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# Drag reduction in flow: Review of applications, mechanism and prediction

Review

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#### Abstract

Drag reduction (DR) agents are used at very low concentrations to accelerate significantly the flow in oil pipeline conduits, oil well operations, flood water disposal, fire fighting, field irrigation, transport of suspensions and slurries, sewer systems, water heating and cooling systems, airplane tank filling, marine systems, and biomedical systems including blood flow. DR agents are typically high molecular mass polymers; this review discusses a mechanism explaining how DR occurs using such agents. All pertinent experimental findings are challenged with that mechanism and all are shown to support it. In industrial applications DR agents undergo mechanical degradation in turbulent flow. An equation predicting the degradation as a function of time is presented and successfully confronted with experimental data. Experimental methods of determination of DR are outlined. Finally a connection between DR and flocculation is discussed.

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Keywords: Drag reduction; Turbulent flow; Petroleum transport; Polymer solvation; Flocculation

#### Contents

1.	Basic definitions	409
2.	Applications	410
3.	Manifestations and characteristic features of DR	411
4.	Mechanism of drag reduction	412
5.	Mechanical degradation in flow	413
6.	Experimental determination of DR.	414
7.	The flocculation connection	414
	Acknowledgements	415
	References	415

## 1. Basic definitions

To begin, there are two main types of flow: laminar and turbulent. In a cylindrical conduit one can visualize the laminar flow as a series of co-axial cylinders oriented along the flow

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*E-mail address:* brostow@unt.edu. *URL:* http://www.unt.edu/LAPOM/ direction; such a flow structure is known as *telescopic shear*. The central part of the fluid which includes the axis has the highest velocity  $u_0$ . The velocity at the wall is necessarily zero, with intermediate velocities in-between. A schematic representation is shown in Fig. 1. Another way to create laminar flow is between two parallel plates, one moving and one stationary, as shown in Fig. 2. Similarities – as well as differences – between this and the preceding case are evident.

Non-laminar flow is called turbulent flow. A picturesque definition is "eddies within eddies within eddies".

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W. Brostow/Journal of Industrial and Engineering Chemistry 14 (2008) 409-416



Fig. 1. Laminar flow at velocity u in a cylindrical conduit.

For both types of flow, the flowing fluid has its motion imposed by an applied shearing force F; the shear stress is

$$\tau = \frac{F}{A} \tag{1}$$

where A is the surface area to which the force is applied.

Consider now the case displayed in Fig. 2: the moving plate has the velocity u.

Consider the velocity  $u_1$  seen in Fig. 2 at a certain level below the moving plate. By the definition of velocity we have

$$u_1 = \frac{\mathrm{d}x_1}{\mathrm{d}t} \tag{2}$$

where  $x_1$  is the horizontal coordinate (in this case at the front of the moving fluid) while *t* is time.

Going vertically down along the  $x_2$ -axis, we have velocities going down from u (adjacent to the moving plate) to 0 (adjacent to the stationary plate). To quantify that vertical velocity gradient, we write

$$\frac{\mathrm{d}u_1}{\mathrm{d}x_2} = \frac{\mathrm{d}(\mathrm{d}x_1/\mathrm{d}t)}{\mathrm{d}x_2} \tag{3}$$

Now we recall a simple rule from calculus: in two consecutive differentiations the order does not affect the result. Therefore

$$\frac{\mathrm{d}u_1}{\mathrm{d}x_2} = \frac{\mathrm{d}(\mathrm{d}x_1/\mathrm{d}t)}{\mathrm{d}x_2} = \frac{\mathrm{d}(\mathrm{d}x_1/\mathrm{d}x_2)}{\mathrm{d}t} = \frac{\mathrm{d}\Gamma}{\mathrm{d}t} \tag{4}$$

where we have introduced the shear rate (strain rate)

$$\Gamma = \frac{\mathrm{d}x_1}{\mathrm{d}x_2} \tag{5}$$



Fig. 2. Laminar flow between parallel plates. The shearing force F acts on the top plate as indicated. The velocity  $u_i$  decreases going down along the vector  $x_2$  since the velocity at the bottom plate is necessarily 0.

