Polymer turbulent drag reduction near the theta point

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Abstract – Turbulent drag reduction efficiencies (%DR) of aqueous poly(ethylene oxide) solutions at various distances \( \tau \equiv \frac{T_\theta - T}{T_\theta} \) away from the theta temperature \( T_\theta \) are studied. It is found that only the long-time behavior of %DR of the system is sensitive to \( \tau \) in that %DR decays faster for systems closer to the theta-point. Usually, this faster decay is attributed to the faster mechanical molecular degradation (MMD) of polymers in bad solvents produced by turbulence. However, temperature quenches experiments close to \( T_\theta \) show that the apparent faster decrease in %DR for polymers closer to \( T_\theta \) is not due to MMD but rather because of the shrinking of the polymer after they have been injected into the turbulent flow. The relative insensitivity of the initial maximum %DR can be understood if \( T_\theta \) is considered as a function of the flow.

Introduction. – Turbulent drag reduction (DR) is defined as the phenomenon in which the turbulent drag of a flow can be drastically reduced by the addition of even minute amounts of polymers [1]. But this drastic effect will not last forever as the polymer molecules will be broken by the flow through a process known as mechanical molecular degradation (MMD) [2]. Usually, this polymer-induced DR is studied for energy saving applications or to understand the mechanism of DR which is still not fully understood yet [1]. Since it is believed that the DR efficiency (%DR) is related to the conformations of the polymer, Malkin et al. [3] has even proposed that the change in polymer conformations in very dilute solutions can also be studied by the effects of DR. This proposed study is feasible if the effects of turbulent flows on the polymer conformations can be neglected.

It is well known that when a polymer is close to its theta temperature \( T_\theta \), its conformation or radius of gyration (\( \xi \)) can be tuned by varying the distance away from its \( T_\theta \) as: \( \xi \sim \tau^{1/3} \) [4] where \( \tau \) is the reduced temperature: \( \tau \equiv \frac{T_\theta - T}{T_\theta} \). Usually, this transition is difficult to study because of the low concentrations involved to avoid inter-chain interactions [5]. One might think that this scaling behavior can be ideally studied by a turbulent DR experiment as proposed by Malkin. Unfortunately, it is known that a turbulent flow can alter the critical properties of a system such as binary mixtures [6,7] and it might most likely have a similar effect on the \( T_\theta \) for a polymer solution. Although very little is known about the effects of flows on the theta point properties, there are some indirect evidences from DR experiments in bad solvents that the effects of turbulence on the conformations of the polymers could be important.

Empirically, %DR of polymers in good solvents (far from \( T_\theta \)) have been found to be higher than those in poor solvents (close to \( T_\theta \)) (see footnote¹) and vice versa for the degree of MMD [8]. That is: polymers closer to \( T_\theta \) have lower %DR and degrade faster [9]. The fact that %DR depends on the solvent quality is not surprising as it is believed that the DR is produced by polymers in expanded conformations. However, as MMD is associated with the breaking of chemical bonds in the polymer chain, it is highly unlikely that a change in conformation of the polymer in bad solvents will affect this bond-breaking process. A possible explanation for this apparent faster

¹Some authors use poor solvents to mean that the polymer is in the collapsed state. Here poor solvents mean the polymer is not collapsed yet but very close to the \( \theta \)-point.
MMD for polymers close to \( T_\theta \) is that their conformations are strongly coupled to the turbulent flow. The initially DR-capable polymers are not broken by the flow as usually believed but simply not being expanded by the flow any more after they are in the flow for a while. However, this proposed mechanism remains to be tested.

In this letter, we report results of DR experiments carried out in a rotating disk apparatus (RDA) with high molecular weight poly (ethylene oxide) (PEO) in aqueous solution at various distances from \( T_\theta \). It is found that only the long time behavior of %DR of the system is sensitive to \( \tau \) in that %DR decays faster for systems closer to the theta-point. Usually, this faster decay is attributed to the faster mechanical molecular degradation (MMD) of polymers in bad solvents produced by turbulence. However, temperature quenches experiments close to \( T_\theta \) show that the apparent faster decrease in %DR for polymers closer to \( T_\theta \) is not due to MMD but rather because of the shrinking of the polymer after they have been injected into the turbulent flow. The relative insensitivity of the initial maximum %DR can be understood if \( T_\theta \) is considered as a function of the flow and the scaling form: \( \%DR \sim \tau^\alpha \) is proposed to estimate the shift in \( T_\theta \) by the flow.

