

Quiz 1 Polymer Properties January 18, 2017

J. J. Feng [*J. Non-Newt. Fluid Mech.* **116** 55-70 (2003)] developed a semi empirical model to describe electro-spinning of polymer solutions. The figure below shows the experimental arrangement. A fiber mat with nanoscale diameter fibers can be produced on a continuous basis.

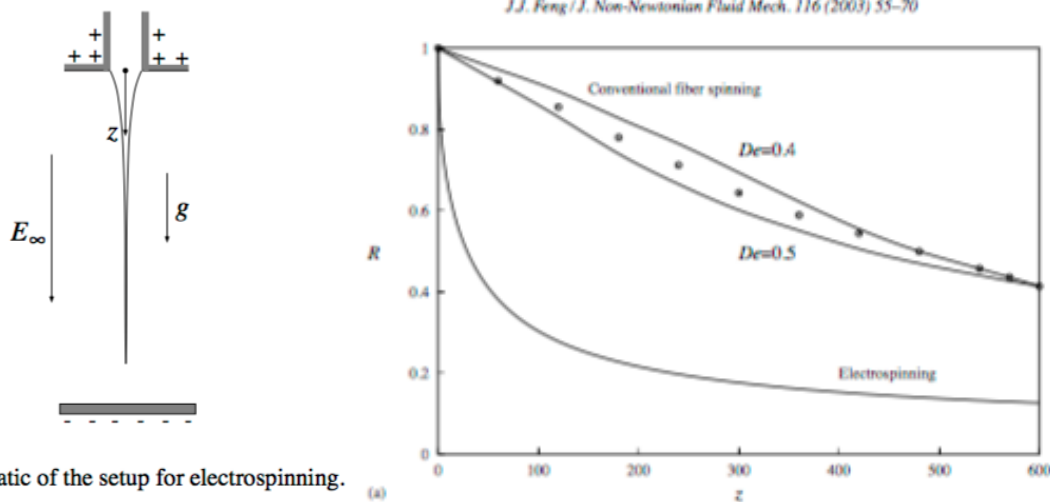


Fig. 1. Schematic of the setup for electrospinning.

In Figure 2 (next page) the Newtonian curves (N) reflects conditions where the Deborah number is small, $De \ll 1$. The Deborah number is the ratio of the materials viscoelastic relaxation time to the time imposed by the process, $\tau_{process} = 1/\dot{\gamma}$.

- Sketch a typical curve of log viscosity versus log shear rate for a polymer showing the Newtonian plateau and the power-law fluid regimes. Indicate where $De = 1$ in this plot.
- For the Newtonian curves (N) in Figure 2 (next page) there is a finite normal stress difference, N_1 , that develops in the electro-spun stream. Define the normal stress difference, N_1 , and explain why it exists for the N curve.
- Considering the stream profile in Figure 1, and Figure 2a (next page), why is there a peak in the normal stress difference, N_1 , at around $z = 100$? (Consider what happens to the strain rate as the stream becomes extremely thin.)
- Under conditions “c” die swell occurs. Explain the origin of die swell. Why does die swell correlate with a dip in curve “c” in Figure 2b?
- Feng mentions that electro spinning typically occurs with De on the order of 10 while conventional fiber spinning occurs for De on the order of 0.5 (plot above). Explain why this is the case.
- Feng discussed the melt strength, which involves stretching of polymer chains between entanglements, during the spinning process as measured by the Trouton or elongational viscosity. Obtain an expression for the force on a chain between entanglements based on a Gaussian probability function and the Boltzmann probability expression.

