## Question 1

(i) To start, we recognize the following relationships on the stress and strain

$$
\begin{gather*}
\gamma=\gamma_{k}+\gamma_{2}  \tag{1}\\
\tau=G_{k} \gamma_{k}+\mu_{k} \dot{\gamma}_{k}=\mu_{2} \dot{\gamma}_{2}
\end{gather*}
$$

Therefore, the following relationships are also true

$$
\begin{gather*}
\dot{\gamma}=\dot{\gamma}_{k}+\dot{\gamma}_{2} \\
\dot{\tau}=G_{k} \dot{\gamma}_{k}+\mu_{k} \ddot{\gamma}_{k}=\mu_{2} \ddot{\gamma}_{2} \tag{2}
\end{gather*}
$$

By substituting the results for strain in Eq. 1, $\dot{\gamma}_{k}=\dot{\gamma}-\dot{\gamma}_{2}$ into our stress equation, we get

$$
\begin{equation*}
\dot{\tau}=G_{k}\left(\dot{\gamma}-\dot{\gamma}_{2}\right)+\mu_{k}\left(\ddot{\gamma}-\ddot{\gamma}_{2}\right) \tag{3}
\end{equation*}
$$

Furthermore, by substituting the result $\dot{\gamma}_{2}=\tau / \mu_{2}$ we have

$$
\begin{equation*}
\dot{\tau}=G_{k}\left(\dot{\gamma}-\frac{\tau}{\mu_{2}}\right)+\mu_{k}\left(\ddot{\gamma}-\frac{\dot{\tau}}{\mu_{s}}\right) \tag{4}
\end{equation*}
$$

We can rearrange this result and we obtain

$$
\begin{equation*}
\tau+\left(1+\frac{\mu_{2}}{\mu_{k}}\right) \lambda_{k} \dot{\tau}=\mu_{2} \dot{\gamma}+\lambda_{k} \mu_{2} \ddot{\gamma} \tag{5}
\end{equation*}
$$

where $\lambda_{k} \equiv \mu_{k} / G_{k}$. The Jeffreys model is given by

$$
\begin{equation*}
\tau+\lambda_{m} \dot{\tau}=\left(\mu_{m}+\mu_{s}\right) \dot{\gamma}+\lambda_{m} \mu_{s} \ddot{\gamma} \tag{6}
\end{equation*}
$$

So we can map the parameters from the new model to the Jeffreys model parameters by

$$
\begin{align*}
& \lambda_{m}=\left(1+\frac{\mu_{2}}{\mu_{k}}\right) \lambda_{k} \\
& \mu_{m}+\mu_{s}=\mu_{2}  \tag{7}\\
& \lambda_{m} \mu_{s}=\lambda_{k} \mu_{2}
\end{align*}
$$

which also gives

$$
\begin{align*}
\mu_{2} & =\mu_{m}+\mu_{s} \\
\mu_{k} & =\mu_{s}\left(1+\frac{\mu_{s}}{\mu_{m}}\right) \\
\lambda_{k} & =\lambda_{m} \frac{\mu_{s}}{\mu_{m}+\mu_{s}}  \tag{8}\\
G_{k} & =G_{m}\left(1+\frac{\mu_{s}}{\mu_{m}}\right)^{2}
\end{align*}
$$

where $G_{m} \equiv \mu_{m} / \lambda_{m}$.
(ii) We can integrate the Jeffreys model by using an integrating factor as we discussed in class. Hence we take Eq. 6 and replace the left hand side by

$$
\begin{equation*}
\lambda_{m} \frac{\partial}{\partial t}\left\{\tau \exp \left(\frac{t}{\lambda_{m}}\right)\right\}=\exp \left(\frac{t}{\lambda_{m}}\right)\left\{\left(\mu_{m}+\mu_{s}\right) \dot{\gamma}+\lambda_{m} \mu_{s} \ddot{\gamma}\right\} \tag{9}
\end{equation*}
$$

