2.341J MACROMOLECULAR HYDRODYNAMICS   **Spring 2012**

QUIZ 2

OPEN QUIZ WHEN TOLD

THERE ARE TWO PROBLEMS
OF EQUAL WEIGHT

Please answer each question in a SEPARATE book

You may use the course textbook (DPL) and your class notes

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Problem 1: The Jeffreys Model for Polymer Solutions [15 points]

We have seen in class that a simple model for a dilute polymer solution is the linear Jeffreys model consisting of a Maxwell element (spring G_m and dashpot μ_m together in series) joined in parallel with a Newtonian dashpot μ_s for the solvent (see sketch below left). This is equivalent to the linear limit of the Hookean Dumbbell model derived in class from kinetic theory.
Imagine that a colleague of yours has proposed an alternate 3 parameter model as shown in the sketch below right that consists of a spring G_K and dashpot μ_K in parallel, which are then joined in series with another dashpot μ_2
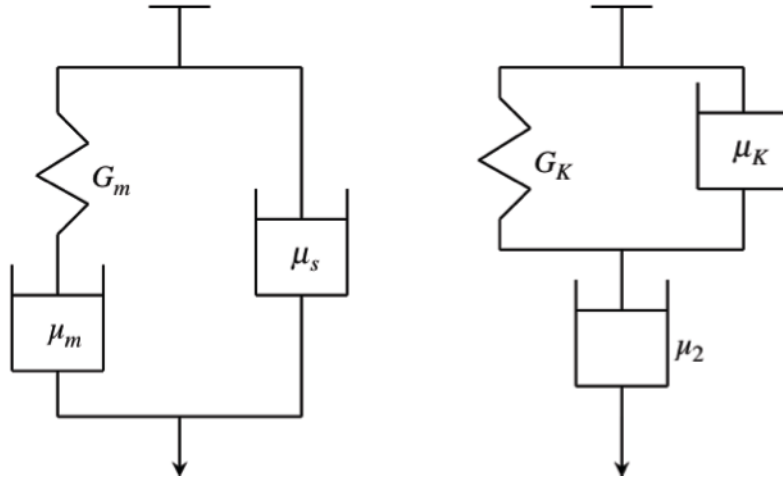
a) [4 points] Derive the appropriate constitutive equation as a differential equation for the total stress $\tau(t)$ for this new 3-parameter linear viscoelastic model. Compare your result with the result derived in class for the Jeffrey's model (left hand sketch). Show that the two equations are, in fact, identical in functional form and relate the 3 parameters in the new model (G_K, μ_K and μ_2 to the 3 parameters G_m, μ_m μ_s from the Jeffrey's model.
    => Given this equivalence, which formulation you use to consider a particular problem is thus a matter of which is easier from a mathematical or physical viewpoint as we show below.

b) [3 points] Integrate the form of the constitutive equation for the Jeffreys model (i.e. corresponding to the left hand sketch) to find an explicit expression for the total stress $\tau(t)$ predicted by the model as a function of time. Sketch clearly the evolution of stress in this model for a stress relaxation experiment following the cessation of steady shear flow at a shear rate $\dot{\gamma}_0$. Clearly label the value of the initial stress and indicate any jumps or discontinuities and the final value of the stress.

c) [3 points] Calculate the predicted response of the complex modulus $G^*(\omega)$ of the model to Small Amplitude Oscillatory Shear flow with $\gamma(t) = \gamma_0 \sin \omega t$. Sketch the predicted form of the functions $G'(\omega), G''(\omega)$. Hint; you can either use complex variables to solve this problem directly, or recognize that both of these two constitutive models are <u>linear</u> viscoelastic models and therefore consist of linear combinations of results that you already are familiar with.

d) [3 points] Use the equations you derived for the <u>new</u> model representation (i.e. the one shown in the righthand sketch above) to calculate the predicted creep compliance $J(t)$ following imposition of a constant stress $\tau(t) = \tau_0 H(t)$. Once again, sketch the form of the model response $J(t)$.

e) [2 point]. What does this 3 parameter model predict for the extensional viscosity $\eta_E^+ \equiv \left((\tau_{zz} - \tau_{xx})/\dot{\varepsilon}_0 \right)$ in an ideal uniaxial elongational flow with $b = 0$ and $\dot{\varepsilon}(t) = \dot{\varepsilon}_0 H(t)$. The velocity field for this flow has been given in class and corresponds to an irrotational flow with $v_z = \dot{\varepsilon}_0 z$. Does the model predict any extensional strain-hardening – which we know is an important observed response in real polymeric fluids.

Problem 2: DNA Polymer Physics [15 points]

Consider an aqueous solution of DNA with molar mass $M = 1.1 \times 10^8$ g/mol corresponding to $n = 1.64 \times 10^5$ base pairs. Assume that the ionic strength is high enough to ignore excluded volume interactions. Assume, if needed, the density is 1.0 g/mL.

(a) [3 points] What is the contour length R_{max} of this DNA if $l = 0.34$ nm per base pair? What is the overlap concentration if the Kuhn length is $b = 300$ nm (approximately 1000 base pairs)?

(b) [3 points] Assuming that the entanglement concentration $c_e \approx 10c^*$ estimate the contour length of an entanglement strand at $c = 0.5$ mg/mL. What is the molar mass of entanglement strand at this concentration? Estimate the plateau modulus at the concentration of 0.5 mg/mL at 30 °C.

(c) [3 points] Estimate the relaxation time and the viscosity of the DNA solution at the concentration 0.5 mg/mL at 30 °C. Assume the solvent viscosity is $\eta_s = 10^{-3}$ Pa s.

(d) [3 points] What is the relaxation time of a melt of these DNA chains? Estimate how the relaxation time would change if an enzyme attacked these DNA chains, and turned it into a melt where $M' = 1.1 \times 10^6$ as the average molecular weight.

(e) [3 points] In the Hatsopoulos Microfluids Lab (HML), we can measure the relaxation time of the dilute solution of DNA chains of molecular weight M, using capillary breakup rheometer (CaBER). What will your best guess for relaxation time be?

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