

DYNAMICAL BEHAVIOR OF AN OLDROYD FLUID UNDER UNSTEADY LINEAR FLOW

Farith M. Absi Salas, farith78@yahoo.com

Francisco Ricardo da Cunha, frcunha@unb.br

Universidade de Brasilia - Brazil, Brasilia - DF, Campus Universitário Darcy Ribeiro

Abstract. *In this article we study the nonlinear frequency response of a FENE-dumbbell fluid undergoing an oscillatory shear. We start with a description of the dimensionless governing equations and differential constitutive models of the elastic liquid examined. The non-dimensional measure of the elastic stresses defines the Deborah number, which is the ratio of the relaxation time of the material to the time for the liquid to flow through the region of interest. We describe the implementation of the simulation technique based on a fourth order Runge Kutta scheme. Oscillatory flows of the FENE-dumbbell version of the Oldroyd-B constitutive equation at low Reynolds numbers are explored at different Deborah numbers. The nonlinear frequency response of the elastic fluid under an oscillatory shear at arbitrary frequency forcing and Deborah numbers are explored from a dynamical system point of view, in terms of phase diagrams and power spectra of the macromolecule conformation tensor and elastic stresses.*

Keywords: *frequency response, nonlinear fluid, unsteady shear, Oldroyd fluid.*

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 time and 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 well-known (Bird et al, 1987). 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 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 the context of elastic liquid under oscillatory shear flow, the excitation frequency ω is relevant in the approach of oscillatory energy stored mechanism. Hence the influence of this parameter on the rheological response of the fluid will be explored in a wide range in terms of viscoelastic functions. Such quantities represents the energy stored as a consequence of the viscous and elastic polymer characteristics under an oscillatory shear flow.

2. MICROSTRUCTURAL MODEL

2.1 Scaling analysis

Dilute polymer solutions (no overlapping of the macromolecules) behavior can be idealized as being a polymer chain composed of two beads representing drag forces, linked to a Hookean spring representing elastic forces. This configuration bead-and-spring is called a dumbbell (Bird et al, 1987; Tanner, 2000). In this model a macromolecule is composed of N rigid segments (each corresponding to an individual monomers) of length δ , with each individual monomer randomly oriented with respect to the adjoining segments. The equilibrium configuration distribution of the macromolecule is then given by a random walk of N steps each of length δ . In this model the mean end-to-end distance of the polymer, a is proportional to $N^{1/2}\delta$ as required by the central limit theorem, which is smaller than the length of the polymer chain by a factor of $N^{1/2}$.

In a flow, the distribution of polymer configurations will be affected by the local velocity gradient. In an shear flow the difference in the fluid velocity acting on the two halves of the polymer will cause the molecule to extend. The extension is opposed by Brownian motion which tend to restore the equilibrium distribution.

Let us examine the equilibrium condition between Brownian and viscous forces and consider, for instance, the simplest linear Hookean spring for modeling the restoring Brownian force. The vector \mathbf{r} between the centers of the two beads represents the end-to-end distance of the polymer molecule. We express the elastic force as being $F_B = Gr$, where G denotes the spring constant given by $G = 3KT/a^2$ (e.g. Flory, 1969). Here a denotes the equilibrium length of the macromolecule (i.e. a typical value of $|\mathbf{r}| = r$ for the elastic regime where a linear spring model makes sense.), K is the Boltzmann constant and T the absolute temperature.

The hydrodynamic interactions between the molecule and the solvent is represented by the viscous drag on the beads. So, in a dumbbell model the viscous force is defined as the force exerted over an isolated spherical particle of ratio a by the solvent with viscosity μ . At low Reynolds number, the expression is given by the Stokes law, namely, $F_V = 6\pi\mu a dr/dt$. At the thermodynamic equilibrium state, the balance between the viscous and the restoring forces acting on the macromolecule leads to

$$\frac{dr}{dt} = \frac{G}{C_v} r, \quad (1)$$

where $C_v = 6\pi\mu a$. Integrating the equation (1) for the initial condition $r(0) = r_0$, one obtains:

$$r(t) = r_0 \exp\left(\frac{t}{\tau}\right), \quad (2)$$

where $\tau = C_v/G = 2\pi\mu a^3/KT$ denotes the relaxation time of an extended macromolecule to the randomly-coiled state. Since N is equal to the molecular weight of the polymer (M) divided by the molecular weight of a single monomer (M_i), $N = M/M_i$ it results that the macromolecule relaxation time is proportional to $M^{3/2}$.

2.2 Fundamental parameters

In defining the Reynolds number, Re for a polymer solution, we need to define carefully what is meant by the viscosity μ , since both shear and extensional viscosity vary with shear-rate. Conventionally μ is taken to be the shear viscosity in the limit of small shear rates. Most polymeric fluids are highly viscous and so we consider the limit where Re is small. For the flow of a fluid density ρ and viscosity μ past a body of length scale a with velocity scale u_c , Re is defined to be $Re = \rho u_c a / \mu$.

In the context of elastic liquids a fundamental parameter is the Deborah number, that is defined as the ratio of the relaxation time and a characteristic time of the flow, i.e. $De = \tau/t_f$, where τ denotes the relaxation time of the polymer. The relaxation time measures the ability of the macromolecules to recoil to their equilibrium condition after stretching. The flow time scale t_f is defined as the ratio of a velocity u_c and a length a , characteristics of the flow. For $De \ll 1$ means weak flow and the fluid behaves closely to a Newtonian fluid. In this limit, Brownian motion prevents the polymer from becoming highly extended, and the macromolecule distribution remains close to the randomly coiled distribution. We denote this limit as being the elastic regime, with $r \sim a$. For large values of Deborah (i.e. $De \sim 1$), however, the flow is strong enough to overcome the Brownian relaxation and so the polymer may become greatly extended, so that the mean end-to-end distance becomes large compared to its values in the randomly-coiled distribution, i.e. $r \gg a$. This second regime will correspond to the anisotropic limit of the macromolecule. For strong flows $De \sim 1$ the macromolecule stretching produces anisotropy in the flow and non-linear effects as normal-stress-difference.

A second important dimensionless parameter is the extensibility of the polymer, L defined as being the ratio of the full stretched length ($\ell = N\delta$) to the average length corresponding to the end-to-end distance in the randomly coiled state of

the macromolecule, a , i.e. $L = N\delta/a$. In the present work, while Deborah can be interpreted as a measure of the polymer elasticity on the flow, L will denote a measure of the flow anisotropy created by the macromolecule orientation.

The final dimensionless group is a measure of the effective volume fraction of the macromolecule evaluated at the randomly coiled state, namely $\phi = 4\pi a^3 n/3$, where n is the number of molecules, N_m per unit of volume, i.e. $n = N_m/V$. For the solution to be dilute, ϕ must be much less than unit, therefore the polymer contribution to the fluid stress will be negligible unless the polymer become highly extended.

3. GOVERNING EQUATIONS

The balance equations are the conservation of mass and of momentum

$$\nabla \cdot \mathbf{u} = 0, \quad \nabla \cdot \Sigma = \mathbf{0} \quad (3)$$

where inertia is neglected.

3.1 Constitutive Equation

In general, the stress tensor for an elastic liquid is given by the following constitutive equation

$$\Sigma = -p\mathbf{I} + \sigma \quad (4)$$

with the deviatoric stress σ given by the following expression

$$\sigma = 2\mu_s(\phi, \dot{\gamma})\mathbf{D} + \bar{\sigma}_B, \quad (5)$$

where p is the mechanical pressure, \mathbf{I} is the unit tensor, $\mu_s(\phi, \dot{\gamma})$ is the shear viscosity as a function of the volume fraction ϕ and the shear rate $\dot{\gamma}$, $\bar{\sigma}_B$ is the elastic stress contribution due to the presence of macromolecules and \mathbf{D} is the rate of the strain tensor, $\mathbf{D} = (\nabla \mathbf{u} + \nabla \mathbf{u}^T)/2$.

