

# Effects of molar mass, concentration and thermodynamic conditions on polymer-induced flow drag reduction

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## Abstract

Drag reduction in Taylor flow of polystyrene solutions is investigated using a commercial rheometer equipped with a standard double-gap sample holder with axial symmetry. The dependence of drag reduction on various factors, including polymer molar mass, polymer concentration, and thermodynamic conditions is studied. Drag reduction induced by polystyrene in toluene is found to increase with increasing polymer concentration in the dilute concentration regime. It is also seen that molecules with high molar mass of the polymer promote drag reduction. In terms of hydrodynamic volume fraction normalisation, it is found that most of the drag reduction effect occurs at volume fractions below 0.2. It is observed that drag reduction is favoured by good thermodynamic conditions of the polymer–solvent system. Both the flow induced extension of the polymer chains and the hydrodynamic volume fraction occupied by the polymer molecules seem to play an important role for the drag reduction effect.

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## 1. Introduction

It is well known that when small amounts of certain high molar mass polymers are dissolved in a liquid, the frictional drag associated with turbulent flow through conduits can be significantly reduced [1]. The drag reduction phenomenon implies that polymer solutions undergoing flow in a pipe require a lower pressure drop to maintain the same flow rate. This effect has in recent years been the subject of intensive experimental [2–12], theoretical [13–21] and simulation [22–24] research. The drag reduction behaviour depends on various factors [1], including type of polymer, polymer molar mass, concentration, temperature, thermodynamic conditions of

the system, and turbulence intensity. Although the detailed mechanism of drag reduction is not entirely understood, the consensus is that this phenomenon is associated with the viscoelasticity of polymer solutions where both alignment and elongation of the polymer chains can play an important role. Two processes, the stretching of the chains by the velocity gradients and the relaxation due to the elasticity of the molecules, determine the deformation of polymer chains [21]. In the scenario of Tabor and de Gennes [16] and de Gennes [17] the polymers in turbulent flow exhibit elastic response even at very low concentrations. As a result, the polymer chains store up some of the cascading energy of turbulence and this energy is not dissipated by viscosity, giving rise to an effective drag reduction. There are different theoretical approaches that address this issue, but all models predict reduction of turbulence generation and dissipation. A problem that may arise in polymer solutions exposed to strong extensional flows is related

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to macromolecular degradation [25–28]. It has been found [29–33] that chain scission occurs around the chain midpoint, indicating that the chains are highly extended when they break.

In many of the previous studies of drag reduction, most of the measurements have been conducted using a pipe flow apparatus, where driving the fluid through a looping channel generally produces turbulence. In many cases, the experiments were performed in non-uniform and ill-defined shear fields. There is only a few extensional flow experiments carried out in uniform shear fields under controlled conditions [30]. In a recent investigation [34], laminar and Taylor flows were studied in a cell with Taylor–Couette geometry. The experimental set-up consisted of a commercial rheometer equipped with a standard double-gap sample holder with axial symmetry.

This double-gap geometry is also utilized in the present work, where the effect of extensional flow on dilute solutions of polystyrene at different thermodynamic conditions will be explored. We will show that this experimental arrangement constitutes a powerful method to investigate drag reduction effects in dilute polymer solutions. In this paper, the effects of polymer concentration, molar mass, and changes in thermodynamic conditions (measurements from good solvent conditions to the upper critical solution temperature) on drag reduction will be scrutinized with the aid of this device. With this experimental setup, the region of fully developed turbulence will not be reached [34], but polymer induced drag reduction in Taylor flows will be probed. We will show that the drastic change of the thermodynamic conditions and the accompanying conformational alteration of the macromolecules will have a significant impact on the drag reduction behaviour.

