uniquely defined by the entrance conditions and the channel geometry [14]. They did not change in time, and there was always some constant difference in concentration between neighboring points.

The basic condition of linearity in low $Re$ flows can be changed by adding flexible high molecular weight polymers to the working liquid [15]. Solutions of those poly-
mers are known as non-Newtonian visco-elastic fluids [15]. Mechanical stress in these fluids depends on the flow history with some characteristic relaxation time, $\lambda$, which for dilute solutions is a time of relaxation of individual polymer molecules. Another specific property of the polymer solutions is the non-linear dependence of the polymer contribution to the stress on the rate of deformation in the flow, $\nabla V$ [15]. This non-linearity usually becomes significant, when the Weissenberg number, $Wi = \lambda \nabla V$, becomes on the order of unity. The non-linear growth of the elastic polymer stresses is especially striking in extensional flows at $Wi > 1/2$, where apparent viscosity of polymer solutions can rise by up to three orders of magnitude as the total deformation increases [16]. In pure shear flows the major non-linear elastic effect shows up in the appearance of negative normal stress along the flow direction. It leads to the well known effect of rod climbing [15,17] and causes purely elastic instabilities in curvilinear flows of viscous polymer solutions in table-top set-ups, when inertial effects are virtually absent [18]. The non-linear polymer stresses in curvilinear shear flows can also lead to elastic turbulence, a random multi-scale three-dimensional flow, which can develop at arbitrarily low $Re$ [19]. Elastic turbulence causes sharp growth of the flow resistance [19,20], and it was found to generate efficient mixing in a table-top curvilinear channel [21].

Recently it was shown that the non-linear elasticity of the polymer solutions can cause a purely elastic transition and non-linear growth of flow resistance in a microscopic channel with contractions [22]. Those non-linear effects, however, were due to regions of fast extensional flow near the contractions, where individual polymer molecules are expected to partially unravel at $Wi > 1/2$ [23,24]. The non-linearity in resistance was the most dramatic feature of the transition and it became quite significant before any substantial changes in the flow pattern could be seen [22]. Therefore the non-linear resistance could be understood as a simple additive effect of individual molecules forced through the contractions. Although the flow became rather irregular at higher flow rates, the fluctuating flow regions were mostly near the contractions, and no detailed study of those fluctuations was made.

If the basic linear flow is a pure shear as in Ref. [19–21], a non-linear elastic transition can only occur through a major reorganization of the flow structure. In Ref. [19–21] the secondary flow generated above the instability threshold had well expressed turbulent features and involved irregular fluid motion in a broad range of temporal and spatial scales. That implies an essentially collective effect of the polymer molecules on the flow, and the polymer solution behaving as a visco-elastic continuum. If the size of the set-up is reduced to a micro-scale, non-homogeneity in the polymer concentration and extension of polymer molecules stretched in the flow may become comparable with the size of the set-up, and larger than size of some of the generated vortices. Therefore, whether or not the purely elastic instability and elastic turbulence can be reproduced in a microscopic shear flow is still an open question.

Here we show that a fully developed chaotic flow similar to the elastic turbulence can be generated in a flat curvilinear microscopic channel with smooth walls and uniform width at arbitrarily low $Re$, if the working liquid contains a small amount of high molecular weight polymers. The flow is characterized by significant non-linear growth in resistance, randomly fluctuating velocity field and chaotic three-dimensional mixing patterns. It is further shown that stirring by the flow results in efficient mixing in the micro-channel with characteristic mixing length significantly shorter compared with the "herringbone" patterning method reported before [14]. The characteristic mixing times for solutions of macromolecules are reduced by three to four orders of magnitude compared with molecular diffusion.

II. MATERIALS AND METHODS.

A. Device fabrication.

The micro-channel devices consist of a silicon elastomer (Sylgard 184 by Dow Corning) chip sealed to a #1 microscope cover glass. The channel structure of the chip was fabricated using the technique of soft lithography [1]. First, a negative master mold was fabricated in UV-curable epoxy (SOTEC micro-systems SU8-1070) by using conventional photolithography. The epoxy was spun onto a silicon wafer at 1800 rpm for 60 s to create a 100 $\mu m$ layer and patterned by using a high-resolution negative transparency mask. Liquid elastomer was poured on the mold to a thickness of $=5mm$ and cured in an 80C oven for 1 hr 30 min. After that the elastomer was peeled off the mold, trimmed to its final size and liquid feeding ports were punched by using a 20-gauge luer stub. The patterned side of the chip was bonded to the cover glass by overnight baking in the 80C oven.