The macroscopic behavior of a dilute solution of macromolecules is obtained by averaging a property for a single molecule over an large ensemble of identical molecules. We then derive an equation for $\bar{\sigma}_B$ which correlates the average microscopic behavior of macromolecules with the macroscopic response of the fluid.

3.2 Non-linear Stress

Since we are treating with dilute polymer solutions, the shear viscosity may be considered as being a linear function of the volume fraction only, i.e. $\mu_s(\phi, \dot{\gamma}) \approx \mu(1 - c\phi)$. For a dilute aqueous solution of polyacrylamide-PAMA, the best fitting constant is found to be $c = 0.0128$ (Andreotti et al., 2003).

Now, the non-Newtonian average contribution stress due to the macromolecules is given by a volume average over a volume V sufficiently large to contain a meaningful number of macromolecules, that is

$$\bar{\sigma}_B = \lim_{V \rightarrow \infty} \frac{1}{V} \int_0^V \sigma_B d\mathbf{x} = n \langle \sigma_B \rangle, \quad (6)$$

where $\langle \rangle$ represents an ensemble average.

According to the scaling analysis presented in §1, the elastic restoring force can be written as

$$\mathbf{F}_B = G\mathbf{r}, \quad (7)$$

and the associated stress tensor for one macromolecule is given by the dyadic $\sigma_B = G\mathbf{r}\mathbf{r}$. Taking the average over N_m macromolecules within a sufficiently large volume V , one obtains

$$\langle \sigma_B \rangle = G \left(\frac{1}{N_m} \sum_{s=1}^{N_m} \mathbf{r}\mathbf{r} \right). \quad (8)$$

Since $n = N_m/V$, $\bar{\sigma}_B = n \langle \sigma_B \rangle = nG \langle \mathbf{r}\mathbf{r} \rangle$.

We define the conformation tensor or the moment of inertia tensor of the deformable macromolecule as being

$$\mathbf{B}(t) = \langle \mathbf{r}\mathbf{r} \rangle = \frac{1}{N_m} \sum_{s=1}^{N_m} \mathbf{r}\mathbf{r}. \quad (9)$$

Note that \mathbf{B} is by definition symmetric and positive definite tensor.

Rewriting the Eq. (5) in terms of the conformation tensor it leads to:

$$\boldsymbol{\sigma} = 2\mu_s(\phi)\mathbf{D} + nG\mathbf{B}(t). \quad (10)$$

3.3 Time evolution of \mathbf{B}

The closure problem of the constitutive equation, Eq. (10) requires a time evolution equation for the conformation tensor $\mathbf{B}(t)$. Turning back to the scaling analysis given in §(2.1), the balance between elastic and viscous forces gives

$$6\pi\mu a \frac{d\mathbf{r}}{dt} + G\mathbf{r} = 0. \quad (11)$$

Now, multiplying both sides of the Eq. (11) by \mathbf{r} , subtracting the rigid body translation and adopting a frame of reference rotating and deforming with the macromolecule, after averaging one obtains:

$$3\pi\mu a \frac{\delta\mathbf{B}}{\delta t} + G\mathbf{B} - KTI = 0. \quad (12)$$

Here $\delta/\delta t$ is the upper convective time derivative or the Oldroyd derivative that is material frame indifference. It is simply the rate of change of \mathbf{B} seen by an observer translating and deforming with the macromolecule

$$\frac{\delta\mathbf{B}}{\delta t} = \frac{D\mathbf{B}}{Dt} - \nabla\mathbf{u} \cdot \mathbf{B} - \mathbf{B} \cdot \nabla\mathbf{u}^T, \quad (13)$$

Now, writing Eq. (12) in terms of the Oldroyd derivative given by Eq. (13) and after rearranging the equation, we find

$$\frac{D\mathbf{B}}{Dt} = \nabla\mathbf{u} \cdot \mathbf{B} + \mathbf{B} \cdot \nabla\mathbf{u}^T - \frac{2}{\tau} [\mathbf{B} - (a^2/3)\mathbf{I}], \quad (14)$$

where D/Dt denotes the translational material derivative. Here, the first term on the right-hand side in equation (14) represents the stretching of the macromolecule by the flow, and the second term represents the relaxation of the polymer due to Brownian motion.

It should be important to note that by few algebraic manipulation, taking the Oldroyd derivative of the stress Eq. (10) and using the microstructure equation (12) it is straightforward to show that the pair of constitutive equation given by Eqs. (10) and (14), reduces to the most common Oldroyd-B fluid (Bird et al., 1987), namely:

$$\hat{\boldsymbol{\sigma}} + \lambda \frac{\delta\hat{\boldsymbol{\sigma}}}{\delta t} = 2\mu(\phi) \left(\mathbf{D} + \lambda \frac{\delta\mathbf{D}}{\delta t} \right), \quad (15)$$

with $\hat{\boldsymbol{\sigma}} = \boldsymbol{\sigma} - nKTI$ and the material constant $\lambda = \tau/2$.

In this work we will keep the form of a pair of constitutive equations in order to explore the explicit dependence of the microstructure given by the behavior of the second moment tensor \mathbf{B} .

3.4 Non-linear bead-and-spring model.

A dumbbell model with a drag correction and a non-linear spring force which gives a finite limit to the spring extension is considered. A Hookean spring may produces unlimited elongation of the dumbbell. Such a behavior is not only unrealistic but can also lead to numerical difficulties as unlimited values of the stress tensor. These difficulties can at least be partially eliminated by limiting the extensibility of the macromolecule (Rallison and Hinch, 1988). Changing the linear spring law to one with a finite extension, i.e. $Gf(r)$, yields to a dumbbell-FENE model, where $f(r)$ is the nonlinear spring law. Actually the correct spring law for a random-chain model was proposed by Flory (1969) as being $f(r) = (\ell/3r)F^{-1}(r/\ell)$, where $F(z) = \coth(z) - 1/z$ is the Langevin function. Because this law is difficult to work mathematically, we use instead a simpler law with the same qualitative behavior such as first proposed by Warner (1972)

$$f(r) = \frac{l^2}{l^2 - r^2} \quad \text{with} \quad r^2 = \text{tr}(\mathbf{B}). \quad (16)$$

Note that as r tends to the rigid fibre limit l , the polymer reaches its limits of maximum extensibility, whereas in the case of small distortions of the macromolecules $r \sim a$ (i.e. randomly-coiled state), $f(r) \sim 1$ (i.e. linear spring law would be appropriated). In addition, the FENE dumbbell model described above needs also to take account of the variation in the hydrodynamic drag for $r \sim l$. In this respect this model is strictly valid only for small values of r . As the polymer expands, the size of the object on which the frictional force of the fluid acts increase. The viscous drag increases with the largest linear dimension and so the size of the beads should increase roughly with $r = \text{tr}(\mathbf{B})^{1/2}$ (Hinch, 1977).