## 2. Experimental

A number of standard polystyrene (PS) samples with weight average molar masses of  $1.0 \times 10^6$ ,  $3.0 \times 10^6$ ,  $6.5 \times 10^6$ ,  $8 \times 10^6$ ,  $20 \times 10^6$ , and  $30 \times 10^6$  g/mol (data provided by the manufacturers; Pressure Chemical Co., Pittsburgh, PA. and Toyo Soda Manufacturing, Japan) were utilized. All fractions have narrow molar mass distributions ( $M_w/M_n \leq 1.2$ ) and were used without further purification. The solvents used were toluene (good solvent for PS), toluene (82.5 wt.)/methanol (17.5 wt.%) (this mixture is a  $\theta$  solvent for PS at approximately 25 °C [35,36]), and *trans*-decalin (T-D,  $\theta$  solvent for PS at 21 °C [37]) (P.a. grade solvents from Fluka, used without further purification). The measurements were carried out in the dilute concentration regime ( $c[\eta] < 1$ , where  $c$  is the polymer concentration and  $[\eta]$  is the intrinsic viscosity). All solutions were prepared by

weighing. Great care was exercised in the preparation of samples to obtain homogeneous solutions.

The rheological measurements were conducted with the aid of the Physica USD 200 rheometer (Physica Messtechnik GmbH, Stuttgart, Germany) equipped with a double-gap measuring geometry (see Fig. 1), with the active rotor height  $H = 111.0$  mm and with radii  $R_1 = 22.25$  mm,  $R_2 = 22.75$  mm,  $R_3 = 23.50$  mm, and  $R_4 = 24.00$  mm, respectively. The double-gap sample holder is stationary, while the thin-walled cylindrical tube placed in the sample can rotate about the axis of the cylinder symmetry. The maximum speed of rotation of this instrument is 3000 rpm (revolutions per minute), which corresponds to a maximum geometrically averaged shear rate of  $15\,000\text{ s}^{-1}$ . The sample volume is 22.5 ml. By using the axial symmetric double-gap cell, the rheometer was found to maintain its excellent characteristics even at angular velocities corresponding to well developed Taylor vortices. The speed of rotation is not sufficient to reach the onset of full turbulence [34] in these experiments, but polymer-induced drag reduction in Taylor flows will be reported. In this study, we have

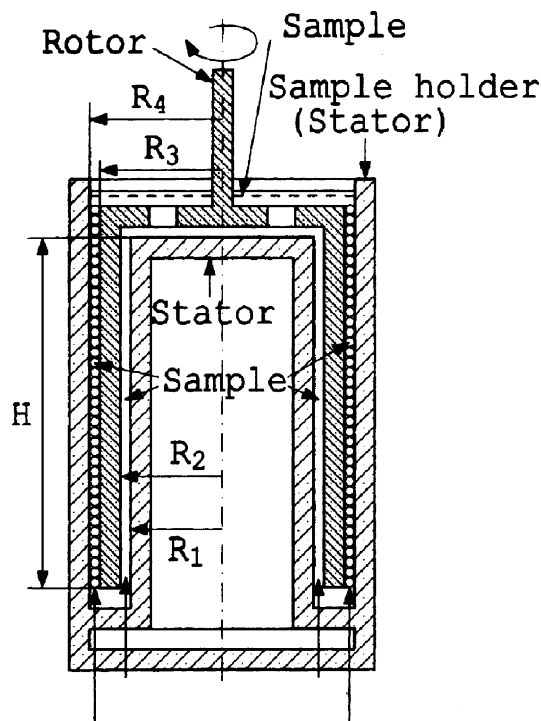


Fig. 1. A schematic illustration of the utilised double-gap sample holder with axial symmetry. The sample holder is stationary, while the thin-walled cylindrical tube placed in the liquid can rotate about the axis of the cylinder symmetry. When the rotor angular velocity exceeds a certain minimum value, Taylor vortices appear in the outer half of the sample.

used the rotor speed of rotation as a variable, but this quantity can readily be converted to the Reynolds number [34]. Details about the experimental setup and the measuring procedure have been published elsewhere [34].

In this work, measurements were conducted at different temperatures. The measuring device is equipped with a temperature unit that provides a rapid change of temperature and gives a very good temperature control ( $\pm 0.1$  °C) over an extended time.

The fluid flow results are presented in terms of the nominal shear viscosity [34], which is defined as  $\eta \equiv \tau(R_2 - R_1)/\omega R_1$ , where  $\tau$  is the shear stress and  $\omega$  is the angular velocity. In most experiments, the reproducibility of the nominal shear viscosity is better than  $\pm 2.5\%$  even for well-developed Taylor flow.