Integrating this result from the appropriate limits, we have

$$
\begin{equation*}
\tau(t) \exp \left(\frac{t}{\lambda_{m}}\right)=\frac{1}{\lambda_{m}} \int_{-\infty}^{t} \exp \left(\frac{t^{\prime}}{\lambda_{m}}\right)\left\{\left(\mu_{m}+\mu_{s}\right) \dot{\gamma}\left(t^{\prime}\right)+\lambda_{m} \mu_{s} \ddot{\gamma}\left(t^{\prime}\right)\right\} d t^{\prime} \tag{10}
\end{equation*}
$$

So that we have

$$
\begin{equation*}
\tau(t)=\frac{1}{\lambda_{m}} \int_{-\infty}^{t} \exp \left(-\frac{t-t^{\prime}}{\lambda_{m}}\right)\left\{\left(\mu_{m}+\mu_{s}\right) \dot{\gamma}\left(t^{\prime}\right)+\lambda_{m} \mu_{s} \ddot{\gamma}\left(t^{\prime}\right)\right\} d t^{\prime} \tag{11}
\end{equation*}
$$

Next, we can eliminate the terms with $\ddot{\gamma}$ by using integration by parts on the term with $\ddot{\gamma}$.

$$
\begin{equation*}
\tau(t)=\frac{1}{\lambda_{m}} \int_{-\infty}^{t} \exp \left(-\frac{t-t^{\prime}}{\lambda_{m}}\right)\left(\mu_{m}+\mu_{s}\right) \dot{\gamma}\left(t^{\prime}\right) d t^{\prime}+\left.\exp \left(-\frac{t-t^{\prime}}{\lambda_{m}}\right) \mu_{s} \dot{\gamma}\left(t^{\prime}\right)\right|_{t^{\prime}=-\infty} ^{t^{\prime}=t}-\frac{1}{\lambda_{m}} \int_{-\infty}^{t} \exp \left(-\frac{t-t^{\prime}}{\lambda_{m}}\right) \mu_{s} \dot{\gamma}\left(t^{\prime}\right) d t^{\prime} \tag{12}
\end{equation*}
$$

which, provided $\dot{\gamma}$ is finite at $t^{\prime}=-\infty$, reduces to

$$
\begin{equation*}
\tau(t)=\frac{1}{\lambda_{m}} \int_{-\infty}^{t} \exp \left(-\frac{t-t^{\prime}}{\lambda_{m}}\right) \mu_{m} \dot{\gamma}\left(t^{\prime}\right) d t^{\prime}+\mu_{s} \dot{\gamma}(t) \tag{13}
\end{equation*}
$$

For a cessation of steady shear test, we have $\dot{\gamma}(t)=\dot{\gamma}_{0}(1-H(t))=\dot{\gamma}_{0} H(-t)$, where $H(t)$ is the Heaviside function. We take Eq. 13 and substitute in the strain rate function to obtain

$$
\begin{align*}
\tau(t) & =\frac{1}{\lambda_{m}} \int_{-\infty}^{t} \exp \left(-\frac{t-t^{\prime}}{\lambda_{m}}\right) \mu_{m} \dot{\gamma}_{0} H\left(-t^{\prime}\right) d t^{\prime}+\mu_{s} \dot{\gamma}_{0} H(-t) \\
\tau(t) & =\frac{1}{\lambda_{m}} \int_{-\infty}^{0} \exp \left(-\frac{t-t^{\prime}}{\lambda_{m}}\right) \mu_{m} \dot{\gamma}_{0} d t^{\prime}+\mu_{s} \dot{\gamma}_{0} H(-t)  \tag{14}\\
\tau(t) & =\exp \left(-\frac{t-t^{\prime}}{\lambda_{m}}\right) \mu_{m} \dot{\gamma}_{0}+\mu_{s} \dot{\gamma}_{0} H(-t)
\end{align*}
$$