After incorporating into the model the corrections discussed above, the constitutive equations for the stress tensor and the conformation tensor are written respectively as being

$$\boldsymbol{\sigma} = 2\mu_s(\phi)\mathbf{D} + nGf(r)\mathbf{B}(t), \quad (17)$$

$$\frac{d\mathbf{B}}{dt} = \nabla\mathbf{u} \cdot \mathbf{B} + \mathbf{B} \cdot \nabla\mathbf{u}^T - \frac{2af(r)}{\tau[\text{tr}(\mathbf{B})]^{1/2}} [\mathbf{B} - (a^2/3)\mathbf{I}]. \quad (18)$$

Eqs. (17) and (18) can be made dimensionless with appropriate scales. Using u_c and a as the reference speed and the reference length respectively, the flow is characterized by the Deborah number $De = 2\pi\mu a^2 u_c / KT$; for an oscillatory shear motion with shear rate $\dot{\gamma} = \dot{\gamma}_0 \cos(\omega t)$, with amplitude $\dot{\gamma}_0 = \omega\gamma_0$, the characteristic velocity $u_c = a\dot{\gamma}$. As mentioned before the other parameter of interest are the particle volume fraction ϕ and the extensibility of the polymer $L = l/a$. The dimensionless constitutive equations expressed in terms of the stress $\tilde{\boldsymbol{\sigma}}$ and the conformation tensor $\tilde{\mathbf{B}}$ of the polymer are respectively

$$\tilde{\boldsymbol{\sigma}} = \tilde{\mu}(\phi)\tilde{\mathbf{D}} + \frac{9\phi f(R)}{2De}\tilde{\mathbf{B}}, \quad (19)$$

$$\frac{d\tilde{\mathbf{B}}}{d\tilde{t}} = De(\tilde{\nabla}\tilde{\mathbf{u}} \cdot \tilde{\mathbf{B}} + \tilde{\mathbf{B}} \cdot (\tilde{\nabla}\tilde{\mathbf{u}})^T) - \frac{2f(R)}{[\text{tr}(\tilde{\mathbf{B}})]^{1/2}} \left(\tilde{\mathbf{B}} - \frac{\mathbf{I}}{3} \right), \quad (20)$$

where $\tilde{\boldsymbol{\sigma}} = a\boldsymbol{\sigma}/\mu u_c$, $\tilde{\mu} = \mu_s/\mu$, μ is the solvent viscosity, $\tilde{\mathbf{B}} = \mathbf{r}\mathbf{r}/a^2$, $R = r/a$ and the spring function in terms of the dimensionless quantities R and L is given by $f(R) = L^2/(L^2 - R^2)$. By examining the right-hand side term in the equation (20), it becomes clear that for large Deborah, the contribution of the first term responsible for the stretching of the polymer is dominant compared to the contribution for the polymer relaxation. One can see that this is possible only if one considers high relaxation time macromolecule compared to the time scale of the flow. The above pair of constitutive equations should be a reasonable approximation for describing oscillatory shear flows of very dilute polymer solutions.

4. ANALYTICAL RESULTS

In the linear limit where low deformations of the macromolecules are considered ($\gamma \ll 1$), 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 $f(R) = 1$ and $R = 1$ as a consequence of macromolecules random coiled configuration.

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

4.1 Linear Viscoelastic Regime

In the case of elastic limit, when $f(R) = 1$, $De \ll 1$ and $R \sim 1$, the components of the governing equation (20) of \mathbf{B} evolution reduces simply to

$$\frac{d\tilde{B}_{12}}{d\tilde{t}} = De\tilde{B}_{22}\cos(\tilde{\omega}\tilde{t}) - 2\left(\tilde{B}_{12}\right). \quad (21)$$

$$\frac{d\tilde{B}_{11}}{d\tilde{t}} = De(\tilde{B}_{12} + \tilde{B}_{21})\cos(\tilde{\omega}\tilde{t}) - 2\left(\tilde{B}_{11}\right) + \frac{2}{3}. \quad (22)$$

$$\frac{d\tilde{B}_{22}}{d\tilde{t}} = -2\left(\tilde{B}_{22} - \frac{1}{3}\right). \quad (23)$$

Integrating Eq. (23) gives $\tilde{B}_{22} = 1/3$. Taken this value into Eq. (21) considering the macromolecules isotropic random configuration as initial condition, i.e., $\mathbf{B}(0) = \mathbf{I}/3$, we integrate the equation (21) and obtain the component \tilde{B}_{12} , as:

$$\tilde{B}_{12} = \frac{1}{3} \frac{De}{(\tilde{\omega}^2 + 4)} [2\cos(\tilde{\omega}\tilde{t}) + \tilde{\omega} \text{sen}(\tilde{\omega}\tilde{t})] \quad (24)$$

Now substituting the component \tilde{B}_{12} in the Eq. (19), an expression for the shear stress in terms of a sum of cosine and sine functions is given by:

$$\tilde{\sigma}_{12} = \left[\tilde{\mu}(\phi) + \frac{3\phi}{(\tilde{\omega}^2 + 4)} \right] \cos(\tilde{\omega}\tilde{t}) + \frac{3\phi\tilde{\omega}}{2(\tilde{\omega}^2 + 4)} \text{sen}(\tilde{\omega}\tilde{t}) \quad (25)$$

In the context of linear viscoelastic theory ($De \ll 1$), the product coefficient of cosine and sine functions in Eq. (25) are denoted as the viscous and elastic modules, respectively, as:

$$\eta' = \tilde{\mu}(\phi) + \frac{3\phi}{(\tilde{\omega}^2 + 4)} \quad \eta'' = \frac{3\phi\tilde{\omega}}{2(\tilde{\omega}^2 + 4)}. \quad (26)$$

The η' function is associated to the viscous energy dissipation and represent the module "in phase" with the excitation. The η'' is associated with the stored energy during the macromolecules deformation and denote s the module "out phase" with respect to excitation.

complementarity with the analytic result above, we present the integration of Eq. (22) for the normal component \tilde{B}_{11} , resulting in

$$\tilde{B}_{11} = \frac{1}{3} + \left[\frac{4De^2}{12(\tilde{\omega}^2 + 4)} + \frac{4De^2 - 2De^2\tilde{\omega}^2}{12(\tilde{\omega}^2 + 4)(\tilde{\omega}^2 + 1)} \cos(2\tilde{\omega}\tilde{t}) + \frac{6De^2\tilde{\omega}}{12(\tilde{\omega}^2 + 4)(\tilde{\omega}^2 + 1)} \text{sen}(2\tilde{\omega}\tilde{t}) \right] \quad (27)$$

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. (19), we have:

$$\tilde{\sigma}_{11} = \frac{3\phi}{2De} + \frac{3\phi De}{2(\tilde{\omega}^2 + 4)} + \frac{3\phi De(2 - \tilde{\omega}^2)}{4(\tilde{\omega}^2 + 4)(\tilde{\omega}^2 + 1)} \cos(2\tilde{\omega}\tilde{t}) + \frac{9\phi De\tilde{\omega}}{4(\tilde{\omega}^2 + 4)(\tilde{\omega}^2 + 1)} \text{sen}(2\tilde{\omega}\tilde{t}) \quad (28)$$

and

$$\tilde{\sigma}_{22} = \frac{3\phi}{2De} \quad (29)$$

From Eqs. (28) and (29) it can be seen that for an asymptotic limit where $De \rightarrow 0$, all of numerator terms with De tend to zero and the normal stresses $\tilde{\sigma}_{11} \rightarrow \tilde{\sigma}_{22}$. Therefore the first normal difference stresses defined as $N_1 = \tilde{\sigma}_{11} - \tilde{\sigma}_{22}$ is negligible for a linear viscoelastic regime.

