The Charged FENE-P Dumbbell model: explaining the rheology of dilute polyelectrolyte solutions

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A robust model of dilute polyelectrolyte solutions is constructed based on kinetic theory arguments. The polyelectrolyte molecules are modelled by finitely elongated non-linear elastic dumbbells with beads carrying identical effective charges. The electric interaction between the beads is described in a simplified way through an electrostatic Coulomb force. With two pre-averaging approximations, the constitutive equations of the fluid model are formulated in closed form; and its rheological properties in steady and transient shear and elongational flows are investigated by analytical and simple numerical means. It is found that despite its simplicity, the model shows an excellent qualitative agreement with the results obtained by advanced numerical simulations of polyelectrolyte solutions and predicts most of the experimentally observed features of such fluids.

1. Introduction

Polymeric liquids – liquids containing extremely long molecules – are of great importance for modern engineering and biotechnological applications. On the contrast to liquids consisting of small molecules, polymeric liquids are non-Newtonian: they do not obey the laws of classical fluid mechanics and often behave strictly opposite to what one could expect from “ordinary” fluids (Bird et al.\textsuperscript{1987a}, ch. 2).

Some synthetic and biological polymers are polyelectrolytes: They dissociate in water and become electrically charged. The segments of polyelectrolyte molecules carry electric charges of identical sign: this leads to repulsive electric forces, acting between different parts of the molecular chain. Such forces make polyelectrolyte molecules more rigid, and therefore mechanically different from their electrically neutral analogues.

One of the specific features of polyelectrolytes is that their rheological properties are strongly sensitive to kind and amount of ions present in the solvent. When the charged segments of a polyelectrolyte molecule attract ions of the opposite sign, e.g. from a dissolved salt, they effectively lose charge due to screening. The polymer molecules change their dynamical properties and become more flexible, which strongly affects the rheological behaviour of the solution (Lake\textsuperscript{1989}).

Two major fields where flows of polyelectrolyte solutions are important, are biotechnology (Spagnolie\textsuperscript{2014}; Maitz\textsuperscript{2015}) and enhanced oil recovery (Lake\textsuperscript{1989}; Weaver et al.\textsuperscript{2011}). In both cases, transient flows in non-trivial geometries are involved. In addition, the salinity of the solvent may vary, making the flows of polyelectrolytes more complicated compared to those of uncharged polymers.

To understand the dynamics of such flows – even qualitatively – it is necessary to use

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advanced tensor models based on microscopic physics to adequately describe the forces
governing the fluid motion; and these models must take the polyelectrolyte nature of the
polymer into account. Dumbbell models (Bird et al. 1987b, ch. 13-14) are a relatively
simple class of fluid models for polymer solutions, derived from microscopic kinetic
theory. Each polymer molecule is thought of as composed of two identical spherical
beads connected by a spring (elastic dumbbell) or simply a rigid rod (rigid dumbbell).
The configuration of each dumbbell is completely specified by the connector vector, $Q$,
pointing from one bead to another. Then, the properties of the molecules are defined by
the connector force law, $F_c(Q)$. In particular, the Warner force law (Warner 1972) has
been found physically relevant:

$$F_c(Q) = \frac{HQ}{1 - (Q/Q_0)^2}.$$  

This law describes a non-linear spring of finite extensibility: the extension of the spring
cannot exceed $Q_0$, and the spring is Hookean with stiffness $H$ at small extensions.
Finite extensibility proves to be a crucial property for understanding the flow of polymer
solutions. The resulting macroscopic fluid model is known as the FENE (finitely elongated
non-linear elastic) dumbbell model (Armstrong 1974a,b). A pre-averaging approximation
(closure) made by Peterlin (1966) allows to formulate the constitutive equations in closed
form, facilitating both analytical investigation and numerical simulations of the fluid
model. This updated version of the model is now known as FENE-P (“P” for Peterlin)
and is probably the best dumbbell model to date. It is, however, restricted to electrically
neutral or weakly hydrolysed polymers.

The pioneering attempt of constructing a dumbbell model describing polyelectrolyte
solutions is that of King & Eisenberg (1972), who considered a Hookean dumbbell
model modified by the presence of effective charges, interacting through an electrostatic
Coulomb force. Then, Dunlap & Leal (1984) constructed an analogous fluid model
based on FENE dumbbells; however, they adopted conformation-dependent friction.
No closed-form constitutive equation was derived; and numerical simulations revealed
a hysteretic behaviour of viscosity and relative elongation with respect to flow strength.
Ait-Kadi et al. (1988) extended this work and formulated a constitutive equation for the
model of Dunlap & Leal (1984), using a conformation tensor approach. Since then, the
focus has been kept on implementing advanced numerical methods and improving the
modelling of the electric repulsion between the charged polyelectrolyte parts: Andrews
et al. (1998) considered screened Coulombic interactions using Nonequilibrium Brownian
Dynamics and Configuration-Biased Monte Carlo simulations of charged Fraenkel bead-
spring-chains; Jiang & Chen (2001) studied the impact of taking electroviscous effects
into account; and Zhou & Chen (2006) investigated numerically the role played by
hydrodynamic interaction.

In the present research, we are aiming at developing an effective phenomenological fluid
model, which can be used to understand the rheology of polyelectrolyte solutions and
describe qualitatively their behaviour in complex flows. Such a model must encapsulate
all the crucial features of polyelectrolytes: orientability, non-linearity, finite extensibility,
and variable intrinsic rigidity of the molecules – and at the same time be as simple
as possible without suffering from pathologies of early kinetic theory models. For these
reasons, we take the successful FENE-P dumbbell model as our starting point. Although
screened Coulombic interactions (with Debye-Hückel approximation) are a proper way
to describe the repulsion between charged parts of polyelectrolyte molecules, this would
also lead to substantial mathematical complexity. Therefore, we adopt the concept of
The paper is organised as follows. In section 2, the underlying assumptions of the new polymer fluid model are specified and the closed-form constitutive equations are derived. Then, the constitutive equations are used to obtain the material functions predicted by the model; the results for steady and transient flows are presented in sections 3 and 4, respectively. Section 5 is devoted to explaining how the specific model parameter \( E \) can in principle be related to actual concentration of salt in the solvent. The results are discussed in section 6; and conclusions are presented in section 7.

Throughout the paper, SI units are used. Scalars (such as density \( \rho \), temperature \( T \) and shear rate \( \dot{\gamma} \)) are written with lightface italic font; vectors (such as force \( \mathbf{F} \) and velocity \( \mathbf{v} \)) – with boldface Latin; while second-order tensors (like rate-of-strain tensor \( \dot{\gamma} \) and stress tensor \( \tau \)) – with boldface Greek. For the stress tensor, the sign convention of Bird et al. (1987a) is adopted.

2. The constitutive equations

The FENE dumbbell model is assumed applicable when the solution is sufficiently dilute, so that the polymer molecules interact with the molecules of the Newtonian solvent much stronger than with each other. The polymer-solvent interactions are typically described by an isotropic Stokes’s law with conformation-independent coefficient \( \zeta \) (Bird et al. 1987b §13.1). It has been found that macroscopically the polymer contribution to the stress tensor of the solution depends on three parameters: the ”ideal-gas” pressure \( nkT \) (where \( n \) is the number concentration of the dumbbells, \( k \) Boltzmann’s constant, and \( T \) the thermodynamic temperature); the dimensionless non-linearity parameter \( b = HQ^2/kT \); and a time constant, which we shall find it most convenient to define by:

\[
\lambda = \lambda_Q = \frac{Q^2}{12kT}.
\]

More commonly, \( \lambda_H = 3\lambda_Q/b = \zeta/4H \) is used in literature. Our alternative choice of the time constant will be motivated below.