In dimensionless form, this result is

$$
\begin{equation*}
\frac{\tau(t)}{\mu_{m} \dot{\gamma}_{0}}=\exp \left(-\frac{t-t^{\prime}}{\lambda_{m}}\right)+\beta H(-t) \tag{15}
\end{equation*}
$$

where $\beta \equiv \mu_{s} / \mu_{m}$. So we see that the initial stress is $\tau\left(t=0^{-}\right)=\left(\mu_{m}+\mu_{s}\right) \dot{\gamma}$, and that the stress instantaneously drops to $\tau\left(t=0^{+}\right)=\mu_{m} \dot{\gamma}$, since the solvent no longer contributes to the stress once the shearing is stopped.
(iii) To determine the complex modulus $G^{*}(\omega)$ it is convenient to use complex variables $\exp (i \omega t)=\cos (\omega t)+i \sin (\omega t)$, where $i \equiv \sqrt{-1}$. Note, that ultimately, we are concerned only with the real part of this complex variable. So we have

$$
\begin{gather*}
\gamma(t)=\operatorname{Re}\left\{-i \gamma_{0} \exp (i \omega t)\right\} \\
\dot{\gamma}(t)=\operatorname{Re}\left\{\gamma_{0} \omega \exp (i \omega t)\right\}  \tag{16}\\
\ddot{\gamma}(t)=\operatorname{Re}\left\{i \gamma_{0} \omega^{2} \exp (i \omega t)\right\}
\end{gather*}
$$

We also assume that the stress will take the form $\tau(t)=\operatorname{Re}\left\{\left(G^{\prime}(\omega)+i G^{\prime \prime}(\omega)\right)\left(-i \gamma_{0} \exp (i \omega t)\right)\right\}=$ $\operatorname{Re}\left\{\left(-i G^{\prime}(\omega)+G^{\prime \prime}(\omega)\right) \gamma_{0} \exp (i \omega t)\right\}$, (or equivalently $\tau(t)=G^{\prime}(\omega) \gamma_{0} \sin (\omega t)+G^{\prime \prime}(\omega) \gamma_{0} \cos (\omega t)$, when only the real part is considered). When we substitute these results in to Eq. 6 and ignore the Real operator $\operatorname{Re}\}$ which can be taken as implicit, we have

[^0]
$\left(-i G^{\prime}(\omega)+G^{\prime \prime}(\omega)\right) \gamma_{0} \exp (i \omega t)+i \lambda \omega\left(-i G^{\prime}(\omega)+G^{\prime \prime}(\omega)\right) \gamma_{0} \exp (i \omega t)=\left(\mu_{m}+\mu_{s}\right) \gamma_{0} \omega \exp (i \omega t)+i \lambda \mu_{s} \gamma_{0} \omega^{2} \exp (i \omega t)$
where we are writing $\lambda=\lambda_{m}$ for simplicity. Simplifying, we have
\[

$$
\begin{equation*}
\left(-i G^{\prime}(\omega)+G^{\prime \prime}(\omega)\right)(1+i \lambda \omega)=\left(\mu_{m}+\mu_{s}\right) \omega+i \lambda \mu_{s} \omega^{2} \tag{18}
\end{equation*}
$$

\]

which is

$$
\begin{equation*}
-i G^{\prime}(\omega)+G^{\prime \prime}(\omega)=\frac{\left(\mu_{m}+\mu_{s}\right) \omega+i \lambda \mu_{s} \omega^{2}}{1+i \lambda \omega} \tag{19}
\end{equation*}
$$

To obtain a real number in the denominator, we multiply the denominator and the numerator by the complex conjugate of the denominator $(1-i \lambda \omega)$.

$$
\begin{equation*}
-i G^{\prime}(\omega)+G^{\prime \prime}(\omega)=\frac{\left(\mu_{m}+\mu_{s}\right) \omega(1-i \lambda \omega)+i \lambda \mu_{s} \omega^{2}(1-i \lambda \omega)}{1+(\lambda \omega)^{2}} \tag{20}
\end{equation*}
$$

Simplifying, we have

$$
\begin{equation*}
-i G^{\prime}(\omega)+G^{\prime \prime}(\omega)=-i \frac{\mu_{m} \lambda(\lambda \omega)^{2}}{1+(\lambda \omega)^{2}}+\frac{\mu_{m} \lambda(\lambda \omega)}{1+(\lambda \omega)^{2}}+\mu_{s} \omega \tag{21}
\end{equation*}
$$