B. Experimental set-up.

A snapshot of our first microfluidic set-up is shown in Fig.1. It has a uniform thickness $d = 100\mu m$. Its main active element is a curvilinear channel with square cross-section. It is a chain of 40 identical segments, which are couples of interconnected half-rings with inner and outer radii $R_i = 100\mu m$ and $R_o = 200\mu m$, respectively, Fig.1b. It has the same proportions as the table-top channel, which was used in the elasticity induced mixing experiments reported before [21], but its dimensions are reduced by a factor of 30. Because of the periodic
structure of the channel, it is convenient to use the number of a segment, \( N \), starting from the inlet as a discrete linear coordinate along the channel. The auxiliary rectilinear channel (b) has width of 90 \( \mu m \) and total length of about 72.5 mm. Channel (b) and the comparator region (c) serve to make differential in situ measurements of flux vs. pressure by the method described in Ref. [22].

C. Flow control.

The flow in the micro-channels was generated and controlled by pressure differences between the inlets and the outlet, Fig.1a. The pressures were generated hydrostastically using long vertical rails with precise rulers and sliding stages. Working liquids were kept in 30 ml plastic syringes, which were held upright, open to the atmosphere and connected to the two inlets and the outlet by plastic tubing with internal diameter of 0.76 mm. The pressure drop in the tubing was estimated below 1\% of the total. The two syringes feeding the inlets were attached to the sliding stages. The difference in liquid elevation between these two syringes and the outlet syringe was measured and adjusted with a precision of about 0.1 mm corresponding to 1 Pa in pressure. Dependence of the volumetric low rate, \( Q \), in the curvilinear channel on the pressure difference between inlet 1 and outlet, Fig.1, was determined with a relative precision of about 0.5\% using an in-situ measurement technique described elsewhere [22]. A syringe pump (PHD 2000 by Harvard Apparatus Inc.) with a 50 ml gastight Hamilton syringe was used for an absolute flow rate calibration.

D. Polymer solutions.

The polymer used was polyacrylamide, PAAm, by Polysciences Inc. with high molecular weight \( M_w = 1.8 \times 10^7 \), which was the same polymer sample as in Ref. [21]. It was dissolved at identical concentrations of 80 ppm by weight in two Newtonian solvents with different viscosities. The solvent for the low viscosity solution 1 was a 35\% solution of sucrose in water with 1\% of NaCl added to fix the ionic contents. The Newtonian viscosity of the solvent, \( \eta_s \), was 4.2 mPas at the room temperature of 22C. The viscosity of solution 1, \( \eta_1 \), was 5.6 mPas at a shear rate of 50 s\(^{-1}\), suggesting a dilute polymer solution. The Newtonian solvent for the high viscosity solution 2 was sugar syrup containing 64.4\% sucrose and 1\% of NaCl in water. The viscosity of solvent 2 was 114 mPas at 22C, and the viscosity of solution 2 was 138 mPas at a shear rate of 2 s\(^{-1}\). The polymer relaxation time, \( \lambda \), of solution 2 measured by phase shift between stress and shear rate in an oscillatory flow regime was 1.1 s. The measurements of viscosity and relaxation time were made using a high precision rheometer (AR1000 by TA Instruments). Relaxation time of solution 1 was estimated as 0.04 s with the assumption that \( \lambda \) scales linearly with \( \eta_s \) [15].