In addition, from Eqs. (28) and (29) we can define N_1 for a linear regime where $De \rightarrow 0$, as:

$$N_1 = \frac{3\phi De}{2(\tilde{\omega}^2 + 4)} + \frac{3\phi De(2 - \tilde{\omega}^2)}{4(\tilde{\omega}^2 + 4)(\tilde{\omega}^2 + 1)} \cos(2\tilde{\omega}\tilde{t}) + \frac{9\phi De\tilde{\omega}}{4(\tilde{\omega}^2 + 4)(\tilde{\omega}^2 + 1)} \text{sen}(2\tilde{\omega}\tilde{t}) \quad (30)$$

Finally note that for an oscillatory shear excitation with frequency $\tilde{\omega}$, the first normal stress difference N_1 show a rheological response with frequency $2\tilde{\omega}$.

5. NUMERICAL RESULTS

We start this section with a brief description of the integration numerical method used to obtain the components of the conformation tensor \tilde{B}_{ij} . Then we show nonlinear results of the elastic fluid under an oscillatory shear at arbitrary frequency forcing and Deborah numbers.

5.1 Four Order Runge-Kutta Procedure

In this section we describe the method used to obtain numerical results for the macromolecule configurations and elastic stresses under strong oscillatory shear flows. Numerical integrations are performed on the ordinary differential equations of the conformation tensor components given by:

$$\frac{d\tilde{B}_{ij}}{dt} = De \left(\frac{\partial \tilde{u}_i}{\partial \tilde{x}_k} \tilde{B}_{kj} + \tilde{B}_{ik} \frac{\partial \tilde{u}_j}{\partial \tilde{x}_k} \right) - \frac{2f(R)}{R} \left(\tilde{B}_{ij} - \frac{\delta_{ij}}{3} \right), \quad (31)$$

A critical point in order to achieve the convergence of the method is the choice of the time step Δt . For a oscillatory shear flow, the convergence of the method show a strong dependence with the excitation frequency $\tilde{\omega}$. For this reason we define the time step from scaling analysis of the flow in terms of $\tilde{\omega}$, given by:

$$\Delta t = \min \left\{ 10^{-3}, \frac{10^{-1}}{\tilde{\omega}} \right\} \quad (32)$$

The four order Runge-Kutta procedure is based on the temporal derivatives evaluation in four point inside of integration time interval t_n to t_{n+1} . We obtain the solution of the vector \mathbf{x}_{n+1} in time $t = t_{n+1}$ from the knowledge of \mathbf{x}_n in $t = t_n$ and the weighted mean of the functions k_1, k_2, k_3 e k_4 , where $\mathbf{x} = (\tilde{B}_{11}, \tilde{B}_{12}, \tilde{B}_{13}, \dots, \tilde{B}_{33})$.

The functions k_1, k_2, k_3 e k_4 are expressed in terms of time step Δt and function $f(t_n, \mathbf{x}_n)$ in different points in the interval of integration. Since the function $f(t_n, \mathbf{x}_n) = f(\tilde{t}, \tilde{B}_{ij}) = d\tilde{B}_{ij}/d\tilde{t}$ is dependent of the flow velocity profile, we denote the components of the ordinary differential equation (31) considering the velocity profile for a oscillatory shear, given by $\tilde{\mathbf{u}} = (\tilde{x}_2, 0, 0)\cos(\tilde{\omega}\tilde{t})$, as:

$$\frac{d\tilde{B}_{11}}{dt} = 2De\tilde{B}_{12}\cos(\omega t) - \frac{2f(R)}{R} \left(\tilde{B}_{11} - \frac{1}{3} \right) \quad (33)$$

$$\frac{d\tilde{B}_{22}}{dt} = -\frac{2f(R)}{R} \left(\tilde{B}_{22} - \frac{1}{3} \right) \quad (34)$$

$$\frac{d\tilde{B}_{12}}{dt} = De\tilde{B}_{22}\cos(\omega t) - \frac{2f(R)}{R}\tilde{B}_{12}. \quad (35)$$

Note that $\tilde{B}_{21} = \tilde{B}_{12}, \tilde{B}_{13} = \tilde{B}_{31} = \tilde{B}_{23} = \tilde{B}_{32} = \tilde{B}_{33} = 0$. The Eqs. (33) to (35) represents a "coupled" system of ordinary differential equations that will be solve with the numerical scheme presented above. Such solutions will be in terms of the conformation tensor components \tilde{B}_{ij} .

For nonlinear frequency domain results, the quantities of interest are evaluated in terms of its Fourier coefficients. Therefore the Fast Fourier Transform (FFT) subroutine is incorporated into the numerical code to obtain the power spectrum of the quantities $\tilde{B}_{ij}, \tilde{\sigma}_{ij}$ and N_1 . The FFT subroutine was implemented from IMSL90 numerical library. Such subroutine gives the Fourier coefficients of a signal for a fluid excitation frequency $\tilde{\omega}$. From these coefficients we also examine the viscoelastic modules η' and η'' as functions of excitation frequency $\tilde{\omega}$.

5.2 Nonlinear Results

The numerical results in time and frequency domain using the procedure described above will be show next. Such results are given in terms of components of the conformation tensor \mathbf{B} , shear stress $\tilde{\sigma}_{12}$ and the first normal stress difference N_1 . The nonlinear response of these quantities are explored for strong oscillatory shear flows ($De > 1$). In the numerical simulations the physical parameters are fixed as $\phi = 300ppm$ and $L = 80$. In time domain results the dimensionless excitation frequency is fixed as $\tilde{\omega} = 1$

Figures (1) and (2) show the normal and shear components of \mathbf{B} , respectively, as a function of dimensionless time. Such quantities represent the temporal evolution of macromolecules configuration under an oscillatory shear flow with a velocity profile as $\tilde{\mathbf{u}} = (\tilde{x}_2 \cos(\tilde{\omega}t), 0, 0)$. In the linear viscoelastic regime where $De \ll 1$ the macromolecules remain its random configuration in which solvent viscous forces can not be able to deform such configuration. Hence the oscillation amplitude of \tilde{B}_{11} is smaller than \tilde{B}_{12} . When the flow intensity increase ($De > 1$), the amplitude of \tilde{B}_{11} grow as a consequence of the macromolecule stretching by the flow. This anisotropic configuration of the macromolecules give rise to a normal stress difference as we will show later.

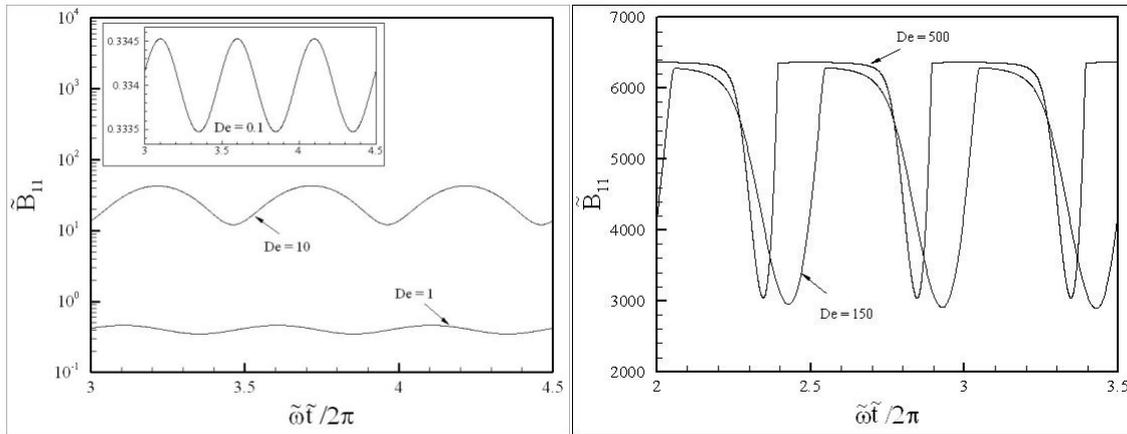


Figure 1. Conformation tensor component \tilde{B}_{11} as a function time with $De = 0.1, 1, 10, 150, 500, L = 80, \phi = 300 \text{ ppm}$ and $\tilde{\omega} = 1$.