Recognizing that $\mu_{m}=G_{m} \lambda_{m}$, we have

$$
\begin{gather*}
G^{\prime}(\omega)=G_{m} \frac{(\lambda \omega)^{2}}{1+(\lambda \omega)^{2}}  \tag{22}\\
G^{\prime \prime}(\omega)=G_{m} \frac{\lambda \omega}{1+(\lambda \omega)^{2}}+\mu_{s} \omega
\end{gather*}
$$

Again, there is a viscous and a viscoelastic contribution to $G^{\prime \prime}$ only. In dimensionless form these results are

$$
\begin{gather*}
\frac{G^{\prime}(\omega)}{G_{m}}=\frac{(\lambda \omega)^{2}}{1+(\lambda \omega)^{2}}  \tag{23}\\
\frac{G^{\prime \prime}(\omega)}{G_{m}}=\frac{\lambda \omega( }{1+(\lambda \omega)^{2}}+\beta \lambda \omega
\end{gather*}
$$

The complex modulus is defined as $G^{*}(\omega) \equiv\left|-i G^{\prime}(\omega)+G^{\prime \prime}(\omega)\right|=\sqrt{G^{\prime 2}(\omega)+G^{\prime \prime 2}(\omega)}$, so we have the following plots. (See overleaf.)
(iv) For a creep compliance test, we instantly apply a constant stress of $\tau_{0}$ for all time $t>0$. Since we now wish to solve for the strain as a function of time, neither the differential form of the governing equation for the mechanical model given in Eq. 6 nor the integral form given in Eq. 13 is very convenient. Instead, it is useful to reconsider the original equations for stress and strain given in Eq. 1 for our new model, because strains add linearly for elements in series. We can solve for the two strains independently and then add them together to determine the total strain in time. The initial condition for the solvent strain is $\gamma_{2}(0)=0$.

Solving for the solvent, we have

$$
\begin{equation*}
\tau(t)=\tau_{0} H(t)=\mu_{2} \dot{\gamma}_{2} \tag{24}
\end{equation*}
$$

Hence $\gamma_{2}=\frac{\tau_{0}}{\mu_{s}} t$.
For the viscoelastic element, we have

$$
\begin{equation*}
\tau(t)=\tau_{0} H(t)=G_{k} \gamma_{k}+\mu_{k} \dot{\gamma}_{k} \tag{25}
\end{equation*}
$$

This is a first order, ordinary differential equation in $\gamma$ with a constant on the left side for all $t>0$. We can solve this equation to obtain ${ }^{1}$

$$
\begin{equation*}
\gamma_{k}(t)=\frac{\tau_{0}}{G_{k}}\left\{1-\exp \left(\frac{-t}{\lambda_{k}}\right)\right\} \tag{26}
\end{equation*}
$$

This result is consistent with the initial condition at $t=0$ that $\gamma_{k}=0$ and $\dot{\gamma}_{k}=\tau_{0} / \mu_{k}$.
The total strain is therefore

$$
\begin{equation*}
\gamma(t)=\frac{\tau_{0}}{\mu_{s}} t+\frac{\tau_{0}}{G_{k}}\left\{1-\exp \left(\frac{-t}{\lambda_{k}}\right)\right\} \tag{27}
\end{equation*}
$$

The compliance is defined $J(t) \equiv \gamma(t) / \tau_{0}$, and for a creep test with the Jeffreys model we obtain

$$
\begin{equation*}
J(t)=\frac{1}{\mu_{s}} t+\frac{1}{G_{k}}\left\{1-\exp \left(\frac{-t}{\lambda_{k}}\right)\right\} \tag{28}
\end{equation*}
$$

The normalized compliance is defined as $J(t) \equiv \gamma(t) / \tau_{0}$, and for the creep test we can thus write

$$
\begin{equation*}
J(t) G_{k}=\frac{1}{\beta} \frac{t}{\lambda_{k}}+\left\{1-\exp \left(\frac{-t}{\lambda_{k}}\right)\right\} \tag{29}
\end{equation*}
$$