The overlap concentration \( c^* \), taken as a concentration at which the viscosity ratio reached \( \eta/\eta_s = 2 \), was 200 ppm by weight for solvent 2, corresponding to molecular concentration of \( n = 8.76 \times 10^{12} \) cm\(^{-3}\). Characteristic size of the polymer coils at rest can be estimated from this as \( n^{-1/3} \approx 0.5 \mu m \), and characteristic distance between them at 80 ppm by weight can be estimated as 0.7 \( \mu m \). These estimates are well supported by the data on PAAm taken from the literature [25]. One can use the Mark-Houwink scaling relation for PAAm, 
\[
[\eta] = 6.31 \times 10^{-3} M_w^{0.8} \quad \text{(in ml/g)} \quad [25],
\]
where \([\eta]\) is the intrinsic viscosity of the polymer defined as \([\eta] = \frac{m_\text{poly}}{m_\text{soln}}|_{c \to 0} \). At molecular weight \( M_w = 1.8 \times 10^7 \) one gets \([\eta] = 4020 \) ml/g. Defining \( c^* = 1/[\eta] \) [15] we obtain \( c^* = 250 \) ppm by weight for an aqueous solution in a good agreement with the above estimate. Further, we can compare the estimated size of the PAAm coils with the data obtained from light scattering Ref [25]. Plugging in \( M_w = 1.8 \times 10^7 \) into an interpolation relation from Ref. [15], one gets \( R_g \approx 0.4 \mu m \) for the radius of gyration of the coils, which is rather consistent with the above estimate obtained from \( c^* \).

It is worth noting that \( c^* = 200 \) ppm is very close to the value found for \( \lambda \)-phage DNA [26], which has a comparable molecular weight of \( 3.1 \times 10^7 \). Radius of gyration of the \( \lambda \)-phage DNA was found to be 0.73 \( \mu m \) [27], which is quite in line with the above estimate for the PAAm coil size. The full contour length of a PAAm molecule having \( M_w = 1.8 \times 10^7 \) and thus consisting of 2.5 \( \times 10^8 \) monomers (having molecular weight 71.08 g/mol) can be estimated as about 50 \( \mu m \), if a monomer length of 0.2 nm is assumed. It is significantly larger than the contour length of the \( \lambda \)-phage DNA (which is equal to about 16 \( \mu m \)) and twice smaller than the micro-channel diameter.

The experiments on mixing were carried out with polymer solution 2, and then fluorescent dyes with low diffusivities were added to the solution and used as tracers. Those were a few different samples of fluorescein-conjugated Dextran, FITCD, by Sigma with average molecular weights, \( M_1 \), varying from 10 kDa to 2 MDa. In spite of the relatively high molecular weight of FITCD it did not have any measurable influence on the solution rheology due to high rigidity of the polysaccharide molecules. Diffusion coefficients of the FITCD samples in water were estimated using the data in Ref. [28], giving values from \( 9.1 \times 10^{-7} \) to \( 7.4 \times 10^{-8} \) cm\(^2\)/s that corresponded to a broad range of biological macromolecules. The diffusion coefficients in solvent 2 were estimated with assumption that \( D \sim 1/\eta_s \), resulting in \( D_1 = 6.6 \times 10^{-9} \) and \( D_2 = 5.4 \times 10^{-10} \) cm\(^2\)/s for 10 kDa and 2 MDa FITCD, respectively.
E. Measuring flow velocity.

Measurements of the flow velocity in the micro-channel were carried out using custom developed microscopic particle image velocimetry, micro-PIV. The polymer solution was seeded with 0.2 µm yellow-green fluorescent beads (Polysciences), and epifluorescent imaging of the flow in the micro-channel, Fig. 1, was made with an inverted microscope (Olympus IMT2) and narrow band excitation and emission filters in the dichroic filter cube. The objective was a LWD 20×, N.A. = 0.40, and the images were projected onto a CCD array with 480 × 480 pixel resolution (PixelFly camera by PCO, Germany) and digitized to 12 bits. The snapshots of the flow were taken with even time intervals of 40 ms, and digitally post-processed. Images of out-of-focus particles were disregarded. Velocity field was found by cross-correlating positions of the particles in two consecutive snapshots, and the particle velocity vectors were neighbor-validated. (The calculated velocity field corresponded to the time interval between the two snapshots.) The collected time series represented velocity values measured at equal distances from interconnections of two half-rings at N = 35, and averaged over a 20 × 20µm square region at the middle of the channel and over 4 µm across the channel mid-plane.

F. Measuring tracer concentration profiles.

Concentrations of the fluorescent dyes, which were used as passive tracers in the experiments on mixing in the channel, were measured using a commercial confocal microscope (Fluoview FV500 by Olympus). It was equipped with a 40× N.A. = 0.85 infinity corrected objective and a 12 bit photomultiplier. The scanning was done at a rate of 56 lines per second and 512 pixels per line corresponding to a step of 0.18 µm per pixel.