**Experiments.** – The RDA used here is similar to other experiments [10,11]. The device consists of an aluminum (Al) disk with dimensions of 7.0 cm in radius (\( r \)) and 0.30 cm in thickness, enclosed in a cylindrical, temperature-controlled Al container (inner diameter = 16.3 cm and height = 5.5 cm). A transducer is used to monitor the torque on the rotating disk. Turbulence is produced for \( Re > 3 \times 10^5 \) with \( Re = \rho r^2 \omega / \eta \), where \( \rho \) and \( \eta \) are the fluid density and viscosity, respectively. The temperature of the system is maintained with a stability of ±0.5°C. Torques are measured to give: %DR = (\( T_S - T_F \))/\( T_S \) × 100, where \( T_F \) and \( T_S \) are the torques needed to maintain the disk to rotate at a particular \( \theta \) with and without polymer, respectively.

Polymer stock solutions are prepared by dissolving weighted amount of PEO (average molecular weights, \( M_\omega = 4.0 \times 10^6 \) g/mol, polydispersity = 3.0) in aqueous solutions of sodium acetate (CH\(_3\)COONa) (\( M_\omega = 82.03 \) g/mol) with three different concentrations of 0.75 M, 1.5 M, and 2.0 M. The \( T_\theta \) for the 0.0 M, 0.75 M, 1.5 M, and 2.0 M samples are 96, 75, 55 and 45°C respectively [12]. The system PEO/water has an inverted coexistence curve [12]. The polymer will be in the expanded form when the temperatures of the solutions are well below these temperatures and shrink when the temperatures are raised. The corresponding viscosities (intrinsic viscosities) of the samples at 25°C are 0.94 cP (456 ml/g), 1.13 cP (371 ml/g), 1.42 cP (285 ml/g) and 1.68 cP (229 ml/g), respectively. Their corresponding relaxation times are: 4.22 × 10\(^{-4}\) s, 4.12 × 10\(^{-4}\) s, 3.97 × 10\(^{-4}\) s and 3.79 × 10\(^{-4}\) s, respectively. Note that the viscosities of the polymer solutions at 55°C are only about 60% of those at 25°C. Since \( Re \) depends both on \( \omega \) and \( \eta \), \( \omega \) has to be adjusted to keep \( Re \) constant for experiments performed at various temperatures and concentrations.

A DR experiment is started by the injection of the stock solutions of prescribed polymer concentration into the RDA filled with appropriate solutions to give the desired final polymer concentrations. The mixing time of the polymer in the RDA is estimated to be 0.2 s [11] and therefore the addition of polymer to the RDA can be considered as instantaneous in the time scales of the experiments reported below. All aqueous solutions are prepared by deionized water. Note that the final concentrations of the polymer solutions in the experiments reported below are all 50 wppm. For such a dilute concentration, the shear viscosities of the samples are almost shear independent [13,14]. Distance from \( T_\theta \) is changed by either a change in temperature or a change in the salt concentration in the aqueous solutions [12]. The advantage of the addition of salt is that the \( T_\theta \) of the system is closer to room temperature.

**Results.** – Figure 1 shows a typical result for the time dependence of %DR immediately after the injection of the polymer into the RDA at 25°C with \( Re = 1.0 \times 10^6 \).

The salt concentrations and temperature of the solution are chosen in such a way that the samples are at various distance from \( T_\theta \). Figure 1 shows that %DR decreases immediately after the injection. These decreases in %DR are representative for other systems [11] and have been believed to be caused by the MMD of the polymer under turbulence. It can be seen that the decrease in %DR
is faster when the system is closer to $T_\theta$. The inset shows similar degradation behavior for systems with the same salt concentration but at various temperatures. One characteristic observation in fig. 1 is that systems far away from the $\theta$-point do not only degrade slower but also give some finite values of %DR after an extended period (60 min). But for systems close to the $\theta$-point, there seems to be no DR capabilities after a while.