(v) To solve for the start up of this uniaxial extensional flow, we use Eq. 13 in tensorial form to obtain three evolution equations for the three normal stresses.

$$
\begin{gather*}
\tau_{x x}(t)=\tau_{y y}(t)=-\frac{1}{\lambda_{m}} \int_{-\infty}^{t} \exp \left(-\frac{t-t^{\prime}}{\lambda_{m}}\right) \mu_{m} \dot{\varepsilon}_{0} H\left(t^{\prime}\right) d t^{\prime}-\mu_{s} \dot{\varepsilon} H(t) \\
\tau_{z z}(t)=\frac{1}{\lambda_{m}} \int_{-\infty}^{t} \exp \left(-\frac{t-t^{\prime}}{\lambda_{m}}\right) 2 \mu_{m} \dot{\varepsilon}_{0} H\left(t^{\prime}\right) d t^{\prime}+2 \mu_{s} \dot{\varepsilon}_{0} H(t) \tag{30}
\end{gather*}
$$

For times $t>0$, we have

[^1]
\[

$$
\begin{align*}
& \tau_{x x}(t)=\tau_{y y}(t)=-\left(1-\exp \left(-\frac{t}{\lambda_{m}}\right)\right) \mu_{m} \dot{\varepsilon}_{0}-\mu_{s} \dot{\varepsilon}_{0}  \tag{31}\\
& \tau_{z z}(t)=\left(1-\exp \left(-\frac{t}{\lambda_{m}}\right)\right) 2 \mu_{m} \dot{\varepsilon}_{0}+2 \mu_{s} \dot{\varepsilon}_{0}
\end{align*}
$$
\]

Hence the stress in the viscous solvent adapts immediately to the imposed extensional flow, just like a Newtonian fluid, while the stress in the viscoelastic component of the model grows toward steady state with an exponential decay on the time scale $\lambda_{m}$. The extensional viscosity is given by

$$
\begin{equation*}
\eta_{E}^{+} \equiv \frac{\tau_{z z}-\tau_{x x}}{\dot{\varepsilon}_{0}}=\left(1-\exp \left(-\frac{t}{\lambda_{m}}\right)\right) 3 \mu_{m}+3 \mu_{s} \tag{32}
\end{equation*}
$$

So at long times the Trouton ratio is always $\operatorname{Tr} \equiv \frac{\eta_{E}}{\mu_{m}+\mu_{s}}=3$, and so this model does not give rise to extensional strain-hardening. To generate strain-hardening, we need to consider the convected derivative discussed in class.

## Question 2

This problem was based on problem 9.15 on page 408 in Rubinstein \& Colby.
We are given DNA with molar mass $M=1.1 \times 10^{8} \mathrm{~g} / \mathrm{mol}$ corresponding to $n=1.64 \times 10^{5}$ base pairs.
(i) For a base pair length $l=0.34 \mathrm{~nm}$, the contour length is

$$
\begin{equation*}
R_{\max }=n l=\left(1.64 \times 10^{5}\right) \times(0.34 \mathrm{~nm})=5.58 \times 10^{4} \mathrm{~nm}=55.8 \mu \mathrm{~m} \tag{33}
\end{equation*}
$$

Equivalently, we have $R_{\max }=N b$, where $N$ is the number of Kuhn segments and $b$ is the Kuhn segment length. We are given the Kuhn segment length of $b=300 \mathrm{~nm}$, hence the number of Kuhn segments is

$$
\begin{equation*}
N=R_{\max } / b=\left(5.58 \times 10^{4} \mathrm{~nm}\right) /(300 \mathrm{~nm})=186 \tag{34}
\end{equation*}
$$

We can also calculate the root mean square size of the molecule which is $\left\langle R^{2}\right\rangle^{\frac{1}{2}}=\sqrt{N} b=1.27$ $\mu \mathrm{m}$, so it is clearly possible to see a molecule of DNA under a microscope, especially if using fluorescence microscopy.

