NUMERICAL ANALYSIS OF FREE SURFACE FLOWS IN FIBER SPINNING OF CARBON NANOTUBES

C. Halliburton[1], J.A. Lee[2], M. Pasquali[2]

1. NanoJapan Program and Department of Electrical and Computer Engineering, Louisiana State University

2. Department of Chemical and Biomolecular Engineering, Rice University

Fiber spinning is an industrial process that can be applied to solutions of carbon nanotubes (CNTs) to create fibers which exhibit the unique mechanical and electrical properties of CNTs on the macro-scale. This process involves the extrusion of a CNT-superacid solution through a die and subsequent coagulation of the extruded solution in water or air to produce a pure CNT fiber. However, morphological irregularities that appear in the viscous outer layer of the fiber before it has fully solidified may lead to degradation of fiber strength and elasticity. In this viscous outer layer, we suspect that radial buckling too is related to the degradation of properties. In order to describe these irregularities, we have modeled the flow as an isothermal solution and chosen a physical model to take into account the viscoelasticity of the material and examine changes in the stress and radial position profile for various conditions on viscosity (μ) and relaxation time. For example, we may force a μ-profile in space and time to simulate coagulation, where the range of possible values was informed by rheological data of uncoagulated CNTs. Though a 2D model may be necessary to fully capture radial buckling, we first develop a 1D model which will allow us to investigate the effects of axially varying μ on surface profile and stresses within the solution in one dimension along the axis of flow.

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Charles Halliburton[1], J. Alex Lee[2], Matteo Pasquali[2]

1. NanoJapan Program and Department of Electrical and Computer Engineering, Louisiana State University, Baton Rouge, LA
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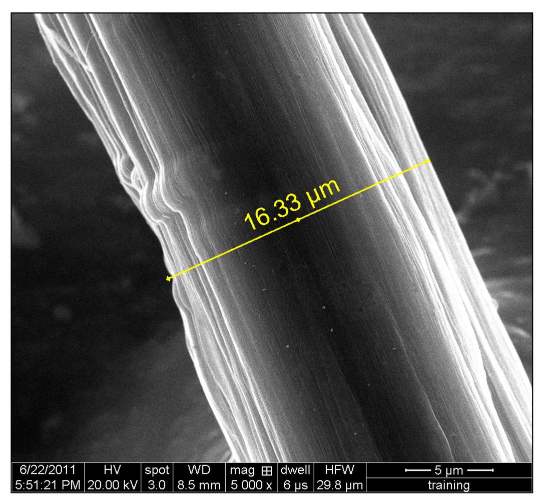
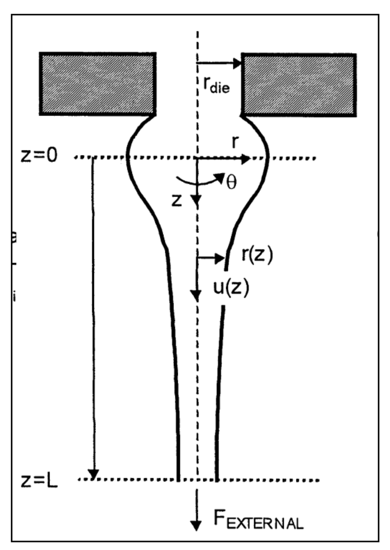
Background

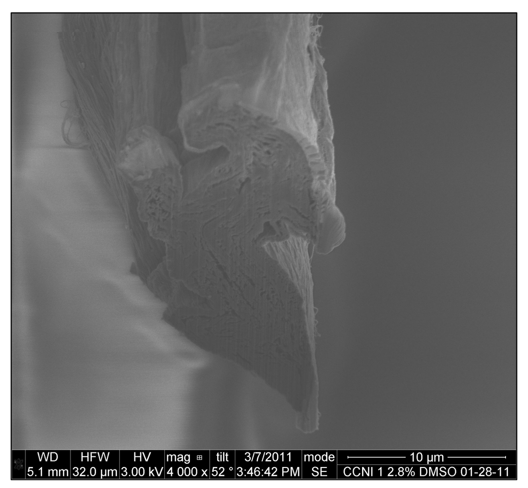
- Fibers can be produced from solutions of carbon nanotubes (CNTs) dissolved in chlorosulphonic acid[1]
- These exhibit CNTs' unique mechanical and electrical properties on the macroscale
- Irregular morphologies in some of these fibers may lead to degradation of material properties
- Morphological features are typically difficult to measure experimentally



CNT fiber (scanning-electron microscopy)



Fiber spinning process[2]



Buckling in CNT fiber (scanning-electron microscopy)

Governing Equations

Key assumptions:

1) 1D
2) Isothermal
3) Relatively inviscid medium

An upper-convected Maxwell (UCM) constitutive equation was chosen to model stress:

$$\boldsymbol{\tau} + \lambda \frac{\delta \boldsymbol{\tau}}{\delta t} = \mu(\nabla \boldsymbol{u} + (\nabla \boldsymbol{u})^T) \quad (1)$$

UCM takes into account stress relaxation, and thus is suitable for modeling a viscoelastic fluid.