Although the long time DR capability of a polymer is sensitive to its distance away from its theta-point as shown in fig. 1, the maximum initial %DR in fig. 1 seems to be not the case. Figure 2 shows the temperature dependence of the initial %DR at various salt concentrations with $Re = 1 \times 10^6$. There are two important features in fig. 2. First, all the measured initial %DR decrease when the temperature of the systems approach their corresponding $T_\theta$: similar to the effect of MMD. However, the measured initial %DR for systems with various $T_\theta$ seem to not too sensitive to their corresponding $T_\theta$. These two findings are in contradiction if MMD is sensitive to $T_\theta$. To check for the effects of MMD, GPC experiments have been performed and the results\(^2\) show that MMD is not important here. Furthermore, since data in fig. 2 are all early time measurements, one can safely neglect the effects of MMD. Therefore the decrease in %DR in fig. 2 must be caused by the change in the polymer conformation. Since %DR increases with the size of a polymer in general [1], fig. 2 is consistent with the equilibrium picture that $\xi$ decreases as the system is getting closer to $T_\theta$. If the system is in equilibrium, a scaling relation between %DR and $\tau$ might exist. The inset of fig. 2 is an attempt to search for such a scaling relation by plotting of the same data of fig. 2 as a function of $\tau$ in a log-log form and it is clear that there is no such scaling relation.

Here we consider a different explanation for the observed apparent MMD in fig. 1. When a polymer of size $\xi$ is under a shear flow of shear rate $\gamma$, the force acting on the polymer to stretch it is: $F_{ext} \sim \gamma \xi^\nu$ with $\nu = 1$. In the case of turbulence, presumably one can assume a statistically similar relation but then $\nu$ might not be one. This relation says that if the force to stretch the polymer is the same, a stronger shear is needed for a smaller $\xi$. Since there is a distribution of shear rates both spatially and temporally in a turbulent flow [15], there will be a distribution of the stretched polymers. For a fixed turbulent strength, the number of fully stretched polymers will then increase with $\xi$. Intuitively, %DR should also increase with the number of stretched polymers and therefore assumes a higher value when the system is far from $T_\theta$. With this picture, one does not need MMD to explain the observed decrease in %DR shown in fig. 1 if the number of stretched polymers is a decreasing function of time.

If the picture discussed above is correct, the polymers in the case of $T-T_\theta = 30K$ shown in fig. 1 are not degraded after 20 min. but simply not being stretched any more by the flow to produce DR. These polymers should recover their DR-capabilities if they can be made more easily stretched; i.e. far from $T_\theta$. To test this idea, experiments with temperature quenches are performed. Figure 3 shows the results of the changes of %DR as a function of time when the temperature of the system is switched between two preset values. It can be seen from the figure that the usual degradation of %DR can be observed when the temperature is set close to $T_\theta$. However, when the temperature of the system is changed to a value far from $T_\theta$, %DR of the system recovers; indicating that the polymers are not completely broken by the flow even when nearly zero %DR has been observed. Figure 3 also shows that this phenomenon is reversible when the temperature of the system is quenched back to its original value.

In order to understand why the initially DR-capable polymers fail to maintain their DR-capabilities after they have been in the turbulent flow for a while, one needs to consider how our DR experiments are being performed. In most DR experiments, when the polymer solution is injected into the turbulent flow, a very high shear exists close to the outlet of the needle because of the high mean flow velocity. Presumably, most of the polymers are being fully stretched immediately after they enter the turbulent flow. These stretched polymers will produce the initial high value of %DR. Once they are being stretched, the shear rate needed to maintain the stretched state can be much smaller. However, since turbulence is

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\(^2\)The peak molecular weight of the polymer is found to decreased from $1.5 \times 10^6$ to about $4.2 \times 10^5$ after the drag reduction experiments such as those shown in fig. 1.
The solid symbols represent the changes of %DR when the scale in figs. 1 and 3 originates from the non-space-filling observed in figs. 1 and 3. Note that although the slow time after the injection and therefore produce the phenomena stretched polymer will be a decreasing function of time to wait for a relatively high shear to get stretched less equilibrium size. Once that happens, the polymer will be in a collapsed state as observed in our experiments. Intuitively, the flow-induced shift, \( \Delta T_\theta (\equiv T'_\theta - T_\theta) \) should be a function of salt concentration when the flow condition is fixed; similar to the equilibrium condition.