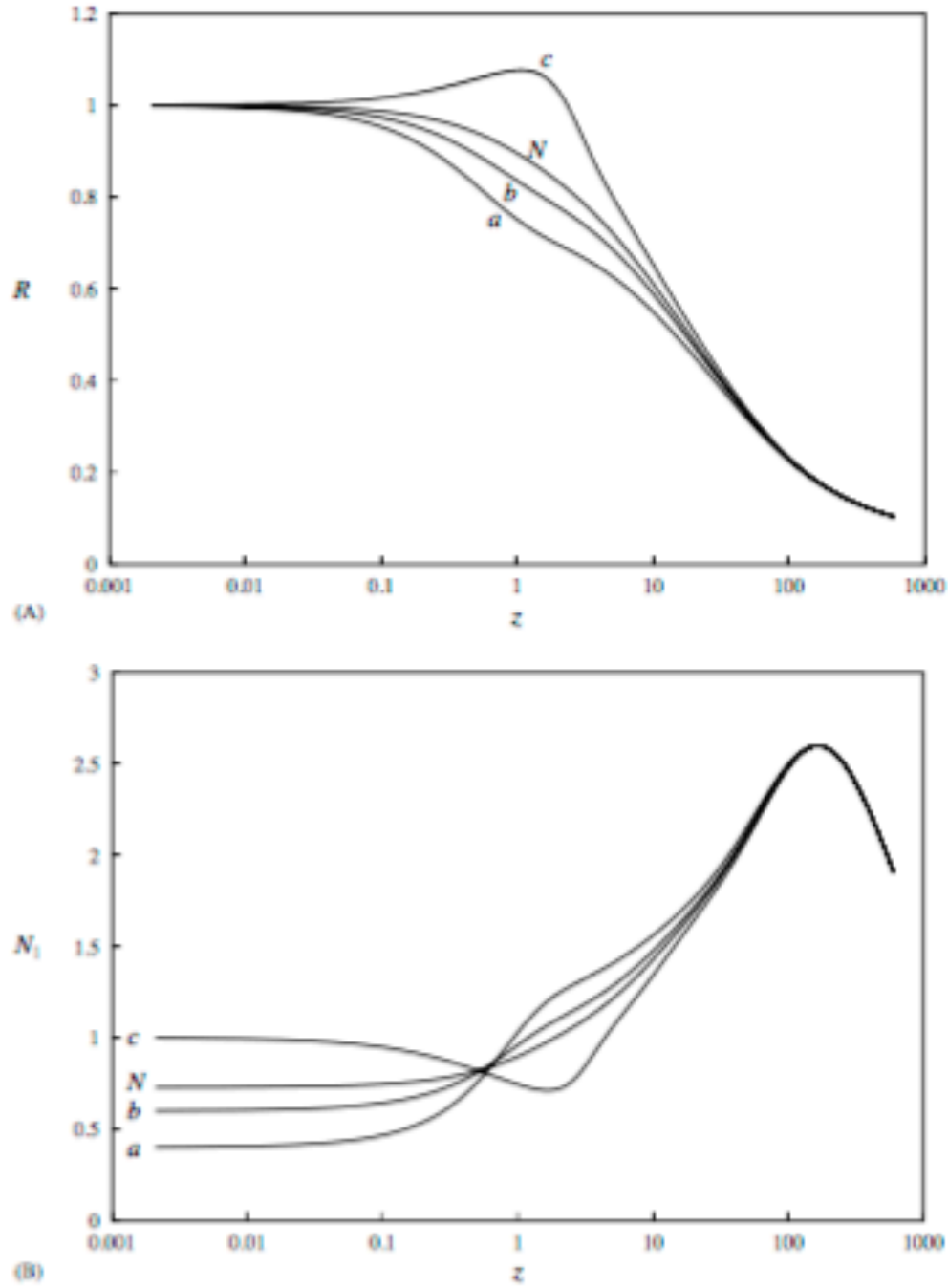
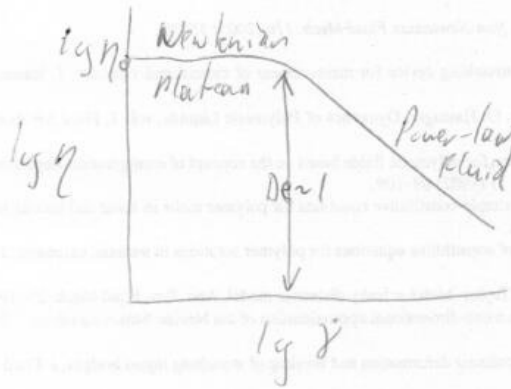


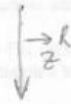
Fig. 2. Effects of the stress boundary condition on (A) jet radius $R(z)$ and (B) normal stress difference $N_1(z) = \tau_{zz}(z) - \tau_{\theta\theta}(z)$. For curves a , b and c , $\tau_{\theta\theta}(0) = -0.13$, -0.20 and -0.33 with $\tau_{zz}(0)/\tau_{\theta\theta}(0) = -2$. Curve N corresponds to the Newtonian condition in Eqs. (20) and (21).

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a)



b)



$$\tau_{zz} - \tau_{rr} = N_1$$

$$\tau_{zz} = \frac{dF_z}{dA_z}$$

Tensile Stress

$$\tau_{rr} = \frac{dF_r}{dA_r}$$

Normal Stress

A normal stress develops when there is a complex structure in the fluid that can convert "zz" stress into "rr" stress. This occurs when the polymer deforms.

In the Newtonian condition $\tau_{viscous} \ll \tau_{process}$ so the chains relax but there is still a conversion of τ_{zz} to τ_{rr} .

c) The stream has an exponential profile and becomes very thin where the maximum in N_1 occurs. The rate of strain becomes very high for the thin stream as reflected in the elevated N_1 . Once the stream reaches the order of molecules on the nanoscale it can't hold the high strain and it relaxes so N_1 drops.

d) Die swell occurs when there is deformation of the polymer chains in the flow stream that relax to lead to swelling of the stream. It seems that as the stream swells the normal stress difference drops since the act of swelling relaxes the chain deformation.

e) A large De is needed for electrospinning since it is necessary for the polymer chains to be highly deformed to make nanoscale fibers.

f)

The Gaussian Chain

Boltzman Probability
For a Thermally Equilibrated System

$$P_b(R) = \exp\left(-\frac{E(R)}{kT}\right)$$

Gaussian Probability
For a Chain of End to End Distance R

$$P(R) = \left(\frac{3}{2\pi\sigma^2}\right)^{3/2} \exp\left(-\frac{3(R)^2}{2(\sigma)^2}\right)$$

By Comparison The Energy to stretch a Thermally Equilibrated Chain Can be Written

$$E = kT \frac{3R^2}{2nl_k^2}$$



$$F = \frac{dE}{dR} = \frac{3kT}{nl_k^2} R = k_{spr} R$$



Assumptions:
-Gaussian Chain
-Thermally Equilibrated
-Small Perturbation of Structure (so it is still Gaussian after the deformation)