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MATHEMATICAL MODELING AND SIMULATION OF THE RHEOLOGICAL BEHAVIOR OF AN ELASTIC LIQUID UNDERGOING DIFFERENT SHEAR FLOWS.

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Abstract. *In this work the rheological behavior of an elastic liquid composed of an ambient Newtonian fluid and a dilute polymeric is examined under steady and unsteady shear flows. The elastic liquid is described by a standard FENE-Dumbbell model of two equations under conditions of different flows: steady simple shear and oscillatory shear. The governing equations are non-dimensionalized based on the relaxation time of the elastic liquid and the viscosity of the ambient Newtonian fluid. The Deborah number* (De) *is the relevant non-dimensional physical parameter which measures the relative importance between the fluid relaxation time and a typical flow time. We investigate different quantities such as the first normal stress difference as a function of the Deborah number in steady shear. We show the typical dependence of the first normal stress with the square of the Deborah number for small value of this parameter. An asymptotic solution for small* De *(i.e.,* $De \ll 1$*) is also presented under condition of the macromolecules close to the equilibrium and a constant spring function. This behavior* $\mathcal{O}(De^2)$ *is also observed experimentally with an aqueous solution of anionic polyacrylamide under steady simple shear. A very good agreement is observed between the numerical solution based on a Runge-Kutta integration, the asymptotic solution and experimental data. The elastic and viscous modules as a function of frequency and* De *for both linear and nonlinear viscoelastic regimes are also obtained numerically in this work by calculating the Fourier coefficient of the stress. Again, we proposed an asymptotic solution for* $De \ll 1$ *for the elastic liquid experimenting an oscillatory shear. Finally a brief analysis of non-dimensional first normal stress difference* $\tilde{N}_1$ *is presented where we estimate the output of this function from the asymptotic limit* $De \ll 1$*. The Fourier coefficients of this second normal stress are also examined in this work.*

Keywords: *Elastic liquids, Dumbell model, Frequency response.*

1. Introduction

The rheological response of non-Newtonian fluid under complex flows is of interest of many industrial processes. The accurate characterization of dilute polymer solutions under steady and unsteady shear flows are important in many applications such drag reduction in turbulent flows by polymer additives. In a previous work (Absi et al., 2005) we explore the nonlinear response of an elastic liquid under steady extensional and steady simple shear flows. Complementarily, in this article we will present a dynamical response under strong oscillatory shear flows in frequency domains. Such responses will be given in terms of rheological quantities as shear and normal stresses and viscoelastic modules.

The elastic liquid examined in this work is obtained with the addition of few ppm of a polymer in the solvent characterizing a dilute polymeric solution. In dilute solutions the rheological properties of the system are a reflection of the mechanical properties of the individual polymer chains and the number of chains in the bulk solution. However, even in such dilute systems, the mechanical properties of the individual chains and, hence, the bulk solution are strongly dependent on the type of flow.

The rheological behavior of the common Oldroyd constitutive equation is a well explored subject in the current literature (Bird et al, 1987). In order to understand the physics in this constitutive equation for elastic liquids, it is helpful to look at a micro-structural model which leads to an Oldroyd-like-constitutive equation. Rather than studying the rheological performance and mathematical structure of the coupled flow equations, we retreat to some physical model of the microstructure which generates the constitutive equation. In this article it is considered a bead-and-spring model (i.e., Dumbell model) of polymer solutions.

We describe a microstructure analysis based on a macromolecule closely to the simplest version of the bead-and-spring model (i.e. dumbbell model) introduced by Kuhn and Kuhn (1945) and discussed in details by Hinch (1977) and Rallison and Hinch (1988) with a finite spring correction, i.e. a FENE (i.e. finitely extensible non-linear elastic) model. The original empirical FENE spring force was first proposed for dumbbells by Warner (1972). Scaling arguments based on a balance between viscous drag and restoring Brownian forces lead to a time dependence partial differential equation for the macromolecule conformation tensor. In particular this tensor gives an explicit information about the internal structure of the fluid.

The model identifies three relevant physical parameters: the Deborah number, defined as the ratio between the relaxation time of the polymer and a characteristic time of the flow, the volume fraction of the polymer, and the parameter of extensibility of the polymer which is the ratio of the full stretched length and the average length in the thermodynamic equilibrium state of the macromolecule. We apply a non-linear spring model which gives a finite limit of macromolecule extension and a drag correction in the way suggested by Rallison and Hinch (1988).

In this article we have examine different quantities such as the first normal stress difference as a function of the Deborah number in steady shear. In particular, we explore the dependence of the first normal stress with tof the Deborah number. A very good agreement is observed between the numerical solution based on a Runge-Kutta integration, the asymptotic solution and experimental data. The elastic and viscous modules as a function of frequency and De for both linear and nonlinear viscoelastic regimes are also obtained numerically in this work by calculating the Fourier coefficient of the stress signal.

2. Mathematical Modeling

We describe a microstruture analysis based on a macromolecule closely to the simplest version of the bead-and-spring model (i.e. dumbell model) introduced by Kuhn and Kuhn (1945) and discussed in details by Hinch (1977) and Ralison and Hinch (1988) with a finite spring corretion, i.e. a FENE (i.e. finitely extensible non-linear elastic) model. In this way we obtain the closed system of equations:

$$\boldsymbol{\sigma} = 2\mu_s(\phi)\mathbf{D} + nGf(r)\mathbf{B}(t), \tag{1}$$

$$\frac{D\mathbf{B}}{Dt} = \nabla\mathbf{u}\cdot\mathbf{B} + \mathbf{B}\cdot(\nabla\mathbf{u})^T - \frac{2af(r)}{\tau\sqrt{tr(\mathbf{B})}}\left(\mathbf{B} - \frac{a^2}{3}\mathbf{I}\right), \tag{2}$$

where $\boldsymbol{\sigma}$ is the stress tensor, $\mathbf{u}$ is the Euclerina velocity field, τ is the polymer relaxation time. From this theoretical model in particular, $\tau = 2\pi\mu a^3/KT$. Otherwise the polymer relaxation time can be determined experientially. The quantity $G = 3KT/a^2$ represents the spring constant, n denotes the number of molecules per unit of volume given by $n = 3\phi/4\pi a^3$ and $\phi \ll 1$ is the effective volume fraction in the polymeric liquid. The function $f(r) = \ell^2/(\ell^2 - r^2)$ represents the non-linear spring law to a dumbbell-FENE model, ℓ denotes the limit of rigid fibre where the polymer reaches the its maximum extensibility, a is the tip-to-tip length of the macromolecule in the case of small distortions (i.e. randomly-coiled state). The vector $\mathbf{r}$ is the distance vector between the centre of the two dumbell beads and in fact represents the end-to-end distance of the polymer in the randomly coiled state.

