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Thermo-electro-hydrodynamic model for electrospinning process

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Abstract

Ultra-fine polymer fibers, obtained by electrospinning, have a wide range of potential applications such as fluid filtration, biomedicine, catalyst supports, drug delivery, tissue engineering, nanowires, to just say few. Yet theoretical modeling the spinning process remains a bottleneck severely hampering further improvement in both quality and efficiency. This paper establishes a mathematical model to explore the physics behind electrospinning. When electrical force is dominant over the other forces, Bratu equation is derived, which can explain the instability (bifurcation) in electrospinning. A variational model is also established.

Keywords: electrospinning, electrospun nanofiber, mathematical model, Bratu equation, bifurcation, instability, variational principle.

1. Introduction

Structured polymer fibers with diameters in the range from several micrometers down to tens of nanometers are of considerable interest for various kinds of applications. It is now possible to produce a low cost, high-value, high-strength fiber from a biodegradable and renewable waste product for easing the environmental concerns. For instance, pore structured electrospun nanofibrous membrane as wound dressing [1] can exudates fluid from the wound so as to prevent either building up under the covering, or wound desiccation. The electrospun nanofibrous membrane shows controlled liquid evaporation, excellent oxygen permeability, and promoted fluid drainage capacity, meanwhile still can inhibit exogenous microorganism invasion because its ultra-fine pores. Other examples include thin fibers for filtration application [2,3], bone tissue engineering [4], drug delivery [5], catalyst supports[6], fiber mats serving as reinforcing component in composite systems[7], fiber templates for the preparation of functional nanotubes [8].

Electrospinning is a method of producing superfine fibers with diameters ranging from 10 μm down to 10 *nm* by forcing a molten polymer or a polymer solution through a spinneret by an electric field. Under the influence of the electrostatic field, a pendant droplet of the polymer solution at the capillary tip is deformed into a conical shape (Taylor cone)[9]. If the voltage surpasses a threshold value, electrostatic forces overcome the surface tension, and a charged fine jet is ejected. The jet moves towards a ground plate acting as a counter electrode. The controlling parameters of the process are hydrostatic pressure in the capillary tube and external electric field. Viscosity, conductivity, dielectric permeability, surface tension, and temperature gradient affect the process as well. The electrospinning process, invented by Formhals [10] in 1934, was studied in detail by many researchers [11~23], but almost all models in open literature do not take thermal effect into account. For a polymer with high molten temperature, thermal factor is critical for the process. So a rigorous thermo-electro- hydrodynamics description of electrospinning is needed for better understanding of the process.

2. Governing Equations of thermo-electro-hydrodynamics

Spivak *et al.*[16,17] established a model of steady state jet in the electrospinning process (see notations in section 3):

1) Equation of mass balance gives

$$\nabla \cdot \boldsymbol{u} = 0 . \tag{1}$$

2) Linear momentum balance is

$$\rho(\boldsymbol{u} \cdot \nabla)\boldsymbol{u} = \nabla T^m + \nabla T^e . \tag{2}$$

3) Electric charge balance reads

$$\nabla \cdot \boldsymbol{J} = 0 . \tag{3}$$

The right hand side of Eq.(2) is the sum of viscous and electric forces.

This is a simple model without considering thermal effect. In this paper, we consider the couple effects of thermal, electricity, and hydrodynamics. A complete set of balance laws governing the general thermo-electro-hydrodynamics flows has been derived by and Ko & Dulikravich[24] and Eringen & Maugin [25,26]. It consists of modified Maxwell's equations governing electrical field in a moving fluid, the modified Navier-Stokes equations governing heat and fluid flow under the influence of electric field, and constitutive equations describing behavior of the fluid (see notations in section 3):

$$\frac{\partial q_e}{\partial t} + \nabla \cdot \boldsymbol{J} = 0 , \tag{4}$$

$$\rho \frac{D\boldsymbol{u}}{Dt} = \nabla \cdot \boldsymbol{t} + \rho \boldsymbol{f} + q_e \boldsymbol{E} + (\nabla \boldsymbol{E}) \cdot \boldsymbol{P} , \tag{5}$$

$$\rho c_p \frac{DT}{Dt} = Q_h + \nabla \cdot \boldsymbol{q} + \boldsymbol{J} \cdot \boldsymbol{E} + \boldsymbol{E} \cdot \frac{D\boldsymbol{P}}{Dt} . \tag{6}$$

This set of conservation laws can constitute a closed system when it is supplemented by appropriate constitutive equations for the field variables such as polarization. The most general theory of constitutive equations determining the polarization, electric conduction current, heat flux, and Cauchy stress tensor has been developed by Eringen and Maugin [25,26].

$$\boldsymbol{P} = \varepsilon_p \boldsymbol{E} , \tag{7}$$

$$\boldsymbol{J} = k\boldsymbol{E} + \sigma \boldsymbol{u} + \sigma_T \nabla T , \tag{8}$$

$$\boldsymbol{q} = \kappa \nabla T + \kappa_E \boldsymbol{E} , \tag{9}$$

$$\boldsymbol{t} = -\tilde{p}\underline{\underline{\boldsymbol{I}}} + \eta[\nabla \underline{\boldsymbol{v}} + (\nabla \underline{\boldsymbol{v}})^t] . \tag{10}$$

Here, coefficients ε_p, μ_m, k, σ, σ_T, κ, κ_E, η are material properties and depend only on temperature in the case of an incompressible fluid. For the physical importance of these properties, see review papers by Ko and Dulikravich [24]. Eq.(10) is valid only for Newtonian flows.