The fluid resists the motion; a measure of that resistance is viscosity  $\eta$  – which we can now define in terms of quantities already known

$$\tau = \frac{\eta \, d\Gamma}{dt} \tag{6}$$

Incidentally, here lies the main difference between fluids and elastic solids; in the latter the stress is proportional to strain (not to the strain rate).

Armed with the above definitions, we return to the story of laminar and turbulent flow. We need just one more definition, that of the Reynolds number

$$N_{Re} = \frac{Du_{\mathrm{av}\rho}}{\eta} \tag{7}$$

where *D* is the conduit diameter (applicable strictly to the cylindrical conduit in Fig. 1),  $u_{av}$  is the average flow velocity and  $\rho$  is the fluid mass density (typically in g cm<sup>-3</sup>). A rule-of-thumb which applies to various fluids is that for

$$N_{Re} > 1.7 \times 10^4 \,\mathrm{s}^{-1} \tag{8}$$

we have turbulent flow while for lower Reynolds numbers the flow is laminar [1].

We can now (at last ...) consider the topic of this review: drag reduction (DR). While the phenomenon of DR can take place in laminar flow, its occurrence in turbulent flow is of very large interest. As already discussed, the velocity of fluid particles at the walls in Fig. 1 or at the immobile plate in Fig. 2 is naught. The operation of disc brakes in a car provide a simple analogy of this situation. The implication: the immobile plate in Fig. 2, or likewise the immobile walls of the circular conduit in Fig. 1, cause *drag*. *DR occurs when an additive put into the fluid increases the average flow velocity*.

Section 2 now follows with discussion of a long list of applications of the DR phenomenon. In Section 3 then we shall discuss experimental findings regarding DR. Section 4 encompasses the presentation of a model that explains all these findings. In Section 5 there is a description of mechanical degradation in flow (MDF), which gradually lowers the effectiveness of the DR agent. A quantitative model allowing prediction of MDF and thus of DR as a function of time is presented. We then briefly outline experimental methods of DR determination. Finally, we discuss connection of DR to flocculation.

#### 2. Applications

DR as defined above has numerous applications in a variety of fields. To give the first example, large urban agglomerations in India – and in other countries as well – find their sewer systems inadequate in the face of doubled or tripled populations. An alternative to *digging out the entire municipal sewer system* and replacing it by conduits with larger diameters is the use of DR agents. First of all, this is a much faster and cheaper solution. More importantly, however, it is not a temporary palliative only. Later on larger diameter pipes would have to be replaced periodically by still larger ones. By contrast, when the population continues to increase still more as it always does, a DR agent at increasing concentrations can continue to keep the sewage situation under control.

Other applications of the DR phenomenon are as follows:

- oil pipelines, such as the Alaska pipeline
- oil well operations
- flood water disposal
- fire fighting
- field irrigation
- transport of suspensions and slurries
- water heating and cooling systems
- airplane tank filling
- marine systems (ocean thermal energy conversion systems)

In fact, until I and my collaborators started working on DR, I did not know that at every major airport around the world DR agents are in use. Otherwise filling tanks of passenger planes with fuel would take approximately twice as much time.

The above list is *not* complete; it is limited to technologies created by humans. DR occurs also – without our intervention – in human and animal blood flow [2–4]. Without DR, humans and animals *would have to eat multiple amounts of food* as compared to their current food consumption. Imagine what would happen if DR agents provided by Nature were not present; blood circulation would be insufficient without eating much more food, and since the amounts of food for humans and animals are not unlimited, all these species would become extinct. In other words, living organisms other than plants would disappear!

