School of Engineering
Institute of Materials
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Polymer Science 2024

Exercise 3 – Solution

1. Suppose that the potential inter-chain interaction energy is $U = -Ar^{-6} + Br^{-12}$ per mole of repeating unit of a polymer, and that the molar volume of a repeating unit is $V \sim r^3$.
   a) Express U as a function of V, and find V_0, the value of V which corresponds to E_{coh}, i.e. a minimum of U. Show that the compression modulus is

$$K = -V_0 \frac{\partial^2 U}{\partial V^2}\bigg|_0 = \frac{8E_{coh}}{V_0}$$

   b) Estimate the compression modulus of a polymer with $\delta = 18\ (\mathrm{J/cm^3})^{1/2}$

$$U = -Ar^{-6} + Br^{-12} = -AV^{-2} + BV^{-4} \qquad \frac{\partial U}{\partial V} = 2AV^{-3} - 4BV^{-5} \qquad \frac{\partial^2 U}{\partial V^2} = -6AV^{-4} + 20BV^{-6}$$

$$\frac{\partial U}{\partial V} = 0 \rightarrow 2AV^{-3} = 4BV^{-5} \rightarrow V_0^2 = \frac{2B}{A} \qquad U_0 = -A\frac{A}{2B} + B\frac{A^2}{4B^2} = -\frac{A^2}{4B}$$

$$\frac{\partial^2 U}{\partial V^2}\bigg|_0 = -6A\frac{A^2}{4B^2} + 20B\frac{A^3}{8B^3} = \frac{A^3}{B^2} \qquad -V_0\frac{\partial^2 U}{\partial V^2}\bigg|_0 = -\frac{V_0^2}{V_0}\frac{A^3}{B^2} = -\frac{1}{V_0}\frac{2B}{A}\frac{A^3}{B^2} = \frac{8U_0}{V_0}$$

$$\delta = \sqrt{\frac{E_{coh}}{V_0}}$$

$$K = 8\frac{E_{coh}}{V_0} = 8\delta^2 = 8 \cdot 18^2 J/cm^3 = 2600\ J/cm^3 \equiv 2.6\ GPa$$

2. Why is the glass transition not a “second-order thermodynamic transition”?

First-order phase transitions exhibit a discontinuity in the first derivative of the free energy with respect to a certain thermodynamic variable. This is, for

example, the case for a melting/crystallization transition. The glass transition is often referred to as a second order transition because it does not involve a discontinuous change in enthalpy but, instead, the heat capacity changes (Slide 129).

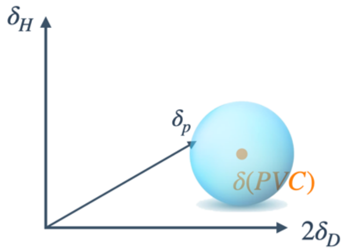
This is, however, not a thermodynamic transition insofar as it describes the way from an equilibrium state (dynamic), i.e. the rubbery state in the case of a polymer, into an out-of-equilibrium state, i.e. the glassy state. In the glassy state the chain movements (in particular, conformational changes) are frozen at the time scale of the measurement (see question 4), they can no longer adjust their conformations in order to reach a state of equilibrium, which changes with temperature. This therefore implies that the nature of the glassy state (as well as the experimental value of T_g) depends on the measurement speed!

3. It is well known that polyvinylchloride (PVC) is not miscible with its own monomer (VC). This gives the polymer a characteristic particle structure that remains even after melt processing, which is often detrimental for its mechanical properties. The solubility parameters (in (Mpa)$^{1/2}$) of PVC are $\delta_D = 18.2$, $\delta_P = 7.5$, $\delta_H = 8.3$, $R_{A0} = 3.5$, where R_{A0} is the radius of its *solubility sphere* in the '$2\delta_D$-δ_P-δ_H space' (the necessity of doubling the δ_D axis is based on experimental observations). The solubility parameter values of VC are: $\delta_D = 15.4$, $\delta_P = 8.1$, $\delta_H = 2.4$. Confirm that PVC is immiscible with VC on the basis of these data.