In order to describe qualitatively the electric repulsion between the charged sections of the polyelectrolyte chain, we assume the beads to carry identical effective charges \( q \) and the relative permittivity of the solvent to be \( \varepsilon \). This modifies the connector force by an additional electrostatic Coulomb force, so that

\[
F_c = \frac{HQ}{1 - (Q/Q_0)^2} - \frac{q^2}{4\pi\varepsilon_0\varepsilon} \frac{Q}{Q^3}, \tag{2.2}
\]

where \( \varepsilon_0 \) is the permittivity of vacuum.

Like for other dumbbell models, the stress tensor dilute polymer solutions can be split into a sum of solvent and polymer contributions:

\[
\tau = \tau_s + \tau_p. \tag{2.3}
\]

Of these the latter, \( \tau_p \), can be written in two forms – the Kramers form and the Giesekus form, respectively (Kramers 1944; Giesekus 1962; see also Bird et al. 1987b §13.3):

\[
\tau_p = -n\langle QF_c \rangle + nkT\delta, \tag{2.4}
\]

\[
\tau_p = \frac{1}{4}n\zeta\langle QQ \rangle_{(1)}. \tag{2.5}
\]
Here the angular brackets denote the configuration-space average, see \cite{Bird1987b} §13.1 for details; $\delta$ is the unit tensor; while the subscript "(1)" stands for the upper-convected time derivative, introduced by Oldroyd \cite{Oldroyd1950} to express the rate of change of tensor properties of a fluid element in a coordinate system deforming with the fluid.

Substituting the modified connector force \eqref{eq:modified_force} into the Kramers expression for the stress tensor \eqref{eq:stress_tensor}, one gets:

$$
\tau_p = -nH\left\langle \frac{QQ}{1 - (Q/Q_0)^2} \right\rangle + \frac{\eta a^2}{4\pi\varepsilon_0\varepsilon} \left\langle \frac{QQ}{Q^3} \right\rangle + nkT\delta. \quad \text{(2.6)}
$$

In order to obtain the constitutive equation in closed form, this expression must be approximated by pre-averaging the first two terms. This is implemented as follows:

$$
\left\langle \frac{QQ}{1 - (Q/Q_0)^2} \right\rangle \approx \left\langle \frac{QQ}{Q_0^2} \right\rangle, \quad \text{(2.7)}
$$

$$
\left\langle \frac{QQ}{Q^3} \right\rangle \approx \left\langle \frac{QQ}{(Q_0^2)^{3/2}} \right\rangle. \quad \text{(2.8)}
$$

Approximation \eqref{eq:approx_1} is the Peterlin’s closure, introduced when he established the FENE-P dumbbell polymer model \cite{Peterlin1966}. The corresponding approximation for the Coulomb term, \eqref{eq:approx_2}, is established by analogous arguments. We propose the abbreviation C-FENE-P for the present extended polymer model, where ”C” stays for ”charged”.

In what follows, it will be convenient to introduce the dimensionless ratio

$$
E = \frac{q^2/4\pi\varepsilon_0\varepsilon Q_0}{kT} \quad \text{(2.9)}
$$

between the characteristic potential energy of the electric repulsion and the thermal energy scale of the dumbbells. Larger values of $E$ correspond to ”stiffer” dumbbells, i.e. to increased electrostatic repulsion between the beads. In the limit $E \to 0$, the original (uncharged) FENE-P model is recovered, while the dumbbells become rigid as $E \to \infty$.

Furthermore, we introduce the mean-square relative dumbbell elongation, $x$, as:

$$
x = \left\langle \frac{Q^2}{Q_0^2} \right\rangle. \quad \text{(2.10)}
$$

Making use of pre-averaging approximations \eqref{eq:approx_1} - \eqref{eq:approx_2} and notations \eqref{eq:dimensionless_ratio} - \eqref{eq:mean_square_elongation}, \eqref{eq:stress_tensor} can be rewritten as:

$$
\tau_p = -nH\frac{\left\langle QQ \right\rangle}{1 - x} + nH \frac{E}{b} \frac{\left\langle QQ \right\rangle}{x^{3/2}} + nkT\delta. \quad \text{(2.11)}
$$

With the definition of the C-FENE-P $Z$-factor as:

$$
Z = \frac{1}{1 - x} \frac{E}{b} \frac{1}{x^{3/2}}, \quad \text{(2.12)}
$$

\eqref{eq:stress_tensor} reduces to:

$$
\tau_p = -nHZ\left\langle QQ \right\rangle + nkT\delta. \quad \text{(2.13)}
$$

Expression \eqref{eq:final_stress_tensor} is identical in form to the corresponding equation of the FENE-P dumbbell model \cite{Bird1980}. One can still proceed by taking the Oldroyd derivatives of both sides of the equation, eliminating $\left\langle QQ \right\rangle_{(1)}$ using the Giesekus form of the stress tensor \eqref{eq:stress_tensor_giesekus} and then eliminating $\left\langle QQ \right\rangle$ using \eqref{eq:final_stress_tensor} once more. The result is:

$$
\frac{b}{3}Z\tau_p + \lambda \tau_{p(1)} - \lambda \{\tau_p - nkT\delta\} \frac{D_t}{\ln Z} = -nkT\lambda \dot{\gamma}, \quad \text{(2.14)}
$$
where $\dot{\gamma} = (\nabla v) + (\nabla v)^T$ is the rate-of-strain tensor, while $D_t$ stands for the material derivative. This result is identical to the constitutive equation of the FENE-P dumbbells. Thus, the difference between the FENE-P and the C-FENE-P models is exclusively the appearance of $E$ in the $Z$-factor.

Taking the trace of (2.11) and making some simple rearrangements, one arrives at:

$$Zx = 3 \frac{b}{E} \left( 1 - \frac{\text{tr} \tau_p}{3nkT} \right). \tag{2.15}$$

Combining this with the definition of the $Z$-factor (2.12) leads to the following algebraic equation for $x$:

$$\frac{1}{1-x} - \frac{E}{b\sqrt{x}} = Z_0, \tag{2.16}$$

where

$$Z_0 = 1 + 3 \frac{b}{E} \left( 1 - \frac{\text{tr} \tau_p}{3nkT} \right) \tag{2.17}$$

is the $Z$-factor of the original FENE-P dumbbell model.

In order to facilitate the solution of equation (2.16) with respect to $x$, we introduce $X = 1/x$. Then, (2.16) becomes:

$$\left( Z_0 - 1 \right) + \frac{E}{b\sqrt{X}} = \frac{1}{X - 1}. \tag{2.18}$$

We further introduce $F(s, \alpha)$ as the unique real solution of the equation

$$s + \alpha\sqrt{y} = \frac{1}{y - 1} \tag{2.19}$$

with respect to $y$, assuming $\alpha \geq 0$ and $s > 0$. Some properties of this function will be used in this research. In particular, at fixed $s$, $F$ is a monotonically decreasing function of $\alpha$; and at fixed $\alpha$, $F$ is monotonically decreasing as $s$ increases. Furthermore, $F(s, \alpha) > 1$ on its domain, with

$$\lim_{s \to \infty} F(s, \alpha) = \lim_{\alpha \to \infty} F(s, \alpha) = 1; \tag{2.20}$$

and finally, $F(s, 0) = 1 + 1/s$. Then:

$$X = F(Z_0 - 1, E/b); \tag{2.21}$$

and from (2.15):

$$Z = (Z_0 - 1)F(Z_0 - 1, E/b). \tag{2.22}$$

The constitutive equations are therefore completely formulated through expressions (2.14), (2.17), and (2.22).

One observes that the C-FENE-P dumbbell model contains four parameters: $(nkT)$, $b$, $\lambda$, and $E$. Of these, the first three are precisely those of the original FENE-P dumbbell model, while $E$ is specific to C-FENE-P and describes the intrinsic rigidity of polyelectrolyte molecules: A larger value of $E$ implies a more rigid molecule. This parameter also accounts for salt-sensitivity of polyelectrolyte molecules, the connection between $E$ and the actual salt concentration in the solvent being inverse: higher salinity means lower values of $E$, and vice versa.