III. RESULTS.

We measured volumetric flux rate, Q, of solution 1 through the curvilinear channel, Fig.1, in a broad range of applied pressures and calculated the resistance factor, Z = P/Q, where ∆P is pressure drop per segment. The resistance factor is a constant proportional to viscosity for Newtonian fluids in linear, low Re regime, and it can be used as a measure of turbulent flow resistance in large channels at high Re. Fig. 2 shows dependence of Z on Q for solution 1, after Z is divided by a resistance factor, Z0, found for a Newtonian liquid with the same viscosity, η. The ratio Z/Z0 is constant equal to unity in the linear regime at low Q. At Q of about 8.5 nl/s, however, a non-linear transition occurs; Z/Z0 starts to grow and reaches a factor of about 2.8 at high Q. The Reynolds number for the channel flow can be defined as Re = Qρ/(ηd) . It was 0.017 at the transition point and 0.14 at highest Q, that we tried, so that the inertial effects were always negligible. The Weissenberg number can be defined as W_i = 4λQ/d^3, and its estimated value at the transition point is 1.4, which is comparable with W_i found at purely elastic transitions in macroscopic set-ups [18,19,21,29].

In order to get detailed information about structure of the flow above the non-linear transition we used solution 2 with high viscosity and large λ. The polymer relaxation time defines both characteristic time of changes in the flow and the inverse of flow velocity in the elastic non-linear regime [15,29]. Therefore, the non-linear flow in solution 2 was expected to be much slower, and measurements of its characteristics were expected to be more feasible with the standard video microscopy techniques. Using the micro-PIV we measured flow velocity in the middle of the curvilinear channel. Dependence of RMS of fluctuations of the longitudinal component of the flow velocity, V_1 rms , (which is the velocity component along the main flow) on ∆P is shown in Fig.3. The fluctuations are virtually absent in the linear regime at low pressure. At ∆P of about 50 Pa, however, V_1 starts to fluctuate, and V_1 rms begins to grow quickly and non-linearly. It can be learned from the inset in Fig.3 that the longitudinal component of the flow velocity, V_1, grows linearly at low ∆P, but its growth slows down at the same critical ∆P of about 50 Pa, which is another evidence for a non-linear elastic flow transition taking place. At the transition point, the average longitudinal flow velocity, estimated from the micro-PIV measurements in different points across the channel, was V_1 ≈ 80µm/s. That gives estimates of Q ≈ 0.8 nl/s, Re ≈ 8 × 10^{-5} and W_i ≈ 3.5 for the elastic non-linear transition. This value of the Weissenberg number is very close to W_i ≈ 3.2 found for the transition to chaotic flow in the table-top curvilinear channel in Ref. [21].

A typical time series of V_1 above the transition is shown in Fig.4a. The velocity is strongly fluctuating and its time dependence has well expressed chaotic appearance. The chaotic character of the velocity fluctuations is confirmed by analysis of its time correlations. The velocity autocorrelation function shown in Fig. 4b does not have distinct peaks and decays uniformly.

For the experiments on mixing the design of the micro-channel was slightly modified to enable side by side injection of two streams of solution 2, one with and one without FITCD, to the channel inlet, Fig.5a. Apart from c_0 = 280 ppm by weight of FITCD added to one of them the polymer solutions were identical and were injected at equal flow rates by careful adjustment of the driving pressures, Fig. 5a. The set-up was first tested with the plain solvents without PAAm added. The flow appeared laminar at all ∆P that we applied, and the interface between the streams with and without FITCD remained smooth and sharp along the whole channel with only mi-
nor smearing by diffusion, Fig. 5b.

The situation was similar with the polymer solutions in the linear regime at low $\Delta P$. However, when the driving pressure was raised above the non-linear transition threshold, fluctuating flow velocity produced significant stirring and complex and chaotically changing tracer concentration profiles, Fig. 5c, d. We studied mixing in the channel in detail at $\Delta P = 134$ Pa, corresponding to a flow rate about twice above the non-linear transition threshold (cf. Ref. [21]) and $V_1$ of about $173 \mu m/s$. Variation of the tracer concentration profiles with time at different distances from the inlet is illustrated by the space-time plots in Fig. 6a,b. One can observe that the tracer concentration appears to fluctuate quite randomly without any apparent scale in time or space. Next, one can see in Fig. 6a, taken at $N = 12$, that the left side of the channel, where the tracer was initially injected, looks much brighter and has much higher average concentration of the tracer. Although also noticeable in Fig.6b taken further downstream, at $N = 18$, this feature is clearly weaker there. Thus, stirring by the fluctuating velocity field seems to create a more symmetric distribution of the tracer between the two sides of the channel.