Still further, the occurrence of DR in blood flow and the fact we know it takes place make possible atherosclerosis prevention [2–4]. Atherosclerosis is the process of deposition of fatty substances, cholesterol, cellular waste products, calcium and built-up of still other substances as plaque in the inner lining of an artery. It usually occurs in large and medium-size arteries and may cause hardening of arteries. Plaques can grow large enough to reduce significantly the blood flow through arteries. Plaques that rupture can cause blood clots; in turn the clots can block blood flow or else break off and travel to other parts of the body. Thus, DR in blood flow performs two roles: flow acceleration as in other applications and also slowing down plaque formation in blood arteries.

In spite of so many different positive applications, DR provided by polymeric agents is not without shadows; mechanical degradation in flow takes place. Flow turbulence causes the polymeric chains providing DR to undergo scission. We shall address this issue in particular in Section 5.

# 3. Manifestations and characteristic features of DR

The reason the present author started working in the area of DR was in response to a challenge. In the Spring of 1980 Jacques Zakin, Ohio State University, Columbus, told this author that the DR phenomenon is unexplained – in spite of its

numerous applications. Actually, a number of explanations have been provided but each of them was able to explain only *a part* of the experimental findings. Clearly a model which would explain all facts was needed – and therein was the challenge.

The original list of findings concerning DR was based on papers by Zakin and Houston [5,6]. Currently the main agreed-upon items on the list are as follows:

- (a) DR is directly proportional to the molecular mass *M* of the polymer, regardless of liquid (solvent) type.
- (b) The concentration of DR agent required for a given level of drag reduction is several times higher in a poor solvent. We recall that solvents can be classified as good, theta (=Flory) and poor [7,8].
- (c) More MDF occurs in a poor solvent under fixed flow conditions than in a good solvent under the same flow conditions. MDF stops at some time, so that further flow turbulence does not make the chains which already underwent scission any shorter. We define the limiting molecular weight

$$M_{\infty} = \lim M \tag{9}$$

It has been proven in experiments [5,6] that  $M_{\infty}$  values in poor solvents are lower than in good ones.

- (d) Bond scission in flow along chain backbones does not occur exclusively at chain midpoints (as some authors hypothesized) nor is it random.
- (e)  $M_{\infty}$  is independent of the initial molecular weight  $M_0$  before the flow start. MDF in polydisperse systems occurs mostly by breaking large macromolecules.
- (f) Shear degradation at a given shear stress is independent of the viscosity of the solvent.
- (g) Entanglements do not play a major role in MDF.
- (h) The degradation rate increases or remains the same as the DR agent concentration is decreased.
- (i) Taking photographs of flowing liquids containing DR agents, Donohue et al. [9] observed low speed streaks originating from a conduit wall. They have found that such streaks lift off but after neither oscillating nor bursting return to the wall.
- (j) Hunston and Reischman [10] have shown that only polymeric chains above a certain length participate in DR.
- (k) Long ago Flory [11] has found values of configurational dimensions of polymers in solution often twice as large as calculated from the freely jointed chain model [7,8,12].
- Kulicke et al. [13] have demonstrated that single chains can also cause DR. This agrees with practical applications of the DR phenomenon which involve sometimes concentrations as low as 10 ppm.
- (m) DR takes place also in laminar flow.
- (n) Injecting a DR agent into the center of a pipe results in practically instant drag reduction [14,15].

Among the experimental findings listed above, for a long time (c) was considered very puzzling. By definition, in poor solvents the liquid volume pervaded by each polymer chain is small [7,8]. The macromolecular chains 'keeping their own

company' were expected to defend themselves against scission better than those in good solvents; the latter are extended over large volumes and thus were expected to be 'attacked' more by flow turbulence. According to this reasoning, more MDF should occur in good solvents – while experiments were showing the contrary.

#### 4. Mechanism of drag reduction

Given the practical importance of DR, various explanations how it occurs have been advanced. Models based on fluid mechanics were of the continuum type, did not take into account discrete polymer + solvent interactions and were not successful. The starting point for a successful model of DR was the puzzling observation (c) named above. Clearly 'closer cooperation' between the macromolecular chains and the solvent molecules provided more and more stable DR.