where δ/ δt is Oldroyd's convected derivative

CNT fiber spinning shares characteristics with polymer melts spinning:

i) Primarily extensional flow
ii) Non-Newtonian
iii) Viscoelastic behavior

Assuming velocity only varies along z and neglecting gravity, the constitutive equation in x and z reduces to

$$\tau_{zz} + \lambda\left(\frac{\partial \tau_{zz}}{\partial t} + u_z \frac{\partial \tau_{zz}}{\partial z} - 2\frac{\partial u_z}{\partial z}\tau_{zz}\right) = 2\mu\left(\frac{\partial u_z}{\partial z}\right) \quad (2)$$

$$\tau_{xx} + \lambda\left(\frac{\partial \tau_{xx}}{\partial t} + u_z \frac{\partial \tau_{xx}}{\partial z}\right) = 2\mu\left(\frac{\partial u_z}{\partial z}\right) \quad (3)$$

The reduced momentum balance in z is

$$\rho\left(\frac{\partial u_z}{\partial t} + u_z \frac{\partial u_z}{\partial z}\right) = \frac{\partial \tau_{zz}}{\partial z} \quad (4)$$

Boundary Conditions

Assuming constant volumetric flow rate,

$$u_z(t_{0,}z) = \frac{Q}{\pi[r(z)]^2} \quad (5)$$

If we assume the fiber is fully solidified at the chill roll, then

$$u_z(t z_f) = u_f \quad (6)$$

If we know the velocity at some point on the boundary, all velocities there may be determined by applying (9) and assuming an initial radial profile, r(z)

Start-up transients are not treated here, but we assume that prior to observing the flow, stress gradients near the endpoint have become negligible, allowing us to introduce two more boundary conditions,

$$\tau_{xx} = 2\mu\frac{\partial u_z}{\partial z} \qquad \tau_{zz} = \frac{2\mu}{\left(\frac{\partial u_z}{\partial z}\right)^{-1} - 2\lambda} \quad (7), (8)$$

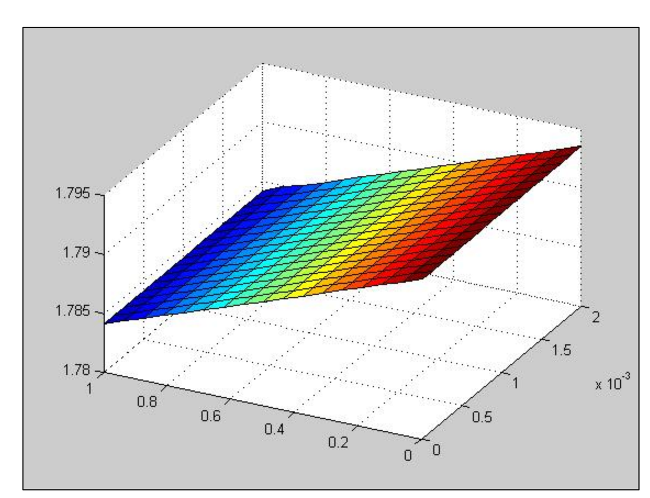
where

$$\frac{\partial u_z}{\partial z} = \frac{2Qm}{\pi(r_f + a(1-z))^3} \quad (9)$$

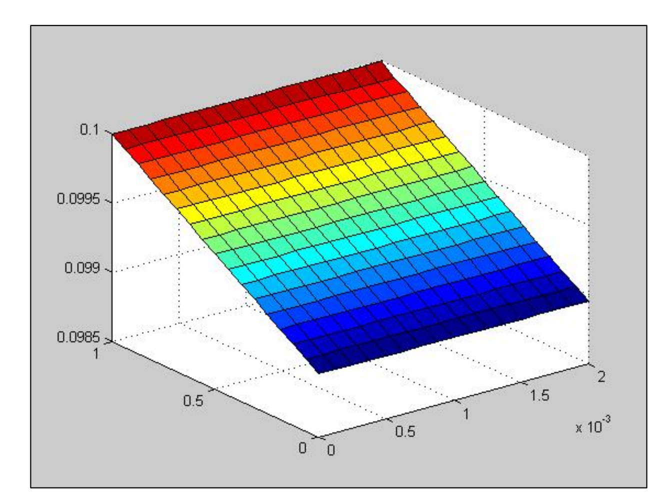
We use a solution from the literature for a high Deborah number polymer at steady state as an initial condition for T and P[3]

Discussion

- A solution was obtained by a forward Euler method for velocity and first and third normal stresses, but the method's limited stability prevents examining the system over long run times

