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Effects of non-linear rheology on electrospinning process: A model study

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ABSTRACT

We develop an analytical bead-spring model to investigate the role of non-linear rheology on the dynamics of electrified jets in the early stage of the electrospinning process. Qualitative arguments, parameter studies as well as numerical simulations, show that the elongation of the charged jet filament is significantly reduced in the presence of a non-zero yield stress. This may have beneficial implications for the optimal design of future electrospinning experiments.

1. Introduction

The dynamics of charged polymers in external fields is an important problem in non-equilibrium thermodynamics, with many applications in science and engineering (Doshi and Reneker, 1995; Andrady, 2008). In particular, such dynamics lies at the heart of electrospinning experiments, whereby charged polymer jets are electrospun to produce nanosized fibers; these are used for several applications, as reinforcing elements in composite materials, as building blocks of non-wetting surfaces layers on ordinary textiles, of very thin polymeric separation membranes, and of nanoelectronic and nanophotonic devices (Pisignano, 2013; Agarwal et al., 2013; Arinstein et al., 2007; Mannarino and Rutledge, 2012). In a typical electrospinning experiment, a charged polymer liquid is ejected at the nozzle and is accelerated by an externally applied electrostatic field until it reaches down to a charged plate, where the fibers are finally collected. During the process, two different regimes take place: an initial stable phase, where the steady jet is accelerated by the field in a straight path away from the spinneret (the ejecting apparatus); a second stage, in which an electrostatic-driven bending instability arises before the jet reaches down to a collector (most often a grounded or biased plane), where the fibers are finally deposited. In particular, any small disturbance, either a mechanical vibration at the nozzle or hydrodynamic perturbations within the experimental apparatus, misaligning the jet axis, would lead the jet into a region of chaotic bending instability (Reneker et al., 2000). The stretching of the electrically driven jet is thus governed by the competition between electrostatics and fluid viscoelastic rheology.

The prime goal of electrospinning experiments is to minimize the radius of the collected fibers. By a simple argument of mass conservation, this is tantamount to maximizing the jet length by the time it reaches the collecting plane. Consequently, the bending instability is a desirable effect, as long it can be kept under control in experiments. By the same argument, it is therefore of interest to minimize the length of the initial stable jet region. Analyzing such stable region is also relevant for an effective comparison with results coming from electrospinning experiments studied in real-time by means of high-speed cameras (Camposeo et al., 2013) or X-ray phase-contrast imaging (Greenfeld et al., 2012).

In the last years, with the upsurge of interest in nanotechnology, electrospinning has made the object of comprehensive studies, from both modelling (Carroll and Joo, 2006) and experimental viepoints (Theron et al., 2005) (for a review see Carroll et al., 2008). Two families of models have been developed: the first treats the jet filament as obeying the equations of continuum mechanics (Spivak et al., 2000; Feng, 2002, 2003; Hohman et al., 2001a,b). Within the second one, the jet is viewed as a series of discrete elements obeying the equations of Newtonian mechanics (Reneker et al., 2000; Yarin et al., 2001). More precisely, the jet is regarded as a series of

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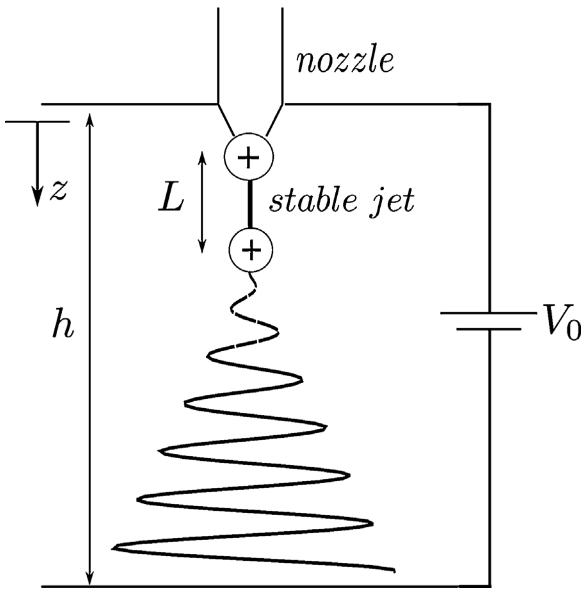

Fig. 1. The experimental set up and reference system of the stable jet region, with the origin at the nozzle orifice and z coordinate axis pointing down (figure not to scale).

charged beads, connected by viscoelastic springs. Both approaches above typically assume Newtonian fluids, with a linear strain-stress constitutive relation. On the other hand, in a recent time, the use of viscoelastic fluids has also been investigated in a number of papers, both theoretical and experimental, for the case of power-law (Feng, 2002; Spivak et al., 2000) and other viscoelastic fluids (Carroll and Joo, 2006, 2011), with special attention to the instability region.