For $De > 10$ the oscillation amplitude of \tilde{B}_{11} is one order magnitude bigger than \tilde{B}_{12} . This result denote a predominant nonlinear elastic response. Fig. (1) also shows the component \tilde{B}_{12} as a time function with $De > 100$. In this case the oscillation amplitude reach to a constant limit despite of Deborah number increases. Such amplitude limit is a consequence of the fully stretch of the macromolecules by the flow. Similarly as \tilde{B}_{11} response, the amplitude of oscillation of \tilde{B}_{12} increase with De as showing in Fig (2). The normal components \tilde{B}_{22} and \tilde{B}_{33} are constants with $\tilde{B}_{22} = \tilde{B}_{33} = 1/3$.

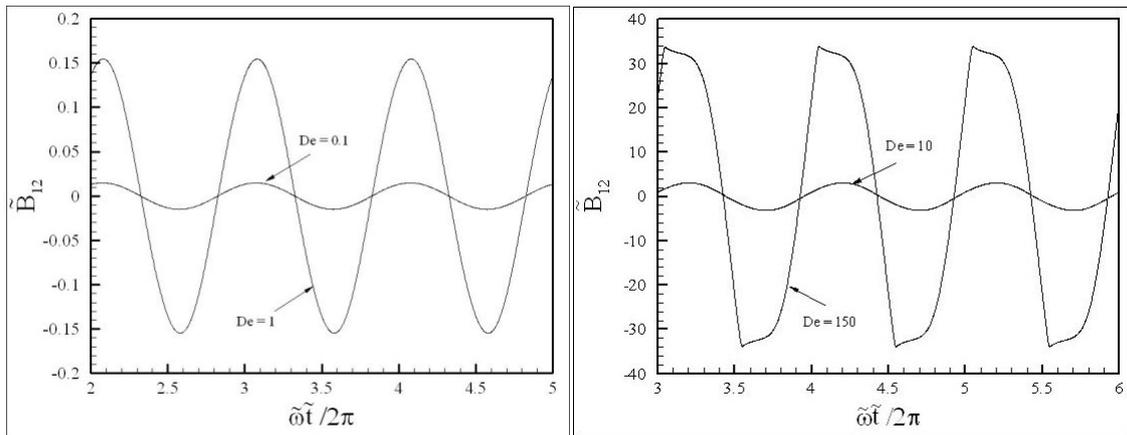


Figure 2. Conformation tensor component \tilde{B}_{12} as a function time with $De = 0.1, 1, 10, 150, L = 80, \phi = 300 \text{ ppm}$ and $\tilde{\omega} = 1$.

In shear flows one of the most relevant aspect of interest is the polymer response in terms of shear stress $\tilde{\sigma}_{12}$. In Fig. (3) we plot the dimensionless shear stress as a time functions for several De . Firstly we examine a weak flow with $De = 0.1$. A linear response of the polymer is observed as a reflect of equilibrium between the elastic and viscous forces. For low values of De , the oscillation amplitude is small and the oscillation frequency response is the same of excitation. In addition, the linear response of $\tilde{\sigma}_{12}$ in steady shear flow is obtained with $\tilde{\omega} = 0$. Note that the maximum oscillation amplitude value correspond to the constant value of $\tilde{\sigma}_{12}$ in steady case. It is important to note that this linear result can be obtained analytically from Eq. (25).

Nonlinear results of the polymer at $De = 10$ and $De = 150$ are also showed in Fig. (3). In strong flows where $De \gg 1$, the elastic forces are dominant and the macromolecules are stretching in same direction of the flow. Such

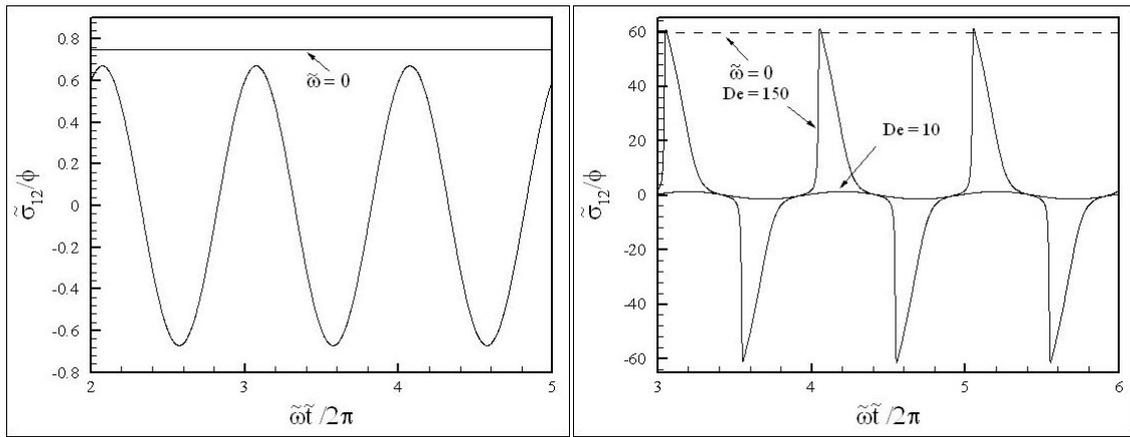


Figure 3. Dimensionless shear stress $\tilde{\sigma}_{12}$ as a function of time with $De = 0.1, 10, 150, L = 80, \phi = 300 \text{ ppm}$ and $\tilde{\omega} = 1$.

macromolecule deformation is bigger as the Deborah number increase. For $De = 10$ the oscillation amplitude of shear stress is bigger than the linear case. For $De = 150$ this amplitude reach to a maximum in which the macromolecule is considered fully extended. The wave form of the curve for $De = 150$ have a complex form as a consequence of the several oscillation modes that the macromolecule responses. In addition we compare the shear stress considering a steady simple shear flow doing $\tilde{\omega} = 0$. The value of maximum amplitude is the same in both cases.

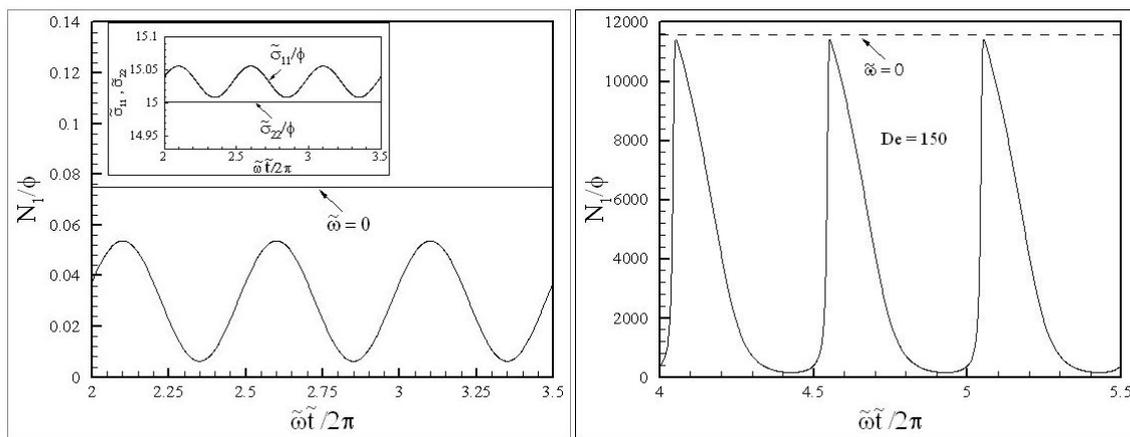


Figure 4. First normal stress difference N_1 as a function of time for two limits with $De = 0.1$ and $De = 150, L = 80, \phi = 300 \text{ ppm}$ and $\tilde{\omega} = 1$.