A model was created in 1983 [16] and is now depicted in Fig. 3. A domain flows as a unit, with some perturbation to its shape caused by the turbulence along the way. Here we see the reason for drag reduction: individual solvent molecules solvated by polymer chains are not 'attacked' individually by eddies of the turbulence. When such an attack occurs, the solvent molecules defend themselves collectively. The solvent molecules inside the domains are protected even more than those which by solvation are attached to macromolecular chains outside.

The model assumes that in each polymer chain there are two kinds of sequences, good (oriented along the flow direction or close to it, and strongly solvated, can be called oak-like) and poor (oriented more or less perpendicularly to the flow, poorly solvated, can be called willow-like). Statistical mechanical calculations have been made based on that model [17–19]. The results show effects of variation of the proportion of good/poor sequences on solution properties.

Indirect support for the model shown in Fig. 3 was provided by Springer and his coworkers [20,21] who reported the existence of long-range heterogeneities in polymer solutions. Brownian dynamics computer simulations of flowing dilute polymer solutions [22,23] have demonstrated that at short times and high shear rates the polymer chains become less entangled and less intertwined as flow continues, enlarging pervaded volumes.



Fig. 3. Mechanism of drag reduction. Average distance between chain sequences on the outside of the domain oriented along the flow is d; average widths of good and poor sequences are  $d_g$  and  $d_p$  in obvious notation.

Still, the model represented in Fig. 3 was a hypothesis without a direct experimental evidence supporting it. A breakthrough came in 1999. As one can easily infer from Fig. 3, the larger is the volume pervaded by polymer chains, the higher is DR. Acoustic measurements of the solvation numbers and of DR efficacy have shown that indeed *the solvation numbers go symbatically with that efficacy* [24]. This result provides us also with a tool to choose between several polymers as candidates for a DR agent for a given fluid: the higher the solvation number calculated from the ultrasound velocity, the better will be the DR efficacy.

We can now consider the facts listed in the preceding Section in the light of the DR mechanism represented in Fig. 3:

- (a) Clearly higher *M* means longer chains and thus larger domains corresponding to those seen in Fig. 3. This has been observed in non-aqueous solvents as well as in aqueous media [25].
- (b) The solvated domains in poor solvents are necessarily smaller than in good ones and thus less effective as drag reducers.
- (c) Solvated domains in poor solvents are smaller, hence the fraction of the total volume in the fluid taken by solvated molecules is smaller than in good solvents.
- (d) Therefore, in poor solvents there is less 'defense' against polymer chain scission.
- (e) The assumption that scission occurs at each chain at its midpoint never had any foundation. The scission is not random either since the sequence location in the domain (good or poor in Fig. 3) is important.
- (f) As a consequence of scission caused by turbulence, the chains become eventually so short that turbulence becomes 'powerless' and cannot cut the chains to pieces anymore;
- (g) Clearly solvation is important rather than viscosity. Some of the continuum models assumed substantial viscosity changes to explain DR. As noted above, DR at the DR agent concentration such as 10 ppm is possible. Viscosity difference between the pure fluid and the fluid containing a DR agent is then very small.
- (h) Again Fig. 3 tells us that entanglements are not decisive for DR. Earlier assumptions that chain entanglements are important here seem to be connected to the false model of 'critical polymer concentration  $c^*$ '. If we call the average liquid volume pervaded by an individual polymer chain  $v_i$ , then  $V(c^*) = nv_i$ , where V is the total volume of the fluid and *n* is the number of dissolved polymeric chains. Thus, one assumes here that each chain pervades a different volume in the fluid as long as this is possible. Such a situation is represented in Fig. 4. There are 9 spaces (cells) with the volume  $v_i$  each and n = 9. Each chain takes a different cell and there is no overlap. The occupation number in each cell = 1. Clearly this is only one of many possible ways of filling 9 cells - and *all other* such ways include overlaps. This problem was analyzed by Wolff and the present author in terms of combinatorial statistics [26] and the negligible probability of the configuration displayed in Fig. 4 was demonstrated. Moreover, none

