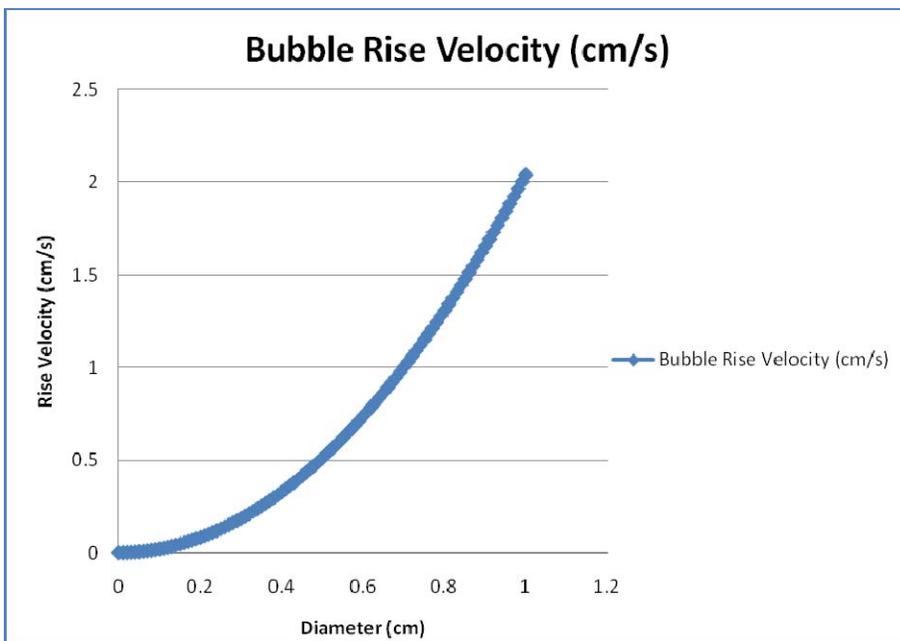


SAMPLE ANSWERS TO HW SET 3A

Copied below are some examples of (more or less) successful answers to the HW problems that were originally due on Sept. 26th. I selected these examples to give everyone an idea on how to solve each problem- don't read anything into why I chose what examples I did. Mostly, I've selected answers that seem straight-forward.

1. Calculate the rate of rise of spherical bubbles of different sizes (from 10 microns to 1 cm) in a molten glass tank, glass density 2.5 g/cm³ and a viscosity of 10² P. How long will it take bubbles of different sizes to rise 100 cm under these conditions?

Example 1:

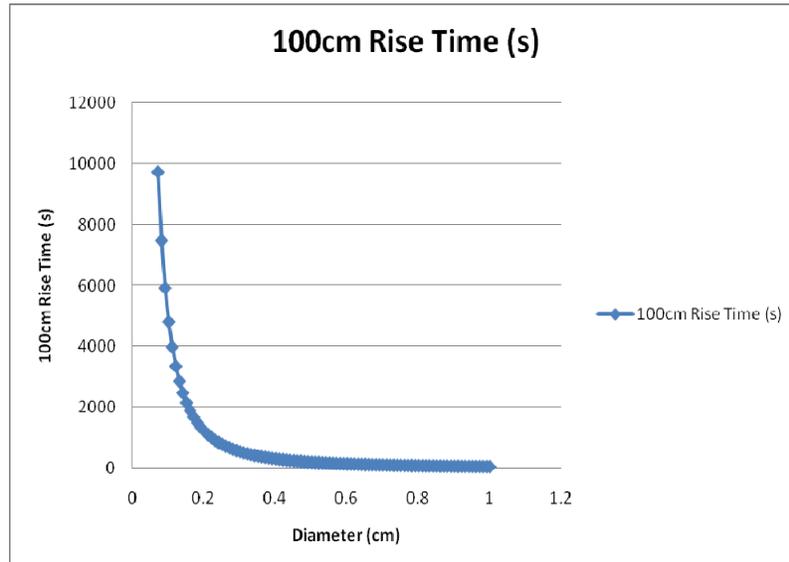


Use of the formula $V = d^2 * g * (\rho_{\text{bubble}} - \rho_{\text{liquid}}) / (12 * \eta)$ gives the above curve for the glass melt of density 2.5 g/cm³ and viscosity of 10² P, assuming the bubbles have the density of dry air (approximately 0.0012 g/cm³). The velocity-diameter curve shows a quadratic relationship, since the velocity varies with the square of the bubble diameter. Some rise velocities are given in the table below:

Diameter (cm)	Rise Velocity (cm/s)
0.001	2.04069E-06
0.01	0.000204069
0.1	0.020406867
1	2.040686667

Since velocity is equal to the rise distance divided by the rise time, rearrangement of the velocity equation gives the formula $t_{\text{rise}} = (12 * y * \eta) / (d^2 * g * (\rho_{\text{bubble}} - \rho_{\text{liquid}}))$, where y is the

vertical rise distance of 100cm. The rise time thus varies inversely with the square of the bubble diameter, leading to the curve shown below.