A comparison of the first normal stress difference N_1 as a time function for two Deborah number is plotted in Fig. (4) In left side of this figure we show the viscoelastic linear case in which the macromolecules are not significantly deformed by the flow and the normal stresses $\tilde{\sigma}_{11}$ and $\tilde{\sigma}_{22}$ have the same magnitude (insert). Therefore the oscillation amplitude of N_1 is close to zero in oscillatory and steady shear cases (where $\tilde{\omega} = 0$), as the figure show. Such result are according with the asymptotic linear Eqs. (28) and (29). When Deborah number increases, the oscillation amplitude grow and the response of the macromolecules departure from a isotropic equilibrium regime to nonlinear regime in which the anisotropy of the normal stresses leads to the appearance of the first normal stress difference N_1 . This behavior can be explained from a physical point of view considering that the viscous forces acting on the polymer are strong enough for a fully stretch of the macromolecules in "11" direction. With the fully stretched macromolecules oriented in same direction of $\tilde{\sigma}_{11}$, this term become predominant when compared with $\tilde{\sigma}_{22}$. For this reason the appearance of N_1 can be considered an important measure of the polymer nonlinear response.

In Fig. (5) phase diagrams are shown in terms of $\tilde{\sigma}_{12}$ and N_1 considering four values of Deborah number. These diagrams are plotted in order to verify a nonlinearity response of the polymer. This is achieved plotting $\tilde{\sigma}_{12}$ versus its derivative $d\tilde{\sigma}_{12}/d\tilde{t}$ and N_1 versus $dN_1/d\tilde{t}$, as Fig (5) show. For $De = 0.1$ a linear case is considered in which the phase diagram show a circular curve denoting a linear response of the polymer. In this case the "phase difference" between $\tilde{\sigma}_{12}$ and its derivative is near to $\pi/2$. As expected, in linear regime the diagram for shear stress $\tilde{\sigma}_{12}$ show a bigger magnitude when compared to the diagram for N_1 . Increasing de intensity of the flow, i.e., increasing De , a distortion of a linear

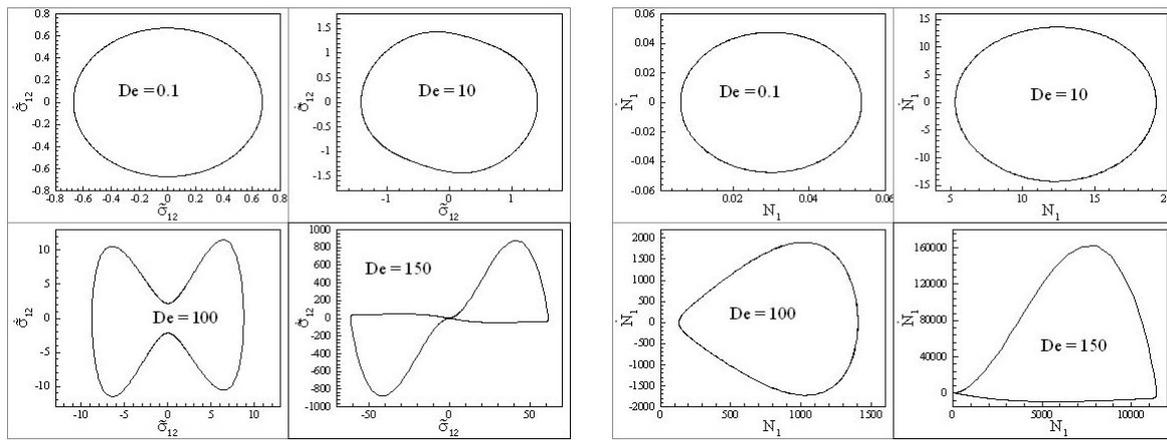


Figure 5. Phase diagrams of the quantities: $\tilde{\sigma}_{12}$ versus its derivative $d\tilde{\sigma}_{12}/d\tilde{t}$ and N_1 versus $dN_1/d\tilde{t}$. Each diagrams for a different Deborah number, with $De = 0.1, 10, 100, 150$. $L = 80$, $\phi = 300$ ppm and $\tilde{\omega} = 1$

circular curve is verify as a consequence of the nonlinearities incorporated by the polymer. In a nonlinear case where $De = 10$, it can be seen a level distortion of the curve and the increase of the amplitude for both quantities $\tilde{\sigma}_{12}$ and N_1 and its derivatives, respectively. More complex responses can be observed for $De = 100$ and $De = 150$. For $De = 100$ the curve is clearly distorted and the amplitude of $\tilde{\sigma}_{12}$ and its derivative has a one order magnitude bigger than the case for $De = 10$. The quantity N_1 and its derivative has a similar behavior of shear stresses for $De = 100$, however, the amplitude of N_1 versus $dN_1/d\tilde{t}$ is significantly larger indicating a strong nonlinear response of the polymer due to the anisotropy of the normal stresses. In a nonlinear limit where $De = 150$ the amplitude of $\tilde{\sigma}_{12}$ and $d\tilde{\sigma}_{12}/d\tilde{t}$ increase 100 times compared with the case of $De = 100$. In contrast of previous cases, the term N_1 show positives values for $De = 150$, denoting that N_1 oscillate always between positive values.

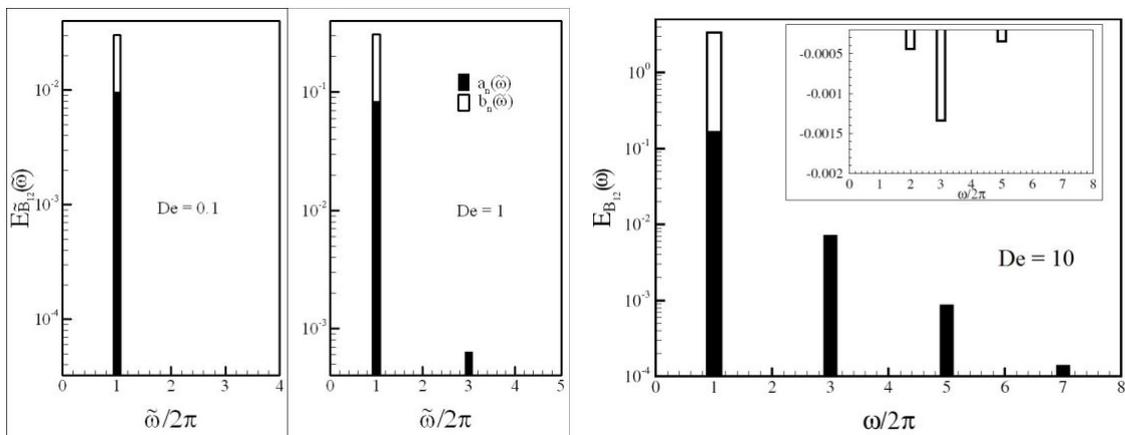


Figure 6. Power spectrum of Fourier coefficients $a_n(\tilde{\omega})$ and $b_n(\tilde{\omega})$ for \tilde{B}_{12} , with $\tilde{\omega} = 2\pi$, $De = 0.1, 1, 10$, $\phi = 300$ ppm, $= 80$

In previous results the rheological response of the quantities of interest in time domain were presented. In addition, results in frequency domain in terms of conformation tensor component \tilde{B}_{12} , shear stress $\tilde{\sigma}_{12}$ and first normal stress difference N_1 will be examined next for a given excitation frequency $\tilde{\omega}$. Such results are obtained with the application of the FFT (Fast Fourier Transform) to the time response of the polymer under an strong oscillatory shear flow.