In this work the quantities are made non-dimensional using the following characteristic scales: a for length, τ for time, velocity a/τ and viscosity of the ambient fluid μ to viscosity. The non-dimensional quantities are defined as follows: $\tilde{\mathbf{B}} = \mathbf{B}/a^2$, $\tilde{\boldsymbol{\sigma}} = \boldsymbol{\sigma}\tau/\mu$, $\tilde{t} = t/\tau$, $R = r/a$, $L = \ell/a$, $\tilde{\mathbf{D}} = \mathbf{D}\tau$, $\mathbf{u} = \tilde{\mathbf{u}}a/\tau$. For the non-dimensional viscosity we used the Einstein theory (1956) where $\mu_s(\phi) = \mu(1 + c\phi)$, and we write:

$$\tilde{\mu}(\phi) = \frac{\mu_s(\phi)}{\mu} = 1 + c\phi. \tag{3}$$

For a dilute aqueous solution of polyacrylamide-PAMA, the best fitting constant is found to be $c = 1.53 \times 10^5$.

Now, the governing equations written in terms of non-dimensional quantities is given by:

$$\tilde{\boldsymbol{\sigma}} = 2\tilde{\mu}(\phi)\tilde{\mathbf{D}} + \frac{9}{2}\phi f(R)\tilde{\mathbf{B}}, \tag{4}$$

$$\frac{d\tilde{\mathbf{B}}}{d\tilde{t}} = \tilde{\nabla}\tilde{\mathbf{u}}\cdot\tilde{\mathbf{B}} + \tilde{\mathbf{B}}\cdot(\tilde{\nabla}\tilde{\mathbf{u}})^T - \frac{2f(R)}{\sqrt{tr(\tilde{\mathbf{B}})}}\left(\tilde{\mathbf{B}} - \frac{1}{3}\mathbf{I}\right). \tag{5}$$

In the present context $f(R) = L^2/(L^2 - R^2)$ is the spring nonlinear constant of the Dumbell-model and $R = \sqrt{tr(\tilde{\mathbf{B}})}$.

3. Experimental and computacional procedure

Our numerical approach deals with the resolution of the system of equations given by (4) and (5), using fourth order runge-kutta procedure. The non-dimensional time step, $\tilde{dt}$, used is controlled by the time scales involved in the problem, mainly the relaxation time τ and frequency ω, for steady simple shear and oscillatory shear, respectively, as:

$$\tilde{dt} = 10^{-3} \times \min\{1, De^{-1}\} \text{ and } \tilde{dt} = 10^{-3} \times \min\{1, De^{-1}, (\tilde{\omega})^{-1}\}, \tag{6}$$

where $De = \tau\dot{\gamma}$ and $\tilde{\omega} = \tau\omega$.

Experimental data are obtained from tests in a rheometer Anton Paar Physica MCR 301 model. The fluid investigated is a polyacrylamide (PAMA) in the volume fraction $\phi = 400\, ppm$, which is submitted the already mentioned shear flows and the data obtained after an appropriated statistical treatment of the ones over several experimental realizations.

From the numerical results we obtain the non-dimensional first normal stress diference $N_1 = \sigma_{11} - \sigma_{22}$, for the simple shear, both for the general numerical case and for the analytical-asymptotic limit, $De \ll 1$. We shall also present a comparison between the experimental data for $N_1 \times De$ and the simulation results and asymptotic solution in the regime of $De \to 0$. For the experimental case $N_1 = 2G'(\omega \to 0)$, otherwise, N_1 is obtained from the oscillatory shear experiment, for the limit $\omega \to 0$, i.e., using the Cox-Merz relation, Bird et al (1987). In the linear viscoelastic regime the shear stress can be written in terms of its Fourier coefficients in-phase and out-phase with the the forcing $\dot{\gamma}_0 \cos(\omega t)$ as following:

$$\sigma(t) = \eta'(\omega)\dot{\gamma}_0 \cos(\omega t) + \eta''(\omega)\dot{\gamma}_0 \sin(\omega t), \tag{7}$$

where ω is the forcing frequency.

4. Analytical and Numerical results for steady simple shear

The dimensional steady simple sher flow is given: $\mathbf{u}(t) = (\dot{\gamma}x_2, 0, 0)$. Now, make $\mathbf{u}(t)$ non-dimensional using our characteristic velocity scale $u_c = a/\tau$ results,

$$\tilde{\mathbf{u}}(\tilde{t}) = (De\, \tilde{x}_2, 0, 0), \ \text{ where } \ De = \tau\dot{\gamma}, \tag{8}$$

here $\tilde{x}_2 = x_2/a$.

A simple asymptotic solution already explored by Absi et al. can be determined in the asymptotic limit of $De \ll 1$. Under this condition the macromolecule is pretty close to the random coiled equilibrium configuration so that $f(R) \sim 1$ and $R \sim 1$. After solving the steady solution of the governing equation (5) we found that:

$$\tilde{B}_{22}(\tilde{t}) = \tilde{B}_{33}(\tilde{t}) = \frac{1}{3}, \tag{9}$$

$$\tilde{B}_{12}(\tilde{t}) = \frac{1}{6}De, \tag{10}$$

and

$$\tilde{B}_{11}(\tilde{t}) = \frac{1}{6}De^2 + \frac{1}{3}. \tag{11}$$

Now, using the equations (9) and (11) in the Eq. (4), and considering that non-dimensional first normal stress difference is given by $\tilde{N}_1 = \tilde{\sigma}_{11} - \tilde{\sigma}_{22}$, we obtain:

$$\tilde{N}_1(\phi, De) = \frac{3}{4}\phi De^2, \tag{12}$$

for the asymptotic limit $De \ll 1$ where we assume $f(R) \sim 1$ and $R \sim 1$.

