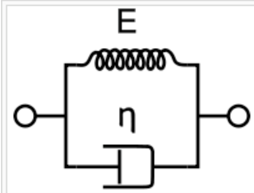
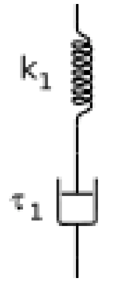
070601 Polymer Properties Quiz 8

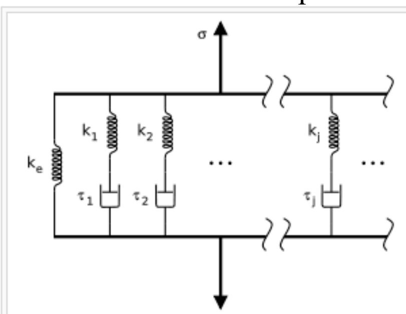
1) The Voigt Model and the Maxwell Model (1850's to 1880's) were used to describe viscoelastic properties of solids and liquids many years prior to the Rouse Model and prior to the development of the molecular Dumb Bell Model in physics.



Schematic representation of Kelvin-Voigt model.



a) Describe the Dumb Bell Model and compare it to these two models.
b) In the Voigt model the stress (force) of the system is the sum of the stress for the two components (strain is equal) while for the Maxwell model the strain (position) is the sum of the strains for the two components, a spring and a dash pot (stress is equal). Show which of these conditions is inherent to the Dumb Bell Model.
c) The Voigt and Maxwell Models are often combined in more complex relaxation models need to describe solid-like features in liquids and liquid-like features in solids.



Schematic of Maxwell-Weichert Model

Explain how the Dumb Bell model might be modified to accommodate more complex relaxations.
d) Is it physically possible for a system to display more than one relaxation time? Explain.
e) Write the constitutive equations involving the friction factor and the spring constant and show by unit analysis that the units of the relaxation time are time, $\tau = \xi_{vis}/k_{spr}$.

2) a) What is the difference between the Rouse Model and the Dumb Bell Model?
b) What is the difference between the Maxwell-Weichert Model shown above and the Rouse Model?
c) In a simple analysis, such as shown for the Maxwell-Weichert Model above, how many relaxation times would a Rouse chain display?
d) How is the size of a Rouse unit determined?
e) Would the number of relxation times displayed by the Rouse chain depend on the definition of a Rouse unit?

3) The dynamics of chains in dilute solutions in good solvents are often modeled using the Rouse theory.

a) What assumptions are involved in the use of the Rouse theory?
b) Are these assumptions appropriate for a chain in a dilute solution in a good solvent?
c) In order for the Rouse chain's dynamic properties to not depend on the size of a Rouse unit $\left(\xi_R / a_R^2\right) = \text{constant}$, where a_R is the size of a Rouse unit and ξ_R is the friction factor of the Rouse unit. What does this mean in terms of the solvent interaction with the chain coil? (For a Gaussian chain $a_R^2 \sim N_R l^2$.)
d) The Mark-Houwink parameter, "a", relates the intrinsic viscosity to the molecular weight,
$[\eta] = kN^a$. What is the value of "a" for the chain of part c?
e) How does the value of "a" in part d compare with the expected value for a non-draining Gaussian Chain and a non-draining excluded volume chain?

4) a) Write the force balance (Langevin Equation) for a Rouse chain.
b) Why is inertia ignored in this force balance?
c) What term would be included if inertia were not ignored?
d) What effect would inertia have on the response of the Rouse chain?
e) Explain how the expression $e^{il\delta}$ is part of the equation for a wave.

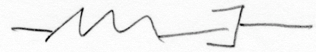
5) The Rouse Model results in a relaxation time of the form, $\tau = \dfrac{\xi_R}{4b_R \sin^2\left(\delta/2\right)}$, while the Dumb Bell model results in a relaxation time of the form, $\tau = \dfrac{\xi_R}{b_R}$.

a) Explain the similarities between these two expressions. (Why would they be similar?)
b) Explain the differences between these two expressions.
c) Calculate the values of δ for a cyclic chain of length N.
d) Calculate the values of δ for a linear chain of length N.
e) Explain the difference between these two in terms of the structure of a cyclic chain.

