

## CHAPTER IV

### THEORIES AND DISCUSSION

#### 4.1 Lumley's Viscous Theory (Lumley, 1973)

Lumley kept the viscosity in the viscous sublayer at its Newtonian value, but he assumed an increased viscosity in the turbulent regions (buffer layer and inertia sublayer). This implies that, at any distance  $y$  from the wall, the Kolmogorov limit  $l_k$  is shifted upwards. The net result is a shrinkage of the turbulent domain outside the viscous sublayer or in the buffer layer, whose size increases with polymer concentration. It is then natural to expect that the turbulent wall friction will be reduced.

##### 4.1.1 Range of Eddy Sizes

(a) Inertia sublayer. At any distance from the wall, there are eddies lying between two limits; the first is the largest size which is given by the distance  $y$  itself and the rest is the smallest size which is given by the Kolmogorov microscale,  $l_k$ .

$$l_k \equiv \frac{V^{3/4}_{(sol,s,y^o)}}{\varepsilon^{1/4}} \quad (4.1)$$

The main difference is that the rate of energy dissipation per unit mass,  $\varepsilon$  is a function of the distance to the wall:

$$\varepsilon = \frac{u_*^3}{\kappa y} \quad (4.2)$$

Thus

$$l_k \equiv \frac{V^{3/4}_{(sol,s,y^o)}}{\varepsilon^{1/4}} = \left( \frac{\kappa y V^3_{(sol,s,y^o)}}{u_*^3} \right)^{1/4} \quad (4.3)$$

where  $\kappa$  is the von Karmen's constant.

(b) Peak of Dissipation Spectrum. At the peak of the dissipation spectrum for Newtonian turbulence, the shortest scales in the flow

occur. The energy dissipation rate is  $\varepsilon = \frac{u_*^4}{4\nu_{(sol,s,\dot{\gamma}^o)}}$ , so the Kolmogorov

microscale,  $l_k$  can be written as:

$$l_k \approx \frac{\sqrt{2}\nu_{(sol,s,\dot{\gamma}^o)}}{u_*} \quad (4.3)$$

Here  $\nu_{(sol,s,\dot{\gamma}^o)}$  used to define  $l_k$  is the apparent solution kinematic shear viscosity at an arbitrary shear strain rate  $\dot{\gamma}^o$  (1/sec).

In Lumley's theory, elongational viscosity is the key parameter; therefore, we replace  $\nu_{(sol,s,\dot{\gamma}^o)}$  in equation 4.1 with  $\nu_{(sol,e,e^o)}$ , the corresponding solution kinematic elongational viscosity at an arbitrary elongational strain rate  $e^o$ . The Kolmogorov microscale, in terms of elongational viscosity, can be written as:

$$l_k \equiv \frac{\nu_{(sol,e,e^o)}^{3/4}}{\varepsilon^{1/4}} \quad (4.4)$$

In the buffer layer,  $\nu_{(sol,e,e^o)}$  is expected to increase and can become substantially greater than  $\nu_{(sol,s,\dot{\gamma}^o)}$ , due to the expansion of polymer chain size by the strong fluctuating strain rate field, whereas the apparent solution viscosity in the viscous sublayer remains unchanged.

### 4.1.2 Lumley-Einstein model

In the scaling relation  $\varepsilon^{-1/4} \nu_{(sol,e,e^0)}$ ,  $\nu_{(sol,e,e^0)}$  depends on expanded hydrodynamic radius,  $R_h'$  through the Einstein equation  $\eta = \eta_s (1 + \frac{5}{2} n V_h')$  where  $n$  is number of chains per unit volume and  $V_h'$  is nonequilibrium polymer hydrodynamic volume. In the buffer layer,  $\eta$  increases substantially due to the increase in  $V_h'$  which in turn affects  $l_k$ . The scaling dependence of  $l_k$  on  $R_h'$  in the buffer layer can be written as:

In the limit  $1 \gg n V_h'$  (dilute regime)

$$l_k \propto \varepsilon^{-1/4} \nu^{3/4} \cong \varepsilon^{-1/4} \rho^{3/4} \eta_s^{3/4} (1 + \frac{15}{8} n V_h'), \quad (4.5)$$

where  $n = \frac{c_p N_A}{N M_o}$ ,  $R_h' \propto N^{3/5}$  (Flory law),  $M_o$  is molecular weight of monomer,

$N$  is the degree of polymerization,  $\rho$  is the solution density and  $N_A$  is the Avogadro number.