Fig. (1) shows the variation of the first normal stress N_1/ϕ as a function of the De number. The insert in the figure presents the details of the regime of smaller De as N_1/ϕ varies quadratically with De. An excellent agreement between the simulation results and the asymptotic predictions can be observed as $De \to 0$. However, we can see that for $De \sim 1$ the quadratic dependence of N_1 on De breaks and a quite nonlinear regime of the fluid response is reached. In this nonlinear regime the assumptions of $R \sim 1$ and $f(R) \sim 1$ is not valid, and the asymptotic solution is not able to describe the nonlinear elastic behavior of the flow.

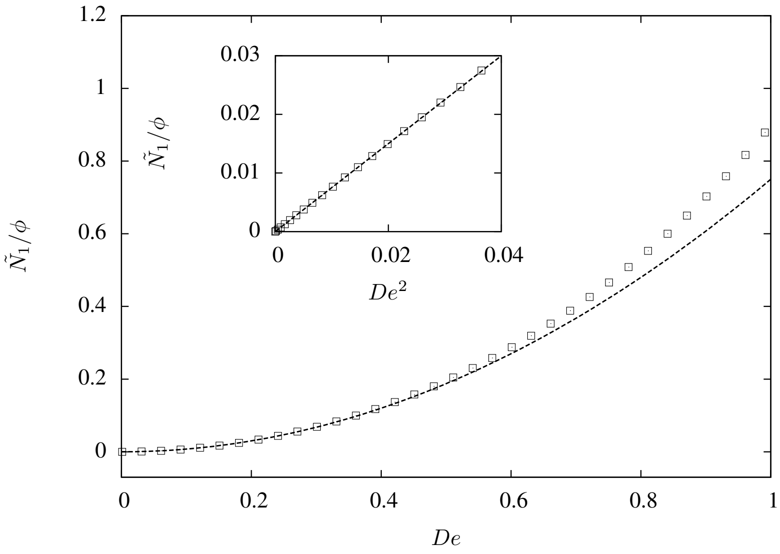


Figure 1. Non-dimensional first normal stress difference (as described above) as function of the Deborah number. Dotted line represents the analytical solution (12). The open squares denotes the numerical solution give by (4) and (5). The insert in the plot shows details of the comparison between simulation results and asymptotic prediction for small De ($De \leq 0.2$). For $\phi = 400\,ppm$ and $L = 60$.

In this way our model is in agreement with the theory of Barnes et al. and Absi et al., since the same, determined that for this type of flow, to the limit of small shear rates of deformation, $\dot{\gamma}$, we have that the first normal stress difference is proportional to the square of the shear rate, i.e, $N_1 = A\,De^2 + \mathcal{O}(De^4)$ where A e B are constants.

A general expression for a calibration of the theoretical model using the experimental data is:

$$\tilde{N}_1(\phi, De) \sim K\,De^2. \tag{13}$$

Here K can be evaluated by the experimental data $\tilde{N}_1 \times De^2$. In the table (1) we presented the experimental data of $\tilde{N}_1$, which was obtained by the relation of Cox-Merz, Bird et al (1987). What was done next was to determine the value of the constant K, where we obtained $K = 15500$, and compare this constant with our coefficient $3\phi/4$ of our analytical solution (12), as follows:

$$\frac{3}{4}\phi q = K, \tag{14}$$

where the constant q is introduced in order to calibrate the experimental data and numerical values for that specific type of fluid.

Table 1. Experimental data of non-dimensional first normal stress difference $\tilde{N}_1$ and related values of De^2 of a polyacrylamide solution (PAMA) with $\phi = 400\,ppm$.

De^2	$\tilde{N}_1$	Error $\tilde{N}_1$
2.50E-06	3.87E-02	7.00E-03
4.54E-06	7.67E-02	7.41E-03
6.86E-06	1.12E-01	1.09E-02
1.05E-05	1.48E-01	1.69E-02

With this constant of calibration q, we obtain new numerical values for $\tilde{N}_1$, and a comparison between the experimental data (given by table (1)) and the new numerical values can be seen in the Figure (2). Realize that even for De very small we have that the experimental measure already differs from the numerical and analytical solution. This is due to the Cox-Merz relationship, where $N_1 = 2G'$ for $\omega \to 0$ or $De \to 0$, thus the linear regime of the experiment is limited to very small values of parameter De.

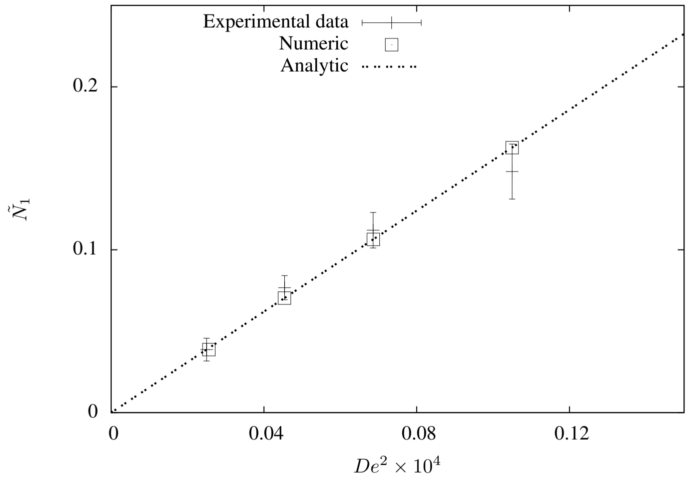


Figure 2. Comparison between numerical values and experimental data for a non-dimensional first normal stress difference. We also present the analytical solution. Parameters $\phi = 400\,ppm$ and $L = 60$.

In order to know where the asymptotic limit begins to deviate from the numerical solution, with the addition of the calibration constant q, we calculate, in the table (2), the relative error between these two solutions and determine that it is greater than one percent for $De > 0.25$. This limit of $De \sim 0.25$ also corresponds the Deborah number in which the De^2 dependence of $\tilde{N}_1$ breaks. Therefore, the stretching of the macromolecule in stronger flows introduces elastic nonlinear effects to the reponse of the fluid. Thus, the model given by equations (4) and (5) allows the variation of De for a wide range before we leave the linear regime.

