Quiz 11
Polymer Physics
April 5, 2017

a) The harmonic mean is used to average rates for example the harmonic mean of v_1 and v_2 is $v_{hm} = \frac{2v_1v_2}{v_1+v_2} = \frac{2}{1/v_1 + 1/v_2}$. How does the RPA equation for scattering compare with a harmonic mean? In what way is the scattered intensity a rate?

b) To consider scattering from a polydisperse sample the scattered intensity is considered an arithmetic mean of the component scatterers. $I_{total} = \sum p(R) I_R$, where p(R) is the probability of the component with size R. Why would a harmonic mean be appropriate for intertwined polymer chains and an arithmetic mean be appropriate for a polydisperse sample of the same chain? From a scattering perspective what is the difference between polydisperse components of the same material and two different materials that are mixed?

c) Use a force balance for Newton's second law, F = ma, and Stokes law to calculate the relaxation time for Brownian motion.

d) For a creep experiment sketch the change in length versus time showing the elastic, viscous and anelastic parts. Which component displays a time constant?

e) Describe the Boltzmann superposition principle.

Answers: Quiz 11
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a) The RPA equation:

$$\frac{1}{S(q)} = \frac{1}{\phi_1 N_1 S_D(q,R_{g1})} + \frac{1}{\phi_2 N_2 S_D(q,R_{g2})} - 2\chi \qquad \text{(7) (RPA Blend)}$$

is a harmonic mean of the scattering from two components of a blend. The scattered intensity is measured as a rate, counts per time. So it might make sense that the average rate is calculated in this way. This kind of average would be used if you had a certain interest rate for the first half of a year and a different interest rate for the second half of a year. For velocities you would travel the same distance at two different velocities. If you spent the same amount of time at the two velocities you would use an arithmetic mean.

b) For polydisperse materials the components are viewed as contributing to the overall intensity independently. It is as if there were layers of the different components that sum to give the total. The components are independent of each other. For the RPA equation the inverse sum relies on interaction between the two components. This is the internal field in the derivation of the RPA. So the two situations are conceptually different. There is no internal field between the components for the polydisperse sample.

c)

$$m\,(dV/dt) = -6\pi\eta_s a\,V$$

$$V = V_0\exp(-6\pi\eta_s a\,(t_1 - t_2)/m) = V_0\exp(-(t_1 - t_2)/\tau_V)$$

$$\tau_V = m/(6\pi\eta_s a)$$

d)

Creep Experiment

$$\varepsilon_{11} = \sigma_{11}/E$$

$$d\varepsilon_{12}/dt = \sigma_{12}/\eta$$

$$\varepsilon_{11} = k\,(1 - \exp(-t/\tau))$$

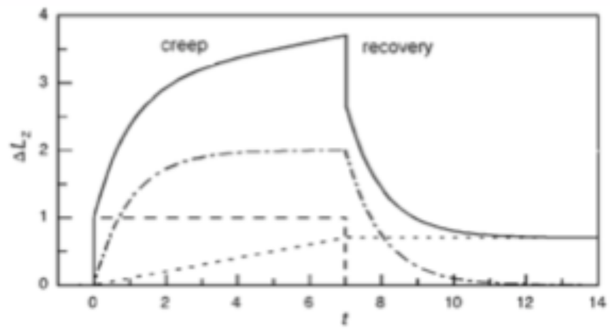

Fig. 6.1. Creep curve of a polymer sample under tension (schematic). The elongation ΔL_z induced by a constant force applied at zero time is set up by a superposition of an instantaneous elastic response (*dashed line*), a retarded anelastic part (*dash-dot line*), and viscous flow (*dotted line*). An irreversible elongation is retained after an unloading and the completion of the recovery process

e)

Boltzmann Superposition

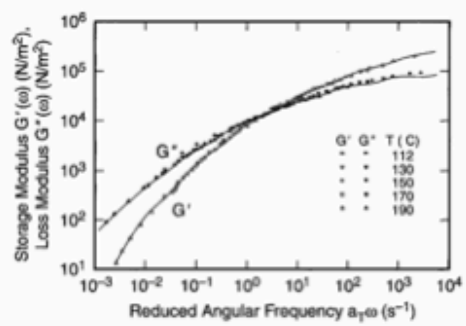

Figure 1.11 Storage and loss moduli for a low density polyethylene "Melt I." (These data were measured at several temperatures and shifted along the frequency axis by a "shift factor" a_T to form collapsed curves; see Section 3.5.2). The lines are empirical fits of Eqs. (3-25a) and (3-25b) to the data. (From Laun 1978, reprinted with permission from Steinkopff Publishers.)

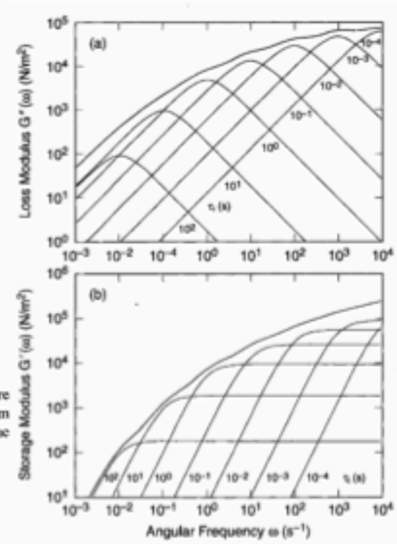

Figure 3.9 (a) Loss modulus G'' and (b) storage modulus G' versus frequency computed from Eqs. (3-25a) and (3-25b) for the eight modes given in Table 3-1 for Melt I, a polyethylene melt. Summing up over all the modes gives the "envelope" curves shown; these curves are reproduced in Fig. 1-11, where they are seen to represent accurately the linear data for this melt. (From Laun 1978, reprinted with permission from Steinkopff Publishers.)