### 3. Results and discussion

The use of polymers may lead to their mechanical degradation in strong extensional flow. This rupture of polymer chains usually develops in course of time and this phenomenon affects the nominal shear-viscosity [32]. In this study, the measurements were usually carried out by first increasing the speed gradually from 0 to 3000 rpm, and back again using a sweep rate of 10 rpm s<sup>-1</sup>. Since the up-ramp curve and the down-ramp curve can be superimposed on each other, it can be argued that no significant mechanical degradation of the polymer occurs during the time of measurement. However, even in Taylor flow rupture of polymer chains has been observed [12,34] if the chains are exposed to high shear rates for some time. This is also the case for the present systems (data not shown), but this issue is not addressed in this work because the measurements reported here have been carried out over short times where no degradation effect was detected.

Fig. 2 shows the influence of polymer concentration on the drag reduction for toluene in the presence of PS (toluene is a good solvent for PS) of a molar mass of  $8 \times 10^6$  g/mol. In Fig. 2a, the nominal shear viscosity  $\eta$  is plotted as a function of the speed of rotation  $n$  for different concentrations. The conspicuous features are that the shear viscosity curve is moved vertically to higher values as the concentration increases, and the onset of Taylor flow is shifted toward higher values of  $n$  with increasing polymer concentration. The former feature is attributed to the trivial increase of the Newtonian viscosity with increasing concentration, while the latter phenomenon can probably be ascribed to the gradual suppression of the turbulence intensity as the polymer concentration increases. These effects obstruct a direct comparison of the drag reduction effect at the different polymer concentrations. To take into account the viscosity effect and the difference in the onset of Taylor

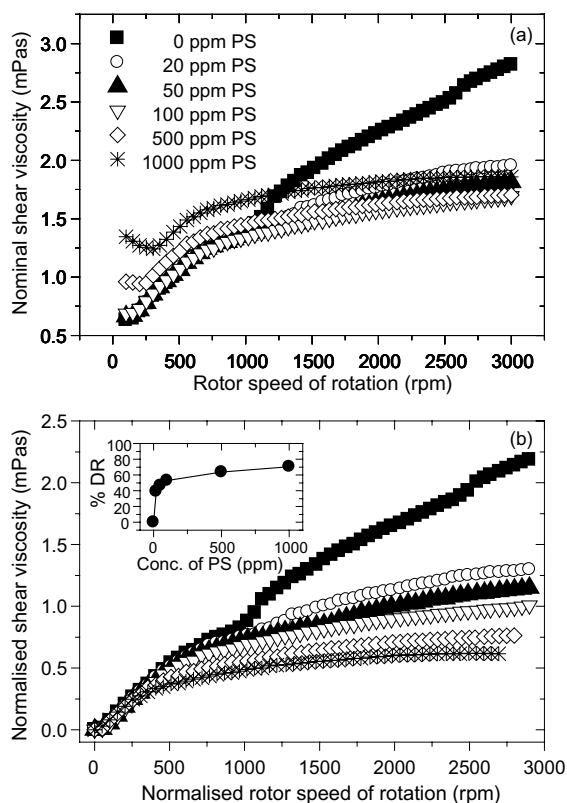


Fig. 2. (a) Nominal shear viscosity as a function of rotor speed of rotation at 20 °C for toluene without and in the presence of the indicated concentrations of polystyrene of a molar mass of  $8 \times 10^6$  g/mol. (b) Plot of the normalised shear viscosity as a function of the normalised rotor speed of rotation (these quantities are defined in the text) for the data in (a). The inset plot shows the effect of concentration on the percent drag reduction, calculated with the aid of Eq. (1). The drag reduction has been calculated at a fixed normalised rotor speed of rotation of 2700 rpm.

flow, the normalized shear viscosity  $\eta_N$  ( $\eta_N = \eta_T - \eta_{T,o}$ ) is plotted as a function of the normalized rotor speed of rotation  $n_N$  ( $n_N = n_T - n_{T,o}$ ) in Fig. 2b. Here the subscripts T and T,o denote considered values in the Taylor flow region and the onset of this region, respectively. In this case, this procedure is employed to account for the polymer-induced viscosity change and the alteration of the Taylor flow domain with concentration. An analogous method can be used to take into account changes of these parameters due to, e.g., temperature effects.