Overlap occurs when the volume of each polymer $\frac{4}{3} \pi\left\langle R^{2}\right\rangle^{3 / 2}$ is roughly equal to the total system volume divided by the number of polymers $M / c^{*} N_{A}$, where $N_{A}$ is Avagadro's number.

$$
\begin{equation*}
c^{*} \approx \frac{M}{N_{A}} \frac{1}{\frac{4}{3} \pi\left\langle R^{2}\right\rangle^{\frac{3}{2}}}=\frac{M}{N_{A}} \frac{1}{\frac{4}{3} \pi\left(N b^{2}\right)^{3 / 2}}=6.36 \times 10^{-4} \mathrm{mg} / \mathrm{mL} \tag{35}
\end{equation*}
$$

Some students could have also used

$$
\begin{equation*}
c^{*} \approx \phi^{*} \frac{M_{0}}{b^{3} N_{A}}=\frac{M}{N_{A}} \frac{1}{\left(N b^{2}\right)^{3 / 2}}=1.52 \times 10^{-3} \mathrm{mg} / \mathrm{mL} \tag{36}
\end{equation*}
$$

where $M_{0}=M / N$ is the monomer molecular weight and we use the scaling $\phi^{*} \sim N^{-1 / 2}$.
Note that these results are just approximate and that we could have used the Fox-Flory equation given by Eq. 8.37 in Rubinstein \& Colby, in which case we have

$$
\begin{equation*}
c^{*} \approx \frac{1}{[\eta]} \approx \frac{M}{\Phi\left\langle R^{2}\right\rangle^{3 / 2}}=6.42 \times 10^{-3} \mathrm{mg} / \mathrm{mL} \tag{37}
\end{equation*}
$$

where $\Phi=0.425 N_{A}=2.5 \times 10^{23} \mathrm{~mol}^{-1}$ is a universal constant.
(ii) Given that the entanglement concentration is $c_{e}=10 c^{*}=6.36 \times 10^{-3} \mathrm{mg} / \mathrm{mL}$, where we have used our first result for $c^{*}$ above, we note that for the solution concentration of $c=0.5 \mathrm{mg} / \mathrm{mL}$ the system is in the entangled regime. To determine the contour length of an entanglement strand, we need the volume fraction at the entanglement concentration. To find this quantity, we must first find the volume fraction at the overlap concentration, $\phi^{*}$. We can use the expression in Eq. 36

$$
\begin{equation*}
\phi^{*} \approx c^{*} \frac{b^{3} N_{A}}{M_{0}}=0.017 \tag{38}
\end{equation*}
$$

The volume fraction at the entanglement concentration is $\phi_{e}=10 \phi^{*}=0.17$. Note that a number of students simply used the formula $\phi^{*} \sim N^{-1 / 2}=0.073$, but this approach gives an erroneous result since it is just a scaling relationship. The conversion factor $A$ for $c=A \phi$ from Eq. 38 that applies for a dilute solution is $A=b^{3} N_{A} / M_{0}=3.6 \times 10^{-2} \mathrm{mg} / \mathrm{mL}$, which is small indicating that a small mass of polymer coil occupies a large volume. On the other hand, in the melt, where $\phi=1, A=\rho$ or the density of the polymer. For intermediate concentrations, $3.6 \times 10^{-2} \mathrm{mg} / \mathrm{mL}<A<10^{3} \mathrm{mg} / \mathrm{mL}$, so without knowing the exact value of the prefactor $A$, we end up using one of these limits. As a consequence, we will notice below that our estimates for modulus, viscosity and relaxation time for semi-dilute solutions of DNA appear to be physically unreasonable in parts (ii) and (iii). However the results for parts (iv) and (v) are reasonable. An example study DNA solutions is Mason, Dhople \& Wirtz, Macromolecules, 31, 3600-3603 (1998). With this in mind, we proceed as follows.

