



Short communication

Alternative derivation of differential constitutive equations of the Oldroyd-B type

P.J. Oliveira

Departamento de Engenharia Electromecânica, Unidade de Materiais Têxteis e Papeleiros, Universidade da Beira Interior, 6201-001 Covilhã, Portugal

ARTICLE INFO

Article history:

Received 18 August 2008

Received in revised form 9 November 2008

Accepted 13 November 2008

Keywords:

Oldroyd models

Rheological equations of state

Differential constitutive equations

Modified FENE-P

ABSTRACT

Now that almost 60 years have passed since the pioneering works of J.G. Oldroyd it seems appropriate as an homage to consider here constitutive equations that can be viewed as generalisations of the by now classical Oldroyd-B model. In this short communication we shall address heuristically the theme of differential constitutive models and will provide an alternative way of deriving a “modified FENE” equation (FENE-M) and inter-relating the PTT and FENE-P-like models.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

In his 1950 classical paper, Oldroyd [1] set out the theoretical basis and principles required by all constitutive equations for the rheological macroscopic behaviour of any material to be physically well posed. Namely that the equations should be written under frame invariance form in co-ordinate systems convected with the material, a notion that came out to be known as the principle of objectivity. He then devised a general integro-differential form of constitutive equation which, under a simplified version with only three independent parameters (see also Oldroyd [2]), has since become one of the most cited and employed differential constitutive equations, the Oldroyd model equation for material B (Oldroyd-B):

$$\boldsymbol{\tau}_{tot} + \lambda \overset{\nabla}{\boldsymbol{\tau}}_{tot} = 2\eta_0 \left(\mathbf{D} + \lambda_r \overset{\nabla}{\mathbf{D}} \right) \quad (1)$$

This is the simplest model which is capable of representing basic viscoelastic behaviour of an incompressible liquid having a constant shear viscosity η_0 , and constant relaxation λ and retardation λ_r times; the symbol $\overset{\nabla}{\boldsymbol{\tau}}$ over the total extra stress tensor $\boldsymbol{\tau}_{tot}$ and the deformation rate tensor \mathbf{D} designates what is nowadays rightly called Oldroyd's upper convected derivative in honour of his influential and decisive contributions to the field of non-Newtonian fluid mechanics. With a simple mathematical manipulation it is possible to split the stress tensor in Eq. (1) into a Newtonian-like contribution of viscosity η_s (s for solvent, even if the fluid in question may

not be a polymer solution) and a polymer-related contribution:

$$\boldsymbol{\tau}_{tot} = \boldsymbol{\tau}_s + \boldsymbol{\tau}_p \quad (2)$$

$$\boldsymbol{\tau} + \lambda \overset{\nabla}{\boldsymbol{\tau}} = 2\eta_p \mathbf{D} \quad (3)$$

where we adopt the simplified notation $\boldsymbol{\tau} \equiv \boldsymbol{\tau}_p$ and η_p is the (constant) polymer viscosity, defined such that:

$$\eta_0 = \eta_s + \eta_p = \beta\eta_0 + (1 - \beta)\eta_0 \quad (4)$$

Decomposition (2) arises naturally in models derived from kinetic theory and is also employed in most numerical simulation works. The solvent viscosity ratio $\beta \equiv \eta_s/\eta_0$ can also be viewed as a retardation time ratio $\beta = \lambda_r/\lambda$.

An interesting and vivid account of Oldroyd's contributions to Rheology in the post-war years is provided in the book by Tanner and Walters [3] where the continuum mechanics approach of Oldroyd is contrasted with the “simple fluid expansion” theory followed by Coleman and Noll [4] in the USA. It would appear today that those two routes eventually lead to equivalent macroscopic differential constitutive equations, e.g. [5]. In later developments, to a large extent conducted by Bird and co-workers [6,7], the basis of constitutive modelling has shifted from a continuum mechanics approach to a more physically sound molecular-based approach also known as “kinetic theory” (in line with the kinetic theory of gases in statistical thermodynamics). Here one looks to a mechanical model for the basic constituent of the macromolecules forming a non-Newtonian liquid, decides on what are the main forces acting on it and thus defining its motion, and after a suitable averaging procedure over the large number of configurations of the basic models forming the structure of the polymer, one goes from the microstructure to the macrostructure relevant at the usual fluid mechanics level. In a beautiful confirmation of Oldroyd's physical

E-mail address: pjpo@ubi.pt.

insight, it has been shown that his “Oldroyd-B model” – proposed in his 1950 paper – is the only one of the continuum mechanics constitutive equations which may be derived without any closure approximation from kinetic theory, when the model for a macromolecule is just a pair of spheres connected by an Hookean spring – the dumbbell model. The derivation is very simple and follows from a balance of advection/affine deformation with the mean motion, and relaxation:

$$\overset{\nabla}{\mathbf{A}} = -\frac{\mathbf{A} - \mathbf{I}}{\lambda} \quad (5)$$

where $\mathbf{A} = \langle \mathbf{Q}\mathbf{Q} \rangle$ is the first moment of the end-to-end distance of the molecular model, averaged over the ensemble of configurations and suitably normalised. Having obtained the conformation tensor \mathbf{A} , we can then employ the following expression, due to Kramers [8], to calculate the “macroscopic” polymer stress which is required to form the momentum balance:

$$\boldsymbol{\tau} = \frac{\eta_p}{\lambda} (\mathbf{A} - \mathbf{I}). \quad (6)$$

In the present study, we have deliberately chosen to write the equations in terms of macroscopic parameters having a well-known meaning, namely the relaxation time λ and the polymer shear viscosity coefficient η_p , since our ultimate interest is to work with macroscopic, differential constitutive equations. In terms of the basic microstructure quantities, these are given by $\lambda = \zeta/4H$ and $\eta_p = nkT\lambda$ ($\zeta \equiv$ Newtonian drag coefficient on a sphere; $H \equiv$ Hookean spring constant; $n \equiv$ number of dumbbells per unit volume; $k \equiv$ Boltzmann constant; $T \equiv$ absolute temperature).