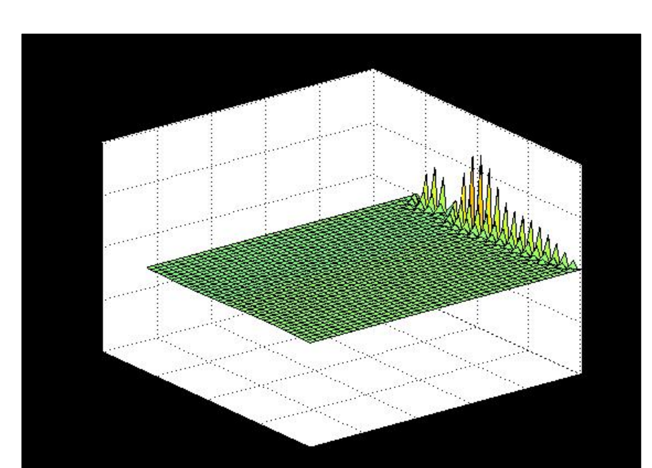


Initial radius is given by ICs on velocity and varies little in time (RHS)

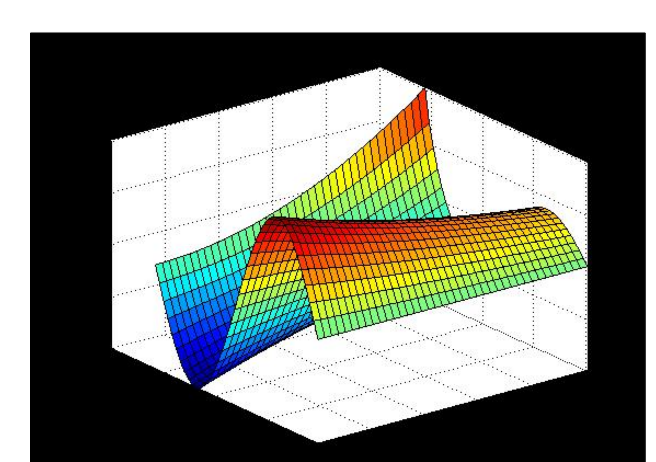


Velocity differs little from the BC in time (RHS)

- Implicit methods could be implemented to better understand the time evolution of features such as a forced viscous or radial profile, based either on the above boundary conditions or w/ steady solutions as ICs



Ex) Explicit solution for a 2nd order diffusion problem

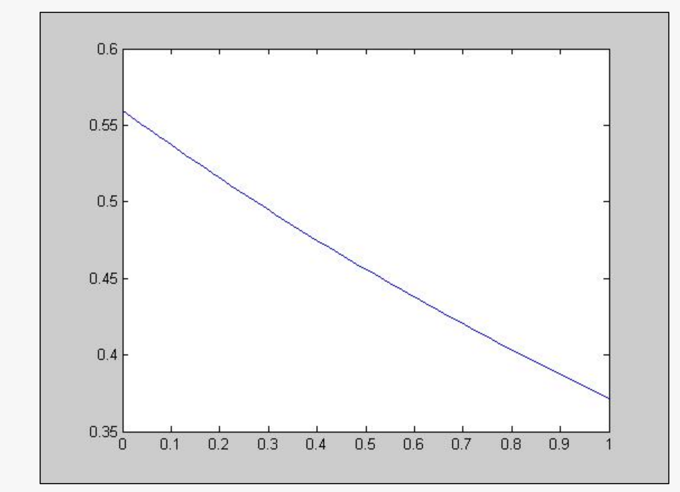


Ex) Implicit solution with identical parameters and domain partition

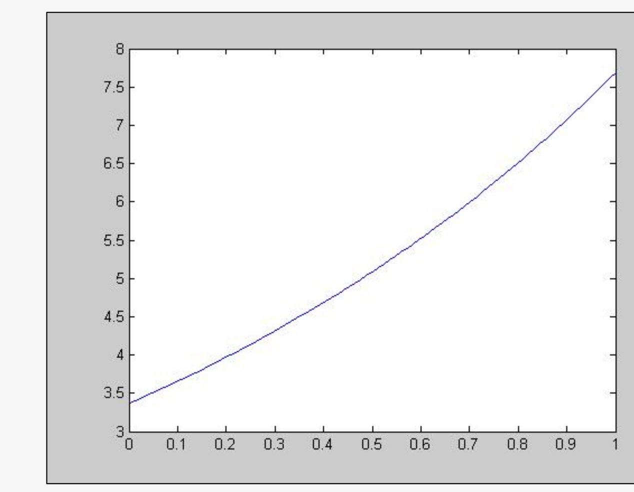
- Because the solution loses mass as acid, it may be necessary to model the flow rate as a function of axial position

Implementations

- A steady-state solution for a polymer melt may be used as an initial condition and perturbed by adjusting the boundary conditions of our model



Newtonian solution for radius vs. axial position[3]



Newtonian solution for third normal stress vs. axial position[3]

- Coagulation may be simulated by forcing an exponential, axially varying viscous profile
- In 2D, a shelling effect believed to cause radial buckling could be treated as a radially varying viscosity and normal stresses computed in the outer shell

Conclusions

- We have here interpreted a CNT-superacid solution as a high Deborah number polymer melt
- Boundary conditions are consistent, given an appropriate choice of process parameters
- We have established a framework for performing numerical simulations of fiber spinning and obtained solutions for certain boundary conditions
- Further examination of the model is needed to better understand time evolution of initial conditions

References

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Contact: Charles Halliburton
challi1@lsu.edu