As is evident from Fig. 2b, this procedure facilitates a direct comparison of the drag reduction effect at different concentrations. The general trend is that the effect of drag reduction grows with increasing polymer concentration. The percent drag reduction (%DR) to quantify the drag reduction efficiency is calculated via the

normalized shear viscosity of the solvent and that of the solution at a fixed value of  $n_N$  through the expression

$$\%DR = 100 - \frac{\eta_{N,\text{solution}} - \eta_{N,\text{solvent}}}{\eta_{N,\text{solvent}} - \eta_{N,\text{o}}} \cdot 100 \quad (1)$$

where  $\eta_N$  is the normalized shear viscosity at the selected value of  $n_N$ , and  $\eta_{N,\text{o}}$  is the normalized shear viscosity at the onset of Taylor flow for the considered system. The effect of concentration on drag reduction in PS–toluene solutions is illustrated in the inset plot of Fig. 2b at a value of  $n_N = 2700$  rpm. The drag reduction effect rises with increasing polymer concentration and levels off as the overlap concentration ( $c[\eta] = 1$ ) is approached. In the theoretical models [14–17] of drag reduction it is usually argued that elastic effects govern the dissipation of turbulent energy. As the polymer concentration increases, the elastic response grows and the turbulence is gradually damped. In this context, it is probably better to consider the hydrodynamic volume fraction of polymer molecules ( $c[\eta]$ ) instead of the polymer concentration. The concentrations given in Fig. 2 for the PS–toluene system cover the interval  $0.019 \leq c[\eta] \leq 0.95$ , where the intrinsic viscosity was estimated from the Mark–Houwink relation  $[\eta] \text{ (dl/g)} = 8.5 \times 10^{-5} \cdot M^{0.74}$  [38]. At the highest value of  $c[\eta]$ , we are close to the concentration ( $c[\eta] = 1$ ) at which neighboring coils begin to overlap. It has been predicted [17] that at concentrations below the overlap concentration ( $c[\eta] < 1$ ), the drag reduction effect should increase steadily with increasing concentration. This behaviour is consistent with that displayed in the inset plot of Fig. 2b. However, it is also argued [17] that at concentrations above the overlap concentration a more complex picture emerges, where the trivial increase of the Newtonian viscosity due to the polymer may become the dominating feature.

The effect of polymer-induced drag reduction in toluene for different molar masses of PS at a fixed concentration (50 ppm) is depicted in Fig. 3. At this low polymer concentration, it is evident that the drag reduction effect can virtually be ignored at molar masses below  $3 \times 10^6$  g/mol, while for the two highest molar masses the drag reduction is approximately 60% (see the inset plot). The results suggest that the effect of drag reduction levels off at high molar masses. This may indicate that the drag reduction is, to some degree, an effect of the length and extension of the polymer chains. We may note that the curve of the drag reduction (see the inset plot of Fig. 3) changes with increasing molar mass in a similar way as it changes with increasing concentration (see the inset plot of Fig. 2). These findings reveal that there is an intricate interplay between concentration and molar mass effects on drag reduction, but it is evident that both factors contribute to laminarity of the flow. Since both the molar mass and concentration of the polymer influence the drag reduction

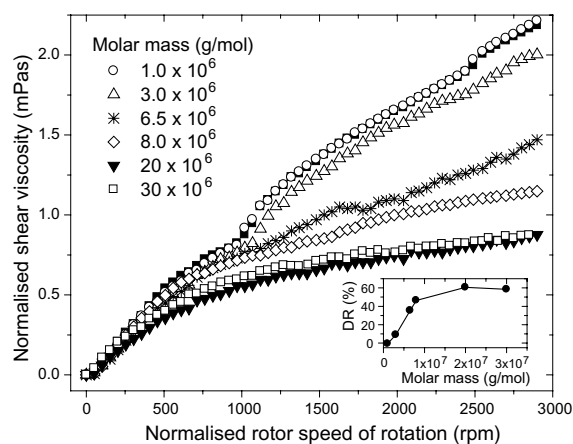


Fig. 3. Plot of the normalised shear viscosity as a function of the normalised rotor speed of rotation (these quantities are defined in the text) at 20 °C for toluene (■) and in the presence of a fixed concentration (50 ppm) of polystyrene at the molar masses indicated. The inset plot shows the effect of molar mass on the percent drag reduction, calculated with the aid of Eq. (1). The drag reduction has been calculated at a fixed normalised rotor speed of rotation of 2700 rpm.