The fluid B equation of Oldroyd can then be readily derived by taking the convective derivative of Eq. (6) and assuming that both η_p and λ are constants (a feature to be relaxed in this short communication) together with the result $\overset{\nabla}{\mathbf{I}} = -2\mathbf{D}$, to obtain, with help of Eq. (5):

$$\lambda \overset{\nabla}{\boldsymbol{\tau}} = \eta_p \left(\overset{\nabla}{\mathbf{A}} - \overset{\nabla}{\mathbf{I}} \right) = \eta_p \left(-\frac{\mathbf{A} - \mathbf{I}}{\lambda} + 2\mathbf{D} \right)$$

and, if Eq. (6) is used again:

$$\lambda \overset{\nabla}{\boldsymbol{\tau}} = \eta_p \left(-\frac{\boldsymbol{\tau}}{\eta_p} + 2\mathbf{D} \right) \Rightarrow \lambda \overset{\nabla}{\boldsymbol{\tau}} + \boldsymbol{\tau} = 2\eta_p \mathbf{D}$$

the same as Eq. (3) above. This is a simple viscoelastic model which can represent, at least qualitatively, many physical phenomena such as purely elastic instabilities [9] or turbulent drag reduction [10]. However the Oldroyd-B model has a number of well-known limitations, the main one being the prediction of infinite extensional stresses at finite extensional rates. Such a limitation can be overcome by more realistic spring force models at the microscopic level: if the Hookean spring model for the interaction between the two dumbbell spheres is replaced by a Warner [11] spring model, which gets stiffer as the spring gets longer, then the problem with infinite extensibility is removed and we obtain the FENE-P model of Bird et al. [12].

This closed form constitutive model required a further approximation first suggest by Peterlin [13] in that the average of a fraction having quadratic terms was in fact replaced by the ratio of averages of square terms. Here a new model parameter arises, $b = HQ_0^2/kT$, which is related to the maximum possible extensibility of a macromolecule (Q_0). The model predicts a variable, shear-thinning polymer viscosity and also a shear-thinning first normal-stress coefficient $\psi_1 = N_1/\dot{\gamma}^2$. The function that controls the rate of decay of both $\eta_p(\dot{\gamma})$ and $\lambda(\dot{\gamma})$ will be designated here by f , and depends on the trace of the stress tensor and the parameter b .

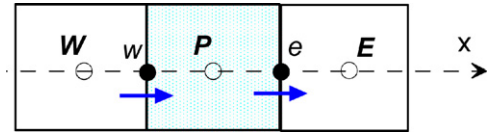


Fig. 1. Schematic of 1D control volumes to illustrate conservativeness.

An empirical adjustment was later proposed by Chilcott and Rallison [14], and used in many works subsequently under the designation of the FENE-CR model; it offers the advantage of a constant viscosity η_p but a shear-thinning relaxation time (or ψ_1), therefore enabling separation of pure elastic effects from shear-thinning viscosity effects which, from a basic standpoint, is very useful.

The aim of the present communication is to show that a modified version of the FENE-P constitutive equation can be derived by following a procedure similar to the one illustrated above for the Oldroyd-B equation, but with allowance for variable relaxation time and polymer viscosity. As a guiding principle for the heuristic derivation followed here, the final constitutive equations should be cast under a “conservative” form, and this topic is discussed in Section 2. The derivation itself is provided in Section 3 and in Section 4 results obtained with the modified model in simple homogeneous time-dependent shear and elongational flows are discussed and compared to predictions with the standard FENE-P model. Finally, some conclusions are given in Section 5. This work was presented at the conference on Complex Flows of Complex Fluids, in Liverpool, in a Session devoted to the memory of J.G. Oldroyd.

2. Background and conservative property

The notion of “conservativeness” was a crucial idea for the present paper as it allowed us to scrutinise and discriminate between constitutive equations. We base this on the fact that the conservative property [15] is necessary in order to obtain discretised equations for numerical simulation techniques that are consistent with the starting differential equations and, within the present context, it is necessary that the “effective” relaxation time λ_{ef} should appear inside the convective or substantial derivative:

$$\frac{D(\lambda_{ef}\boldsymbol{\tau})}{Dt} = \frac{\partial(\lambda_{ef}\boldsymbol{\tau})}{\partial t} + \text{div}(\lambda_{ef}\mathbf{u}\boldsymbol{\tau}) \quad (7)$$

In this way, when such terms are discretised by integration over control volumes, here illustrated in 1D as an example (Fig. 1), using basic interpolation schemes such as the Euler method for the time derivative term, we obtain:

$$\begin{aligned} \frac{\partial(\lambda_{ef}\boldsymbol{\tau})}{\partial t} + \text{div}(\lambda_{ef}\mathbf{u}\boldsymbol{\tau}) &\approx \frac{V_P[(\lambda_{ef}\boldsymbol{\tau})_P^{n+1} - (\lambda_{ef}\boldsymbol{\tau})_P^n]}{\Delta t} + \left(\lambda_{ef}\mathbf{u} \cdot \mathbf{A}\boldsymbol{\tau} \right)_{\text{flux-e}} \\ &- \left(\lambda_{ef}\mathbf{u} \cdot \mathbf{A}\boldsymbol{\tau} \right)_{\text{flux-w}} = \frac{V_P[\lambda_{ef,P}^{n+1}\boldsymbol{\tau}_P^{n+1} - \lambda_{ef,P}^n\boldsymbol{\tau}_P^n]}{\Delta t} \\ &+ \lambda_{ef,e}(\mathbf{u} \cdot \mathbf{A}\boldsymbol{\tau})_e - \lambda_{ef,w}(\mathbf{u} \cdot \mathbf{A}\boldsymbol{\tau})_w \end{aligned} \quad (8)$$

where V_P is the volume of the 1D cell centred at P and $\lambda_{ef,w}$ and $\lambda_{ef,e}$ are determined by interpolation of surrounding λ values. If the relaxation time λ_{ef} was outside the derivative, one would end up with $\lambda_{ef,P}$ on face “e” from integration over cell “P”, but the same flux seen from cell “E” would appear with a relaxation time $\lambda_{ef,E}$; therefore some inconsistency would arise.