In order to validate this observation, we measured time averages of the tracer concentration, $\bar{c}$, at different positions across the channel and at different $N$, Fig.7a. One can see that the cross-channel distribution of $\bar{c}/c_0$ close to the inlet, at $N = 7$, is strongly influenced by the asymmetric conditions at the channel entrance. As one can learn from the curve at $N = 11$, however, the imprint of the initial conditions is clearly fading as the liquid advances downstream and being stirred. Further downstream, at $N = 41$, asymmetry in the tracer distribution introduced by the initial conditions disappears completely. Fading of the initial condition influence with time and restoration of symmetry in flow in statistical sense are both distinct features of chaotic and turbulent flows. Therefore, the curves in Fig. 7a provide further evidence for truly chaotic nature of the flow in the microchannel.

A natural parameter characterizing inhomogeneity of the mixture is standard deviation of the instantaneous local tracer concentration, $c$, from its overall average value $\langle c \rangle = c_0$. It is convenient to divide it by $\langle c \rangle$ and to introduce a dimensionless standard deviation $c_{std} = \sqrt{\langle (c - \langle c \rangle)^2 \rangle}/\langle c \rangle$. At the channel entrance $c_{std}$ is equal to unity, and it becomes zero, when the liquid is perfectly mixed and homogeneous. Dependence of $c_{std}$ on $N$ for two tracers with diffusion coefficients of $D_1 = 6.6 \cdot 10^{-9}$ and $D_2 = 5.4 \cdot 10^{-10} \text{cm}^2/\text{s}$ is shown in Fig.7b in semi-logarithmic scale. One can see that the mixture becomes increasingly homogeneous as the liquid advances downstream, and the parameter $c_{std}$ decays exponentially with $N$ for the both tracers. An exponential decay was also found in the case of elastic turbulence in a macro-channel [21], and it agrees very well with theoretical predictions for the so-called Batchelor regime [30-33] of mixing. The latter corresponds to a flow, which is chaotic in time but essentially ”smooth” in space, in the sense that small eddies are rare, and the main contribution to mixing comes from the largest eddies having the size of the whole system.

The rates of the exponential decays for the two dependencies shown in Fig. 7b were 0.217 and 0.137, corresponding to $\Delta N$ of 4.61 and 7.30, and lengths $L_1 = 4.34 \text{mm}$ and $L_2 = 6.88 \text{mm}$, respectively. The latter can be considered as characteristic mixing distances along the channel for the two tracers. Characteristic mixing times, which can be estimated as $t_{mix} = L/V$, are then found to be $t_{mix,1} = 25 \text{s}$ and $t_{mix,2} = 40 \text{s}$, respectively. In the absence of active stirring, mixing would only occur through molecular diffusion, with characteristic diffusion times across the channel given by $t_{diff} = d^2/D$ resulting in $t_{diff,1} = 1.5 \cdot 10^4 \text{s}$ and $t_{diff,2} = 1.9 \cdot 10^4 \text{s}$, respectively. Therefore, the stirring produced by the chaotic flow in the channel reduces the mixing times for the FITCD macromolecules by three to four orders of magnitude.