effect in a complex manner, it seems that the polymer hydrodynamic volume  $c[\eta]$  is a more adequate quantity to describe the turbulence intensity. At a given concentration (50 ppm), the value of the hydrodynamic volume fraction ( $0.01 \leq c[\eta] \leq 0.13$ ) increases with increasing molar mass. In analyses of drag reduction performance, the models of Walsh [39] and Ryskin [18,40] contain the dimensionless parameter  $c[\eta]$  and a plot of %DR versus  $c[\eta]$  is frequently utilised to obtain a more accurate picture of relative drag reduction efficiency. This type of volume fraction normalisation procedure allows facile comparison of polymer samples despite differences in molar mass and concentration. These effects are usually normalised and a universal description is provided. On the basis of hydrodynamic volume fraction normalisation, drag reduction data from various experimental systems [41–43] have been analysed. In this context it should be noted that the values of the polymer volume fraction are determined from  $[\eta]$  values at zero shear rate, in accordance with the common procedure. However, in principle the apparent intrinsic viscosities measured at shear rates approximating those generated in the drag reduction experiments should have been employed. These measurements have not been undertaken because of experimental difficulties at high shear rates. In the high shear, Taylor flow conditions under which drag reduction performance is measured, the polymer chains will probably be extended and hence higher values of  $[\eta]$  will be measured and thereby larger hydrodynamic volume fractions will be registered.

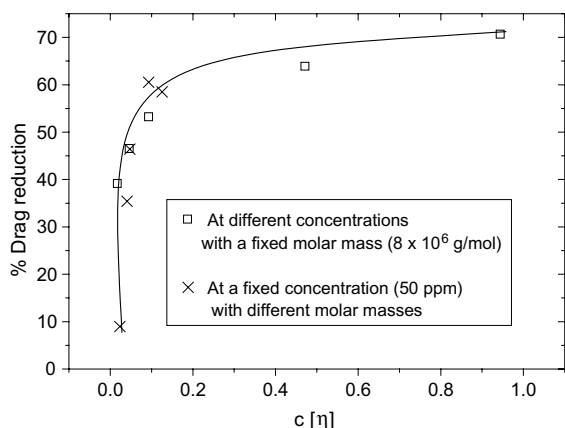


Fig. 4. Percent drag reduction versus  $c[\eta]$  for PS in toluene at different concentrations and molar masses. The data collected in this plot are taken from Figs. 2 and 3. See text for details.

Fig. 4 shows a plot of %DR versus  $c[\eta]$  for PS ( $M = 8 \times 10^6$  g/mol) in toluene at various concentrations (see Fig. 2) and for a constant concentration (50 ppm) of PS of different molar masses (see Fig. 3). The result reveals that most of the drag reduction effect for solutions of PS in toluene has occurred at a polymer volume fraction of approximately 0.2. This finding suggests that the Taylor vortices, to a considerable extent, are damped in the presence of a small amount of polymer. It is possible that even in this dilute concentration regime, the elastic effect [17] of the polymer is sufficient to store up most of the cascading energy of Taylor flow and thereby giving rise to an effective drag reduction. Effects of concentration and molar mass on polymer-induced drag reduction have been reported [2–4,6,44,45] for various polymer–solvent systems.

Fig. 5 compares the drag reduction effect for the system toluene (82.5 wt%)/methanol (17.5 wt%)–PS (close to  $\theta$  solvent conditions [35,36]) and the PS–toluene system at the same concentration and molar mass. The drag reduction effect is more pronounced at good solvent conditions. In dilute solutions at good solvent conditions, the polymer chain is very swollen and makes no knots on itself, while at  $\theta$  solvent conditions it contracts and makes many self-knots [46]. It has been argued [46] that the self-knots of a single coil do not disentangle easily and this suggests that it is more difficult to stretch the polymer chains at poor solvent conditions. This may explain the lower drag reduction efficiency at  $\theta$  solvent conditions, but we should also bear in mind that the hydrodynamic volume fraction is smaller at  $\theta$  solvent conditions and this may also contribute to the observed behaviour. It has been reported [47] that polymers more effectively reduce drag in good than in poor solvents.