We do not know how this notion of “conservativeness” can be established at the micro-structural level, when kinetic theory is applied to construct useful constitutive equations for non-Newtonian materials. However it is interesting to note that a

number of the constitutive equations derived from kinetic theory, in particular the most well-known, turn out to be “conservative”, while some versions of the basic models also in widespread use are not conservative. Next, we discuss in turn some of the common models in terms of whether or not they satisfy conservativeness.

Starting with the constant viscosity models which have mainly been developed to represent Boger fluids, and therefore separate elastic effects from shear-thinning effects, the Oldroyd-B model discussed above (Eq. (3)) is clearly conservative since λ is constant and the question does not arise $\lambda \dot{\tau} = (\dot{\lambda} \tau)$. As mentioned above, an empirical modification was devised by Chilcott and Rallison [14] with a view to limit the extensibility of the Hookean spring inherent to the Oldroyd-B model. This empiricism avoids the problems of infinite elongational viscosity while retaining a constant shear viscosity. The corresponding constitutive equation can be cast under the form (FENE-CR model):

$$\tau + \left(\frac{\lambda}{f} \dot{\tau} \right) = 2\eta_p \mathbf{D} \quad (9)$$

and is therefore conservative since the effective relaxation time ($\lambda_{eff} \equiv \lambda/f$) is inside the derivative. The model has been successfully employed by many workers, e.g. Grillet et al. [16] in viscoelastic cavity flows, and Rocha et al. [17] in cross-slot flow instabilities. A common simplification in steady flows is to consider that spatial variations of $1/f$ are unimportant, thus bringing the effective relaxation time out of the derivative to obtain the FENE-MCR model:

$$\tau + \frac{\lambda}{f} \dot{\tau} = 2\eta_p \mathbf{D} \quad (10)$$

first used by Coates et al. [18] in viscoelastic contraction flows and later by our own team in a number of studies, e.g. Oliveira [19] for vortex shedding of polymeric liquids. In many steady complex (both 2D and 3D) flows of interest there is almost no difference between numerical results obtained from the CR or the MCR models, and the later offers a simpler implementation when τ is used instead of \mathbf{A} . However, Eq. (10) is a non-conservative constitutive equation.

Based on network theory of rubber-like fluids, Phan Thien and Tanner [20,21] developed in 1977 the PTT model which is one of the most widespread non-linear models in use (cf. critical appraisal by Quinzani et al. [22]) and, when the lower convected term in the generalised Jaumann derivative is not considered, by setting the parameter $\xi = 0$ to avoid non-affine deformations, that constitutive equation is usually written as (PTT model):

$$f \tau + \lambda (\dot{\tau}) = 2\eta_p \mathbf{D} \quad (11)$$

with λ and η_p as constant model parameters with the usual meaning. By re-writing this equation as follows, to make clear the shear-thinning effect inherent in both the relaxation time and shear viscosity

$$\tau + \frac{\lambda}{f} \dot{\tau} = 2 \frac{\eta_p}{f} \mathbf{D} \quad (12)$$

it appears, at first sight, as non-conservative (λ/f is outside the derivative). However, the present analysis will show that the above equation may be cast under a conservative form, which arises naturally from the derivation adopted here.

Turning our attention to shear-thinning models of the FENE class referred to in the Introduction, the FENE-P in the original proposition by Bird et al. [12] later (slightly) modified in Bird et al.'s book [7] appears as

$$\lambda \dot{\tau} + Z \tau - \frac{D \ln Z}{Dt} [\lambda \tau + (1 - eb)nkT\lambda \mathbf{I}] = 2(1 - eb)nkT\lambda \mathbf{D} \quad (13)$$

where the stress function was given as

$$Z = 1 + \frac{3}{b} \left[(1 - eb) + \frac{tr(\tau)}{3nkT} \right], \quad \text{with } e = \frac{2}{b(b+2)}. \quad (14)$$

Again, it is not apparent that Eq. (13) is conservative. However, a straightforward manipulation allows us to write the model as

$$\tau + \left(\frac{\lambda}{f} \dot{\tau} \right) = 2 \frac{a\eta_p}{f} \mathbf{D} - \frac{D(a\eta_p/f)}{Dt} \mathbf{I} \quad \left(a = \frac{b+5}{b+2} \quad \text{and} \quad \eta_p = nkT\lambda \frac{b}{b+5} \right) \quad (15)$$

with $f = Z$ of Eq. (14) in agreement with the notation for the other models. Under this form, conservativeness is apparent, with the λ/f inside the convected derivative. In fact, an equation identical to Eq. (15) was derived in 1975 by Tanner [23], who applied a different approximation to deal with the configuration distribution function integrals that arise in the kinetic theory derivation, compared to the approach of Bird and co-workers. Acknowledging this fact, Bird has often referred to Eq. (13) as “Tanner’s equation” (e.g. [6,12]).

The aim of the next section is to obtain a useful constitutive equation that retains the idea of conservativeness while allowing for variable relaxation time λ and polymer viscosity η_p .