Finally, we consider the rigid dumbbell limit, $E \to \infty$. From (2.19) it follows that $y \to 1$ when $\alpha \to \infty$ for a finite $s$. So, one has $F(Z_0 - 1, \infty) = 1$ for finite $Z_0$. This is in agreement with physical expectations: infinitely strong electric repulsion would extend the spring to the upper limit, so that $Q \to Q_0$ and $x \to 1$. This result leads to a new
polymer fluid model with constitutive equations:

\[
Z_{RDB} \tau_p + \lambda \tau_{p(1)} - \lambda \{ \tau_p - nkT \delta \} D_t \ln Z_{RDB} = -nkT \lambda \dot{\gamma},
\]

(2.23)

\[
Z_{RDB} = 1 - \frac{\text{tr} \tau_p}{3nkT}.
\]

(2.24)

We shall refer to this model as the rigid dumbbell (RDB) polymer model. Another rigid dumbbell model, derived using physical assumptions different from ours, has been introduced and investigated earlier by Bird et al. (1971); for details, see (Bird et al. 1987b, ch. 14) and references therein. The two models share a lot of similarities, but they are not equivalent. A detailed comparison between them lies beyond the scope of the present work and shall be discussed elsewhere. In what follows, ”RDB” will refer to the polymer model formulated by (2.23)-(2.24).

Note that neither \(H\) nor \(b\) appear explicitly in (2.23) and (2.24). Moreover, \(H\), and therefore \(b\), is not defined for the rigid dumbbells. As a result, the commonly adopted microscopic time scale \(\lambda_H\) is not applicable in the RDB limit; but \(\lambda_Q\), defined by (2.1), is independent of \(H\) and hence provides a universal microscopic time scale for the FENE-P, C-FENE-P, and RDB models. This justifies our choice \(\lambda = \lambda_Q\).

3. Steady flow material functions

In sections 3 and 4 we shall present the material functions predicted by the C-FENE-P dumbbell and RDB fluid models for some standard flow regimes. The contribution of the Newtonian solvent to the material functions is well understood; therefore, only the polymer contribution to the material functions will be discussed.

3.1. Steady shear flow

Steady shear flow can be locally described by a fluid velocity field given by:

\[
v_1 = v_1(x_2), \quad v_2 = v_3 = 0,
\]

(3.1)

the stress tensor and its Oldroyd derivative having the form:

\[
\tau = \begin{bmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{12} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix} \quad \text{and} \quad \tau_{(1)} = -\begin{bmatrix} 2\tau_{12} & \tau_{22} & 0 \\ \tau_{22} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \dot{\gamma}_{12},
\]

(3.2)

respectively. The rate-of-strain tensor has only one independent non-zero component \(\dot{\gamma} \equiv \dot{\gamma}_{12} = \dot{\gamma}_{21}\), and the three standard steady shear flow material functions – non-Newtonian viscosity, first normal stress coefficient (FNSC), and second normal stress coefficient (SNSC) – are defined, respectively, by:

\[
\tau_{12} = -\eta(\dot{\gamma})\dot{\gamma},
\]

(3.3)

\[
\tau_{11} - \tau_{22} = -\Psi_1(\dot{\gamma})\dot{\gamma}^2,
\]

(3.4)

\[
\tau_{22} - \tau_{33} = -\Psi_2(\dot{\gamma})\dot{\gamma}^2.
\]

(3.5)

The left-hand sides of (3.4) and (3.5) are called the first and the second normal stress differences (FNSD and SNSD), respectively.
Substituting (3.2) into the constitutive equation (2.14) yields:

\[
\frac{b}{3}Z\tau_{11} = 2\lambda\tau_{12}\dot{\gamma}, \quad (3.6)
\]

\[
\frac{b}{3}Z\tau_{12} = -nkT\lambda\dot{\gamma}, \quad (3.7)
\]

\[
\tau_{22} = \tau_{33} = 0. \quad (3.8)
\]

In all but the form of \(Z\) these equations are identical to those arising in the FENE-P dumbbell model. It follows from (3.6)-(3.7) that the FNSC is directly proportional to the square of the viscosity, the coefficient of proportionality being independent of \(E\); and, according to (3.8), the SNSC vanishes identically:

\[
\Psi_1(\dot{\gamma}) = \frac{2}{nkT}\eta^2(\dot{\gamma}), \quad (3.9)
\]

\[
\Psi_2(\dot{\gamma}) = 0. \quad (3.10)
\]

Having eliminated \(\tau_{11}\) from (3.6)-(3.7), one arrives at the following non-linear algebraic relation between the shear stress and the shear rate:

\[
\left(1 + \frac{2\mathcal{I}_{12}^2}{3}\right) \mathcal{F}\left(\frac{3 + 2\mathcal{I}_{12}^2}{b}, \frac{E}{b}\right) \mathcal{I}_{12} = -\lambda\dot{\gamma}, \quad (3.11)
\]

where \(\mathcal{I}_{12} = \tau_{12}/(nkT)\). Equation (3.11) can be solved numerically to calculate steady shear flow properties of the C-FENE-P dumbbells for arbitrary values of \(b\) and \(E\).

The influence of \(E\) on the relative elongation of the dumbbells in steady shear flow is shown in figure 1, left. In general, a higher value of \(E\) leads to larger spring extensions, as expected. This effect is very pronounced at equilibrium and at low-to-medium shear rates. At higher shear rates, the dumbbells are stretched almost to the upper limit by the flow, so that the influence of \(E\) becomes small.

The predicted impact of salinity on the non-Newtonian viscosity is shown in figure 1, right. The C-FENE-P dumbbells demonstrate shear-thinning behaviour, which is typical for polymer solutions. Decreasing \(E\), which is equivalent to increasing the solvent salinity, leads to two noticeable effects. Firstly, the non-Newtonian viscosity decreases at fixed shear rate values. The relative reduction in viscosity is largest at small shear rates and decreases as the shear rate increases, vanishing when \(\dot{\gamma} \to \infty\). Secondly, the onset of shear-thinning is shifted towards higher shear rates.

The asymptotic behaviour of the viscosity curves governed by (3.11) can be studied analytically. At very low shear rates, the viscosity approaches its zero-shear-rate value

\[
\eta_0 = \frac{nkT\lambda}{\mathcal{F}(3/b, E/b)}, \quad (3.12)
\]

which is highly sensitive to \(E\). In the FENE-P limit \((E = 0)\), this result simplifies to:

\[
\eta_{0,FENE} = \frac{3}{b + 3}nkT\lambda; \quad (3.13)
\]

and in the RDB limit \((E \to \infty)\), the zero-shear-rate viscosity is:

\[
\eta_{0,RDB} = nkT\lambda. \quad (3.14)
\]

At very high shear rates, the asymptotic behaviour of the viscosity curves in the RDB, C-FENE-P, and FENE-P models is identical, independent of \(E\), and described by:

\[
\eta \approx \sqrt[3]{\frac{2}{3}} nkT\lambda(\lambda\dot{\gamma})^{-2/3}. \quad (3.15)
\]
Figure 1. The mean-square relative elongation $x$ in steady shear flow (left) and the scaled polymer contribution to the non-Newtonian viscosity (right), as predicted by the C-FENE-P dumbbell model. Both are plotted as functions of the dimensionless shear rate $\lambda \dot{\gamma}$. The viscosity is scaled with respect to the zero-shear-rate viscosity of the FENE-P dumbbells. Different curves correspond to different values of $E$. The coloured lines show the limiting cases $E = 0$ and $E \to \infty$. The black lines are drawn at $\log_{10} E$ varying from $-1$ to $3$ (left) and from $0$ to $3$ (right) with a step of $0.25$, bottom up; the solid black lines correspond to integer values of $\log_{10} E$. The value of the non-linearity parameter, $b$, is set to a moderate value of 50.