In this paper, we investigate the effects of Herschel–Bulkley non-Newtonian rheology on the early stage of the jet dynamics. The main finding is that the jet elongation during such initial stable phase can be considerably slowed down for the case of yield-stress fluids. As a result, the use of yield-stress fluids might prove beneficial for the design of future electrospinning experiments.

2. The model problem

Let us consider the electrical driven liquid jet in the electrospinning experiment. We confine our attention to the initial rectilinear stable jet region and, for simplicity, all variables are assumed to be uniform across the radial section of the jet, and vary along z only, thus configuring a one-dimensional model. The filament is modelled by two charged beads (*dimer*) of mass m and charge e, separated by a distance l, and subjected to the external electrical field V_0/h, h being the distance of the collector plate from the injection point (Fig. 1) and V_0 the applied voltage.

The deformation of the fluid filament is governed by the combined action of electrostatic and viscoelastic forces (gravity and surface tension are neglected), so that the momentum equation reads (Reneker et al., 2000):

$$m\frac{dv}{dt} = -\frac{e^2}{l^2} + \frac{eV_0}{h} + \pi a^2\sigma, \tag{2.1}$$

where a is the cross-section radius of the bead and v the velocity defined as:

$$\frac{dl}{dt} = -v \tag{2.2}$$

For a viscoelastic fluid, the stress σ is governed by the following equation:

$$\frac{d\sigma}{dt} = -\frac{1}{\tau}(\sigma - \sigma_{HB}), \tag{2.3}$$

where τ is the time relaxation constant and σ_{HB} is the Herschel–Bulkley stress (Huang and Garcia, 1998; Burgos et al., 1999) that reads

$$\sigma_{HB} = \sigma_Y + K\left(\frac{dl}{ldt}\right)^n \tag{2.4}$$

In the previous expression, σ_Y is the yield stress, n is the power-law index and $\mu_0 = K|(1/l)(dl/dt)|^{n-1}$ is the effective viscosity with K a prefactor having dimensions $gs^{n-2}\,cm^{-1}$; the case $n=1$ and $\sigma_Y=0$ recovers the Maxwellian fluid model, with $\mu_0 \equiv const$. In the stress Eqs. (2.3) and (2.4), the Maxwell, the power-law and the Herschel–Bulkley models are combined. A large class of polymeric and industrial fluids are described by $\sigma_Y>0$ (Bingham fluid) and $n<1$ (shear-thinning fluid), $n>1$ (shear-thickening fluid) (Bird et al., 1987; Pontrelli, 1997; Pontrelli et al., 2009).

It is expedient to recast the above equations in a nondimensional form by defining a length scale and a reference stress as in Reneker et al. (2000):

$$L = \left(\frac{e^2}{\pi a_0^2 G}\right)^{(1/2)} \qquad G = \frac{\mu_0}{\tau} \tag{2.5}$$

with a_0 the initial radius. With no loss of generality, we assume the initial length of the dimer to be L. Space is scaled in units of the equilibrium length L at which Coulomb repulsion matches the reference viscoelastic stress G, while time is scaled with the relaxation time τ. The following nondimensional groups:

$$Q = \frac{e^2\mu_0^2}{L^3 m G^2} \qquad V = \frac{eV_0\mu_0^2}{hLmG^2} \qquad F = \frac{\pi a_0^2 \mu_0^2}{LmG} \tag{2.6}$$

measure the relative strength of Coulomb, electrical, and viscoelastic forces respectively (Reneker et al., 2000). Note that the above scaling implies $F=Q$. By setting $W = -v$ and applying mass conservation:

$$\pi a^2 l = \pi a_0^2 L$$

the above equations (2.1)–(2.4) take the following nondimensional form:

$$\begin{aligned}
\frac{dl}{dt} &= W \\
\frac{dW}{dt} &= V + \frac{Q}{l^2} - \frac{F\sigma}{l} \\
\frac{d\sigma}{dt} &= \sigma_Y + \left(\frac{W}{l}\right)^n - \sigma
\end{aligned} \tag{2.7}$$

with initial conditions: $l(0)=1$, $W(0)=0$, $\sigma(0)=0$. Eqs. (2.7) describe a dynamical system with non-linear dissipation for $n \neq 1$. It can conveniently be pictured as a particle rolling down the potential energy landscape $E(l)=Q/l-Vl$. Since the conservative potential is purely repulsive, the time-asymptotic state of the system is escape to infinity, i.e. $l\to\infty$ as $t\to\infty$. However, because the system also experiences a non-linear dissipation, its transient dynamics is non-trivial. This may become relevant to electrospinning experiments, as they take place in set-up about and below 1 m size, so that transient effects dominate the scene.

Before discussing numerical results, we firstly present a qualitative analysis of the problem.