3. Derivation of modified equation

From the previous sections, it may be concluded that in general all the differential macroscopic constitutive equations discussed (Eqs. (9)–(15)) may be cast in terms of variable relaxation time and polymer shear viscosity coefficients

$$\lambda_{eff} = \frac{\lambda}{f_\lambda} \quad \text{and} \quad \eta_{p,eff} = \frac{\eta_p}{f_\eta}, \quad (16)$$

as

$$\tau + \left(\frac{\lambda}{f_\lambda} \dot{\tau} \right) = 2 \left(\frac{\eta_p}{f_\eta} \right) \mathbf{D} + \text{other terms} \quad (17)$$

with different functions f_λ and f_η of invariants of τ or \mathbf{D} for the various models, and where $1/f_\lambda$ in the second term on the LHS of Eq. (17) may be either inside or outside the convected derivative. It has become customary to express these functions in terms of the first invariant of the tensor τ , that is the trace of the stress $Tr(\tau) = \tau_{kk}$, and in particular the following forms have been adopted:

- For the FENE-CR and FENE-MCR models

$$f(\tau) \equiv f_\lambda(\tau) = \frac{L^2 + (\lambda/\eta_p)Tr(\tau)}{L^2 - 3}, \quad f_\eta(\tau) = 1; \quad (18)$$

- For the FENE-P model

$$f(\tau) \equiv f_\lambda(\tau) = f_\eta(\tau) = \frac{L^2 + (\lambda/a\eta_p)Tr(\tau)}{L^2 - 3}; \quad (19)$$

- For the PTT model

$$f(\tau) \equiv f_\lambda(\tau) = f_\eta(\tau) = 1 + \left(\frac{\lambda \varepsilon}{\eta_p} \right) Tr(\tau) \quad (20)$$

In these expressions L^2 is the square of the maximum average length of a dumbbell scaled with its equilibrium value, $L^2 \equiv 3Q_0^2/Q_{eq}^2$, having a similar meaning as the b parameter in the FENE-P model which was defined above (Section 1) in terms of micromolecular variables. The two are related by $b = L^2 - 3$ if $e = 0$ as in the original FENE-P [12], or by $b = L^2 - 5$ if $e = 2/b(b+2)$ [7]; in both cases $a = L^2/(L^2 - 3)$ in Eq. (19). In the Phan-Thien and Tanner model [20] two stress functions were initially proposed, a linear one, as above in Eq. (20), and an exponential form $f = \exp((\lambda \varepsilon/\eta_p)Tr(\tau))$ [21], which may be linearised to the same form as above if only the first two terms in the expansion are retained. While the exponential form is better suited to molten polymers, being able to give strain-softening

at high strain rates, the above linear form yields a maximum elongational viscosity proportional to ε , which is often designated as the elongational parameter of the model.

Now, to facilitate the explanation to follow, the polymer viscosity and the relaxation time are assumed to be variables, functions of some measure of τ , and expressed as

$$\eta_p = \eta_p(\tau) \quad \text{and} \quad \lambda = \lambda(\tau) \quad (21)$$

while for the constant zero-shear rate values we shall use the notation:

$$\eta_{p0} \quad \text{and} \quad \lambda_0. \quad (22)$$

From the definition of the upper-convected derivative it is easily concluded that when this operator is applied to any function multiplied by a tensor, one gets:

$$\overset{\nabla}{(f\mathbf{A})} = \left(\frac{Df}{Dt}\right)\mathbf{A} + (\mathbf{A})\overset{\nabla}{f}. \quad (23)$$

We shall assume in the present derivation that the relationship expressing equilibrium between rotation/stretching and relaxation is still valid

$$\overset{\nabla}{\mathbf{A}} = -\frac{\mathbf{A} - \mathbf{I}}{\lambda} \quad (24)$$

and that Kramers' expression [8] for the stress tensor

$$\boldsymbol{\tau} = \frac{\eta_p}{\lambda}(\mathbf{A} - \mathbf{I}) \quad (25)$$

also holds, even when both η_p and λ vary as a function of suitable invariant-dependent variables of the stress or deformation fields.

Applying the upper convected derivative to Eq. (25) gives:

$$\overset{\nabla}{(\lambda\boldsymbol{\tau})} = (\overset{\nabla}{\eta_p\mathbf{A}}) - (\overset{\nabla}{\eta_p\mathbf{I}}) = \frac{D\eta_p}{Dt}\mathbf{A} + \eta_p\overset{\nabla}{\mathbf{A}} - \frac{D\eta_p}{Dt}\mathbf{I} + 2\eta_p\mathbf{D} \quad (26)$$

where expression (23) for the derivative of a product and the result stated in the paragraph below Eq. (6) for the corresponding derivative of the unit tensor \mathbf{I} , were applied. Substituting now Eq. (24) for $\overset{\nabla}{\mathbf{A}}$ in Eq. (26) gives:

$$\overset{\nabla}{(\lambda\boldsymbol{\tau})} = 2\eta_p\mathbf{D} + \frac{D\eta_p}{Dt}(\mathbf{A} - \mathbf{I}) - \eta_p\frac{\mathbf{A} - \mathbf{I}}{\lambda}$$

and using Eq. (25) again results in:

$$\overset{\nabla}{(\lambda\boldsymbol{\tau})} + \boldsymbol{\tau} = 2\eta_p\mathbf{D} + \frac{\lambda\boldsymbol{\tau}}{\eta_p}\frac{D\eta_p}{Dt} \quad (27)$$

Hence the final expression for the modified FENE model (hereafter denoted FENE-M) is given by:

$$\overset{\nabla}{(\lambda\boldsymbol{\tau})} + \left(1 - \frac{\lambda}{\eta_p}\frac{D\eta_p}{Dt}\right)\boldsymbol{\tau} = 2\eta_p\mathbf{D} \quad (28)$$

where it is recalled from Eqs. (16), (21) and (22), both η_p and λ are known functions of the stress (or the strain rate):

$$\eta_p = \frac{\eta_{p0}}{f_\eta} \quad \text{and} \quad \lambda = \frac{\lambda_0}{f_\lambda}. \quad (29)$$

with

$$f_\eta(\tau) = \frac{L_\eta^2 + (\lambda/a\eta_p)\text{Tr}(\boldsymbol{\tau})}{L_\eta^2 - 3} \quad \text{and} \quad f_\lambda(\tau) = \frac{L_\lambda^2 + (\lambda/a\eta_p)\text{Tr}(\boldsymbol{\tau})}{L_\lambda^2 - 3} \quad (30)$$

in accord with Eq. (19).