W. Brostow/Journal of Industrial and Engineering Chemistry 14 (2008) 409-416



Fig. 4. Occupation of 9 spaces by 9 polymeric chains in the primitive and unfounded model. The possibility of overlap has been eliminated on purpose.

of the supporters of the 'critical polymer concentration  $c^*$ ' hypothesis explains how all chain entanglements which were present in the solid state *miraculously disappear* during dissolution. Timid reports in the literature [27] that there are no spectacular changes of properties at  $c^*$  did not receive attention they deserve.

- (i) When the DR agent concentration is decreased, then turbulence causing chain scission has less domains to attack, there is more turbulence per domain.
- (j) Streaks lift off the conduit walls, but it is because they encounter the solvated domains that after neither oscillating nor bursting they return to the wall.
- (k) Short polymeric chains are unable to form domains.
- (1) Solvation results in enlarging the chain dimensions in comparison to the predictions of the freely jointed chain model.
- (m) Precisely because a single chain (of sufficient length) can create a domain, DR occurs at very low DR agent concentrations.
- (n) Solvation can occur and domains can be formed in laminar flow as well.
- (o) The finding of Bewersdorff [14,15] is of course fully supported by the mechanism of DR represented in Fig. 3. However, at the time he reported his results, the finding was significant. Earlier some people were trying to explain DR by wall lubrication, similarly as low friction on metal surfaces with a lubricant. The fact that DR occurs before the conduit walls can be affected by the injected DR agent has ended that series of speculations.

Since we now understand how DR occurs, the next logical question is how can we enhance it. There are a least three approaches which deserve to be named. One advocated by Singh [28–33] consists in taking a polymer and grafting on its chains a second polymer. This should increase the solvent volume pervaded and thus enhance DR (except when the solvent is a poor one for the grafted polymer). A second approach consists in enabling formation of inter-molecular associations in solution that can be destroyed by turbulent flow – but then are re-formed for thermodynamic reasons as reported by Kowalik et al. [34]. A third approach proposed by Bello et al. [35] consists in cross-linking DR polymers at concentrations below those required for gel formation. We know that in all cases when DR occurs, MDF also takes place; this is the subject of the next Section.

## 5. Mechanical degradation in flow

We need to describe quantitatively the drag reduction and its changes with time *t* caused by MDF. Let us call the initial DR at the beginning of the flow  $\lambda_0$  and the fluid viscosity at the same time  $\eta_0$ . Scission of chains caused by MDF results in a lower drag reduction  $\lambda$  and can also lower viscosity  $\eta$ . Then

$$\frac{\lambda}{\lambda_0} = \frac{\eta}{\eta_0} \tag{10}$$

Quite generally, the key property we seek to evaluate MDF is the change of the ratio  $\lambda/\lambda_0$  with time.

An equation for that ratio  $\lambda/\lambda_0$  was derived in [16], used with good results in [19] and amplified in [36]. It reads

$$\frac{\lambda}{\lambda_0} = \frac{1}{1 + W[1 - e^{-t/h_0 + h_1 c + h_2 c^2}]}$$
(11)

Here *W* is the average number of vulnerability points per chain which depends on the good/poor sequences ratio and the turbulent flow velocity;  $h_i$  parameters are constants for a given Reynolds number and the polymer + solvent pair while *c* is the polymer concentration. Eq. (11) contains the quadratic term absent in the original derivation [16] to take now into account the overlap between polymer chains that affects their pervaded volumes [37]. Thus, a single equation for DR takes care of both time and the additive concentration variables.