Finally, in the FENE-P and RDB limits, exact analytical solutions of (3.11) can be obtained. That for the FENE-P dumbbells is well known and can be found, e.g. in (Shogin et al. 2017). In the RDB limit, (3.11) reduces to the following cubic equation for $T_{12}$:

$$\left(1 + \frac{2T_{12}^3}{3}\right)T_{12} = -\lambda \dot{\gamma}. \tag{3.16}$$

This equation has one real solution, which can be obtained, e.g. using the methods described by La Nave & Mazur (2002). The result is:

$$\frac{\eta_{RDB}}{\eta_0, RDB} = \frac{-2^{1/3} + \left(3A + \sqrt{2 + 9A^2}\right)^{2/3}}{2^{2/3} A \left(3A + \sqrt{2 + 9A^2}\right)^{1/3}}, \tag{3.17}$$

where $A = \lambda \dot{\gamma}$ is the dimensionless shear rate.

### 3.2. Steady shearfree flow

The steady simple shearfree flow velocity field is:

$$v_1 = \frac{1}{2} \dot{\varepsilon}x_1, \quad v_2 = \frac{1}{2} \dot{\varepsilon}x_2, \quad v_3 = \dot{\varepsilon}x_3, \tag{3.18}$$

where $\dot{\varepsilon}$ is the time-independent elongation rate, which can take positive and negative values. At $\dot{\varepsilon} > 0$, the flow is called elongational; at $\dot{\varepsilon} < 0$, it is referred to as biaxial stretching.

The rate-of-strain tensor, the stress tensor, and the Oldroyd derivative of the latter
The C-FENE-P dumbbell model

are all diagonal:

\[ \dot{\gamma} = \text{diag}(-\dot{\varepsilon}, -\dot{\varepsilon}, 2\dot{\varepsilon}), \]  
\[ \tau = \text{diag}(\tau_{11}, \tau_{22}, \tau_{33}), \]  
\[ \tau_{(1)} = \text{diag}(\tau_{11}, \tau_{22}, -2\tau_{33})\dot{\varepsilon}, \]

with \( \tau_{11} = \tau_{22} \) due to the flow symmetry. The only material function characterising the fluid in this type of flow is the elongational, or extensional, viscosity, defined by:

\[ \tau_{33} - \tau_{11} = -\bar{\eta}(\dot{\varepsilon})\dot{\varepsilon}. \]  

Substituting (3.19)-(3.21) into the constitutive equation (2.14) leads to:

\[ \frac{b}{3} Z\tau_{11} + \lambda \dot{\varepsilon}\tau_{11} = nkT\lambda \dot{\varepsilon}, \]  
\[ \frac{b}{3} Z\tau_{33} - 2\lambda \dot{\varepsilon}\tau_{33} = -2nkT\lambda \dot{\varepsilon}. \]

Having replaced \( \tau_{11}, \tau_{33}, \) and \( \dot{\varepsilon} \) with dimensionless quantities

\[ T = \frac{2\tau_{11} + \tau_{33}}{nkT}, \]  
\[ D = \frac{\tau_{11} - \tau_{33}}{nkT}, \]  
\[ \Lambda = \lambda \dot{\varepsilon}, \]

one arrives after simple rearrangements at:

\[ \frac{b}{3} ZT + 2\Lambda D = 0, \]  
\[ \frac{b}{3} ZD + \Lambda(T - D) = 3\Lambda. \]

Equations (3.28)-(3.29) can be solved by standard numerical methods. The impact of \( E \) on the elongational viscosity of the C-FENE-P dumbbells is illustrated in figure 2, right. It can be seen that the C-FENE-P dumbbells show elongational thickening at \( \dot{\varepsilon} > 0 \). An increase in salinity (hence, a decrease in \( E \)) leads to an overall drop in the elongational viscosity. The local minimum in \( \bar{\eta} \) at negative elongation rates, which vanishes in the RDB limit, becomes more pronounced as salinity increases.

One can also keep track of the mean-square relative elongation, \( x \), which is shown in figure 2, left. The elongation is smallest at equilibrium and follows the trends similar to those of \( \bar{\eta} \) at \( \dot{\varepsilon} > 0 \).

Some properties of the elongational viscosity curves can be obtained by analytical means. In particular, (3.29) can be used to calculate \( \bar{\eta}_0 \), the elongational viscosity at zero elongation rate. Considering the limit \( \dot{\varepsilon} \to 0 \) and using (3.12) and (3.22) yields the relation \( \bar{\eta}_0 = 3\eta_0 \), which also holds for Newtonian fluids.

At very large positive or negative elongation rates (in the limit \( |\dot{\varepsilon}| \to \infty \)), the relative extension of the dumbbells approaches one; hence, the asymptotic behaviour of the C-FENE-P and FENE-P dumbbells must be identical to that of the RDB model. In the RDB limit, equations (3.28)-(3.29) become:

\[ \left(1 - \frac{T}{3}\right) T + 2\Lambda D = 0, \]  
\[ \left(1 - \frac{T}{3}\right) D + \Lambda(T - D) = 3\Lambda. \]
Figure 2. The mean-square relative elongation $x$ in steady elongational flow (left) and the scaled polymer contribution to the elongational viscosity (right) of the C-FENE-P dumbbells, plotted as a function of the dimensionless elongation rate $\dot{\lambda}$. Different curves correspond to different values of $E$: $E = 0$ and $E \to \infty$ (coloured lines); and $\log_{10} E$ varying from 0 to 3 with a step of $0.25$ (black lines bottom up, solid lines corresponding to integer values of $\log_{10} E$). The value of non-linearity parameter $b = 50$.

This system has three solutions, of which only one:

$$\mathcal{T} = \frac{3}{2} \left(1 - A - \sqrt{1 - 2A + 9A^2}\right),$$

$$\mathcal{D} = \frac{3}{4} \left(-1 + 5A + \sqrt{1 - 2A + 9A^2}\right),$$

provides $\mathcal{T} = \mathcal{D} = 0$ at equilibrium ($A = 0$) and hence is physically relevant. It is seen that at $A \to \infty$, $\mathcal{D} \sim 6A$, and at $A \to -\infty$, $\mathcal{D} \sim 3/2A$. This means that for all the models under consideration (FENE-P, C-FENE-P, and RDB), $\bar{\eta}$ approaches $\bar{\eta}_{+\infty} = 6nkT\lambda$ at large positive elongation rates and $\bar{\eta}_{-\infty} = (3/2)nkT\lambda$ at large negative elongation rates. Equation (3.33) also provides an exact analytical expression for the elongational viscosity in the RDB limit:

$$\frac{\bar{\eta}(A)}{\bar{\eta}_{0,RDB}} = \frac{-1 + 5A + \sqrt{1 - 2A + 9A^2}}{4A}.\tag{3.34}$$

4. Transient shear flow material functions

4.1. Small-amplitude oscillatory shear flow

In small-amplitude oscillatory shear (SAOS) flow, the fluid velocity field is given by:

$$v_1 = \dot{\gamma}_{12}(t)x_2, \quad v_2 = v_3 = 0,$$ \hspace{1cm} (4.1)

where the harmonically oscillating shear rate

$$\dot{\gamma}_{12}(t) = \dot{\gamma}_{21}(t) = \dot{\gamma}_0 \cos(\omega t)$$ \hspace{1cm} (4.2)

is the only independent non-zero component of the rate-of-strain tensor. Here $\dot{\gamma}_0$ is the amplitude of oscillations, and $\omega$ is the angular frequency. The latter is assumed very small, so that the dependency of the stress tensor components on $\dot{\gamma}_0$ is completely described by the lowest-order terms (first order for the shear stresses and second for the normal
stresses). The stress tensor of a fluid undergoing SAOS flow has the general form

\[
\tau(t) = \begin{bmatrix}
\tau_{11}(t) & \tau_{12}(t) & 0 \\
\tau_{12}(t) & \tau_{22}(t) & 0 \\
0 & 0 & \tau_{33}(t)
\end{bmatrix},
\]