Then, 
$$\frac{l_k}{l_{k0}} - 1 \propto \frac{5}{2} n \pi R_h'^3 \propto c_p R_h'^4, \quad (4.6)$$

In the limit  $1 \ll n V_h'$  (non-dilute regime)

$$l_k \propto \varepsilon^{-1/4} \rho^{-3/4} \eta^{3/4} (n V_h')^{3/4}, \quad (4.7)$$

$$l_k \propto c_p^{3/4} R_h'. \quad (4.8)$$

Thus the scaling exponents for Lumley's theory can be summarized and shown in Table 4.1.

**Table 4.1** The scaling exponents of Lumley's theory.

Scaling exponent	$C_p$	$R_h'$	$n V_h' = \phi$
In the limit $1 \gg n V_h'$ , $l_k/l_{k0} - 1$	1	1.33	1
In the limit $1 \ll n V_h'$ , $l_k$	0.75	1	0.75

The predicted correlation between the drag reducing parameters  $l_k$  and  $l_k/l_{ko}-1$  versus polymer hydrodynamic radius and concentration are  $l_k \propto \varepsilon^{-1/4} c_p^{3/4} R_h'$  and  $l_k/l_{ko}-1 \propto \varepsilon^{-1/4} c_p (R_h')^{1.33}$  for the non-dilute and dilute regimes, respectively. In most case, the predicted relationships differ from those obtained from our experimental data (Table 3.7). A similar discrepancy arises when one compares prediction against experiment for the correlation of  $l_k$  and  $l_k/l_{ko}-1$  versus polymer volume fraction,  $\phi$ . One problem is that, in the scaling analysis of the experimental data, equilibrium hydrodynamic radius,  $R_h$  was used instead of expanded hydrodynamic radius,  $R_h'$  which assumes affine deformation and no change in coil hydrodynamics, i.e. non-draining behavior. However, it is interesting that the experimental scaling exponents for  $R_h$  and  $\phi$  on changing molecular weight for the uncharged PAM are relatively close to the Lumley's theory whereas those for the charged HPAM on changing ionic strength differ widely. In the latter, the ratio between  $R_h$  and  $R_h'$  may not be uniform and vary strongly with ionic strength (e. g. at very low ionic strength, the unstretched chain may be very similar to the stretched chain). The theory of Lumley is clearly inadequate to produce a correlation between the drag-reducing efficiency and polymer concentration and hydrodynamic radius for both the uncharged and charged polymers.

#### 4.1.3 Lumley-FENE-P model

FENE-P model is a bead-spring model with a finitely extensible nonlinear elastic spring (Larson, 1999). This model is appropriate in high strain rate field where the relation between the spring force and molecular extension can become highly nonlinear. The solution kinematic elongational viscosity, in the limit of high elongational strain rate, can be shown to be:

$$\nu_{(sol,e,\infty)} = \nu_{(s,e,\infty)} + \nu_{(p,e,\infty)} = \nu_{(s,e,\infty)} + \frac{1}{2} \rho n L^2 \zeta, \quad (4.9)$$

where  $\nu_{(s,e,\infty)}$  is the solvent kinematic elongational viscosity at high elongational strain rate, which is a constant since we restrict our discussion to Newtonian solvent.  $\nu_{(p,e,\infty)}$  is the contribution of polymer to the kinematic elongational viscosity at high elongational strain rate.  $L=Nb_k$  and  $b_k$  is the effective length of each link.  $\zeta$  is the bead drag coefficient. Thus the Kolmogorov microscale of Lumley-FENE-P model is:

$$l_k = (\nu_{(s,e,\infty)} + \frac{1}{2} \rho n L^2 \zeta)^{3/4} \varepsilon^{-1/4} . \quad (4.10)$$