Table 2. Experimental data of non-dimensional first normal stress difference $\tilde{N}_1$, analytical solution $\tilde{N}_1 = 15500De^2$ and relative error of both.

De	$\tilde{N}_1$	$15500De^2$	Relative Error: $(\tilde{N}_1 - 15500De^2)/15500De^2$
1.00E-003	1.5499E-002	1.550E-002	3.702E-004
5.49E-002	46.791	46.7852	1.323E-004
0.104	169.136	168.8915	1.446E-003
0.153	368.101	366.7876	3.584E-003
0.2032	644.670	640.4712	6.555E-003
0.2482	964.5852	955.0425	9.992E-003
0.2527	1000.2149	989.9447	1.038E-002

5. Analytical and Numerical results for oscillatory shear

In the linear limit where low deformations of the macromolecules are considered $(De \ll 1)$, the rheological response of the polymer fall in the linear viscoelastic theory. In such limit the assumption of linear spring model is valid for the analysis of shear and normal stresses. This imply that the correction function become $f(R) \sim 1$ and $R \sim 1$ as a consequence of macromolecules random coiled configuration.

In a oscillatory shear flow with strain-rate given by $\dot{\gamma} = \gamma_0\omega\cos(\omega t) = \dot{\gamma}_0\cos(\omega t)$ the velocity field is given by, $\mathbf{u} = (\dot{\gamma}_0\cos(\omega t)x_2, 0, 0)$ or in non-dimensional terms $\tilde{\mathbf{u}} = \left(\tilde{x}_2\, De\cos(\tilde{\omega}\tilde{t}), 0, 0\right)$ where $De = \dot{\gamma}_0\tau$ and $\tilde{\omega} = \tau\omega$.

5.1 Linear viscoelastic regime

In the case of elastic limit, when $De \ll 1$, the solution of the governing equation (5), provides us:

$$\tilde{B}_{33}(\tilde{t}) = \tilde{B}_{22}(\tilde{t}) = \frac{1}{3}, \tag{15}$$

$$\tilde{B}_{12}(\tilde{t}) = \frac{De}{3}\Big(\frac{\tilde{\omega}\sin(\tilde{\omega}\tilde{t}) + 2\cos(\tilde{\omega}\tilde{t})}{\tilde{\omega}^2+4}\Big), \tag{16}$$

and

$$\tilde{B}_{11}(\tilde{t}) = \frac{1}{3} + \frac{1}{3}\frac{De^2}{(\tilde{\omega}^2+4)} + \frac{1}{6}\frac{(2De^2 - De^2\tilde{\omega}^2)}{(\tilde{\omega}^2+4)(\tilde{\omega}^2+1)}\cos(2\tilde{\omega}\tilde{t}) + \frac{1}{2}\frac{De^2\tilde{\omega}}{(\tilde{\omega}^2+4)(\tilde{\omega}^2+1)}\sin(2\tilde{\omega}\tilde{t}). \tag{17}$$

Now substituing the component $\tilde{B}_{12}(\tilde{t})$, Eq. (16), into the Eq.(4), an expression for the shear stress in terms of the the in-phase and out-of-phase components of the stress is obtained,

$$\tilde{\sigma}_{12}(\tilde{t}) = \Big(De\,\tilde{\mu}(\phi) + \frac{3\phi\,De}{(\tilde{\omega}^2+4)}\Big)\cos(\tilde{\omega}\tilde{t}) + \frac{3\tilde{\omega}\phi\,De}{2(\tilde{\omega}^2+4)}\sin(\tilde{\omega}\tilde{t}). \tag{18}$$

In addition making equation (7) non-dimensional by using τ as time scale and μ as viscosity of fluid ambient, we obtain:

$$\tilde{\sigma}_{12}(\tilde{t}) = \frac{\sigma_{12}\,\tau}{\mu} = \tilde{\eta}'De\cos(\tilde{\omega}\tilde{t}) + \tilde{\eta}''De\sin(\tilde{\omega}\tilde{t}). \tag{19}$$

Now comparing the equations (18) and (19), in the limit asymptotic $De \ll 1$, we obtain an expression for the viscous and elastic modules, repectively, given by:

$$\tilde{\eta}'(\tilde{\omega}) = \tilde{\mu}(\phi) + \frac{3\phi}{(\tilde{\omega}^2+4)} \Longrightarrow \tilde{\eta}'(\tilde{\omega}) - \tilde{\mu}(\phi) = \tilde{\eta}^*(\tilde{\omega}) = \frac{3\phi}{4}\frac{1}{[1+(\tilde{\omega}^*)^2]}, \tag{20}$$

and

$$\tilde{\eta}''(\tilde{\omega}) = \frac{3\tilde{\omega}\phi}{2(\tilde{\omega}^2+4)} \Longrightarrow \tilde{\eta}''(\tilde{\omega}) = \frac{3\phi}{4}\frac{\tilde{\omega}^*}{[1+(\tilde{\omega}^*)^2]}, \tag{21}$$

where $\tilde{\omega}^* = \tilde{\omega}/2$.

It should be important to note that the asymptotic solution of our Dumbel-model recovers the well-known Maxwell model corresponding to the regime of small De numbers. Equations (20) and (21) describes the equivalent Maxwell viscoelastic coefficients for the limit of linear viscoelasticity.