A series of papers by Choi and his coworkers deals with DR [33,38–46] for synthetic polymers, natural ones based on polysaccharides and also for DNA. Among other topics, they have explored the use of the DR phenomenon for cold water piping in an ocean thermal energy conversion (OTEC) system [40]. The group at Inha University deals also with time dependence of DR and MDF. For a number of systems they have found that other  $\lambda(t)$  equations do not work, while Eq. (11) shown above provides good results for the same set of systems [40,43]. This agrees with our own analysis of a variety of solvent + polymeric DR agent systems [16,19,36].

It is instructive to consider the role of the parameter *W* in Eq. (11). In Fig. 5 we see the outcome of applying Eq. (11) to three different polymers [36]: amylopectin (Am), polyacrylamide (PAM) and a copolymer created by grafting acrylamide monomer onto amylopectin (Am-g-PAM). W. Brostow/Journal of Industrial and Engineering Chemistry 14 (2008) 409-416



Fig. 5. Relative drag reduction  $\lambda/\lambda_0$  for aqueous solutions of the Am-*g*-PAM graft co-polymer and for the respective homopolymers as a function of time for 500 ppm concentrations of each drag reducer. Points are experimental, continuous lines calculated from Eq. (11).

In Fig. 5 we observe, above all, large differences in MDF between the three polymers. As for the average number of vulnerability points, we have W = 0.870 for PAM, W = 0.355 for Am and W = 0.251 only for Am-g-PAM. Thus nearly every PAM chain undergoes scission while only one in four Am-g-PAM chains suffers that fate. We see clearly in Fig. 5 how W values affect the time dependence of DR.

Finally consider that DR agents increase the liquid throughput but constitute additional cost. For this reason one wishes to find the lowest necessary concentration of additive. Results reported in [36] tell us that applying concentrations higher than 1000 ppm is not worthwhile. There is no further improvement in retaining drag reduction for longer times. We recall the chain overlap seen in Brownian dynamics computer simulations [22,23]. It seems above 1000 ppm additional polymer chains have little effect on the chain stability with respect to MDF. This is a consequence of the overlap and also tells us how large the domains are.

## 6. Experimental determination of DR

Having discussed in detail the mechanism of DR, we now turn to the question how is DR measured. A turbulent flow rheometer based on the classical design of Hoyt [47] works well. There is a motor-driven syringe; the delivery rate of the syringe is controlled by speed of a small motor. A linear actuator drives the syringe plunger and is coupled to the motor. In the beginning, a full dissolution of a given DR agent is achieved by slow stirring for 6–24 h; the time depends on nature of the fluid, nature of the additive and its concentration. Samples of the solutions are withdrawn from the rheometer at pass numbers such as 10, 20, etc. Clearly time *t* is proportional to the number of passes. Absolute viscosities of the solutions can be determined with an Ubbelhode viscometer as described for instance by Lucas et al. [7].

In a modern procedure of DR determination, Lucas et al. have adapted a capillary viscometer for accurate determination of the pressure drop in turbulent flow regime [25]. Samples of polyacrylamide were synthesized varying the quantity of the polymerization initiator and thus obtaining different molar masses M. Size exclusion chromatography was used to determine M values.

Another method of DR determination based on a rotating disk apparatus has been developed by Choi and his laboratory [37,41,48–50]. A stainless steel disk is enclosed in a cylindrical temperature controlled container. An electric transducer is used to monitor the torque  $t_r$  on the disk rotating at a constant speed of 1800 rpm. The percentage drag reduction is then calculated as

$$\lambda = \left(\frac{1 - t_{\text{rsolution}}}{t_{\text{rliquid}}}\right) \times 100\% \tag{12}$$

where  $t_{rliquid}$  pertains to the original liquid before adding a DR agent.

#### 7. The flocculation connection

As emphasized by Rustum Roy [51] and also by Roald Hoffmann [52], various groups try to compartmentalize disciplines of Science and Engineering and cut them into pieces for their own convenience or benefit. By contrast, our discussion above of DR shows integration of several ostensibly 'unconnected' disciplines.