Example 2:

The velocity of bubble rise was calculated using the corrected Stoke's Formula below where:

v=rate of rise

r=bubble radius

ρ = density of the glass

ρ° =density of the air inside the bubble

g = acceleration of gravity

η = viscosity of the glass

η° = viscosity of the air inside the bubble

$$v = \frac{2r^2(\rho - \rho^{\circ})g}{9\eta} \frac{3\eta + 3\eta^{\circ}}{2\eta + 3\eta^{\circ}}$$

The time for each bubble to rise 100cm was then calculated using the velocity.

ρ (g/cm ³)	η (P)	ρ° (g/cm ³)	η° (P)	d (cm)
2.5	100	1.20E-03	1.78E-04	100

r (cm)	v (cm/s)	t (s)
0.001	8.17E-06	1.22E+07
0.002	3.27E-05	3.06E+06
0.003	7.35E-05	1.36E+06
0.004	1.31E-04	7.65E+05
0.005	2.04E-04	4.90E+05
0.006	2.94E-04	3.40E+05
0.007	4.00E-04	2.50E+05
0.008	5.23E-04	1.91E+05
0.009	6.62E-04	1.51E+05
0.01	8.17E-04	1.22E+05
0.02	3.27E-03	3.06E+04
0.03	7.35E-03	1.36E+04
0.04	1.31E-02	7.65E+03
0.05	2.04E-02	4.90E+03
0.06	2.94E-02	3.40E+03
0.07	4.00E-02	2.50E+03
0.08	5.23E-02	1.91E+03
0.09	6.62E-02	1.51E+03
0.1	8.17E-02	1.22E+03
0.2	3.27E-01	3.06E+02
0.3	7.35E-01	1.36E+02
0.4	1.31E+00	7.65E+01
0.5	2.04E+00	4.90E+01
0.6	2.94E+00	3.40E+01
0.7	4.00E+00	2.50E+01
0.8	5.23E+00	1.91E+01
0.9	6.62E+00	1.51E+01
1	8.17E+00	1.22E+01

In general, almost everyone nailed this problem. The most egregious mistakes involved using a significant density for the gas bubble- in reality, you could ignore the gas density and get a reasonable answer. A few had some problems with units- and so had answers off by some factor of ten. One or two provided answers that I couldn't really decipher.

Average score on the 26 answers submitted: 23.1/25

2. Consider a soda-lime silicate glass fiber in a Littleton softening point experiment. The surface tension of the glass in a dry atmosphere is 300 mN/m and the measured Littleton softening point is 750 °C. When the fiber is equilibrated in a wet atmosphere, the surface tension is reduced to 200 mN/m. By how much does the apparent Littleton softening temperature change?

Example 1:

Problem 2

The equation for η determination via fiber softening is;

$$\eta = \left[\left(Lp + \frac{p^2}{2} \right) \rho g - \frac{\gamma p}{r} \right] / 3 \left(\frac{dp}{dt} \right)$$

where η is glass viscosity in Poise

L is fiber length below the furnace (13.5cm)

p is fiber length within the furnace (10cm)

ρ is glass density, assumed to be a constant (2.596m³)

g is gravity's acceleration (980cm/s²)

γ is surface tension (300g/s² & 200g/s²)

r is fiber radius (0.075cm)

$\left(\frac{dp}{dt} \right)$ is the rate of fiber lengthening (1.67x10⁻³cm/s by definition of the softening point.

$$\eta_{750} = \left[\left((13.5 + 50) \cdot 2.5(980) - \frac{300(10)}{0.075} \right) \right] / 3 \cdot 1.67 \times 10^{-3} = \frac{453250 - 133.3(300)}{0.00501}$$

$$= 10^{7.92} \text{ Pa}\cdot\text{s} = 10^{6.92} \text{ Pa}\cdot\text{s} \sim 10^{6.9164} \text{ Pa}\cdot\text{s}$$

$$\eta_T = \frac{453250 - 133.3(200)}{0.00501} = 10^{7.93} \text{ Pa}\cdot\text{s} = 10^{6.93} \text{ Pa}\cdot\text{s} \sim 10^{6.9302} \text{ Pa}\cdot\text{s}$$