The normal stresses can be calculated from the knowledge of $\tilde{B}_{11}$ and $\tilde{B}_{22}$. Substituting such quantities into the components of Eq. (4), we have:

$$\tilde{\sigma}_{11}(\tilde{t},\tilde{\omega},De) = \frac{3\phi}{2} + \frac{3}{2}\frac{De^2\phi}{(\tilde{\omega}^2+4)} + \frac{3}{4}\frac{\phi De^2(2-\tilde{\omega}^2)}{(\tilde{\omega}^2+4)(\tilde{\omega}^2+1)}\cos(2\tilde{\omega}\tilde{t}) + \frac{9}{4}\frac{\phi De^2\,\tilde{\omega}}{(\tilde{\omega}^2+4)(\tilde{\omega}^2+1)}\sin(2\tilde{\omega}\tilde{t}), \tag{22}$$

and

$$\tilde{\sigma}_{22}(\tilde{t}) = \frac{3\phi}{2}. \tag{23}$$

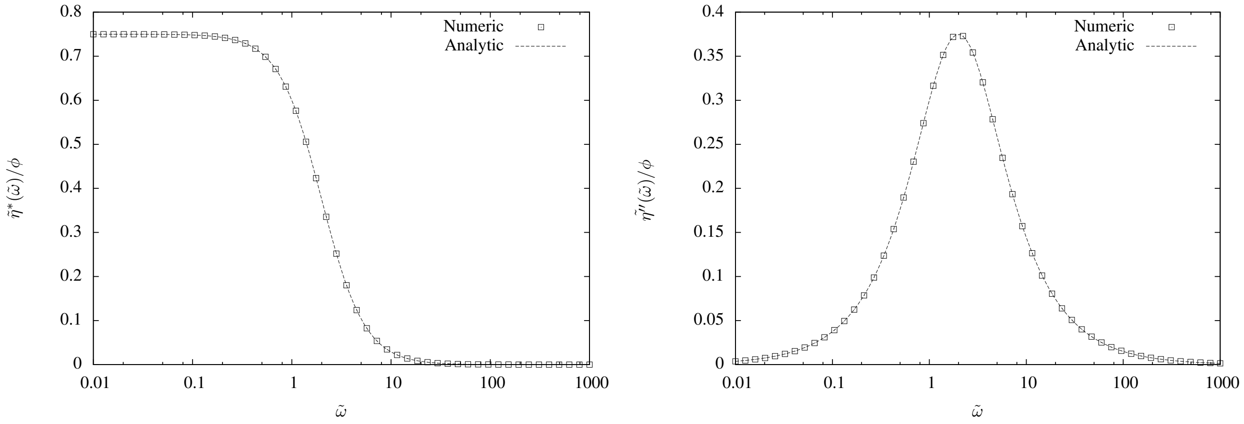
From Eqs. (22) and (23) it can be seen that for an asymptotic limit where $De \to 0$, all of numerator terms with De tend to zero and the normal stresses $\tilde{\sigma}_{11} \to \tilde{\sigma}_{22}$. Therefore the non-dimensional first normal difference stresses defined as $\tilde{N}_1 = \tilde{\sigma}_{11} - \tilde{\sigma}_{22}$ is negligible for a linear viscoelastic regime. In addition, from Eqs. (22) and (23) we can write $\tilde{N}_1$ for a linear regime where, as:

$$\tilde{N}_1(\tilde{t},\tilde{\omega},De) = \frac{3}{2}\frac{De^2\phi}{(\tilde{\omega}^2+4)} + \frac{3}{4}\frac{\phi De^2(2-\tilde{\omega}^2)}{(\tilde{\omega}^2+4)(\tilde{\omega}^2+1)}\cos(2\tilde{\omega}\tilde{t}) + \frac{9}{4}\frac{\phi De^2\,\tilde{\omega}}{(\tilde{\omega}^2+4)(\tilde{\omega}^2+1)}\sin(2\tilde{\omega}\tilde{t}). \tag{24}$$

Finally note that for an oscillatory shear excitation with non-dimensional frequency $\tilde{\omega}$ the non-dimensional first normal stress difference $\tilde{N}_1$ show a rheological response with frequency $2\tilde{\omega}$. And in the case of $\omega = 0$, (steady simple shear) the equation (24) reduces to Eq. (12).

5.2 Linear and non-linear results for viscoelastic modules.

In this section we shall present the results in frequency domain of non-dimensional viscous and elastic modules for $\phi = 400\,ppm$ and $L = 60$. Fig.(3) shows the modules viscous $\tilde{\eta}'$ and elastic $\tilde{\eta}''$ for an asymptotic limit $De \ll 1$ given by Eq.(20). These viscoelastic functions represent the first harmonic fourier coefficients of shear stress in frequency domain, where $\tilde{\eta}'$ represent the term in phase with the shear rate $\dot{\gamma}$ and $\tilde{\eta}''$ the term out of phase.



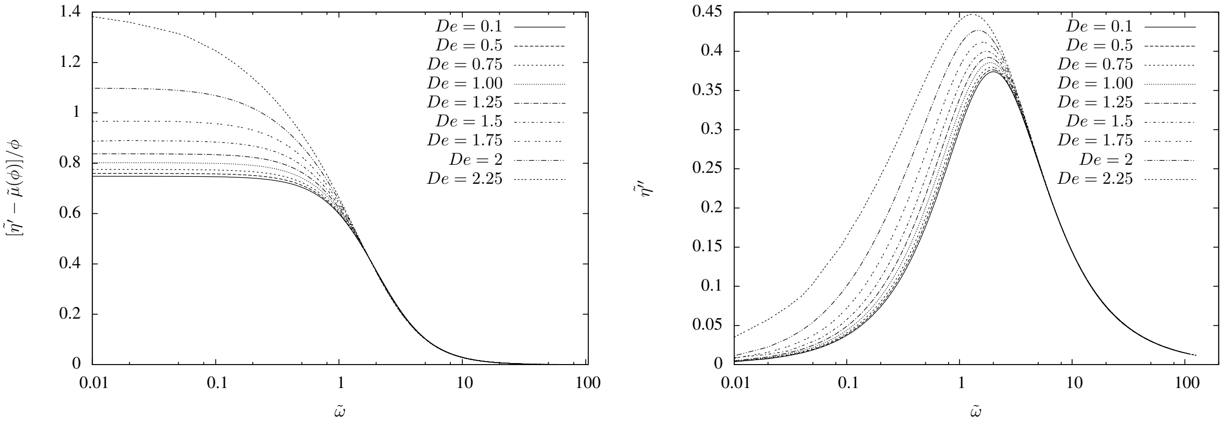
(a) Viscous Module

(b) Elastic Module

Figure 3. Viscous and Elastic modules in the linear regime, dotted line (Asymptotic solution (Maxwell fluid)-Equations (20) and (21)). And the open square denotes the numeric solution for $De = 0.01 \ll 1$. Thus, we see a very good agreement for this two solutions.