In summary, the final equation for the FENE-M model, from Eq. (27) with the added term explicitly underlined, is given by

$$\overset{\nabla}{(\lambda\boldsymbol{\tau})} + \boldsymbol{\tau} = 2\eta_p\mathbf{D} + \frac{\lambda\boldsymbol{\tau}}{\eta_p}\frac{D\eta_p}{Dt} \quad (31)$$

and may be contrasted against the FENE-P equation written here under conservative form:

$$\overset{\nabla}{(\lambda\boldsymbol{\tau})} + \boldsymbol{\tau} = 2\eta_p\mathbf{D} - \frac{D\eta_p}{Dt}\mathbf{I} \quad (32)$$

with $\lambda = \lambda_0/f$ and $\eta_p = a\eta_{p0}/f$ where $f(\tau)$ is given by the function prescribed in Eq. (19). It is clear from (31) and (32) that the last underlined term is different in the two formulations and that, in addition, the modified form offers the possible advantage of allowing different functions for determining λ and η_p , while a single function is used in the FENE-P equation. Such separate control of relaxation time and polymer viscosity may be advantageous in precise, fine-tuning comparisons between predictions and experimental measurements.

A quantitative comparison between predictions of the two models for the basic time-dependent shear and extensional material functions is provided in the next section. It is interesting now to investigate the special case of the modified equation when the two functions f_λ and f_η take the same form f . Writing

$$\eta_p = \frac{\eta_{p0}}{f} \quad \text{and} \quad \lambda = \frac{\lambda_0}{f} \quad (33)$$

and introducing into Eq. (28), we obtain:

$$\lambda\overset{\nabla}{\boldsymbol{\tau}} + \boldsymbol{\tau}\frac{D\lambda}{Dt} + \left(1 - \frac{\lambda_0}{\eta_{p0}}\frac{D\eta_p}{Dt}\right)\boldsymbol{\tau} = 2\eta_p\mathbf{D}$$

or

$$\frac{\lambda_0}{f}\overset{\nabla}{\boldsymbol{\tau}} + \boldsymbol{\tau}\frac{D(\lambda_0/f)}{Dt} + \left(1 - \frac{\lambda_0}{\eta_{p0}}\frac{D(\eta_{p0}/f)}{Dt}\right)\boldsymbol{\tau} = 2\frac{\eta_{p0}}{f}\mathbf{D}$$

and after cancelling out the term multiplied by the stress tensor, we finally get the result:

$$\lambda_0\overset{\nabla}{\boldsymbol{\tau}} + f\boldsymbol{\tau} = 2\eta_{p0}\mathbf{D} \quad (34)$$

This equation, with the change of notation of λ for λ_0 , and η_p for η_{p0} , is nothing but the PTT equation (cf. Eq. (11)). It is therefore a beneficial additional outcome of the present derivation to allow a direct connection to be made between the apparently dissimilar FENE-P and PTT family of models. In some recent papers, in particular in Tanner and Nasser [24], a degree of familiarity has already been established between the network-based models, such as the PTT, and recent developments in reptation models like the Pom–Pom of McLeish and Larson [25], which were based on microphysical ideas following the older tube and reptation models of [26,27]. Just as here, the connection suggested in e.g. [24] is made at a macromolecular level, that is, by looking at the various macroscopic differential constitutive equations, rather than at a more detailed microphysical level.

4. Illustrative results

Steady-state material functions predicted by Eqs. (31) and (32) do coincide in rheometric homogeneous flows (such as simple steady shear and purely elongational flows) and so we shall consider here some simple transient flows. Of course, in complex steady flows differences will always arise due to the distinct convective viscosity terms. Fig. 2 shows curves of shear stress growth upon inception of shear flow as a function of time. Stresses are scaled in such a way that we effectively plot the transient shear viscosity function $((\eta^+(t, \dot{\gamma}) - \eta_s)/\eta_{p0})$; note: all results shown were obtained with $\eta_s = 0$ and time is scaled with the relaxation time, while the parameter for each curve is the imposed shear rate $\dot{\gamma}$ scaled as a Weissenberg number, $We = \lambda\dot{\gamma}$, and taking the values 1, 10 and 100. The solid lines are for the standard FENE-P model with $L^2 = 100$ ($b = 95$), a common mid-range value, and the dashed lines

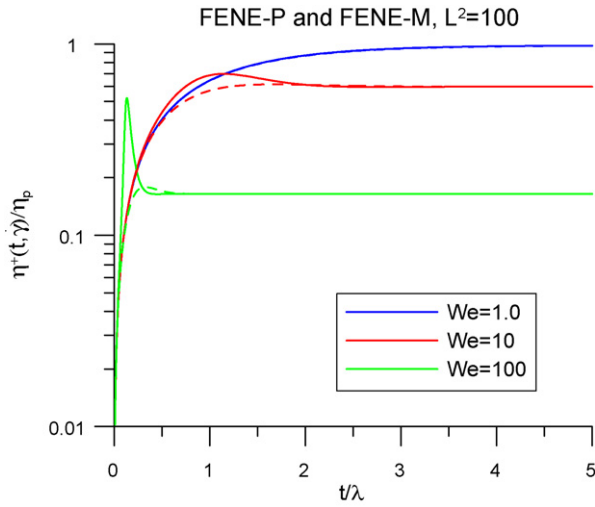


Fig. 2. Comparison of shear viscosity functions in the start-up of shear flow: FENE-P (solid lines) and FENE-M (dashed lines) at extensibility $L^2 = 100$ and various $We = \lambda \dot{\gamma}$.