(4.3)

with

\[
\tau(t) = \partial_t \tau - \begin{bmatrix}
2\tau_{12}(t) & \tau_{22}(t) & 0 \\
\tau_{22}(t) & 0 & 0 \\
0 & 0 & 0
\end{bmatrix} \dot{\gamma}_{12}(t).
\]

(4.4)

For polymer solutions, the shear stress oscillates around zero with frequency \(\omega\); however, on the contrast to Newtonian liquids, the oscillations are not in phase with those of the shear rate. The normal stresses also oscillate around non-zero mean values with the double frequency \(2\omega\) (Bird et al. 1987a §3.4). The properties of the fluid in SAOS flow are then described by eight material functions defined by:

\[
\tau_{12} = -\eta'(\omega)\dot{\gamma}_0 \cos(\omega t) - \eta''(\omega)\dot{\gamma}_0 \sin(\omega t),
\]

(4.5)

\[
\tau_{11} - \tau_{22} = -\Psi_1^d(\omega)\dot{\gamma}_0^2 - \Psi_1^s(\omega)\dot{\gamma}_0^2 \cos(2\omega t) - \Psi_1''(\omega)\dot{\gamma}_0^2 \sin(2\omega t),
\]

(4.6)

\[
\tau_{22} - \tau_{33} = -\Psi_2^d(\omega)\dot{\gamma}_0^2 - \Psi_2^s(\omega)\dot{\gamma}_0^2 \cos(2\omega t) - \Psi_2''(\omega)\dot{\gamma}_0^2 \sin(2\omega t).
\]

(4.7)

Six of these functions are often combined to form the complex quantities \(\eta' + i\eta'', \Psi_1^d, i\Psi_1^s, \Psi_2^d, i\Psi_2^s, \Psi_2''\), called the complex viscosity, the complex FNSC, and the complex SNSC, respectively; \(\Psi_1^d\) and \(\Psi_2^d\) are the first and the second normal stress displacement coefficients. The in-phase (“real”) components, \(\eta', \Psi_1^d, \Psi_2^d\), describe the direct response of the fluid and can be associated with energy loss due to dissipation. The out-of-phase (“imaginary”) components, \(\eta'', \Psi_1^s, \Psi_2^s\), arise because the long polymer molecules do not react instantly to rapid flow changes. This leads to a latency, described by phase shifts. This latency can be interpreted as “elasticity” of the flow and associated with energy storage (Ferry 1980; Mezger 2014).

One can also replace the complex viscosity components, \(\eta'\) and \(\eta''\), by the storage and loss moduli, \(G'\) and \(G''\), defined, respectively, by:

\[
G' = \eta' \omega, \quad G'' = \eta'' \omega.
\]

(4.8)

These (“elastic”) moduli are often considered in literature and measured in experiments. The expressions for the SAOS flow material functions of the C-FENE-P dumbbells can be obtained analytically. Substituting (4.3)-(4.4) into the constitutive equation (2.14), keeping only the lowest-order terms in \(\dot{\gamma}_{12}\), combining and rearranging the scalar equations, one gets:

\[
(\tau_{11} - \tau_{33}) + \lambda_e \partial_t (\tau_{11} - \tau_{22}) - 2\lambda_e \tau_{12} \dot{\gamma}_{12} = 0,
\]

(4.9)

\[
(\tau_{22} - \tau_{33}) + \lambda_e \partial_t (\tau_{22} - \tau_{33}) = 0,
\]

(4.10)

\[
\tau_{12} + \lambda_e \dot{\tau}_{12} = -\eta_0 \dot{\gamma}_{12},
\]

(4.11)

where we have introduced the ”experimental” time constant \(\lambda_e\) by

\[
\lambda_e(b, E) = \frac{\eta_0}{nkT} = \frac{\lambda}{F(3/b, E/b)}.
\]

(4.12)

with \(\eta_0\) as the zero-shear-rate viscosity of the C-FENE-P dumbbells given by (3.12). Substituting (4.5)-(4.7) turn equations (4.9)-(4.11) into identities which hold for all values of \((\omega t)\). This leads to eight algebraic equations for the material functions. Then, the SAOS flow material functions can be written in scaled form as functions of the dimensionless
frequency, $\Lambda_e = \lambda_e \omega$:

\[
\frac{\eta'}{\eta_0} = \frac{1}{1 + \Lambda^2_e}, \quad (4.13)
\]

\[
\frac{\eta''}{\eta_0} = \frac{\Lambda_e}{1 + \Lambda^2_e}, \quad (4.14)
\]

\[
\frac{\Psi_1^d}{\Psi_{1,0}} = \frac{1}{2(1 + \Lambda^2_e)}, \quad (4.15)
\]

\[
\frac{\Psi_1'}{\Psi_{1,0}} = \frac{1 - 2\Lambda^2_e}{2(1 + \Lambda^2_e)(1 + 4\Lambda^2_e)}, \quad (4.16)
\]

\[
\frac{\Psi_1''}{\Psi_{1,0}} = \frac{3\Lambda_e}{2(1 + \Lambda^2_e)(1 + 4\Lambda^2_e)}, \quad (4.17)
\]

while the three material functions describing the SNSD – $\Psi_2^d$, $\Psi_2'$, and $\Psi_2''$ – all vanish.

Then, the elastic moduli can be written as:

\[
\frac{G'}{nkT} = \frac{\Lambda^2_e}{1 + \Lambda^2_e}, \quad (4.18)
\]

\[
\frac{G''}{nkT} = \frac{\Lambda_e}{1 + \Lambda^2_e}. \quad (4.19)
\]

The scaled material functions, given by equations (4.13)-(4.19), are shown in figure 3, where they are plotted against $\Lambda_e$. It can be seen that the in-phase component $\eta'$ of the complex viscosity, associated with energy loss, is a monotonic function of frequency. As follows from (4.13), $\eta' \rightarrow \eta_0$ at low frequencies, and shows a well-pronounced power-law region ($\eta' \sim \omega^{-2}$) at high frequencies.

The out-of-phase component $\eta''$ of the complex viscosity, associated with energy storage, increases linearly at low frequencies ($\eta'' \sim \omega$) and declines slowly at high frequencies ($\eta'' \sim \omega^{-1}$). The maximum value $\eta'' = \eta_0/2$ of this function at $\Lambda_e = 1$ is also the intersection between the $\eta'$ and $\eta''$ curves.

The first normal stress displacement coefficient, $\Psi_1^d$, is a decreasing function of frequency. At low frequencies, $\Psi_1^d \rightarrow \Psi_{1,0}/2$; and at high frequencies, $\Psi_1^d \sim \omega^{-2}$.

The real component of the complex FNSC, $\Psi_1'$, is the only SAOS material function of the C-FENE-P model which can take negative values. At very low frequencies, $\Psi_1' \rightarrow \Psi_{1,0}/2$. At low-to-moderate frequencies, $\Psi_1'$ decreases with frequency, becoming zero at $\Lambda_e = 1/\sqrt{2} \approx 0.707$, and continues to decline until the minimum point

\[
\Psi_1' = \left(\frac{2\sqrt{2}}{3} - 1\right)\Psi_{1,0} \approx -0.057\Psi_{1,0} \quad (4.20)
\]

is reached at

\[
\Lambda_e = \left[\frac{3 + \sqrt{2}}{2\sqrt{2}}\right]^{1/2} \approx 1.249. \quad (4.21)
\]

Thereafter, $\Psi_1'$ starts to increase with frequency, approaching zero from below, with $\Psi_1' \sim \omega^{-2}$ at high frequencies.