However, there is still more. It is difficult to get solid constituents out of a liquid solution or suspension. Fine particles with diameters on the order of 10  $\mu$ m will not settle out of suspension by gravity alone in an economically reasonable amount of time. Addition of flocculants to liquid suspensions causes aggregation of particles in so-called flocs, increasing the ease and rate of their removal. Therefore flocculation has a variety of applications, including mineral processing, treatment of industrial effluents, and municipal sewage sludge purification. Obtaining metals from ores would not be possible without the slurry processing step. As for municipal sludge purification, Meireles et al. [53] report producing a water soluble cellulose flocculant from sugar cane bagasse - which in the city of Uberlándia serves well for the purpose: the turbidity of water is reduced by some 42 %. Flocculants play as we realize multiple roles: not only synthesis from sugar cane bagasse is economical but otherwise bagasse itself would become waste; the use of flocculants reduces environmental contamination, including that by industrial effluents or municipal sewage; depletion of raw materials including potable, industrial and agricultural water - is slowed down.

The same polymers that act as DR agents are typically also flocculation agents. Why? There must be a common or similar mechanism. As shown in Fig. 3, a polymeric chain pervades a large volume of the fluid by solvation. *We assume that the same*  process pushes solid particulate matter out of solution in the flocculation process [54]. If this is true, then more solvation means larger pervaded volumes and larger radii of gyration  $R_G$  of the chains. The radius of gyration  $R_G$  is the root-mean-square distance of the collection of atoms from their common center of gravity [7,8]:

$$R_{\rm G}^2 = \frac{\sum m_{\rm i} r_{\rm i}^2}{\sum m_{\rm i}} \tag{13}$$

Here  $m_i$  is the mass of the ith atom while  $r_i$  is the vector from the center of gravity to that atom; the summations run over all atoms. There are several methods of experimental determination of  $R_{\rm G}$ .

We have demonstrated the existence of a relationship between  $R_G$  and the velocity y of settling the particulates out of suspension [54], namely

$$y = aR_{\rm G}^b \tag{14}$$

where a and b are parameters characteristic for a given suspension medium, that is both the dispersed phase and the majority liquid phase. An illustration is provided in Fig. 6. More results are supporting our model [55].

The phenomenon of drag reduction has been apparently discovered by Toms in 1948 [56]. Our knowledge on DR and flocculation is still growing. At the end of 2007 DR results for turbulent flow near the theta point of the solvent have been reported by Choi and coworkers [57]. A DR agent was added to the poly(ethylene oxide) (PEO) aqueous solutions together with CH<sub>3</sub>COONa. The salt brought the solution closer to the theta point, thus making the solvent poorer than before for the PEO drag reducing agent. The result was a rapid drop in DR with time – explained by polymer shrinkage. Flory et al. [58] have demonstrated that polymer chain dimensions are the same in an amorphous solid and in a good solvent (athermal mixing) liquid. They note that "the gratifying agreement between results obtained by these unrelated methods lends substantial support to the assumption that the molecular conformation in the



Fig. 6. Illustration of Eq. (14) for several systems with flocculating agents.

amorphous state is not appreciably affected by interactions between neighboring chains. The related assumption [59] that the chains of a cross-linked network contribute additively to its elastic free energy likewise is validated". The second assumption has received later still more support from results in the Flory laboratory [60]: the change in the Helmholtz function on swelling consists of independent mechanical (size change) and thermodynamic (mixing a polymer with a low molecular mass liquid) terms. Recall now a discussion of the solvent quality by Lucas et al. [7] or by Gedde [8]. Thus, the explanation in terms of shrinkage [57] when going from a good solvent towards a theta solvent fits with the drag reduction mechanism shown in Fig. 3 and with the totality of results discussed above.

We find that the advancement of a model and mechanism for drag reduction is not self-limiting. The experimental findings and mechanism described in previous sections propels our understanding of another field – flocculation – along with the informed development of improved agents for drag reduction.

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416

#### W. Brostow/Journal of Industrial and Engineering Chemistry 14 (2008) 409-416

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