Quiz 8 Polymer Physics 11/18/00

The Rouse model represents a polymer coil as a series of beads and springs.

a) The Rouse spring has a spring constant based on rubber elasticity theory. This is sometimes called the ideal rubber law in analogy to an ideal gas.
-What is the association between an ideal rubber and an ideal gas?

b) The Maxwell model for visco-elasticity is based on a dash pot (viscous element) and a spring (Hookean elastic). This is similar to the Rouse model.
-What is the difference between the Maxwell model and the Rouse model consider:
-The assumptions involved in defining a Rouse unit,
-The molecular and theoretical basis of a Rouse spring,
-The molecular and theoretical basis for a Rouse bead,
-The ability of the 2 models to predict behavior in terms of molecular features.

c) The relaxation time for a Maxwell element is the viscosity of the dash pot divided by the spring constant for the spring, $\tau = \eta/k_{spr}$. The following expression, $\tau = \zeta_R/\{4b_R \sin^2(\delta/2)\}$, was obtain for a Rouse chain of infinite molecular weight.
-What are the similarities between the two relaxation times?
-What are the differences?
-Describe the terms in the Rouse relaxation time with respect to the Rouse Model.
-What is δ and what values can it take for an infinite chain?

d) The term "Free-Draining" is often associated with the Rouse model. Free draining means that solvent or other polymer chains have no effect on the dynamic response of a chain, i.e. the solvent can freely move in and out of the Rouse chain.
-Explain why free-draining might be associated with the Rouse model.
-Why would the ratio of the Rouse friction factor, to the mean square Rouse size, ζ_R/a_R^2, be constant in the number of mer units for a Rouse unit under a free-draining model?

e) The Rouse model is in some ways identical in dynamic behavior to the dumb bell model. This similarity relies on the dominance of the lowest order modes on the dynamic response as will be discussed in class.
-Give expressions for the relaxation time for the dumb-bell and Rouse models.
-How does the dumb-bell model compare with a Maxwell element in terms of the relaxation time?

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a) Both the ideal rubber and the ideal gas assume no change in enthalpy with deformation. That is, both are based on a purely entropic response for the systems. Because of this, both cases result in a responding force that is proportional to temperature.

b) The difference between the Maxwell model and the Rouse model involves the molecular basis for the springs and viscous elements in the Rouse model. The Rouse units are physically linked to the real structure of the chain while the Maxwell units are empirical constructions. The Rouse unit must be large enough so that rubber elasticity and Stokes law can be applied but small enough so that a preferred direction of dynamic response can be observed, i.e. the definition of a Rouse unit is identical to the definition of a sub-volume element, "v" in our discussion of the fluctuation dissipation theroem. The Rouse spring will follow, $b_R = 3kT/a_R^2$. The Rouse bead will follow $F_R = \zeta_R\ dz_{l/}dt$. Where ζ_R is the friction faction for a Rouse bead that follows the ideal rubber law, $\zeta_R = 3kT/\langle a_R^2\rangle$.

c) The similarity is that the viscosity, η and the friction factor ζ_R describe viscous features for the system and the spring constant, k, and rubber elasticity term, b_R, describe Hookean behavior. The phase factor, δ, gives a description of the temporal relationship in response between Rouse units. For an infinite chain δ is a continuous function between $-\pi$ and π. The Rouse equation is based on molecular structure while the Maxwell equation is empirical, i.e. the viscosity and spring constant do not have a connection with the structure of the material in any real way.

d) The "free-draining limit" pertains to polymers in dilute solution. Under a non-draining assumption the coil is assumed to trap all solvent molecules within the coil leading to the expected behavior or the intrinsic viscosity for theta and good solvents (Mark-Houwink parameter of 0.5 and 0.8 respectively). For a "free draining coil", i.e. a Rouse coil, no solvent is trapped and only the effect of the added Rouse segments or chain units with molecular weight is observed. The Mark-Houwink parameter is 1.0 under these conditions. The assumption that (ζ_R/a_R^2) is constant means that each chain unit or Rouse segment adds linearly to the dynamic response. For a free draining chain the size of the Rouse unit is of no consequence.

e) The Rouse expression is given in question "a". The dumb-bell model yields $\tau = \zeta_R/k_{spr}$. The dumb-bell model is basically the same as a Maxwell model.