The imaginary component of the complex FNSC, $\Psi_1''$, increases linearly at low frequencies ($\Psi_1'' \sim \omega$), reaching a maximum value of

\[
\Psi_1'' = \frac{9}{23 + 5\sqrt{73}}\Psi_{1,0} \approx 0.316\Psi_{1,0} \quad (4.22)
\]
Figure 3. The scaled polymer contribution to the material functions of the C-FENE-P dumbbells in SAOS flow, plotted against the experimental dimensionless frequency $\lambda_e \omega$. Top left: the complex viscosity components. Top right: the elastic moduli. Bottom: the complex FNSC components and the first normal stress displacement coefficient.

at

$$\Lambda_e = \frac{1}{2} \left[ \frac{\sqrt{73} - 5}{6} \right]^{1/2} \approx 0.384,$$

and decays quickly at large frequencies ($\Psi_1'' \sim \omega^{-3}$).

The storage modulus, $G'$, is a monotonically increasing function of frequency. At low frequencies, $G' \sim \omega^2$. At high frequencies, it tends to a constant value, $G'/nkT \to 1$.

The loss modulus, $G''$, increases linearly ($G'' \sim \omega$) at low frequencies, reaching a maximum value $G'' = nkT/2$ at $\Lambda_e = 1$, and then decreases slowly to zero, with $G'' \sim \omega^{-1}$ at high frequencies. The $G'$ and $G''$ curves intersect at the maximum point of $G''$.

Expressions (4.13)-(4.19) show that the SAOS material functions of the C-FENE-P, FENE-P, and RDB fluid models can be written in the same form. However, this form is not suitable for visualising the impact of $E$, since all the scaling factors depend on $E$. To investigate the $E$-dependence, we reformulate (4.13)-(4.19) using salinity-independent scaling factors: the zero-shear-rate viscosity and the zero-shear-rate FNSC of the FENE-P dumbbells, $\eta_0,FENE$ and $\Psi_{1,0,FENE}$, in place of $\eta_0$ and $\Psi_{1,0}$; and $\lambda$ in place of $\lambda_e$.

The dependence of the in-phase complex viscosity component on $E$ is shown in figure 4, top left. It is seen that a decrease in $E$ leads to a reduction in $\eta'$ at lower frequencies, but to an increase in $\eta'$ at higher frequencies; and the onset of “frequency-thinning” is shifted towards higher frequency values as $E$ decreases.
Figure 4. The scaled polymer contribution to the complex viscosity components (top) and the elastic moduli (bottom) of the C-FENE-P dumbbell solution undergoing SAOS flow, plotted against the dimensionless frequency \( \lambda \omega \). Both components are scaled with respect to the zero-shear-rate viscosity of the FENE-P dumbbells. The curves for different values of \( E \) are shown: \( E = 0 \) and \( E \to \infty \) (coloured lines); and \( \log_{10} E \) varying from \(-1\) to 2 with a step of 0.25 (black lines bottom up at low frequencies, solid lines corresponding to integer values of \( \log_{10} E \)). The non-linearity parameter \( b = 50 \).

The impact of \( E \) on the out-of-phase complex viscosity component is visualised in figure 4 top right. A decrease in \( E \) mostly affects the low- and mid-frequency regions of the curves: the values of \( \eta'' \) are reduced, and the maximum is shifted towards higher frequencies. At very high frequencies, \( E \) has no effect on \( \eta'' \): the curves of the C-FENE-P, FENE-P, and RDB models are asymptotically identical.

The storage and loss moduli are found to depend on \( E \) in a relatively simple way, see figure 4 bottom. If the curves are plotted using a log-log scale, a reduction in \( E \) results in a translation of both \( G' \) and \( G'' \) curves to the right; the maximum values of both moduli thus remain unchanged.

The \( E \)-dependence of the SAOS material functions related to the FNSD is shown in figure 5. At low and moderate frequencies, \( \Psi_{1}'' \) is affected in a way similar to \( \eta \) (figure 5 bottom), and \( \Psi_{1}'' \) - similar to \( \eta'' \) (figure 5 top right). The impact of \( E \) on \( \Psi_{1}' \) is more complex, but still follows the same general trend: A decrease in \( E \) leads to an overall reduction in the magnitude of \( \Psi_{1}' \) and shifts the characteristic points towards higher frequencies (figure 5 top left). At high frequencies, all three material functions are insensitive to \( E \).
4.2. Start-up and relaxation of steady shear flow

Start-up and relaxation of steady shear flow are two closely related transient shear flows. The velocity field in these flows is described by (4.1); the stress tensor and its Oldroyd derivative are given by (4.3)-(4.4); while the only independent non-zero component of the rate-of-strain tensor is:

\[ \dot{\gamma}(t) \equiv \dot{\gamma}_{12}(t) = \dot{\gamma}_{21}(t) = \dot{\gamma}_0 H(\pm t), \tag{4.24} \]

where \( \dot{\gamma}_0 \) is a constant, and \( H(t) \) is the Heaviside step-function; by this reason, these flows are known in experimental rheology as step-rate tests, see e.g. [Mezger 2014].

Choosing the positive sign in (4.24) corresponds to the start-up case. The fluid is at rest at \( t < 0 \); a constant shear rate \( \dot{\gamma}_0 \) is suddenly applied at \( t = 0 \); and after a while, shear and normal stresses build up and reach their steady shear flow values.

On the contrast, the negative sign in (4.24) yields the relaxation case, which is the inverse situation. The fluid undergoes steady shear flow with constant shear rate \( \dot{\gamma}_0 \) at \( t < 0 \); the flow is instantaneously stopped (the shear rate is removed) at \( t = 0 \); and the stresses decay after some time, as the fluid returns to equilibrium.
The material functions of the fluid in this kind of flow are defined by:

\[
\tau_{12} = -\eta^\pm(\dot{\gamma}_0, t)\dot{\gamma}_0, \quad (4.25)
\]

\[
\tau_{11} - \tau_{22} = -\Psi^\pm_1(\dot{\gamma}_0, t)\dot{\gamma}_0^2, \quad (4.26)
\]

\[
\tau_{22} - \tau_{33} = -\Psi^\pm_2(\dot{\gamma}_0, t)\dot{\gamma}_0^2, \quad (4.27)
\]

and are known as the shear stress, FNSD, and SNSD growth (+) or relaxation (−) functions, respectively. When presented graphically, these material functions are commonly normalised using their steady-state values \(\eta(\dot{\gamma}_0), \Psi_1(\dot{\gamma}_0), \) and \(\Psi_2(\dot{\gamma}_0).\)

Substituting (4.3)-(4.4) into the constitutive equation of the C-FENE-P dumbbells (2.14), introducing dimensionless quantities

\[
T_{12} = \frac{\tau_{12}}{nkT}, \quad (4.28)
\]

\[
T = \frac{\tau_{11} + \tau_{22} + \tau_{33}}{nkT}, \quad (4.29)
\]

\[
D_1 = \frac{\tau_{11} - \tau_{22}}{nkT}, \quad (4.30)
\]

\[
D_2 = \frac{\tau_{22} - \tau_{33}}{nkT}, \quad (4.31)
\]

\[
\bar{t} = t/\lambda, \quad (4.32)
\]

\[
\Lambda(\bar{t}) = \lambda(\dot{\gamma}_0)H(\pm \bar{t}), \quad (4.33)
\]

and rearranging leads to the following system of ordinary differential equations:

\[
\frac{b}{3} Z T_{12} + \partial_{\bar{t}} T_{12} - T_{12} \partial_{\bar{t}} \ln Z = -\Lambda(\bar{t}), \quad (4.34)
\]

\[
\frac{b}{3} Z T + \partial_{\bar{t}} T - (T - 3) \partial_{\bar{t}} \ln Z - 2T_{12} \Lambda(\bar{t}) = 0, \quad (4.35)
\]

\[
\frac{b}{3} Z D_1 + \partial_{\bar{t}} D_1 - D_1 \partial_{\bar{t}} \ln Z - 2T_{12} \Lambda(\bar{t}) = 0, \quad (4.36)
\]

\[
\frac{b}{3} Z D_2 + \partial_{\bar{t}} D_2 - D_2 \partial_{\bar{t}} \ln Z = 0. \quad (4.37)
\]

The expression for the \(Z\)-factor, (2.22), completes the system. The initial conditions can be imposed at any fixed \(\bar{t} < 0,\) where the stress tensor components are set to zero (start-up case) or to their steady shear flow values (relaxation case).