Fig. 6 shows the effect of drag reduction in solutions of PS ( $M = 8 \times 10^6$  g/mol) in *trans*-decalin at a fixed

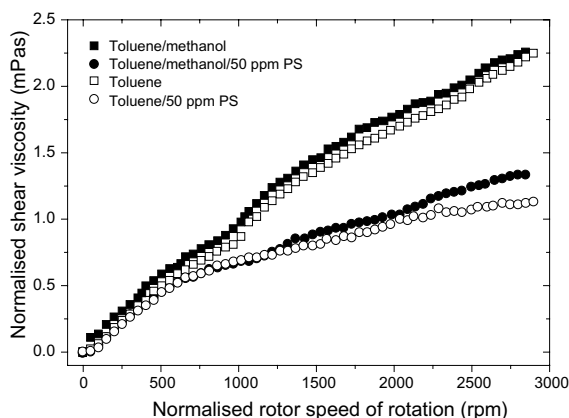


Fig. 5. Normalised shear viscosity as a function of the normalised rotor speed of rotation (these quantities are defined in the text) at 20 °C for toluene and a mixture (close to  $\theta$  conditions) of toluene (82.5 wt%)/methanol (17.5 wt%) without polymer and in the presence of a given concentration (50 ppm) of polystyrene with a molar mass of  $8 \times 10^6$  g/mol.

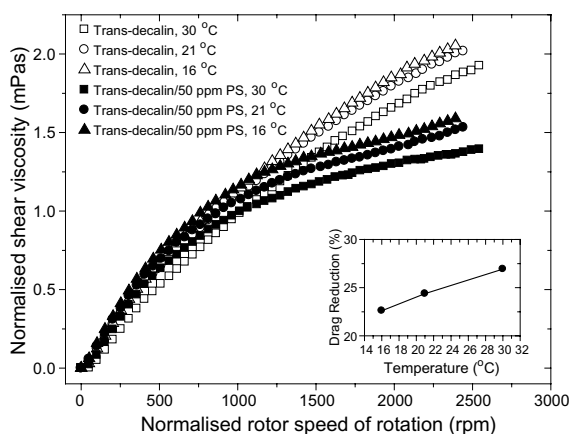


Fig. 6. Normalised shear viscosity as a function of the normalised rotor speed of rotation (these quantities are defined in the text) for *trans*-decalin and in the presence of polystyrene (concentration of 50 ppm and molar mass of  $8 \times 10^6$  g/mol) at temperatures of 16 °C (close to the UCST), 21 °C ( $\theta$  temperature), and 30 °C (marginal solvent conditions). The inset plot shows the effect of temperature on the percent drag reduction, calculated with the aid of Eq. (1). The drag reduction has been calculated at a fixed normalised rotor speed of rotation of 2390 rpm.

polymer concentration (50 ppm) at various thermodynamic conditions [37], ranging from marginal solvent conditions (30 °C) to the upper critical solution temperature (16 °C). The inset plot reveals that the drag reduction effect decreases as the thermodynamic conditions become poorer. Osmotic pressure measurements [37] on the PS/T–D systems have revealed that the  $\theta$

temperature is 21 °C and the thermodynamic conditions become better as the temperature is increased. For the considered molar mass, the upper critical solution temperature (UCST) is close to 16 °C [48,49]. As the UCST is approached, the single polymer chains assume a more contracted conformation (a globule) and the self-knots of the coil should increase. This suggests that the flow induced chain extension should be suppressed as the thermodynamic conditions become poorer. However, again we must remember that the value of  $c[\eta]$  will also decrease with decreasing temperature.

To summarise, the present study has shown that drag reduction in Taylor flow in solutions of PS in toluene is affected by concentration and molar mass of the polymer. High molar mass and concentrations up to the overlap concentration promote the drag reduction effect. On the basis of hydrodynamic volume fraction normalisation, it is shown that an essential part of the drag reduction effect occurs at volume fractions below 0.2. The drag reduction behaviour of solutions of PS is strongly affected by the thermodynamic conditions of the system. It is found that improved thermodynamic conditions of the considered polymer–solvent system favour drag reduction. The results from this work suggest that both the flow induced extension of the polymer chains and the magnitude of the hydrodynamic volume fraction of the polymer damp the Taylor vortices.

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