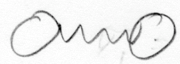
ANSWERS: 070601 Polymer Properties Quiz 8

ANSWERS QUIZ 8 ①

1) a) DumbBell model is similar to the Maxwell Model



$\sigma_1 = E\varepsilon \qquad \eta \frac{d\varepsilon}{dt} = \sigma_2$



$\xi_{vis} \frac{dz}{dt} = K_{spr} z$

$F_1 = F_2$

$\boxed{\tau = \frac{\xi}{K_{spr}}}$

For Maxwell $\sigma_1 = \sigma_2$

$E\varepsilon = \eta \frac{d\varepsilon}{dt}$

$\boxed{\tau = \left(\frac{\eta}{E}\right)}$

b) DumbBell follows stress is equal (Maxwell) since we equate the forces.

c) Similar to the mechanical model we could envision molecular structures that display various relaxation elements joined in different molecular topologies.

d) Yes. In the Maxwell-Weichert model any number of different relaxation times are displayed. Similarly, the modes of Rouse relaxation each have a distinct relaxation time

c)

$$F_{vis} = \zeta \frac{dz}{dt}$$

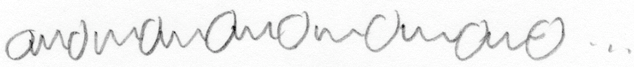
$$F_{elast} = K_{spr} z$$

$$K_{spr} = \frac{\text{Force}}{\text{distance}} \qquad \zeta = \frac{\text{Force time}}{\text{distance}}$$

so

$$\tau = \frac{\zeta}{K_{sp}} = \text{time}$$

2) a) Rouse models a series of Dumb Bells connected in series



b) M-W model is a Macroscopic Viscoelastic Model while Rouse is molecular model. M-W is a parallel model; Rouse is series.

(3)

c) Rouse chain displays N_R relaxation times.

d) Arbitrary

e) Yes if $\frac{\zeta_R}{a_R^2} \neq$ constant

No if $\frac{\zeta_R}{a_R^2} =$ constant (Free Draining Assumption)

3) a) - Gaussian Chain

- Free Draining Chain

- Low deformation (Perturbation)

b) For the Most Part No.

c) It means that $\zeta_R = N_R \, \zeta_{1 \text{ Kuhn unit}}$ so each unit adds linearly to the viscous drag. Free Draining

d) "a" = 1 since $[\eta] \sim N_R$

e) Gaussian "a" = 0.5

Excluded Volume "a" = 0.8

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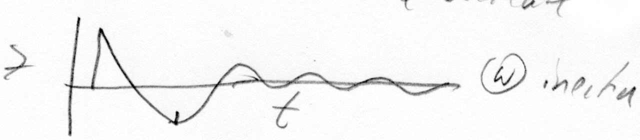
4) a) $\zeta_R \frac{dz}{dt} = b_{spr}\left(z_{\ell+1} + z_{\ell-1} - 2z_\ell\right)$

b) polymer units have almost no mass so

$$\overset{0}{\cancel{m}}\frac{d^2z}{dt^2} \cong 0$$

c) $m\frac{d^2z}{dt^2} = F_{inertial}$

d) Inertia is the restoring force so if significant mass were present the chain would overshoot $0 = z$ & oscillate



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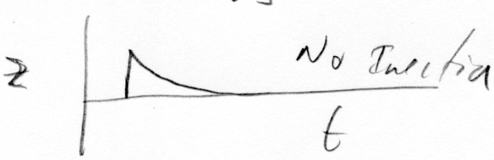

e) $e^{i\ell\delta} = \cos(\ell\delta) + i\sin(\ell\delta)$

real wave imaginary wave

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5) a)

δ_m has a finite smallest value

for the first order relaxation

lowest order Rouse Mode

Then τ is the longest relaxation time

& the chain behaves like a dumb bell.

b) $\tilde{\tau}_R$ has different values for different modes due to breaking the chain into N_R units.

c) For Cyclic

$$z_\ell = z_{\ell+N}$$

at $z_{\ell+N}$ $\delta = N\delta_m$

&

δ must $= m2\pi$ since it has to be perfectly in phase

so $\boxed{\delta_m = \frac{m\,2\pi}{N}}$ cyclic

d) For Linear

There is no loss (imaginary) part to the wave solution

at $\ell = 0$ or at $\ell = N-1$

For $\ell = 0$ or $(N-1)$ $z_\ell = \exp\left(-\frac{t}{\tau}\right) \exp(i\ell\delta) = \exp\left(-\frac{t}{\tau}\right)[\cos\ell\delta + i\cancel{\sin\ell\delta}]$ 0

So $z = \exp\left(-\frac{t}{\tau}\right) \cos l\delta$ for $l = 0$ or $(N-1)$

$$\frac{dz}{dl} = \exp\left(-\frac{t}{\tau}\right) \sin l\delta \equiv 0$$

$$\frac{dz}{dl} = 0 \text{ at } l = 0 \text{ or } (N-1)$$

so

$$\sin((N-1)\delta_m) = 0$$

$$\boxed{\delta_m = \frac{m\pi}{(N-1)}}$$

Linear

e) $\delta_{m\,\text{Cyclic}} \sim 2 \cdot \delta_{m\,\text{Linear}}$

This is because a cyclic chain is like 2 Linear chains hooked together