Since \(D_2 = 0\) both in equilibrium and in steady shear flow (see section 3.1), it follows from (4.37) that \(D_2(\bar{t}) = 0\) identically. The rest of the system can be solved numerically. We are using the standard methods implemented in Wolfram Mathematica for this purpose.

The results for the start-up case are shown in figure 6. At very low values of \(\lambda\dot{\gamma}_0\) the material functions grow monotonically, approaching their steady-state values (figure 6 top). At higher \(\lambda\dot{\gamma}_0\), they typically undergo one or several oscillations around the steady-state value before they stabilise; and a stress overshoot, i.e. a time interval where the stresses are higher than their steady-state values, is clearly seen (figure 6 middle and bottom). The overshoot, however, is not observed in the RDB limit. It it also seen that at higher \(\lambda\dot{\gamma}_0\), the relative magnitude of overshoots increases and their points of maximum are shifted towards earlier times; it takes less time for the stresses to approach their steady-state values; and for any fixed \(\lambda\dot{\gamma}_0\), the shear stress builds up and stabilises faster than the FNSD.

The material functions describing the start-up case depend strongly on \(E\). At low \(\lambda\dot{\gamma}_0\),
Figure 6. The normalised polymer contribution to the shear stress (left) and FNSD (right) growth functions of the C-FENE-P dumbbells, plotted against the dimensionless time $t/\lambda$ at $\lambda\gamma_0 = 10$ (top); $\lambda\gamma_0 = 100$ (middle); and $\lambda\gamma_0 = 500$ (bottom). The coloured lines show the limiting cases $E = 0$ and $E \to \infty$. The black lines are drawn at $\log_{10} E$ varying from $-1$ to $3$ with a step of $0.25$, bottom up at late times; solid black lines correspond to integer values of $\log_{10} E$. All curves are plotted at $b = 50$.

A decrease in $E$ results in a general increase in $\eta^+ / \eta(\gamma_0)$ and $\Psi_1^+ / \Psi_1(\gamma_0)$ (figure 6 top). At higher values of $\lambda\gamma_0$, the impact of $E$ becomes more complex. Firstly, a shear stress overshoot appears (figure 6 middle left and bottom left). As $E$ decreases, the overshoot is shifted towards later times. At the same time, the overshoot magnitude increases, passes a maximum, and then decreases, reaching its final value in the FENE-P dumbbell limit ($E = 0$). The situation is qualitatively similar for the FNSD (figure 6 middle right and bottom right); however, the FNSD overshoot magnitude increases monotonically as $E$ decreases, reaching its maximal value at $E = 0$. 

The C-FENE-P dumbbell model
In other words, an increase in solvent salinity can either increase or decrease the relative shear stress overshoot, depending on values of $\lambda \dot{\gamma}_0$ and $E$; but always increases the FNSD overshoot.

The numerical results for the relaxation case are presented in figure 7. Both the shear stress and the FNSD relaxation functions decay monotonically, quickly approaching zero; the curves for $\eta^-/\eta(\dot{\gamma}_0)$ and $\Psi_1^-/\Psi_1(\dot{\gamma}_0)$ overlap. At higher $\lambda \dot{\gamma}_0$ (figure 7, bottom), equilibrium is reached faster than at lower $\lambda \dot{\gamma}_0$ (figure 7, top).

At later times, the material functions decay exponentially. In figure 7, this is seen as regions where the curves become straight lines. The exponential decay is preceded by a region of faster-than-exponential decrease at early times. An analysis of the system (4.34)-(4.37) shows that the eigenvalues of its linearised version corresponding to $T_{12}$ and $D_1$ both equal $-\mathcal{F}(3/b, E/b)$; hence,

$$\frac{\eta^-}{\eta(\dot{\gamma}_0)} \sim \frac{\Psi_1^-}{\Psi_1(\dot{\gamma}_0)} \sim \exp[-\mathcal{F}(3/b, E/b)t]$$

asymptotically. Our numerical simulations confirm this result.

The impact of $E$ on $\eta^-$ and $\Psi_1^-$ is two-fold. Firstly, the region of fast decrease at early times, which is abrupt and step-like at large $E$, becomes smoother and less pronounced, as $E$ decreases (figure 7 right). Secondly, a decrease in $E$ leads to a faster decay rate.
in the exponential regime at late times, since \( \mathcal{F}(3/b, E/b) \) is a decreasing function of \( E \). This effect is seen in figure [7] left.

5. Relating \( E \) to actual salt concentration

Although qualitative understanding of polyelectrolyte flows is our primary goal, it is also important to find a way to relate the model parameter \( E \) to the actual concentration of salt in the solution. Here we demonstrate that this relation can be established from a set of measurements of a single material function – the non-Newtonian viscosity.

According to Stavland et al. (2013), the impact of salinity can be quantified using the relative retained zero-shear-rate intrinsic viscosity, \( \chi \), defined by:

\[
\chi = \frac{[\eta] - [\eta]_{\infty \text{sal}}}{[\eta]_{0 \text{sal}} - [\eta]_{\infty \text{sal}}},
\]

where \([\eta]\), \([\eta]_{0 \text{sal}}\), and \([\eta]_{\infty \text{sal}}\) are the values of the zero-shear-rate intrinsic viscosity at a particular salt concentration, at zero salinity, and at very high ("infinite") salinity, respectively. Since for dilute solutions the intrinsic viscosity is directly proportional to the polymer contribution to the non-Newtonian viscosity, (5.1) can be written as:

\[
\chi = \frac{\eta_0(E) - \eta_0(0)}{\eta_0(0) - \eta_0(E_0)},
\]

with \( E = E_0 \) at zero salinity and \( E \to 0 \) at large salt concentrations (note that \( \chi = 1 \) at zero salinity and \( \chi \to 0 \) at very high salinities). For the C-FENE-P dumbbells, using (3.12) and rearranging, one gets:

\[
\mathcal{F}(3/b, E/b) = \frac{(b + 3)\chi^{-1}\mathcal{F}_0}{b + 3 + 3\mathcal{F}_0(\chi^{-1} - 1)},
\]

where \( \mathcal{F}_0 = \mathcal{F}(3/b, E_0/b) \). On the other hand, from the definition of \( \mathcal{F}(s, \alpha) \) and (2.18),

\[
E = \frac{b + 3 - 3\mathcal{F}(3/b, E/b)}{(\mathcal{F}(3/b, E/b) - 1)\sqrt{\mathcal{F}(3/b, E/b)}}.
\]

Combining this with (5.3) results in:

\[
E = -\frac{(3 + b)(3 + b - 3\mathcal{F}_0)}{(3 + b - 3\mathcal{F}_0 - b\chi^{-1}\mathcal{F}_0)\sqrt{\frac{(3 + b)\chi^{-1}\mathcal{F}_0}{3 + b + 3(\chi^{-1} - 1)\mathcal{F}_0}}}.
\]

This dependency of \( E \) on the solvent salinity (expressed through \( \chi^{-1} \)) at different \( E_0 \) is shown in figure [8] It is seen that \( E \to E_0 \) at \( \chi^{-1} \to 1 \), corresponding to zero salinity; while at high salinities (at large values of \( \chi^{-1} \)) and/or low \( E_0 \), \( E \sim \chi \).

Finally, \( \chi \) can be directly related to salinity of the solvent by experiments. In particular, Stavland et al. (2013) have established that for partially hydrolysed polyacrylamide solutions, \( \chi = (1 + KI)^{-\alpha} \), were \( I \) is the so-called modified ionic strength, completely determined by the concentration and type of salt ions in the solution; while \( K \) and \( \alpha \) are positive tuning parameters.
Figure 8. Theoretical dependency of the C-FENE-P model parameter $E$ on the inverse of the relative retained zero-shear-rate (intrinsic) viscosity, $\chi^{-1}$. Note that $\chi^{-1} \rightarrow 1$ at zero salinity and increases when salinity increases. The curves are plotted at $E_0 = 0.1; 1; 10; 100; \text{and} 1000$, bottom up. The value of $b$ is set to 50.