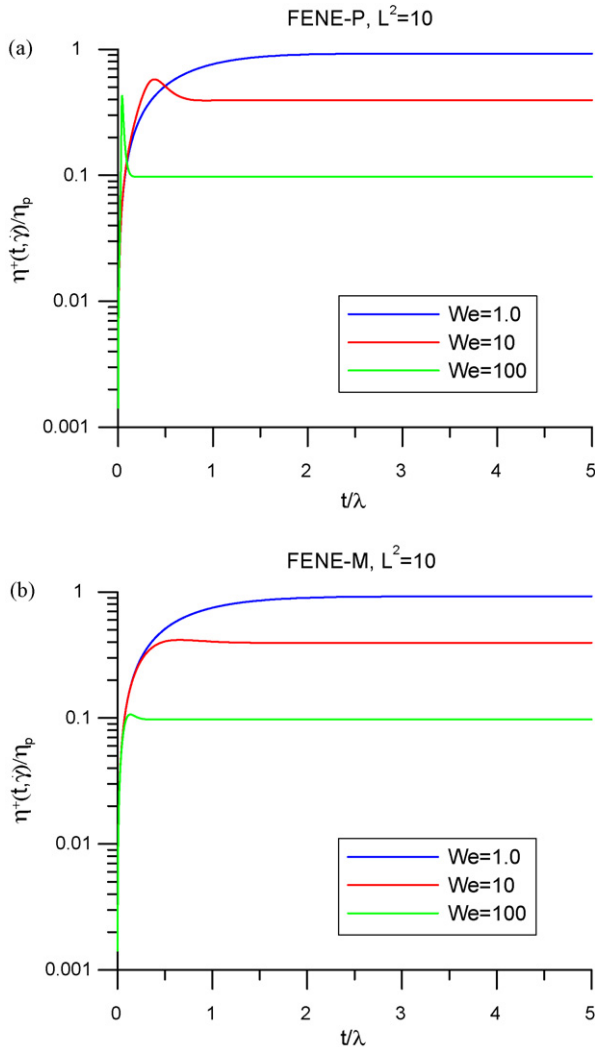


Fig. 3. Comparison of shear viscosity functions in the start-up of shear flow: (a) FENE-P and (b) FENE-M, at extensibility $L^2 = 10$ and various $We = \lambda \dot{\gamma}$.

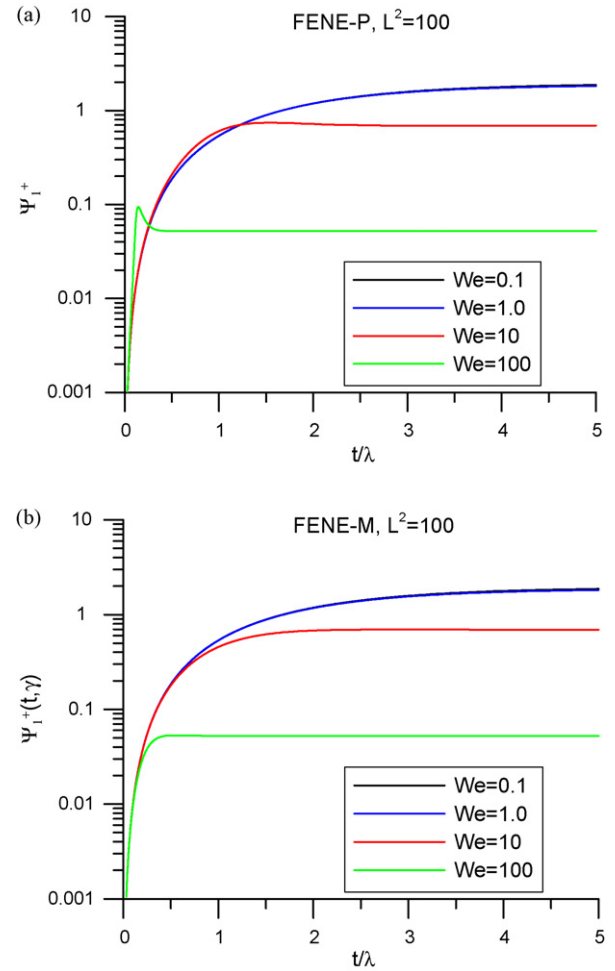


Fig. 4. Comparison of first normal-stress difference coefficients in the start-up of shear flow: (a) FENE-P and (b) FENE-M, at extensibility $L^2 = 100$ and various $We = \lambda \dot{\gamma}$.

are the corresponding results with the modified FENE model (FENE-M of Eq. (31)) with $L_\lambda^2 = L_\eta^2 = L^2 = 100$. Both models produce stress overshoots at high shear rates, although these are significantly accentuated for the FENE-P model, especially when $We \sim 100$, for which the limit imposed by the linear viscoelastic envelope (see Bird et al. [28]; pp. 118–123; 363–364) is violated. When η^+ is scaled with the steady-state $t \rightarrow \infty$ viscosity value, $\eta^+(t, \dot{\gamma})/\eta(\dot{\gamma})$, such an effect becomes even more visible; however, in spite of Bird et al's [28] suggestion that the linear limit ($We = 0$) needs to be respected as a rule, no theoretical proof of such an assertion could be found in the literature, where, it is fair to say, such a problem is hardly ever commented upon. The only reference we could find to this issue is a paper by DeAguiar [29], when a more sophisticated version of the FENE-P model was proposed for concentrated polymer solutions, the Bird-DeAguiar encapsulated FENE model, which was tested against measured data in start-up shear flows. While the experimental data used for comparison by DeAguiar (a 12% solution of polystyrene) fell below the linear viscoelastic envelope, his predictions with the encapsulated FENE model showed overshoots above that limit, much like the situation seen here with the FENE-P model in Figs. 2–4 (Note: Herrchen and Ottinger [32], in a paper discussed below, also mention this issue). A survey of the literature data on actual experiments with dilute and concentrated polymer solutions, such as those by Quinzani et al. [22] with a 5% PIB + C14 solution, shows that the measured start-up material functions remain within the linear viscoelastic limit.

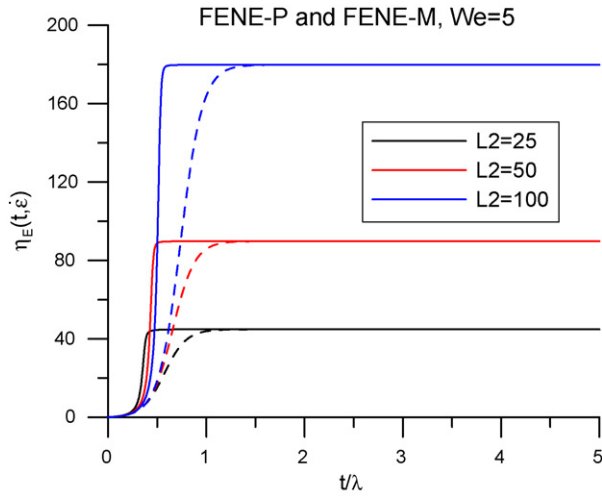


Fig. 5. Elongational viscosity in the start-up of uni-axial extensional flow: FENE-P (solid lines) and FENE-M (dashed lines) at $We = \lambda \dot{\epsilon} = 5$ and various extensibility parameters L^2 .