3. Mathematical Model for One-Dimensional Case

An unsteady flow of an infinite viscous jet pulled from a capillary orifice and accelerated by a constant external electric field is considered in this section.

1) The conservation of mass equation gives

$$\frac{\partial}{\partial t}(r^2) + \frac{\partial}{\partial z}(r^2 u) = 0 , \tag{11}$$

where r is the radius of the jet at axial coordinate z , and u is the axial velocity.

2) Conservation of charge reduces into

$$\begin{aligned} &\frac{\partial}{\partial t}(2\pi r(\sigma + \varepsilon_p E)) + \\ &\frac{\partial}{\partial z}(2\pi r(\sigma + \varepsilon_p E)u + \pi r^2 kE + \pi r^2 \sigma_T \frac{\partial T}{\partial z}) = 0, \end{aligned} \tag{12}$$

where σ is the surface charge density, E the electric field in the axial direction. The current is composed of three parts: (1)The Ohmic bulk conduction current: $J_c = \pi r^2 kE$; (2) Surface convection current: $J_s = 2\pi r \sigma u$; and (3) Current caused by temperature gradient: $J_T = \pi r^2 \sigma_T \partial T / \partial z$.

3) The Navier-Stokes equations becomes

$$\begin{aligned} \frac{\partial u}{\partial t} + u\frac{\partial u}{\partial z} &= -\frac{1}{\rho}\frac{\partial p}{\partial z} + g + \frac{2\sigma E}{\rho r} \\ &+ \frac{1}{r^2}\frac{\partial \tau}{\partial z} + \frac{1}{r^2}\varepsilon_p E \frac{\partial E}{\partial z} , \end{aligned} \tag{13}$$

$$\begin{aligned} &\rho c_p (\frac{\partial T}{\partial t} + u\frac{\partial T}{\partial z}) = Q + \frac{\partial}{\partial z}(k\frac{\partial T}{\partial z} + k_E E) \\ &+ (2\pi r \sigma u + \pi r^2 kE + \pi r^2 \sigma_T \frac{\partial T}{\partial z})E \\ &+ \varepsilon_p E(\frac{\partial E}{\partial t} + u\frac{\partial E}{\partial z}), \end{aligned} \tag{14}$$

where p is the internal pressure of the fluid expressed as

$$p = \kappa\gamma - \frac{\varepsilon - \bar{\varepsilon}}{8\pi} E^2 - \frac{2\pi}{\bar{\varepsilon}} \sigma^2 , \qquad (15)$$

where κ is twice the mean curvature of the interface $\kappa = 1/R_1 + 1/R_2$, where R_1 and R_2 are the principal radii of curvature. ε is the fluid dielectric constant, $\bar{\varepsilon}$ air dielectric constant.

Rheologic behavior of many polymer fluids can be described by power-law constitutive equation in the form:

$$\tau = \mu_0 \frac{\partial u}{\partial z} + \sum_{n=1}^{m} a_n (\frac{\partial u}{\partial z})^{2n+1} . \qquad (16)$$

In addition to conducting bodies, there are also dielectrics. In dielectrics the charges are not completely free to move, but the positive and negative charges that compose the body may be displaced in relation to one another when a field is applied. The body is said to be polarized. The polarization is given in terms of a dipole moment per unit volume ***P***, called the polarization vector. The bound charge or polarization charge in the dielectric is given by

$$q_\rho = -\nabla \cdot \boldsymbol{P} . \qquad (17)$$

In an isotropic linear dielectric case the polarization is assumed to be proportional to the field that causes it, thus

$$\boldsymbol{P} = \varepsilon_p \boldsymbol{E} , \qquad (18)$$

where ε_p is the electric susceptibility.

4. Bratu equation and bifurcation in the process

In this section we consider the steady state jet ignoring the thermal effort. In case electrically generated force is dominant, the momentum equation becomes

$$u \frac{\partial u}{\partial z} = \frac{2\sigma E}{\rho r} . \qquad (19)$$

From the charge balance equation:

$$2r\sigma u + r^2 kE = I ,$$

Eq.(19) can be expressed in the form

$$u \frac{\partial u}{\partial z} = \frac{E(I - r^2 kE)}{\rho r^2 u} . \qquad (20)$$

Introducing a new variable, v, defined as

$$u = e^{-v/6} . \qquad (21)$$

Substituting (21) into (20) results in

$$\frac{\partial v}{\partial z} = -\frac{6E(I - r^2 kE)}{\rho r^2} e^{v/2} = 0 . \qquad (22)$$

Differentiating (22) with respect to z , and assuming $\partial r / \partial z \approx 0$, yields

$$\frac{\partial^2 v}{\partial z^2} = -\frac{3E(I - r^2 kE)}{\rho r^2} e^{v/2} \frac{\partial v}{\partial z} . \qquad (23)$$

In view of (22), Eq.(23) becomes the well-known Bratu equation[27]

$$\frac{\partial^2 v}{\partial z^2} + \lambda e^v = 0 , \qquad (24)$$

where $\lambda = 18E^2 (I - r^2 kE)^2 / \rho^2 r^4$. Eq.(24) comes originally from a simplification of the solid fuel ignition model in thermal combustion theory [28]. There are two solutions to Eq.(24) for values $0 < \lambda < \lambda_c$, and no solutions for $\lambda > \lambda_c$. In case $\lambda = \lambda_c$ there is only one solution.

By the semi-inverse method [30, 31, 32], we can easily obtain various variational principles for electrospinning.

5. Conclusion

We establish general model for the discussed problem, when electric force is in a dominant position, the model turns out to be of Bratu equation; this leads to quite simplification when we study the bifurcation or instability of the process. We will give detailed theoretical results and experimental verification in forthcoming papers.

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