IV. DISCUSSION.

We studied flow of two dilute polymer solutions in a microscopic curvilinear channel. We observed a non-linear transition to occur in the flow at $Re \approx 1.7 \cdot 10^2$, $Wi \approx 1.4$, and $Re \approx 8 \cdot 10^{-5}$, $Wi \approx 3.5$, for solution 1 and solution 2, respectively. The very small and different values of $Re$, and comparable, order of unity values of $Wi$ at the transition threshold for the two solutions indicate that the transition is of purely elastic nature and can occur at arbitrarily low $Re$. A possible explanation of the difference in estimated critical $Wi$ for the two polymer solutions is that the actual polymer relaxation time of solution 1 may be significantly higher than the estimate based on the assumption that $\lambda \sim \eta_s$. A major global feature of the flow above the non-linear elastic transition is fast growth of the resistance, Fig.2. It increases by up to a factor of 2.8 above the resistance for a Newtonian fluid with the same shear flow viscosity, $\eta$, at the same $Q$. Since $Re$ is very low, the whole growth of the flow resistance should be due to increase in the elastic polymer stresses [20]. In a pure shear flow with $\gamma = 240 \text{s}^{-1}$, corresponding to $Q = 60 \text{nl/s}$ (and $Wi \approx 10$), viscosity ratio for polymer solution 1 was $\eta/\eta_s = 1.22$. Hence, the average increase in the polymer shear stresses due to the secondary flow at $Q = 60 \text{nl/s}$ (Fig.2) can be estimated as a factor of about 11. Suggesting linear deformation of the flexible polymer molecules in a shear flow at low to moderate $Wi$ [34], we can estimate extension of the molecules at $Wi = 10$ as $10 \cdot 0.5 \mu m = 5 \mu m$. (Flexible polymer molecules were found to extend linearly with the shear rate, until the extension reached 15-20% of their full length [34].) Additional extension of the polymers due to
the irregular secondary flow, as suggested by the stress growth by the factor of 11, can be estimated as a factor of $\sqrt{11}$ (suggesting that the secondary flow results in an isotropic polymer unravelling and the stress grows as a square of the polymer extension [15]). That brings characteristic size of the extended polymer molecules to $20\mu$m range, less than an order of magnitude smaller than the diameter of the channel, $d = 100\mu$m.

The growth of the elastic stresses due to the fluctuating secondary flow can only occur as a result of significant reorganization of the flow structure and spontaneous generation of regions with strong extensional flow, as in the case of the elastic turbulence [19,20]. (In shear flows polymer contribution to resistance increases slower than linearly with the shear rate, which is called shear thinning,) This suggestion is quite corroborated by the direct flow velocity measurements in solution 2 above the nonlinear transition. Velocity is found to be strongly fluctuating, Figs.3,4, with RMS of the fluctuations reaching as much as 10% of the mean longitudinal velocity at the center of the channel, Fig.3, just as in the tabletop channel in Ref. [21]. The velocity appears to vary randomly in time, Fig.4a, and its auto-correlation function decays quite quickly and does not have any distinct peaks, Fig.4b. These all are clear indications of chaotic nature of the flow in the channel in the nonlinear regime at high $W_\text{i}$. Another evidence of chaos comes from the experiments on mixing, Figs.6,7. Asymmetry in distribution of $\bar{c}/c_0$ across the channel, which is imposed by the conditions at the channel entrance, decays with the distance from the entrance, Fig.7a. Further, $c_{\text{std}}$ exponentially decays with $N$, as it is supposed to be in the chaotic Batchelor regime of mixing [21,32,33].

Experimental results presented in Figs.2-4 and Figs.6,7 and discussed above are fully consistent with a suggestion that the regime of elastic turbulence [19] is being realized in the micro-channel. In fact, the results in Figs.2-4 and Figs.6,7 agree rather well with the measurements in macroscopic systems reported before [19,20]. We find it rather remarkable that although the size of extended molecules may become comparable with the channel diameter, it does not seem to cause any significant new effects in the polymer solution dynamics. An essential feature of turbulent flows is a broad range of spatial scales, at which fluid motion is excited. Unfortunately, limited resolution of the micro-PIV technique did not allow us to explore properties of the flow down to sufficiently small spatial scales and to obtain conclusive data about its spatial structure. Therefore we can only refer to the flow in the micro-channel as being chaotic.

In the experiments with passive tracers, we found that stirring by the chaotic flow results in efficient mixing in the channel, Figs.5-7. So, mixing times for the macromolecules, which we used as tracers, were reduced by three to four orders of magnitude compared with passive molecular diffusion, Fig.7b. It is worth noting that the characteristic distance of $\Delta N = 7.3$ required for mixing of low diffusivity FTICR is comparable with $\Delta N \approx 15$ found in the chaotic flow in the table-top channel Ref. [21]. We further notice that whereas the diffusion time scaled as $1/D$, the time of mixing in the chaotic flow depended on $D$ very weakly. It increased by only 60% between the lower and upper curve in Fig.7b (from $t_{\text{mix},1} = 25$ s and $t_{\text{mix},2} = 40$ s), whereas $D$ dropped by a factor of 12 (from $D_1 = 6.6 \times 10^{-9}$ to $D_2 = 5.4 \times 10^{-10}$ cm$^2$/s). The weak dependence of $t_{\text{mix}}$ on $D$ is quite consistent with theoretical predictions for chaotic flows and the Batchelor regime [30–33]. It implies that the elasticity induced chaotic stirring in the micro-channel can be efficiently used for mixing of liquids with additives of any low diffusivity, such as large molecules of DNA, viruses, particles, and possibly living cells.