In Fig. (6) we show the oscillation modes that the macromolecules responses in terms of \tilde{B}_{12} given an excitation with $\tilde{\omega} = 2\pi$. The Fourier coefficients $a_n(\tilde{\omega})$ and $b_n(\tilde{\omega})$ are showed for 3 values of De . Such coefficients are related to the cosine and sine functions, respectively, denoting a response in phase and "out phase" with respect to the excitation. For a weak flow case where $De = 0.1$ the drag viscous forces are not capable to significantly deform the macromolecules. In this case the macromolecules stay in the random equilibrium and the response reflect the linear behavior in which the fundamental harmonic mode appear in the same excitation frequency, i.e., $\tilde{\omega}/2\pi = 1$. Increasing the intensity of the oscillatory shear flow, such viscous forces are able to deform the random macromolecules configuration. In this nonlinear regime the fluid incorporate others oscillation modes characterizing a nonlinear behavior of the polymer. For

$De = 1$ the elastic forces become predominant and the macromolecules will deform and the nonlinear viscoelastic regime is incorporated by the rheological behavior of the fluid. As Fig.(6) shows, another oscillation mode appear in $\tilde{\omega} = 6\pi$. For $De = 10$ the stretching of the macromolecules is more significant and the elastic energy storage, as a consequence of macromolecules deformation resistance, is distributed in others oscillation modes (10π e 14π). These discrete power spectrum reveals an increase of the complexity of the macromolecules response having the possibility of modes with negative values for $b_n(\tilde{\omega})$ as the "insert" in the Fig (6) show.

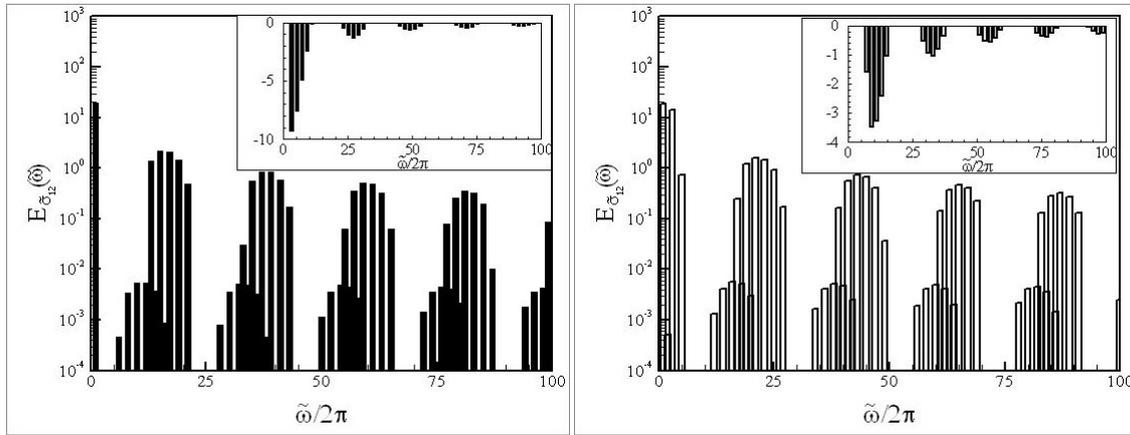


Figure 7. Power spectrum of Fourier coefficients $a(\tilde{\omega})$ and $b(\tilde{\omega})$ for $\tilde{\sigma}_{12}$, with $\tilde{\omega} = 2\pi$, $De = 150$, $\phi = 300$ ppm, $L = 80$

In Fig.(7) and (8) we show power spectrums of shear stresses $\tilde{\sigma}_{12}$ and normal stress difference N_1 for $De = 150$, respectively. Such intensity of the flow is strong enough to the macromolecules reach a fully extended configuration. In this case more complex responses are exposed in terms of many oscillation modes that the polymer responses as a consequence of energy stored in the process of deformation and contraction that the macromolecules are submitted by the oscillatory flow . In Fig. (7) Fourier coefficients $a_n(\tilde{\omega})$ and $b_n(\tilde{\omega})$ associated to the temporal responses of shear stress are presented. The distribution of the modes show in this figure tend to a continuous power spectrum as a consequences of the strong nonlinearity of the polymer response. Note that the firsts "harmonic" modes are dominant and contain larger part of the oscillation energy. In the "insert" of the Fig. (7)the nonlinear response of the polymer show negative values of $a_n(\tilde{\omega})$ and $b_n(\tilde{\omega})$, however most of this modes have values of low magnitude.

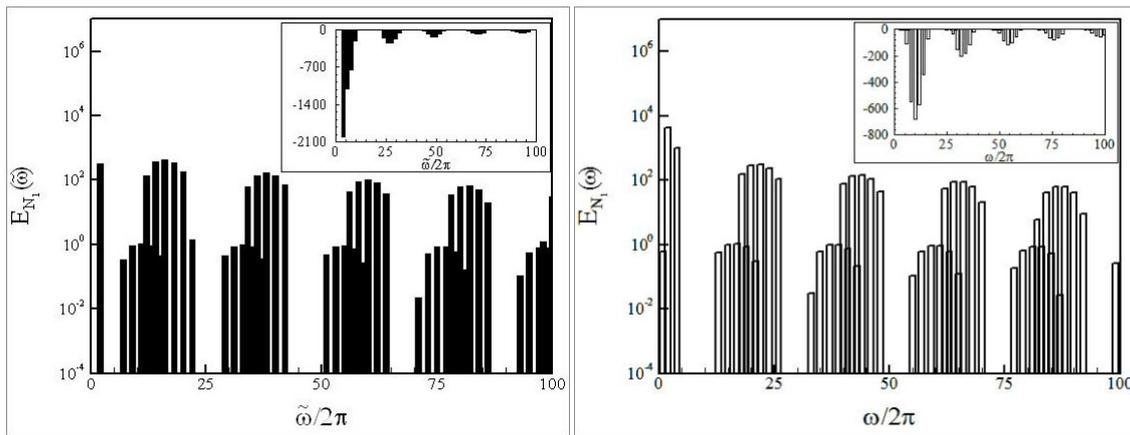


Figure 8. Power spectrum of Fourier coefficients $a(\tilde{\omega})$ and $b(\tilde{\omega})$ for N_1 , with $\tilde{\omega} = 2\pi$, $De = 150$, $\phi = 300$ ppm, $L = 80$

In addition to the nonlinear analysis of the rheological responses of an elastic fluid, Fig. (8) show a power spectrum for first normal stress difference N_1 in terms of Fourier coefficients $a_n(\tilde{\omega})$ and $b_n(\tilde{\omega})$ for $De = 150$. The first normal stresses difference is an anisotropy measure of the elastic stresses and its appearance is a direct consequence of polymer nonlinear behavior. As expected, the energy associated to N_1 is distributed in many oscillation modes and tend to a continuous spectrum. However, this energy is distributed approximately equally between most of the vibration modes and its amplitude reach close to 10^3 larger than the modes associated to $\tilde{\sigma}_{12}$. Note that negative values of some vibration modes have significant magnitude ("Insert"). This result indicate that for $De > 100$, in which the macromolecules are completely deformed, the anisotropy of the normal stresses are the mainly factor in the rheological responses of an elastic

liquid.