We calculate $N_{e}(1)$ using Eq. 9.34 in Rubinstein \& Colby for a $\theta$-solvent

$$
\begin{equation*}
\frac{\phi_{e}}{\phi^{*}}=\frac{c_{e}}{c^{*}}=10=\frac{N_{e}(1)^{\frac{3}{4}}}{N^{\frac{1}{4}}} \tag{39}
\end{equation*}
$$

hence $N_{e}=123$. Therefore the contour length of an entanglement strand is

$$
\begin{equation*}
R_{e}=R_{\max } \frac{N_{e}}{N}=\left(5.58 \times 10^{4} \mathrm{~nm}\right)\left(\frac{123}{186}\right)=3.69 \times 10^{4} \mathrm{~nm}=36.9 \mu \mathrm{~m} \tag{40}
\end{equation*}
$$

Likewise, the molar mass of an entanglement strand is given by

$$
\begin{equation*}
M_{e}=M \frac{N_{e}}{N}=\left(1.1 \times 10^{8} \mathrm{~g} / \mathrm{mol}\right)\left(\frac{123}{186}\right)=7.27 \times 10^{7} \mathrm{~g} / \mathrm{mol} \tag{41}
\end{equation*}
$$

Finally, the plateau modulus at this concentration of $0.5 \mathrm{mg} / \mathrm{mL}$ and $30^{\circ} \mathrm{C}$ can be calculated using

$$
\begin{equation*}
G_{e}(\phi)=G_{e}(1) \phi^{\frac{7}{3}}=\frac{\rho R T}{M_{e}} \phi^{\frac{7}{3}} \tag{42}
\end{equation*}
$$

where we calculate the entanglement modulus first

$$
\begin{equation*}
G_{e}(1)=\frac{\left(10^{6} \mathrm{~g} / \mathrm{m}^{3}\right)(8.314 \mathrm{~J} / \mathrm{mol} . \mathrm{K})(303 \mathrm{~K})}{\left(7.27 \times 10^{7} \mathrm{~g} / \mathrm{mol}\right)}=34.65 \mathrm{~Pa} \tag{43}
\end{equation*}
$$

Now we can obtain the value of $G_{e}(\phi)$ by rewriting the equation as

$$
\begin{equation*}
G_{e}(\phi)=G_{e}(1)\left(\frac{\phi}{\phi^{*}}\right)^{\frac{7}{3}} \phi^{* \frac{7}{3}}=G_{e}(1)\left(\frac{c}{c^{*}}\right)^{\frac{7}{3}} \phi^{* \frac{7}{3}}=(34.65 \mathrm{~Pa})\left(\frac{0.5 \mathrm{mg} / \mathrm{mL}}{6.36 \times 10^{-4} \mathrm{mg} / \mathrm{mL}}\right)^{\frac{7}{3}}(0.017)^{\frac{7}{3}}=14.7 \mathrm{kPa} \tag{44}
\end{equation*}
$$

This number is very large for reasons quoted above.
(iii) The specific viscosity can be estimated by Eq. 9.47 in Rubinstein \& Colby, namely

$$
\begin{equation*}
\eta_{s p}=\left(\frac{\phi}{\phi^{*}}\right)^{\frac{14}{3}} \frac{N^{\frac{2}{3}}}{\left[N_{e}(1)\right]^{2}}=\left(\frac{c}{c^{*}}\right)^{\frac{14}{3}} \frac{N^{\frac{2}{3}}}{\left[N_{e}(1)\right]^{2}}=\left(\frac{0.5 \mathrm{mg} / \mathrm{mL}}{6.36 \times 10^{-4} \mathrm{mg} / \mathrm{mL}}\right)^{\frac{14}{3}} \frac{186^{\frac{2}{3}}}{123^{2}}=7.01 \times 10^{10} \tag{45}
\end{equation*}
$$

So to calculate the solution viscosity, we have

$$
\begin{equation*}
\eta_{s p} \equiv \frac{\eta-\eta_{s}}{\eta_{s}} \approx \frac{\eta}{\eta_{s}}=7.01 \times 10^{10} \tag{46}
\end{equation*}
$$

and hence the solution viscosity is $\eta=\left(7.01 \times 10^{10}\right) \eta_{s}=7.01 \times 10^{7} \mathrm{~Pa} . \mathrm{s}$, which is again quite large.