Solve VFT equation for T

$$\log \eta \text{ (Pa}\cdot\text{s)} = A + B / (T - T_0)$$

~~$$\log \eta = A + B / (T - T_0)$$~~

$$\frac{\log \eta - A}{B} = \frac{1}{T - T_0} \rightarrow T - T_0 = \frac{B}{\log \eta - A} \rightarrow T = \frac{B}{\log \eta - A} + T_0$$

For typical SLS container glass $A = -2.309$; $B = 3922$; $T_0 = 291$

~ these numbers are not exact for our system, yielding low temperatures for given viscosities, however, because the viscosity change is very small, we will approximate ΔT with the numbers.

$$T_{\eta_{750}} = \frac{3922}{6.9164 + 2.309} + 291 = 716.13^\circ\text{C} \quad T_{\eta_T} = \frac{3922}{6.9302 + 2.309} + 291 = 715.50^\circ\text{C}$$

* The temperature changes by approximately 0.6°C (confirmed by SLS window glass values too)

Example 2:

The equation to describe the viscosity of a fiber in a fiber elongation experiment is:

$$\eta = \frac{\left(\frac{Lp + p^2}{2}\right)\rho g - \frac{\gamma}{r}}{3\frac{dp}{dt}}$$

where η is the viscosity, L is the length of fiber outside of the furnace, p is the length of fiber inside the furnace, ρ is the glass density, g is the acceleration of gravity, γ is the surface tension, r is the average radius of the fiber, and dp/dt is the fiber elongation rate. The Littleton softening point experiment has set values for many of these variables, such that $\eta = 10^{6.65}$ Pa·s when $L = 0.135$ m, $p = 0.100$ m, $r = 0.275$ - 0.375 mm, and $dp/dt = 1$ mm/min.

If a glass with a surface tension of $\gamma = 300$ mN/m is subjected to these conditions (and if we assume the average acceptable radius of 0.325 mm), we can back calculate the density of the glass from the above equation to be 2.738 g/cm³.

$$\rho = \frac{3\eta\frac{dp}{dt} + \frac{\gamma}{r}}{g\left(\frac{Lp + p^2}{2}\right)} = \frac{3(10^{6.65} \text{ Pa} \cdot \text{s})\left(\frac{0.001\text{m}}{60 \text{ sec}}\right) + \frac{(0.3 \text{ Nm}^{-1})(0.10\text{m})}{0.000325\text{m}}}{(9.81\text{m} \cdot \text{s}^{-2})\left(\frac{0.135\text{m} \times 0.100\text{m} + (0.100\text{m})^2}{2}\right)} = 2738.4 \text{ kg} \cdot \text{m}^{-3}$$

If this same glass was then equilibrated in a wet atmosphere such that the surface tension was lowered to 200 mN/m, the apparent viscosity would decrease to $10^{6.706}$ Pa·s.

$$\begin{aligned} \eta &= \frac{\left(\frac{Lp + p^2}{2}\right)\rho g - \frac{\gamma}{r}}{3\frac{dp}{dt}} \\ &= \frac{\left(\frac{0.135\text{m} \times 0.100\text{m} + (0.100\text{m})^2}{2}\right)(2738\text{kg} \cdot \text{m}^{-3})(9.81\text{m} \cdot \text{s}^{-2}) - \frac{(0.200\text{N} \cdot \text{m}^{-1})(0.100\text{m})}{0.000325\text{m}}}{3\left(\frac{0.001\text{m}}{60 \text{ sec}}\right)} \\ &= 5082201 \text{ Pa} \cdot \text{s} = 10^{6.706} \text{ Pa} \cdot \text{s} \end{aligned}$$

Examining the viscosity-temperature relationship of a typical soda lime silicate glass will give us the apparent Littleton softening temperature in the wet conditions. We can assume that the viscosity follows a VFT relationship, described by the following equation:

$$\eta = \eta_o \exp\left[\frac{\Delta H}{R(T - T_o)}\right],$$

and we can solve for the pre-exponential factor (η_o), activation energy of viscosity (ΔH), and constant (T_o) by solving simultaneous equations with known values of viscosity and temperature. For a typical soda lime silicate container glass, Varsh gives the following viscosity-temperature values:

η (Pa·s)	T (°C)
10	1450
$10^{6.65}$	750
10^{15}	450

Plugging these values into the VFT equation and solving simultaneously yields the following values for the unknown variables:

Variable	Value
η_o (Pa·s)	1.913E-05
ΔH (J/mol)	154180
T_o (°C)	41.6

We can plug these values back into the VFT equation, along with a viscosity value of $\eta = 10^{6.706}$ Pa·s, to obtain the temperature at which the given viscosity will be observed. The result is 746.6 °C.

$$T = T_o + \frac{\Delta H}{R \ln\left(\frac{\eta}{\eta_o}\right)} = 41.6^\circ C + \frac{154180 J / mol}{(8.314 J / molK) \ln\left(\frac{10^{6.706}}{1.913E-5}\right)} = 746.6^\circ C$$

Therefore, the apparent Littleton softening temperature will decrease by ~ 3.4 °C when the surface tension of the SLS glass drops from 300 mN/m to 200 mN/m when equilibrated in a wet atmosphere.

This problem was tricky. The best approach, I think, was to consider how the apparent viscosity would change with decreasing surface tension (it would appear to decrease because a lower surface tension offers less resistance to the fiber elongation) and then to estimate the temperature change that would produce an equivalent viscosity change. These two examples took this approach. The answers are a bit different, principally because of assumptions about $\eta(T)$, but the approach is solid....

Average score on the 26 answers submitted: 20.8/25

3. Review the 1995 Science article by Angell, then describe and explain in detail the relationship between the change in heat capacity at T_g and the fragility characteristics of the corresponding melt viscosities. On the Angell 'fragility plot' why do all normalized viscosity curves converge at an apparent viscosity of $\sim 10^{-4}$ P as $T_g/T \rightarrow 0$?

Example 1

Problem 3

The key concept tying together heat capacity and melt fragility around the glass transition temperature region is configurational entropy. Because configurational entropy is dictated by the freedom the network has to take on different order, melts which have more freedom to change in their structures have higher configurational entropy. Therefore configurational entropy is directly related to melt fragility, which increases with a looser network structure resulting in starkly non-arrhenius behavior.

Systems with looser structures and thus greater configurational entropy and a high degree of melt fragility also experience a steep change in heat capacity upon cooling through the glass formation region. This is due to the dependence of the heat capacity of a liquid upon the configurational entropy; high entropy correlates to a high heat capacity. However as the system cools through the glass transformation region, the configurational entropy must drop to the values associated with the glassy solid. This drop is rapid and its continuation below the glass transformation range would produce configurational entropy for a disordered state with a value less than that of the ordered state, this has been termed the 'entropy crisis'. To counterbalance this effect and prevent the entropy from dropping to sub-crystalline values, the heat capacity undergoes drastic changes, dropping right at the glass transition. Therefore the glass transition, which has classically been thought of as a purely kinetic process has hidden thermodynamic components.

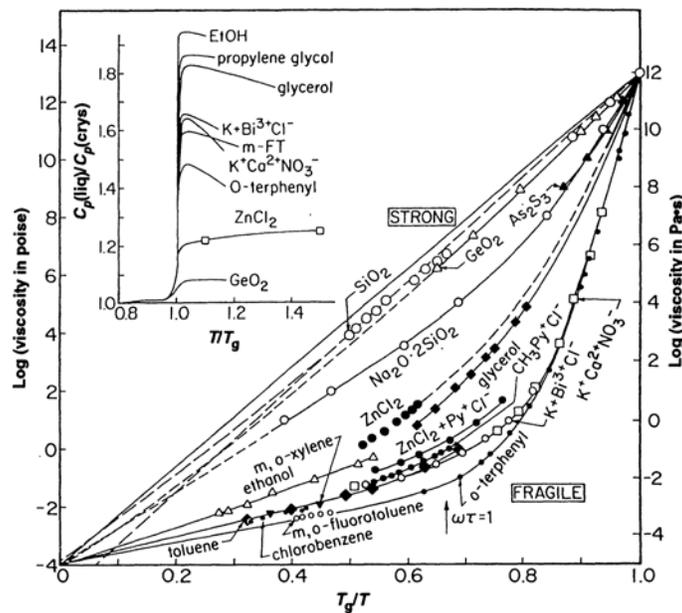
Strong melts which do not have such structural flexibility and thus have smaller configurational energy changes have a smaller 'crisis' upon cooling and thus exhibit a lesser drops in heat capacity.