Fig. (4) presents the viscoelastic functions $\tilde{\eta}'$ and $\tilde{\eta}''$ as a function of excitation frequency for several Deborh numbers De. The values of frequency range between $10^{-2} \leq \tilde{\omega} \leq 10^{2}$. The function $\tilde{\eta}'$ has dissipate characteristics and is denoted as viscous module. As the Fig.(3) shows, this function present a shear thinning behavior in which a reduction of its magnitudes is verified with the increase of the non-dimensional frequency $\tilde{\omega}$. In the linear viscoelastic regime the elastic liquid has a Newtonian behavior in the limits of low and high frequency values, exhibit only viscous characteristics. In both limits the structure of the fluid is not changed by the flow. At low frequency, the characteristic time of the fluid is much smaller than the flow time scale (period of excitation). Under this condition the macromolecule relaxes instantaneously to any disturbance of the flow. The fluid can be seen as an equivalent Newtonian Fluid. On the other hand at high frequency the period of the low forcing is much smaller than the macromolecule relxation time so that the polymer does relax and the elastic effect elastic goes to zero. This corresponds to a viscous limit at high frequency. Considering high values of De and moderate frequencies range, a nonlinear viscoelastic regime is observed in which viscous and viscoelastic effects are present in diferente magnitudes. Hence in viscoelastic nonlinear regime the viscous module $\tilde{\eta}'$ is a function of non-dimensional frequency and of parameter De.

The Fourier coefficient out-of-phase with respect of shear rate is the viscoelastic function $\tilde{\eta}''$ and it is defined as the elastic module. This elastic module is plotted in a wide range of frequencies for several Deborha number from a linear viscoelastic limit $(De = 0.1)$ (Eq. (20)) to a great amplitude of De when compared to the linear case. In a linear regime the Fig.(4)(b) shows a symmetric curve. Such symmetry is gradually lost as the De grow and nonlinear effects are incorporated by the fluid. Of the numerical data, it is seen that in case of strong deformation amplitude De around 2 the magnitude amplitude of $\tilde{\eta}''$ is 4.4 times bigger than the linear viscoelastic regime, for $\tilde{\omega} = 0.1$. Note that in the limit cases of low and high frequencies the elastic effect does not contribute to the stored energy and the fluid remain only viscous characteristic.

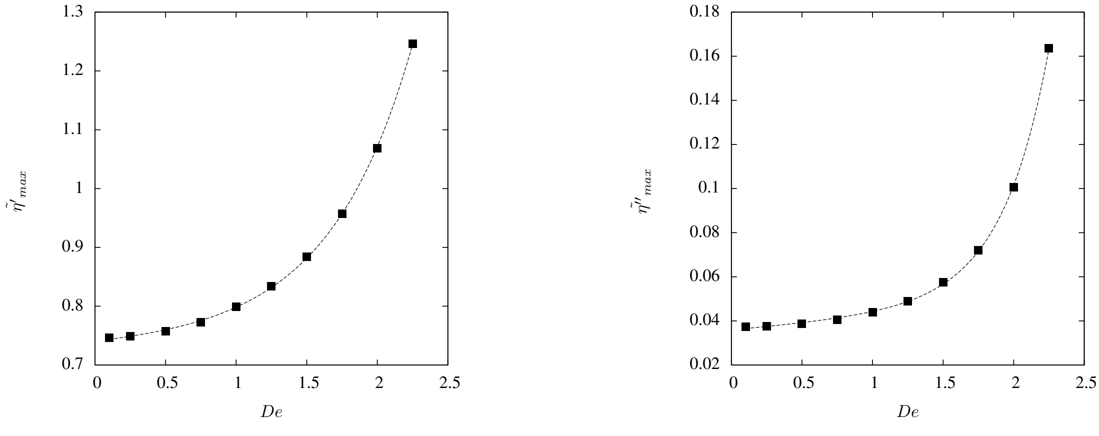


(a) Viscous module

(b) Elastic module

Figure 4. Viscous and Elastic modules for several De. In (a) we see the viscous effects where we notice a small variation, since we subtract the viscous effects of the base fluid, showing only viscous effects of the macromolecules present in the solution. In (b) we have a considerable variation of the elastic modules, for the frequency $\tilde{\omega} = 0.1$, when we go from $De = 0.01$ to $De = 2.25$. This shows that the increase of this parameter causes a great stretch in the macromolecules which causes nonlinear effects in the signal response of $\tilde{\eta''}$.

In addition, the Fig.(5) shows the departure from the linear regime in which the module $\tilde{\eta''}$ has a frequency dependency only. On the other hand, as the elastic liquid is submitted to larger amplitude of shear rate the elastic module $\tilde{\eta''}$ shows a dependence on De as a consequence of a nonlinear viscoelastic regime. It should be important to note that these results are exclusively related to the macromolecule contribution. Therefore we can see that both viscoelastic modulus increase as De number increases due to the stretching of the macromolecules by the stronger flow. For De close to 2.5 the slope of the curve becomes very high, that indicates a possible break-up of the macromolecule microstructure. In conclusion, we can argue that even for a dilute limit of a polymeric solution our numerical simulation is able to explore nonlinear regimes of the a macromolecule response undergoing oscillatory shear at moderate and high forcing amplitude.



(a) Viscous module

(b) Elastic module

Figure 5. Maximum values of viscous and elastic modules in function of De, for $\tilde{\omega} = 0.1$ fixed. The full square denotes the numeric solution and dotted line denotes the fitting $f(De)$ and $g(De)$, where: In (a), $f(De) = 0.7462 + aDe^2 + bDe^4$, with $a = 0.0315$ e $b = 0.0129$. In (b), $g(De) = 0.03733 + cDe^2 + dDe^4$ with $c = -0.00387$ e $d = 0.005459$.