6. Discussion

6.1. Steady shear flow

The influence of salinity on the non-Newtonian viscosity of polyelectrolytes has been subject to extensive experimental studies. Both a decrease in viscosity and a shift of the onset of shear-thinning towards higher shear rate values with increasing salt concentration are shown by e.g. [AitKadi & Carreau 1987], [Tam & Tiu 1989, 1990], [Stavland et al. 2013], and [Stanislavskiy 2018]. It is also reported that polyelectrolytes the molecules of which are intrinsically more rigid demonstrate shear-thinning in a greater degree. The predictions of the C-FENE-P dumbbell model are in excellent qualitative agreement with these experimental results, as illustrated in figure 1.

Much less data is available on the normal stress coefficients and their dependence on salt concentration. The shape of the $\Psi_1(\dot{\gamma})$ curve predicted by the C-FENE-P model is realistic and fully consistent with a qualitative description given by [Bird et al. 1987a, §3.3]. The simple nonlinear relation between $\Psi_1(\dot{\gamma})$ and $\eta(\dot{\gamma})$, expression (3.9), is a generic feature of many dumbbell models. This prediction has been tested experimentally for partially hydrolysed polyacrylamides in a recent study by [Lozhkina 2018]; this relation was proven to be qualitatively correct for solutions of high-molecular-weight polyacrylamides, but to not hold for their lower-molecular-weight counterparts. The second normal stress difference is reported to be very small, $|\Psi_2(\dot{\gamma})| \ll |\Psi_1(\dot{\gamma})|$; hence, it does not play a significant role for most flows of practical interest [Bird et al. 1987a, §3.3]. The second normal stress coefficient vanishes in most of the kinetic theory-based polymer fluid models, see e.g. [Bird et al. 1980], including the C-FENE-P dumbbells.

6.2. Steady elongational flow

The C-FENE-P model predicts monotonic elongational thickening at positive elongation rates. The S-shaped curves, obtained in earlier theoretical works of [Dunlap & Leal 1984] and [Ait-Kadi et al. 1988], are not reproduced by our model. The impact of salinity on the elongational viscosity, as described in section 3.2 and shown in figure 2, is fully consistent with available experimental data [Miles et al. 1983], [AitKadi & Carreau 1987], [Dunlap et al. 1987], [Ferguson et al. 1990], [Anna et al. 1997]. For the negative elongation rates, we found no experimental results for comparison.
6.3. Small-amplitude oscillatory shear flow

The qualitative shape and asymptotic behaviour of the complex viscosity components $\eta'(\omega)$, $\eta''(\omega)$ and the elastic moduli $G'(\omega)$, $G''(\omega)$, as described in section 4.1, are in accordance with physical arguments provided by Bird et al. (1987a, §3.4). A decrease in these material functions with increasing salinity at fixed $\omega$, shown in figure 4, is supported by experimental observations of Tam & Tiu (1989) and Ihebuzor (2019).

Furthermore, the C-FENE-P model predicts a decrease of the experimental time parameter, $\lambda_e$, with increasing salinity; this leads to a shift of the characteristic points, occurring at fixed $\lambda_e\omega$, towards higher frequencies. This matches the experimental results of Ihebuzor (2019), who reported the $G'-G''$ crossover frequency to increase with salinity.

At the same time, the C-FENE-P model is not capable of resolving the quantitative relations between the SAOS material functions; in particular, it predicts that the $G'(\omega)$ and $G''(\omega)$ curves intersect at the point of maximum of $G''(\omega)$, as shown in figure 3, top right. This is not supported by experimental results for polyelectrolytes: as seen from the recent reports of Liu et al. (2017) and Ihebuzor (2019), $G''(\omega)$ continues to increase at frequency values larger than the crossover frequency. This mismatch was expected, since dumbbell models, with their single relaxation time, cannot properly represent a complex oscillator possessing a wide spectrum of relaxation times – which a real polymer molecule is – in cases when the flow pattern changes rapidly. An extension of the C-FENE-P dumbbell model to its bead-spring-chain variant might resolve this issue, but would lead to significant mathematical and computational complexity, which we are intentionally trying to avoid.

Finally, we did not find any experimental works allowing to analyse the results related to the behaviour of the first normal stress difference in SAOS flow.

6.4. Start-up and relaxation of steady shear flow

At fixed salinity, the appearance of shear stress overshoot at the start-up of steady shear flow and the way its magnitude and position depends on the step-rate value $\dot{\gamma}_0$, as described in section 4.2 and shown in figure 6, is in excellent qualitative agreement with experiments of Zebrowski & Fuller (1985) and Islam (2019).

According to our results, a decrease in salinity can either increase or decrease the relative shear stress overshoot magnitude, depending on the polyelectrolyte natural rigidity and the step-rate value $\dot{\gamma}_0$. Interestingly, the same complex effect was predicted by advanced numerical study of Andrews et al. (1998), who used a polymer model more advanced than ours both mechanically (bead-spring-chains in place of dumbbells) and physically (Debye-Hückel potential instead of simple Coulomb force). Experimentally, this effect was recently observed by Åsen (2019) for aqueous solution of partially hydrolysed polyacrylamide. In earlier experiments, in particular those of Zebrowski & Fuller (1985), it was reported that the relative overshoot increases with decreasing salinity, which is also consistent with our results.

In the case of steady shear flow relaxation, the C-FENE-P model predicts a faster return to equilibrium at increasing shear rate values and fixed salinity, as seen in figure 7. This is confirmed by experimental evidence provided by Zebrowski & Fuller (1985) and Islam (2019). Furthermore, our results show that at fixed shear rate value, an increase in salinity leads to a slower decay of shear stresses; this is also in accordance to (Zebrowski & Fuller 1985).

Finally, Islam (2019) investigated the shape of normalised shear stress relaxation functions for commercial partially hydrolysed polyacrylamides. Two clearly distinct regions: a faster-than-exponential decrease at earlier times and an exponential decay
at later times, as predicted by the C-FENE-P model – were observed. Furthermore, the
decay rate in the exponential regime was found to be dictated by the polymer type
and independent of $\dot{\gamma}_0$ and polymer concentration, which is in total agreement with our
theoretical result expressed by (4.38).

No experimental data for comparison was found for the first normal stress difference
growth and relaxation functions.

7. Conclusions

The predictions of the C-FENE-P dumbbell model in steady and transient shear and
elongational flows are in a very good qualitative agreement with most of the available
experimental data for polyelectrolytes. This involves not only the qualitative shape
of the material functions and their dependence on flow parameters, but also the way
how the material functions differ for more and less intrinsically rigid polyelectrolytes
and how they are affected by the solvent salinity. Furthermore, our results are fully
consistent with numerical simulations of advanced polyelectrolyte model of Andrews
et al. (1998). At the same time, the C-FENE-P model is strikingly simple, being in fact
just a slight complication over the uncharged FENE-P dumbbell model. The closed-form
constitutive equation allows to investigate fluid dynamics in shear and shearfree flows
using a combination of analytical and simple numerical methods. In addition, physical
quantities of interest – such as the relative elongation of the polyelectrolyte molecules –
can be easily kept track of under analysis.

Concerning numerical simulation of complex flows, we assume that any computer code
which is capable of solving the equations of motion for a FENE-P dumbbell fluid can be
easily upgraded to tackle the constitutive equation of the C-FENE-P dumbbells.

We believe that the C-FENE-P dumbbell model has all the potential to be a robust
instrument, allowing a qualitative understanding of flow phenomena in complex flows of
dilute polyelectrolyte solutions.

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