In the dilute concentration regime where  $\nu_{(s,e,\infty)} \gg \nu_{(p,e,\infty)}$ :

$$\frac{l_k}{l_{ko}} = l \propto c_p N . \quad (4.11)$$

In the non-dilute concentration regime where  $\nu_{(s,e,\infty)} \ll \nu_{(p,e,\infty)}$ :

$$l_k \propto \varepsilon^{-1/4} c_p^{3/4} N^{3/4} . \quad (4.12)$$

In deriving equation 4.11, Lumley's elongational viscous theory predicts that the Kolmogorov microscale scales linearly with concentration and degree of polymerization in dilute concentration regime. In the non-dilute regime, the scaling exponents are  $3/4$  for both polymer concentration and degree of polymerization. We see that concentration scaling exponent departs substantially from the experimental values, whereas the molecular weight scaling exponent differs widely from the experimental values (Table 3.7).

## 4.2 de Gennes's Elastic Theory

The main idea of this theory is that flexible coils, even in the dilute regime, behave elastically at high Reynolds number. A Kolmogorov cascade remains unaltered by polymer additives only down to a certain limit which is an elastic limit,  $l_e$  where stress due to partially stretched coils (the first scenario) is equal to the Reynolds stress. This limit at which a truncation in the cascade occurs is observable only if  $l_e > l_k$ . The result is (de Gennes, 1990):

$$l_e \propto N^{2.7-2.8x} \varepsilon^{0.5-x} c_p^x \quad (4.12)$$

But we focus on linear, flexible polymers in good solvents, where the Flory law is expected to hold (Flory, 1971; de Gennes, 1984):

$$R_h \cong N^{3/5} a, \quad (4.13)$$

where  $a$  is a monomer size.

Then 
$$l_e \propto (R_h')^{4.5-4.7x} \varepsilon^{0.5-x} c_p^x, \quad (4.14)$$

where exponent  $x$  varies from 0.32 to 0.18 for 2 and 3 dimensional system respectively (de Gennes, 1990).

The scaling exponents for de Gennes's theory are summarized in Table 4.2.

**Table 4.2** The scaling exponents of de Gennes's theory.

Scaling exponent	$C_p$	$N$	$R_h'$
2-D	0.32	1.82	3.00
3-D	0.18	2.20	3.66

Considering the scaling exponent of  $c_p$  obtained from experimental values (Table 3.7), it is approximately the same as that of de Gennes's theory. But the theoretical scaling exponent of  $R_h'$  and  $N$  differs widely from that obtained from the experimental values. These are opposite with Lumley's model; an approximate agreement is obtained for the concentration dependence, but the predicted molecular weight scaling exponent differs widely from experimental values.

Thus we may say that the polymer hydrodynamic radius may not be used as the universal parameter to explain drag reduction mechanism and both theories are inadequate in predicting the dependence of the smallest eddy size on polymer concentration and molecular weight.

### 4.3 Our Proposed Model: Viscoelastic Fluid

We may postulate a universal equilibrium theory for viscoelastic fluids in which the small scales depend on dissipation rate,  $\varepsilon$  the free energy per unit mass,  $\gamma$  and the kinematic viscosity,  $\nu$ .

de Gennes (de Gennes, 1990) proposed anharmonic energy  $F_e = \frac{c}{N} k_B T \lambda^{5/2} = G \lambda^{5/2}$  where  $G$  has the dimensions of one elastic modulus, which is linear in concentration.  $\lambda$  is polymer coil elongation ratio which is defined as  $\lambda = R_h'/R_h$  and  $c/N$  is number of chains per unit volume. Let  $\rho$  be a density of a mixture of solvent and polymer which remains nearly equal to the solvent density,  $\rho_s$ . Therefore  $\gamma$  is equal to:

$$\gamma \cong \frac{F_e}{\rho_s}, \quad (4.15)$$

Then 
$$\gamma \cong \frac{c}{\rho_s N} k_B T \lambda^{5/2}. \quad (4.16)$$

Thus in the viscoelastic theories, we propose  $l_{ve} = f(\varepsilon, \nu, \gamma)$ . Using  $\pi$ -group analysis,  $l_{ve}$  can be shown to be (Appendix B):

$$l_{ve} = \varepsilon^{a-1/4} \nu^{a+3/4} \gamma^{-2a}, \quad (4.17)$$

the viscoelastic velocity scale,  $U_{ve}$  and the viscoelastic time scale,  $\tau_{ve}$  can also be determined similarly as:

$$U_{ve} = \varepsilon^{a+1/4} \nu^{a+1/4} \gamma^{-2a}, \quad (4.18)$$

$$\tau_{ve} = \varepsilon^{a-1/2} \nu^{a+1/2} \gamma^{-2a}, \quad (4.19)$$

where ‘ $a$ ’ is an unknown coefficient. There are three fundamental forces in our problem. The inertial force, with magnitude proportional to and represented by  $\varepsilon$ , tends to deform and breakup eddies thus constituting the process of energy cascade from large to small scales. The viscous force dissipates the eddy kinetic energy by converting it to heat thus providing the viscous truncation. We conjecture that the elastic force can act upon eddies with two opposing roles. The stretched coil springs provides an elastic recoil effect which retards or resists the eddy breakup, generating the so called elastic truncation. On the other hand, partially stretched springs can store kinetic energy, thus resisting energy dissipation and we may expect to find a reduction in size of the smallest eddy. The two opposing elastic effects are consistent with the scaling relation of equations 4.17 to 4.19: there are three possible ranges for ‘ $a$ ’. When ‘ $a < 0$ ’, the elastic effect is to resist eddy breakup, and we obtain the elastic truncation. When ‘ $a > 0$ ’, the elastic effect can store eddy kinetic energy and smaller eddies are able to survive and exist under the same energy dissipation rate. When ‘ $a = 0$ ’, we recover the viscous limit; the three scales become the Kolmogorov microscales;  $l_{ve} = \nu^{3/4} \varepsilon^{-1/4} = l_k$ ,  $U_{ve} = \nu^{1/4} \varepsilon^{1/4} = U_k$  and  $\tau_{ve} = \nu^{1/2} \varepsilon^{-1/2} = \tau_k$ . On the other hand, it is apparent from



equation 4.17 to 4.19 that viscosity must always appear in the above relations; energy must still be dissipated in viscoelastic fluids as well as in viscous fluids.

For viscosity  $\nu$ , we shall replace the usual solution kinematic shear viscosity with solution kinematic elongational viscosity of equation 4.9: FENE-P model and We obtain the scaling relation for the viscoelastic length scale  $l_{ve}$  as:

$$l_{ve} = (v_{(s,e,\infty)} + \frac{1}{2} \rho n L^2 \zeta)^{a+3} \varepsilon^{a-1} ((c / \rho_s N) k_B T \lambda^5)^{-2a}. \quad (4.20)$$

The viscoelastic theory to be proposed is valid only in the limits of non-dilute concentration and infinitely high Reynolds number. Thus in the non-dilute concentration regime where  $v_{(s,e,\infty)} \ll v_{(p,e,\infty)}$ :

$$l_{ve} \propto \varepsilon^{a-1} c_p^{3+4-a} N^{3+3a}. \quad (4.21)$$

The scaling exponent ‘ $a$ ’ is dynamic and depends considerably on Reynolds number through energy dissipation rate,  $\varepsilon$  and degree of polymerization,  $N$ . Presumably, it is not unique.

Considering the scaling exponents obtained from the experimental data, a value of ‘ $a$ ’ was determined as shown in Table 4.3.

On comparing with the present theory’s prediction in the non-dilute concentration regime, approximate agreements with experimental data are probably obtained at higher Reynolds number and higher molecular weight if we take ‘ $a$ ’ to lie between 0.2-0.3, depending whether we want to match concentration or molecular weight dependence more closely. Positive value of ‘ $a$ ’ implies that elasticity promotes small eddies to store kinetic energy. Small discrepancies between our theory and experimental data observed (Table 4.3) arise from polydispersity of the samples and the fact that experiments were

carried out at finite Reynolds number. However, the decrease in the concentration scaling exponent and the increase in the degree of polymerization exponent as Reynolds number increases are consistent with the scaling relation of equation 4.21 when ' $a$ ' increases.

**Table 4.3** Values of ' $a$ ' determined from the experimental data.

Parameters	$Re$	
	5460	1050
$N$	0.08	0.04
$c_p$	0.44	0.33