Finally, in Fig (9) we present the viscoelastic functions η' and η'' as a function of excitation frequency for several deformation amplitude $\tilde{\gamma}_0$. The values of frequency range between $\tilde{\omega}/2\pi = 8.0 \times 10^{-3}$ and $\tilde{\omega}/2\pi = 10^2$. These viscometric functions represent the first harmonic Fourier coefficients of the shear stress in frequency domain, where η' represent the term in phase with the shear rate $\dot{\gamma}$ and η'' the term "out of phase."

The function η' has dissipate characteristics and is denoted as viscous module. As the Fig. (9) show, this function present a shear thinning behavior in which a reduction of its magnitudes is verified with the increase of the 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. Considering high values of shear strain and moderate frequencies range, a nonlinear viscoelastic regime is observed in which viscous and elastic effects are present in same magnitudes. Hence in viscoelastic nonlinear regime the viscous module η' is a function of frequency $\tilde{\omega}$ and shear strain $\tilde{\gamma}$.

The Fourier coefficient "out of phase" with respect of shear rate is the viscoelastic function η'' and it is defined as the elastic module. In the same way of η' , the elastic module is plotted in a wide range of frequencies for several shear strain $\tilde{\gamma}_0$ from a linear viscoelastic limit (Eq. 26) to a great amplitude of deformation $\tilde{\gamma}_0 = 10$. In a linear regime the Fig. (9) show a symmetric curve. Such symmetry is gradually lost as the $\tilde{\gamma}_0$ grow and nonlinear effects are incorporated by the fluid. It is seen that in case of strong deformation amplitude $\tilde{\gamma}_0 = 10$ the magnitude amplitude of η'' is 6 times bigger than the linear viscoelastic regime. 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. In addition, the "insert" of the figure show the departure from the linear regime in which the module η'' has a frequency dependency only. When the elastic fluid is submitted to large deformation amplitudes the elastic module η'' show a dependency of shear strain $\tilde{\gamma}_0$ as a consequence of a nonlinear viscoelastic regime.

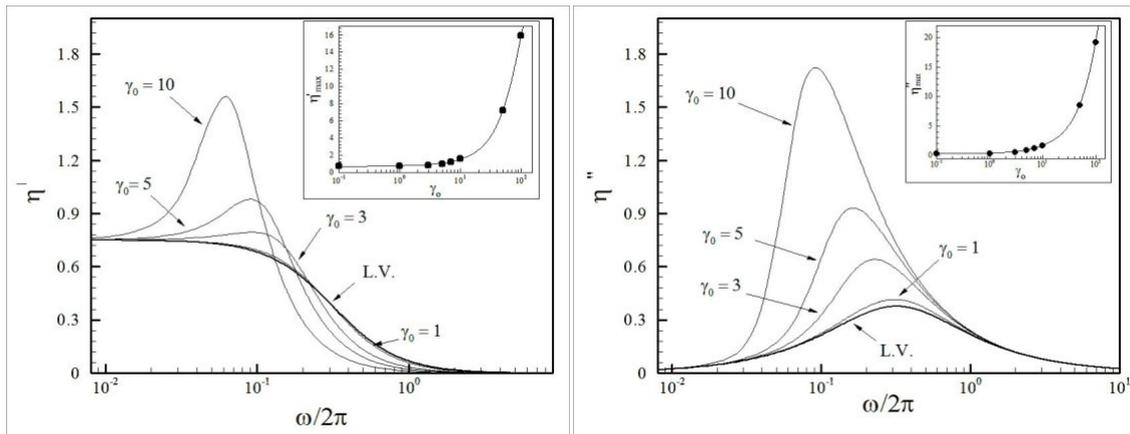


Figure 9. Viscous and elastic modules η' and η'' , respectively, versus $\omega/2\pi$. With $\phi = 300 \text{ ppm}$, $\tau = 80$

6. CONCLUSION

This paper has presented a rheological analysis of elastic liquids under strong oscillatory shear flow for dilute polymer solutions. We have examined a pair of constitutive equations through scaling arguments based on a balance between viscous drag and restoring Brownian forces.

From an asymptotic linear analysis in which $De \rightarrow 0$ the macromolecule was not significantly deform and remains its random coiled configuration. In such regime the viscous and elastics modules was obtained according with the linear viscoelastic theory. As expected, in this linear case the first normal stress difference was negligible.

The four order Runge-Kutta procedure was briefly examined in order to obtain numerical results of the rheological response of macromolecules under an strong oscillatory shear flow in terms of temporal evolution of it configuration given by the conformation tensor B . The nonlinear regime was characterized in terms of shear and normal stresses for high Deborah numbers.

The numerical results was explored in time and frequency domain. For low values of De the equilibrium of viscous and elastic forces acting on the macromolecules reflect a linear behavior of the polymer. In such regime the fluid showed a Newtonian response in which no significant oscillation amplitudes are presents and the phase diagrams showed a circular curve denoting no considerable perturbation by the macromolecules on the flow.

As the values of De increase the nonlinear effects by the presence of the deformed macromolecules could be observed. The nonlinear rheological response of the macromolecules was examined in terms of time evolution of the quantities of interest \tilde{B}_{ij} , $\tilde{\sigma}_{ij}$ and N_1 . In a nonlinear regime such quantities presented a complex behavior such as the appearance of

normal difference stresses N_1 , the significant growth of the oscillation amplitude and distorted phase diagrams of elastic stresses. As the power spectrum results showed, such nonlinear behavior can be explained in part by the presence of many others vibration modes contributing to the nonlinear response of the polymer.

In frequency domain, the viscoelastic functions η' and η'' was examined. The implemented model was validate in the limit of linear viscoelasticity where low deformation amplitude γ_0 was considered. It was shown as the strain amplitude increase nonlinear effects are incorporated by the polymer and the viscous and elastics modules showed a strong dependence with this parameter. Such functions was explored considering the viscous and elastics characteristic that the fluid response into a wide range of frequency and deformation amplitudes.

7. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of CAPES-Brazil, CNPq-Brazil and FINATEC-UnB.

8. REFERENCES

- Absi F.S., Oliveira T.F., Cunha F.R., 2006. A note on the extensional viscosity of elastic liquids under strong flows, *Mechanical Research Communications* 33, 401-414.
- Andreotti, M., Cunha, F.R. and Sousa, A.J., 2003. Investigation of friction affected by additives in turbulent flows in pipelines. *Bol. Tec. Petrobras*, 46, 56. Paper Petrobras PRODUT - Technological Pipeline Award 2002.
- Batchelor, G.K., 1970. Slender-Body theory for particle of arbitrary cross section in stokes flow, *J. Fluid Mechanics*, 44, 419.
- Bird R. B., Armstrong R. C., Hassager O., 1987. *Dynamics of polymeric liquids*, Vol 1, Ed. John Willey and Sons, Inc., New York. RBCM- J. of the Brazilian Soc. Mechanical Sciences, Vol.19, No. 3, pp. 332-340.
- Flory P.J, 1969. *Statistical Mechanics of chain molecules*, Wiley, New York.
- Kuhn, W., Kuhn, H., 1945. Bedeutung beschränkt freier drehbarkeit für die viskosität und stromungsdoppelbrechung von fadenmoleküllösungen, *J. Helv. Chim. Acta* 28, 1533.
- Rallison, J.M, Hinch, E.J, 1988. Do we understand the physics in the constitutive equation?, *J. of Non-Newtonian Fluid Mechanics*, 29, 37.
- Tanner R. I., 2000. *Engineering Rheology*, Pergamon, Oxford.
- Warner H. R., 1972. Kinetic theory and rheology of dilute suspension of finitely extendible dumbbells, *Ind. Eng. Chem. Fundam*, 11, 379.

9. Responsibility notice

The author(s) is (are) the only responsible for the printed material included in this paper