5.3 Brief analysis for the $\tilde{N}_1$ on the Oscillatory Shear.

We present in this subsection some results for the non-dimensional first normal stress difference $\tilde{N}_1$, as the polymer is undergoing an oscillatory shear. As mentioned before, equation (24) represents the asymptotic solution $De \ll 1$. Even in this case, we can already observe a nonlinear effect since $\tilde{N}_1$ scales like De^2 for $De \to 0$.

Figure (6) shows the result for the temporal series of the non-dimensional first normal stress sign as a function of time, for $De = 0.01$ and $\tilde{\omega} = 1$. Under these conditions equation (24) is reduced simply for:

$$\frac{\tilde{N}_1(\tilde{t})}{\phi De^2} = \frac{3}{10} + \frac{3}{40}\cos(2\tilde{t}) + \frac{9}{40}\sin(2\tilde{t}). \tag{25}$$

We can see in the figure (6), a very good agreement between the numeric and the asymprtotic solution for the limit $De \to 0$. As expected the solution is approximately an harmonic function with a very small deviation related to the regime of De^2.

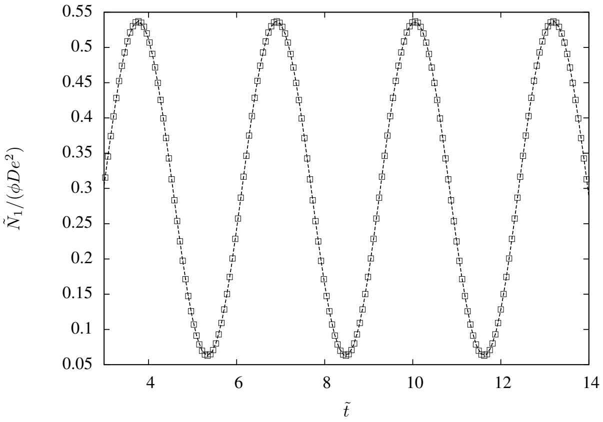


Figure 6. Non-dimensional first normal stress difference as a function of the non-dimensional time. The open squares in this plotes represents the numeric solution in the case $De = 0.01$ and $\tilde{\omega} = 1$. Dotted line represents the asymptotic solution given by equation (25).

Figure (7) presents a comparison between asymptotic and numeric solution for $De = 0.01$ and $10^{-2} \leq \tilde{\omega} \leq 10^2$, of non-dimensional first normal stress difference given by (24). In this case we will consider the viscoelastic modules in-phase and out-of-phase with the non-dimensional shear rate $\dot{\gamma} = De\cos(\tilde{\omega}\tilde{t})$.

Equation (24) can be written in the following form:

$$\frac{\tilde{N}_1(\tilde{t},\tilde{\omega})}{\phi De^2} = \frac{3}{(\tilde{\omega}^2+4)} + \frac{3}{4}\frac{(2-\tilde{\omega}^2)}{(\tilde{\omega}^2+4)(\tilde{\omega}^2+1)}\cos(2\tilde{\omega}\tilde{t}) + \frac{9}{4}\frac{\tilde{\omega}}{(\tilde{\omega}^2+4)(\tilde{\omega}^2+1)}\sin(2\tilde{\omega}\tilde{t}), \tag{26}$$

where we now have the following expression for the in-phase term with the shear rate, given by:

$$\tilde{\beta'}(\tilde{\omega}) = \frac{3}{4}\frac{(2-\tilde{\omega}^2)}{(\tilde{\omega}^2+4)(\tilde{\omega}^2+1)}, \tag{27}$$

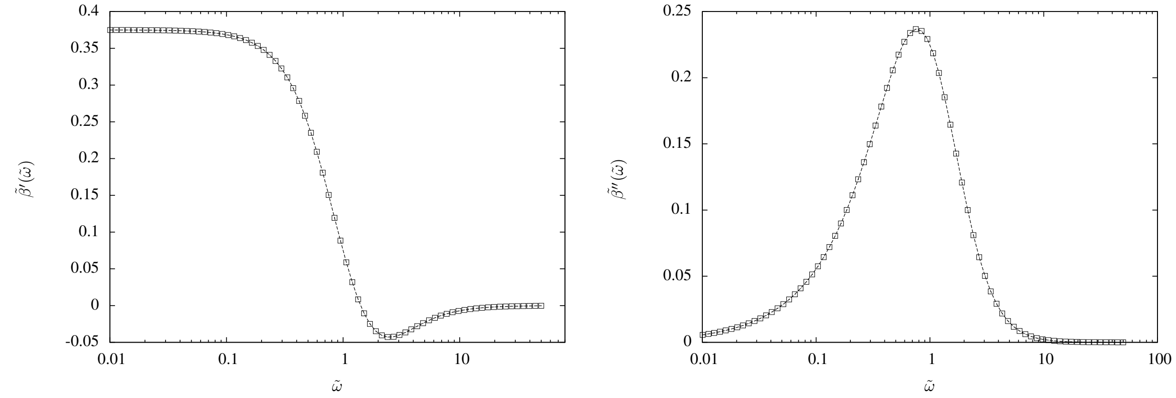
and the analytical expression for the out-of-phase coefficients with the excitation will be given by:

$$\tilde{\beta''}(\tilde{\omega}) = \frac{9}{4}\frac{\tilde{\omega}}{(\tilde{\omega}^2+4)(\tilde{\omega}^2+1)}. \tag{28}$$

Here, $\tilde{\beta'}$ and $\tilde{\beta''}$ represents the fundamental Fourier coefficients in-phase and out-of-phase, respectively, with the flow forcing for the second normal stress difference. These coefficients of the first normal stress difference represents essentially elastic response of the fluid.

Numerically the coefficients $\tilde{\beta'}$ and $\tilde{\beta''}$ are determined by means of a discrete Fourier transform - DFT applied the temporal series of $\tilde{N}_1(\tilde{t},\tilde{\omega})$ for the frequency ranging in the interval $[10^{-2}, 10^2]$. It is clear that the oscillation response of $\tilde{N}_1$ will be on the frequency $2\tilde{\omega}$. Note that there is a slight similarity between the plots shown in figure (7) and figure (3), however $\tilde{\beta'}(\tilde{\omega}) < 0$ for $\tilde{\omega} > \sqrt{2}$. Of course $\tilde{\beta''}(\tilde{\omega}) > 0$ for all $\tilde{\omega} > 0$.