The relaxation time is given by $\tau_{\text {rep }}(\phi) \approx \eta / G_{e}(\phi)=\left(7.01 \times 10^{7} \mathrm{Pa.s}\right) /(14700 \mathrm{~Pa})=4770 \mathrm{~s}$.
(iv) The relaxation time of an entangled melt is given in Eq. 9.8 in Rubinstein \& Colby,

$$
\begin{equation*}
\tau_{\text {rep }} \approx \frac{\zeta b^{2}}{k T} \frac{N^{3}}{N_{e}} \tag{47}
\end{equation*}
$$

Here we have to estimate the drag coefficient in the melt $\zeta$, however the background viscosity is unknown. In the limit of concentrated solution with $\phi$ approaching unity, we can estimate $\zeta \approx \eta_{s} b$. Hence, the relaxation time is

$$
\begin{equation*}
\tau_{\text {rep }} \approx \frac{\eta_{s} b^{3}}{k T} \frac{N^{3}}{N_{e}(1)}=338 \mathrm{~s} \tag{48}
\end{equation*}
$$

In the case of the shortened DNA chains, the molecular weight is less than the entanglement molecular weight calculated above in part (ii). Hence the Rouse relaxation time is relevant in this regime. From Eq. 9.21 in Rubinstein \& Colby, we can determine the Rouse relaxation for the original chain,

$$
\begin{equation*}
\tau_{\text {rep }}=6 \tau_{R}\left(\frac{N}{N_{e}}\right) \tag{49}
\end{equation*}
$$

So the Rouse time of the original chain is $\tau_{R}=37.3 \mathrm{~s}$. Now, the determine the Rouse time of the shortened DNA chains $\tau_{R}^{\prime}$, we have

$$
\begin{equation*}
\frac{\tau_{R}^{\prime}}{\tau_{R}}=\left(\frac{N^{\prime}}{N}\right)^{2} \tag{50}
\end{equation*}
$$

Accordingly, we have

$$
\begin{equation*}
\tau_{R}^{\prime}=\tau_{R}\left(\frac{N^{\prime}}{N}\right)^{2}=(37.3 \mathrm{~s})\left(\frac{1.86}{186}\right)^{2}=3.73 \mathrm{~ms} \tag{51}
\end{equation*}
$$

The result is roughly five orders of magnitude smaller than the relaxation time of the melt.
(v) For a dilute solution of DNA, a CaBER test measures the Zimm relaxation time. The Zimm time is given by Eq. 9.21 from Rubinstein \& Colby

$$
\begin{equation*}
\tau_{Z}=0.163 \frac{\eta_{s} R^{3}}{k T}=0.163 \frac{\eta_{s}(\sqrt{N} b)^{3}}{k T} \tag{52}
\end{equation*}
$$

We note from part (i), that for a molecular weight of $M=1.1 \times 10^{8} \mathrm{~g} / \mathrm{mol}$, we have $N=186$ Kuhn segments. So we estimate that the Zimm relaxation time is

$$
\begin{equation*}
\tau_{Z}=0.163 \frac{\eta_{s} R^{3}}{k T}=0.163 \frac{\left(1 \times 10^{-3} \mathrm{Pa.s}\right) \sqrt{186}\left(3 \times 10^{-7} \mathrm{~m}\right)^{3}}{\left(1.38 \times 10^{-23} \mathrm{~J} / \mathrm{K}\right)(303 \mathrm{~K})}=0.014 \mathrm{~s} \tag{53}
\end{equation*}
$$

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### 2.341J / 10.531J Macromolecular Hydrodynamics

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[^0]:    ${ }^{0}$ Integration by parts is $\left.u v\right|_{x=a} ^{x=b}=\int_{a}^{b} u \frac{d v}{d x} d x+\int_{a}^{b} \frac{d u}{d x} v d x$.

[^1]:    ${ }^{1}$ Eq. 25 can be solved with an integrating factor by $\frac{\partial}{\partial t}\left\{\gamma_{k} \exp \left(\frac{t}{\lambda_{k}}\right)\right\}=\frac{1}{\lambda_{k}} \int_{-\infty}^{t} \exp \left(\frac{t}{\lambda_{k}}\right) \frac{\tau_{0} H(t)}{G_{k}} d t^{\prime}$.