When the extensibility parameter is reduced to $L^2 = 10$, a rather low value which is nevertheless in use due to the critical comments by Purnode and Crochet [30] (see also [33]) regarding the lack of agreement between the physically expected range of L^2 and the values required for the model to predict the experimental data adequately, the predictions follow a trend similar to that of the previous paragraph. Again (Fig. 3a), the FENE-P viscosity growth shows high overshoots at small times, of order $1/We$ relaxation times, that violate the limit imposed by linear viscoelasticity, while the FENE-M (Fig. 3b) shows much reduced overshoots but within the envelope defined by linear viscoelasticity.

The time-dependent normal stresses in Fig. 4, represented as $\Psi_1^+(t, \dot{\gamma})$ versus t/λ , confirm the behaviour observed for the transient viscosity. The FENE-P model predicts localised overshoots that exceed the linear envelope, while the FENE-M model data remains within the limit imposed by the envelope and exhibits very smooth overshoots (almost imperceptible in Fig. 4).

In terms of start-up of uniaxial elongational flow, Fig. 5 shows the results for the two models, presented as elongational viscosity versus normalised time for various typical extensibility parameters

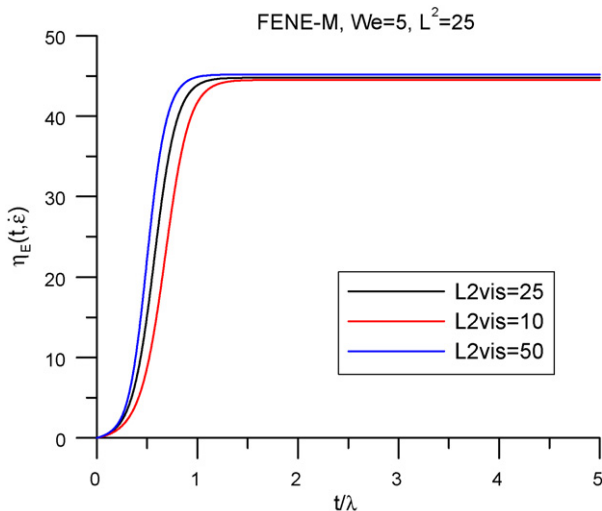


Fig. 6. Sensitivity to varying viscosity extensibility parameter L_{vis}^2 on the elongational viscosity in the start-up of uni-axial extensional flow. FENE-M at $We = \lambda \dot{\epsilon} = 5$ and $L^2 = 25$.

$L^2 = 25, 50$ and 100 . The modified model is represented by dashed lines and shows an asymptotic behaviour similar to the FENE-P, but with a much smoother growth of elongational stresses when the given elongational rate is applied (at $t=0$) and time proceeds. It is clear that the results with the FENE-M are much closer to the actual direct-simulation results with FENE dumbbells without Peterlin's closure approximation, cf. Keunings [31], Herrchen and Ottinger [32], and van Heel et al. [33], a feature that may be relevant to DNS simulations of turbulent flows with drag-reducing liquids. In this case it is important that the model used to represent viscoelasticity, which is averaged over a timescale compatible with the corresponding relaxation time (that is, these simulations are not actually DNS for $t < \lambda$), be able to predict reasonable time-dependent variations in extensionally dominated flows, which are more closely related to the actual flow in turbulent eddies. Clearly, in this respect the FENE-M does a better job than the FENE-P, as judged from the stochastic simulations where hundreds of thousands of FENE molecules are modelled in a flow [31–33].

With the new modified FENE-M model it is possible to have different functions controlling the shear-thinning decay of η_p and λ which is achieved indirectly through the two extensibility parameters L_{η}^2 and L_{λ}^2 as in Eq. (30). A sensitivity study of varying slightly L_{η}^2 around the base value of $L_{\eta}^2 = 25$ is shown in Fig. 6, where the extensional viscosity is plotted against the non-dimensional time in start-up of extensional flow. When L_{η}^2 is varied from 10 to 50 there is a reasonable range of extensional viscosities than can be fitted. Only with more careful measurements of the shear and extensional viscosities can we choose the correct values of those parameters (L_{η}^2 and L_{λ}^2) required in order to obtain quantitative fitting of experimental data, but it is clear that more flexibility is inherent to this model than the FENE-P.

5. Conclusions

A modified FENE-P model is derived heuristically (Eq. (31)) allowing for separate control of both the relaxation time and the polymer viscosity (Eq. (29)) by means of functions of the trace of the stress tensor similar to the Z function of the FENE-P (although with different extensibility parameters, L^2 or b , for λ and η_p , cf. Eqs. (19) and (30)). This modified model predicts overshoots of normal and shear stresses in start-up of shear flow that remain within the linear viscoelastic limit envelope, and the build up of normal stress in the start-up of steady elongational flow is much more gradual than it is with the FENE-P model, being more in-line with micro simulations with FENE dumbbells without closure assumptions. Interestingly, the modified FENE-P model becomes identical to the affine PTT equation ($\xi=0$) written under conservative form, when the two nonlinear spring force functions (f_{λ} and f_n) coincide.

Acknowledgements

The author would like to thank Fundação para a Ciência e Tecnologia (FCT) for financial support through project POCI/EME/58657/2004. The help of Dr. R.J. Poole for very careful proof-reading and correcting the original manuscript is also greatly acknowledged.