I answer the second portion of the question on intuition, backed up on liquid viscosity values from the CRC Handbook. First it must be recognized that the extrapolation of the curves given in Angell's fragility graph to $T_g/T=0$ require an infinite temperature! Therefore, at some point all of these materials would break down and undergo a phase transition into a gas. Thus it seems that 10^{-4} P is roughly the viscosity of a gas near its condensation temperature. CRC values for viscosities of liquids near their boiling point confirm that this is a generic cutoff range for viscosity values. Similarly we could question why all of the curves seem to converge at 10^{13} P at $T_g/T=1$. This is simply because solids cannot strictly be considered viscous liquids and are in a field of their own. However scientist that have considered the possibility of classifying solids as viscous liquids identify them as having viscosities of greater than 10^{13} P.

The first part of the answer discusses the effects of structural changes in supercooled melts near T_g on changes in heat capacity and viscosity. Most answers I received were similar, but most people had problems with the second part of the question. I like the last part of the answer shown above. Turns out that the viscosity (at room temperature and pressure of common gases also fall within the range $10^{-3.5}$ - 10^{-5} Pa·s range, the same range for which the VFT extrapolations for silicate melts converge when $T \rightarrow \infty$. (See Russell et al., Amer. Mineral. 88 1390 (2003).

Example 2

The “Angell” plot of viscosity versus normalized temperature showing strong and fragile liquid behavior is shown below (from C.A. Angell, “Formation of glasses from liquids and biopolymers”, *Science* **267** [5206] 1924-35 (1995)).



Glass transition regions are often described by “the temperature of onset C_p increase, ΔC_p , during heating”. The heat capacity of a material is a measure of a heat energy required to increase the temperature of a quantity of material by a certain temperature interval

$$\left(C_p = \left(\frac{\delta Q}{dT} \right)_p \right),$$

and is affected not only by the molar mass of the substance, but also by the available degrees of freedom and the bonding within the substance. Therefore, structural changes will greatly affect heat capacity.

Strong melts are characterized by having a strong resistance to structural change. As the temperature is increased over a wide temperature range above the T_g , little reorganization of the structure occurs. Often, these glasses have structures similar to that of the corresponding crystal. The lack of structural rearrangement and strong correspondence to the crystalline form

result in Arrhenius behavior of the viscosity with respect to temperature and small changes in heat capacity as the melt passes through the T_g range.

The structures of fragile liquids, however, are very sensitive to temperature changes and undergo more substantial rearrangements upon heating by way of changes in coordination and orientation of the structural units. Fragile liquids often have structures that differ greatly from the corresponding crystalline form. This considerable structural reorganization upon heating through the glass transition region results in non-Arrhenius behavior of the viscosity of the melt and a large change in the heat capacity.

In summary, “strong” liquids experience little structural reorganization upon heating through the T_g region and thus exhibit smaller, more gradual changes in viscosity over a wide temperature range above T_g . The viscosity-temperature relationship demonstrates an Arrhenius dependence and the glass transition region is associated with only a small change in heat capacity. “Fragile” liquids undergo larger structural rearrangements upon heating through the T_g region and thus exhibit more abrupt changes in viscosity with respect to changes in temperature. The viscosity-temperature relationship is non-Arrhenius and the glass transition region is associated with a substantial change in heat capacity.

On Angell’s fragility plot, all normalized viscosities converge as $T_g/T \rightarrow 0$ ($T \rightarrow \infty$). As the temperature increases to infinity, the liquids will all vaporize and will exist in gaseous form. This convergence implies that all gases, regardless of the atomic or molecular make up, will have the same viscosity ($\sim 10^{-4}$ P) at infinitely high temperatures. This phenomena is also demonstrated by the VFT equation for viscosity,

$$\eta = \eta_o \exp\left(\frac{B}{T - T_o}\right).$$

According to the above equation, the viscosities of all substances will approach $\eta \rightarrow \eta_o$ as $T \rightarrow \infty$, regardless of the constants B and T_o , which are dependent on the material composition. This implies that η_o is the same for all materials and is equal to 10^{-4} P (or 10^{-5} Pa·s).