In order to investigate the range of validity of the asymptotic solution, we have compared asymptotic and numerical solutions of the $\tilde{\beta'}$ as a function of De^2 for a frequency $\tilde{\omega} = 0.055$. Figure (8) shows the behavior of the elastic modulus in-phase $\tilde{\beta'}$ as a function of De^2. In addition, table (3) presents the same results and the relative error associated for more details. It is seen that as De varies form 0.45 to 0.50, the change in the relative error is larger than 1%. Therefore the asymptotic regime is limited to De up to 0.5. Therefore, the asymptotic regime is limited to De up to 0.5. As these results are compared with the ones presented in Figure (1) and Table (1) for the case of steady simple shear, it is seen that the linear regime breaks at $De \sim 0.25$ smaller that the oscillatory shear flow where $De \sim 0.5$. This indicate that the oscillatory flow prevents the permanent stretching of the macromolecules and, therefore, limitis the nonlinearity on the flow. Consequently a macromolecule in permanent shear can break-up at De numbers considerable smaller as it compared with the same macromolecule undegoing an oscillatory shear.



(a) $\tilde{\beta}'$.

(b) $\tilde{\beta}''$

Figure 7. In (a): Viscoelastic coefficient in phase with excitation, dashead line denotes the asymptotic solution (27) and the open squares represents the numeric solution for $De = 0.01$. In (b): Viscoelastic coefficient out-of-phase with excitation, dashead line denotes the asymptotic solution (28) and the open square represents the numeric solution for $De = 0.01$.

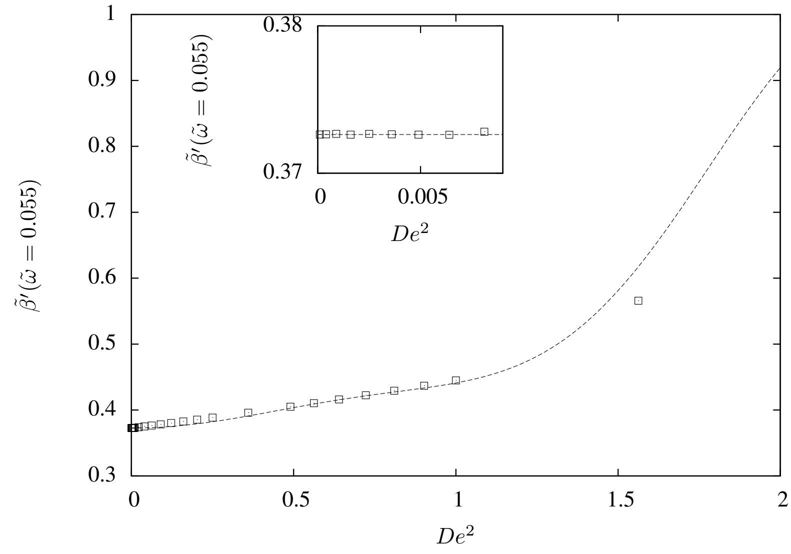


Figure 8. In-phase elastic modulus of the first normal stress difference as a function of De^2, for $\tilde{\omega} = 0.055$. Open square represents the numerical values of $\tilde{\beta}'$ for several De^2, the dotted line denotes the fitting given by: $f(De) = 0.373 + aDe^2 + bDe^4 + cDe^6 + dDe^8 + eDe^{10}$, where $a = 0.165426$, $b = -0.193736$, $c = 0.121118$, $d = -0.0262297$ and $e = 0.00190248$. In the insert, we can see a detail of the $\tilde{\beta}'$ behavior for small De^2. The in-phase modulus is quite constant in the interval considered with a value approximately equat to 0.373.

Table 3. Some numerical values of non-dimensional first normal stress difference $\tilde{N}_1$ and the realtive errors associated.

De^2	$\tilde{\beta}'(\tilde{\omega} = 0.055)$	|Relative Error|
1.000E-004	0.372625	-
3.600E-003	0.372640	5.3671E-005
2.250E-002	0.374004	2.9010E-003
0.2025	0.385443	8.1153E-003
0.2500	0.388571	1.9113E-002

6. Conclusions

In this paper we have theoretically investigated the rheological of elastic liquids undergoing steady and oscillatory shear flows. We have examined a pair of constitutive equation so-called FENE-Dumbell model describing polymeric solution in a very dilute regime. Theoretical results based on asymptotic solutions, experimental data and numerical simulation results for the first normal stress difference as a function of Deborah number, De. have been presented. A very good quantitative agreement between theory and experiments was observed with a simple calibration constant for a polyacrilamide macromolecule. In the frequency domain, the viscoelastic functions $\tilde{\eta}'$ and $\tilde{\eta}''$ were examined. The elastic liquid model was validated by comparison with experimental data the for limit of linear viscoelasticity, i.e. $De \ll 1$. We have shown that as De is increased, nonlinear effects are incorporated by the polymer and the viscous and elastic modules showed a strong dependence on De. There functions were explored considering the viscous and elastic characteristic as the fluid responds to a wide range of frequencies and magnitdes of De. We have seen a dominance of the elastic effects over viscous effects, but at low and high frequency a pure viscous behavior is observed. Another finding of this work was that that even for a dilute limit of a polymeric solution our numerical simulation is able to explore nonlinear regimes of the a macromolecule reponse undegoing oscillatory shear at moderate and high forcing amplitude. The results for the non-dimensional first normal difference $\tilde{N}_1$ from the oscillatory shear flow have indicated that even at the asymptotic limit $De \ll 1$ some nonlinearities on the flow response can be already observed. We have also examined elastic modulus in-phase and out-of-phase from the Fourier coefficient of the first normal stress difference. We have seen that as De is increased further 0.5, the nonlinearities dominated the flow and the asymptotic theory no longer described well the elastic fluid response. In the case of a simple shear flow, this occured at $De = 0.25$, indicanting that nonlinearity are stronger in this case. Moroever a macromolecule is much more streched in steady shear and can break up for Deborah number considerable smaller.

7. ACKNOWLEDGEMENTS

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