References

- [1] J.G. Oldroyd, On the formulation of rheological equations of state, Proc. R. Soc. A 200 (1950) 523–541.
- [2] J.G. Oldroyd, Non-Newtonian effects in steady motion of some idealized elastico-viscous liquids, Proc. R. Soc. A 245 (1958) 278–297.
- [3] R.I. Tanner, K. Walters, Rheology: An Historical Perspective, Elsevier, 1998.
- [4] B.D. Coleman, W. Noll, Foundations of linear viscoelasticity, Rev. Mod. Phys. 33 (1961) 239–249.

- [5] A.S. Lodge, J.H. Stark, On the description of rheological properties of viscoelastic continua: II Proof that Oldroyd's 1950 formalism includes all "simple fluids, *Rheol. Acta* 11 (1972) 119–126.
- [6] R.B. Bird, Kinetic theory of polymeric liquids, *Acc. Chem. Res.* 18 (1985) 364–371.
- [7] R.B. Bird, C.F. Curtiss, R.C. Armstrong, O. Hassager, *Dynamics of Polymeric Liquids*, vol. 2: Kinetic Theory, 2nd ed., John Wiley, New York, 1987.
- [8] H.A. Kramers, The behaviour of macromolecules in inhomogeneous flow, *J. Chem. Phys.* 14 (1946) 415–424.
- [9] M.A. Alves, R.J. Poole, Divergent flow in contractions, *J. Non-Newtonian Fluid Mech.* 144 (2007) 140–148.
- [10] T. Min, J.Y. Yoo, H. Choi, D.D. Joseph, Drag reduction by polymer additives in a turbulent channel flow, *J. Fluid Mech.* 486 (2003) 213–238.
- [11] H.R. Warner Jr., Kinetic theory and rheology of dilute suspensions of finitely extendible dumbbells, *Ind. Eng. Chem. Fundam.* 11 (1972) 379–387.
- [12] R.B. Bird, P.J. Dotson, N.L. Johnson, Polymer solution rheology based on a finitely extensible bead-spring chain model, *J. Non-Newtonian Fluid Mech.* 7 (1980) 213–235.
- [13] A. Peterlin, Hydrodynamics of macromolecules in a velocity field with longitudinal gradient, *J. Polym. Sci. Part B: Polym. Lett.* 4B (1966) 287–291.
- [14] M.D. Chilcott, J.M. Rallison, Creeping flow of dilute polymer solutions past cylinders and spheres, *J. Non-Newtonian Fluid Mech.* 29 (1988) 381–432.
- [15] P.J. Roache, *Computational Fluid Dynamics*, Hermosa Pub., 1970.
- [16] A.M. Grillet, B. Yang, B. Khomami, E.S.G. Shaqfeh, Modeling of viscoelastic lid driven cavity flow using finite element simulations, *J. Non-Newtonian Fluid Mech.* 88 (1999) 99–131.
- [17] G.N. Rocha, R.J. Poole, M.A. Alves, P.J. Oliveira, On extensibility effects in the cross-slot flow bifurcation, *J. Non-Newtonian Fluid Mech.* 156 (2009) 58–69.
- [18] P.J. Coates, R.C. Armstrong, R.A. Brown, Calculation of steady-state viscoelastic flow through axisymmetric contractions with the EEME formulation, *J. Non-Newtonian Fluid Mech.* 42 (1992) 141–188.
- [19] P.J. Oliveira, Method for time-dependent simulations of viscoelastic flows: vortex shedding behind cylinder, *J. Non-Newtonian Fluid Mech.* 101 (2001) 113–137.
- [20] N. Phan-Thien, R.I. Tanner, A new constitutive equation derived from network theory, *J. Non-Newtonian Fluid Mech.* 2 (1977) 353–365.
- [21] N. Phan-Thien, A nonlinear network viscoelastic model, *J. Rheol.* 22 (1978) 259–283.
- [22] L.M. Quinzani, R.C. Armstrong, R.A. Brown, Use of coupled birefringence and LDV studies of flow through a contraction to test constitutive equations for concentrated polymer solutions, *J. Rheol.* 39 (1995) 1201–1228.
- [23] R.I. Tanner, Stresses in dilute solutions of bead-nonlinear-spring micro-molecules. II. Unsteady flows and approximate constitutive relations, *Trans. Soc. Rheol.* 19 (1) (1975) 37–65.
- [24] R.I. Tanner, S. Nasser, Simple constitutive models for linear and branched polymers, *J. Non-Newtonian Fluid Mech.* 116 (2003) 1–17.
- [25] T.C.B. McLeish, R.G. Larson, Molecular constitutive equations for a class of branched polymers: the pom-pom polymer, *J. Rheol.* 42 (1998) 81–110.
- [26] P.G. De Gennes, Reptation of a polymer chain in the presence of fixed obstacles, *J. Chem. Phys.* 55 (1971) 572–579.
- [27] M. Doi, S.F. Edwards, *The Theory of Polymer Dynamics*, Clarendon Press, Oxford, 1986.
- [28] R.B. Bird, R.C. Armstrong, O. Hassager, *Dynamics of Polymeric Liquids*, vol. 1: Fluid Mechanics, 2nd ed., John Wiley, New York, 1987.
- [29] J.R. DeÁguar, An encapsulated dumbbell model for concentrated polymer solutions and melts. II. Calculation of material functions and experimental comparisons, *J. Non-Newtonian Fluid Mech.* 13 (1983) 161–179.
- [30] B. Purnode, M.J. Crochet, Polymer solution characterisation with the FENE-P model, *J. Non-Newtonian Fluid Mech.* 77 (2003) 1–20.
- [31] R. Keunings, On the Peterlin approximation for finitely extensible dumbbells, *J. Non-Newtonian Fluid Mech.* 68 (1997) 85–100.
- [32] M. Herrchen, H.C. Ottinger, A detailed comparison of various FENE dumbbell models, *J. Non-Newtonian Fluid Mech.* 68 (1997) 17–42.
- [33] A.P.G. van Heel, M.A. Hulsen, B.H.A.A. van den Brule, On the selection of parameters in the FENE-P model, *J. Non-Newtonian Fluid Mech.* 75 (1998) 253–271.