The answer to the T_g/T_o part of this last answer is similar to what I received from most people. However, if you did some digging, you could find a couple of explanations for why the limiting viscosity is on the order of 10^{-4} P (or Pa·s). For example, in the Eyring paper I referenced in my viscosity lecture (J. Chem Phys., 4 283 (1936)), the following equation is derived for viscosity (η):

$$\eta = (Nh/V) \exp(E_0/kT) \tag{19}$$

where N is Avogadro’s number, h is Planck’s constant, V is molar volume, and E_0 is the activation energy for viscous flow. Eyring uses a ballpark value for molar volume of 40 cc/mole and so ends up with the approximate expression for viscosity:

$$\eta \approx 10^{-4} \cdot \exp(E_0/kT) \text{ (Pa}\cdot\text{s)} \quad (20)$$

From (20), $\eta \rightarrow 10^{-4} \text{ Pa}\cdot\text{s}$ as $T \rightarrow \infty$.

A second way to consider the limiting viscosity is to use Maxwell's relationship ($\eta = G_\infty \cdot \tau$, where G_∞ is the bulk shear modulus, $\sim 10^{10} \text{ Pa}$, and τ is the relaxation time, now defined as the period for lattice vibrations, about 10^{-14} sec). If we assume that relaxation rates are limited by vibrational rates, then the 'minimum' viscosity will be $10^{-4} \text{ Pa}\cdot\text{s}$.

See CA Angell, J. Non-Cryst. Solids, 131-133, 13-31 (1991); CA Angell et al., J. Appl. Phys., 88 3113-49 (2000) for some more details.

Average score on the 26 answers submitted: 20.0/25

4. *From your review of the literature, identify a family of glasses (or representative compositions) that possess glass thermal expansion coefficients in the range $125\text{-}175 \times 10^{-7}/^\circ\text{C}$ and glass transition temperatures below 450°C . Such glasses could be used for seals to a variety of metals. What are the advantages or disadvantages for using your compositions for such applications?*

Example 1

Glasses in the systems $0.2\text{MoO}_3\text{-}0.3\text{P}_2\text{O}_5\text{-(}0.5\text{-}x\text{)PbO-xPbCl}_2$ ($x > 0.2$) [1] and $x\text{PbF}_2\text{-(}1\text{-}x\text{)[PbO:TeO}_2\text{]}$ [2] possess the properties specified above. The introduction of halide ions into the glass is accompanied by important changes in the glass properties. It can increase the conductivity by increasing both carrier concentration and mobility which is an advantage in the use of these glasses as metal seals.

In these systems, the strong covalent P-O and Mo-O and Te-O bonds in the glassy network are probably replaced by apparently weaker ionic bonds of the $\text{Pb}^{2+}\text{-O}^{2-}$ type. Increasing PbCl_2 and PbF_2 content strongly affects the transformation temperature T_g of these glasses. T_g decreases gradually with the replacement of PbO by PbCl_2 or PbF_2 , which should be correlated with breaking of the network, contributing to its loosening and consequently decreasing the bond strength. This observation is consistent with the decrease in hardness number. The continuous decrease of the hardness number for these glasses reveals that the fragility nature of the network may be increased (i.e. a weaker structure obtained). This behavior can be disadvantageous for the applicability of these glasses as metal seals since the hardness of the

glass is often equated with its resistance to abrasion and may determine the durability of the glass during use.

An open, less rigid or loose structure also favors an increase in the thermal expansion. Therefore, the increase of thermal expansion with increasing PbCl_2 or PbF_2 content can be ascribed to the elongation or rupture of some bonds such as P-O-P , Mo-O-Mo and/or P-O-Mo in addition to Pb-O-P linkages due to accommodation of halide ions. The increasing thermal expansion may also limit the applicability of these glasses as metal seals in certain temperature ranges.

[1] Hassan A. K., J. Phys.: Condens. Matter **11**, 7995 (1999).

[2] El-Damrawi G., Phys. Status Solidi A **177**, 385 (2000).

I included this question as a bit of a throw-away- there are hundreds of examples in the literature of glasses with the requisite properties- including a few papers of my own. (*No* bonus points were given to anyone who cited them!) I was surprised that a number of you did not find an appropriate reference, or if you did find one, you didn't provide a useable citation. I was also trying to find out what you know about glass properties in general.

Average score on the 26 answers submitted: 20.2/25

Overall Homework Scores:

Average: 84.2 (standard deviation = 11.5)

Range: 61-99

I have submitted my scores for this HW set to Lehigh/Clemson to be posted on Blackboard (I think). I intend to scan the 'marked up' pages and send them to each of you- but that will take a bit.

Questions? Be sure to contact me at your convenience!

rkb