The relatively long times of mixing in the chaotic flow of solution 2 are due to high viscosity of the solvent, large $\lambda$ and low flow velocity at the elastic instability threshold. In a much more practically relevant case of water based solutions with the viscosity on the order of 0.001 Pas, $\lambda$ is expected to be about hundred times lower and the flow velocities in the chaotic regime should be about hundred times higher [15,29]. Suggesting qualitatively similar flow conditions [29], we expect characteristic mixing times for the water based solutions to be on 100 ms scale. Since diffusion coefficients for macromolecules are proportional to $1/\eta_s$ [15], the ratio between $t_{\text{diff}}$ and $t_{\text{mix}}$ for the chaotic flow in the water based solutions should be in the same range of $10^3$ to $10^4$.

The characteristic mixing length along the channel for water based solutions should also remain in the same range of about 4-7 mm. It is about 2-3 times shorter than characteristic lengths in the "herring-bone" patterned channel of Ref. [14] at comparable values of Peclet number, $Pe = Vd/D$. Although the method of mixing by elasticity induced chaotic flow necessarily requires addition of polymers to the working liquid, it may be quite practical for many biochemical assays, taking into account the very low concentration of the high molecular weight polymers used. It does not rely on any special patterning of the micro-channels and should be readily compatible with rounded channel profiles used for integrated micro-valves and peristaltic pumps [35], allowing efficient mixing in closed loop microscopic flows [36].

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FIG. 1. (A) Photograph of the micro-fluidic device. The micro-channels were filled with ink for better contrast. (B) Magnified image of a section of the functional curvilinear channel.

FIG. 2. Dependence of normalized resistance, $Z/Z_0$, in flow of solution 1 through the curvilinear channel on the volumetric flow rate, $Q$, in semi-logarithmic scale.

FIG. 3. Dependence of RMS of fluctuations of the longitudinal component of flow velocity, $V_1^{rms}$, on pressure drop per segment, $\Delta P$, in the center of the micro-channel for solution 2. Inset: Dependence of time average of the longitudinal flow velocity, $\bar{V}_1$, in the center of the micro-channel on $\Delta P$.

FIG. 4. (A) Time series of the longitudinal flow velocity, $V_1$, in the center of the micro-channel at $\Delta P = 100$Pa. (B) Auto-correlation function for $V_1$ based on about 6000 individual velocity measurements.

FIG. 5. (A) Epi-fluorescent micro-photograph of the entrance area of a micro-channel used in experiments on mixing. Wide triangular region in front of a curvilinear channel allows to adjust equal flow rates for polymer solutions with (from below) and without FITCD. (B) Confocal photograph of flow in the micro-channel without polymers added. Right wall of the channel is shown by a dotted line from below. (C) Confocal image of mixing in chaotic flow in the micro-channel with solution 2 in it. (D) Confocal image of cross-section of the micro-channel with chaotic flow in solution 2.

FIG. 6. Space-time plots of FITCD distribution across the channel taken at (A) $N = 12$ and (B) $N = 18$. Confocal scanning was done along the same line across the channel in the mid-plane at equal distances from half-ring interconnections, with even time intervals of 0.0177 sec. Profiles of FITCD concentration in consecutive moments of time are plotted from top to bottom.
FIG. 7. (A) Time average of FITCD concentration, $\bar{c}$, divided by $c_0$, as a function of position, $x$, along a line across the channel taken at different distances from the inlet: $N = 7$, $N = 11$, and $N = 41$. The lines across the channel were in the mid-plane at equal distances from half-ring interconnections, just as for the space-time plots in Fig.6. (B) Standard deviation of FITCD concentration from its average value, $c_{std}$, as a function of distance, $N$, from the inlet for two kinds of FITCD with average molecular weights of 10 kDa (triangles) and 2 MDa (squares).