With this concept of \( T'_\theta \), the size of the polymer under turbulence is now only a function of \( \tau \) with respect to \( T'_\theta \). One might think that temperature quench experiments similar to those of fig. 3 can be used to determine \( T'_\theta \) under turbulence. However, it is important to note that zero %DR in fig. 3 does not mean that the polymers have been collapsed. They are just not being stretched by the flows. Here we resort to a scaling assumption to estimate \( \Delta T_\theta \) for the initial time when all the polymers are being stretched and maximal %DR is being produced. If %DR is simply produced by the return of the elastic energy \( w \) stored in the polymer to the flow, as suggested by de Gennes [18], at some length scale \( \ell \) and time scale \( t_\ell \), one could imagine that all these quantities (\( w, \ell \) and \( t_\ell \)) should all be related to the conformation of the polymer or \( \tau \) and the turbulent flow. In such a case, %DR near the \( T'_\theta \) will be in a scaling form. One can then adjust \( \Delta T_\theta \) for various salts concentrations in fig. 2 to get a collapse of all the data point into one single straight line in a log-log plot.

Figure 4 shows the result of such an operation with adjusted \( T'_\theta \) to produce a straight line in the form: %DR \( \sim \tau^\alpha \) with \( \alpha = 2.0 \). In the process of obtaining the straight line in fig. 4, it is found that \( \Delta T_\theta \) is rather sensitive to the salt concentrations; with \( \Delta T_\theta \) being adjusted as 2, 20, 36 and 43 °C for the salt concentrations of 0.0 M, 0.75 M,

\[ \text{Fig. 3: Time dependence of %DR of PEO (50 wppm) in 0.75 M salt solution for four different temperatures at } Re = 8.0 \times 10^3. \]

Discussion. – In equilibrium, the size of a polymer is controlled by its distance from its \( T_\theta \) which is determined solely from the competition between monomer-monomer and monomer-solvent interactions. However, in the presence of turbulence, there is a distribution of \( \xi \) which is determined by the interaction of the flow with the polymers. In general, the effect of flow results in the stretching of polymers. It has been established that there are shifts in the critical temperatures of many critical systems (such as binary fluids and polymer mixtures) under flow [7]. In these later cases, the flows always drive the system further away from the critical point because molecules close to each other (critical clusters) in equilibrium are being torn apart by the flow. Phase transitions would occur only when the temperature of the system under flow is shifted in such a way to provide stronger intermolecular interactions to overcome the effects of the flow.

For a polymer, it is known that its phase transition properties can be changed when it is being pulled by an external force [16,17]. These theoretical studies show that polymers in poor solvent or even collapsed polymers can be stretched. That is, in a sense, the theta-point of the polymer is being shifted. In the case of a polymer being stretched by a flow, the shift of theta-point can, in principle, be determined by the competition of the stretching and relaxation of the polymer. In our current experiments, one can use this concept of a shifted theta-point or \( T'_\theta \). Presumably, \( T'_\theta \) should be higher than the original \( T_\theta \) because the system is now further away from \( T_\theta \) under flow; similar to the shift of critical temperature in a turbulent binary mixture [6]. This phenomenological defined \( T'_\theta \) is consistent with the concept of \( T_\theta \) because, at high enough temperature \( T > T'_\theta \), the polymer will be in a collapsed state as observed in our experiments. One might think that temperature quench experiments similar to those of fig. 3 can be used to determine \( T'_\theta \) under turbulence. However, it is important to note that zero %DR in fig. 3 does not mean that the polymers have been collapsed. They are just not being stretched by the flows. Here we resort to a scaling assumption to estimate \( \Delta T_\theta \) for the initial time when all the polymers are being stretched and maximal %DR is being produced. If %DR is simply produced by the return of the elastic energy \( w \) stored in the polymer to the flow, as suggested by de Gennes [18], at some length scale \( \ell \) and time scale \( t_\ell \), one could imagine that all these quantities (\( w, \ell \) and \( t_\ell \)) should all be related to the conformation of the polymer or \( \tau \) and the turbulent flow. In such a case, %DR near the \( T'_\theta \) will be in a scaling form. One can then adjust \( \Delta T_\theta \) for various salts concentrations in fig. 2 to get a collapse of all the data point into one single straight line in a log-log plot.

In general, the stretching time scale of a polymer is much shorter than its relaxation. At first sight, these two processes cannot be in balance. However, since there is only a small fraction of turbulent fluid is in high shear regime, these two time scales can presumably be balanced in a steady state.

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the turbulent flow and will therefore lead to change in $T_\theta$. It is not clear if the scaling form we argued above could really exist. However, our conclusion that the $T_\theta$ is shifted by the flow and that the effects of salt are nullified by the flow should still hold in general even without the proposed scaling form. The relative insensitivity of the initial maximal %DR is a good evidence of the nullifying effects of the flow.

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