Let the spere's center coordinates be (x, y, z) and its radius be r. A point (a, b, c) will be in the sphere, if

$$(x-a)^2 + (y-b)^2 + (z-c)^2 < r^2$$

In our case, we need to respect the doubling of the δ_D axis. Therefore:



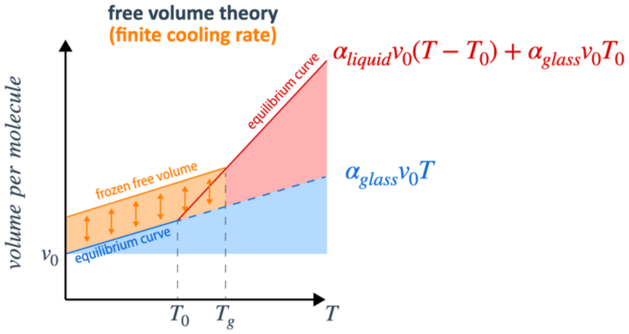
$$R^2_{(PVC-VC)}$$

$$= (2\delta_D(PVC) - 2\delta_D(VC))^2 + (\delta_H(PVC) - \delta_H(VC))^2 + (\delta_p(PVC) - \delta_p(VC))^2$$

$$= 5.6^2 + 5.9^2 + (-0.6)^2 > R^2_{A0}$$

4. Let's try to better understand the theory of "free volume"! As we have seen, at a temperature of absolute 0, each segment of a glassy amorphous polymer will occupy a volume v_o. When the temperature is increased, the molecules start to vibrate and the volume increases. The thermal expansion coefficient of the glass is α_{glass} such that $V = \alpha_{\mathrm{glass}} v_o T$. According to the free volume theory, above a certain temperature T_o, holes begin to appear that are large enough to allow the displacement of chain segments. Thus, conformational changes become possible. We then enter the liquid state (or rubbery state in the case of a polymer, see Slide 132), with a thermal expansion coefficient of α_{liquid}. However, because the glassy state is an out-of-equilibrium state, an average "free volume", v_{fm}, is trapped in the glassy state. v_{fm} is the excess volume compared to a hypothetically "equilibrated" glassy state.

   a) Show that $v_{\mathrm{fm}} = v_o(T - T_o)(\alpha_{\mathrm{liquid}} - \alpha_{\mathrm{glass}})$.



$$v_{fm} = \alpha_{liquid} v_0 (T - T_0) + \alpha_{glass} v_0 T_0 - \alpha_{glass} v_0 T$$

$$v_{fm} = \alpha_{liquid} v_0 (T - T_0) - \alpha_{glass} v_0 (T - T_0)$$

$$v_{fm} = v_0 (T - T_0) \Delta\alpha$$

Therefore, at equilibrium, v_{fm} should disappear at $T = T_o$.

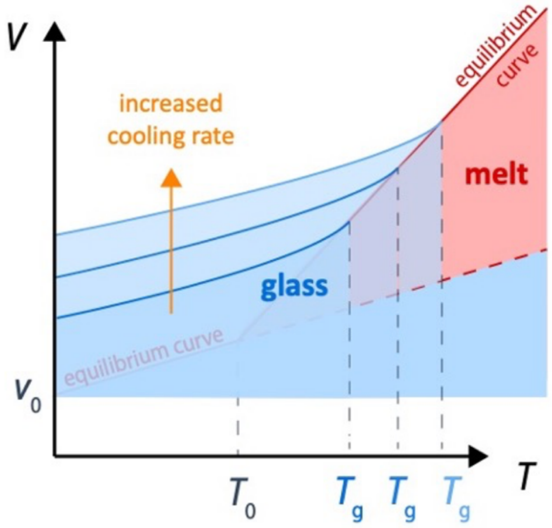
We assume that the probability of finding a hole of size v_o appearing within a certain time interval is proportional to $\exp(-v_o/v_{\mathrm{fm}})$. In other words, the *relaxation time* for these conformational changes is $\tau = \tau_o \exp(v_o/v_{\mathrm{fm}})$ and therefore the viscosity $\eta = \eta_o \exp(v_o/v_{\mathrm{fm}})$.

   b) Express η in terms of T, T_o and the thermal expansion coefficients. What happens to the viscosity of the liquid when T tends towards T_o?

$$\tau = \tau_0 \exp\left(\frac{v_0}{v_{fm}}\right) = \tau_0 \exp\left(\frac{\Delta\alpha^{-1}}{T - T_0}\right) \qquad \eta = \eta_0 \exp\left(\frac{v_0}{v_{fm}}\right) = \eta_0 \exp\left(\frac{\Delta\alpha^{-1}}{T - T_0}\right)$$

Thus, when T tends towards T_o, η becomes infinitely large (therefore, the stained glass windows of old churches do not sink under their own weight!).

c) If we cool at a given speed, we will effectively stop the conformational changes at a temperature, $T > T_0$ (when the viscosity becomes too high to allow conformational changes over the timescale of the experiment). This temperature will be the experimental glass transition temperature, T_g. Draw the evolution of the volume as a function of T for different constant cooling rates, indicate T_g for each rate.

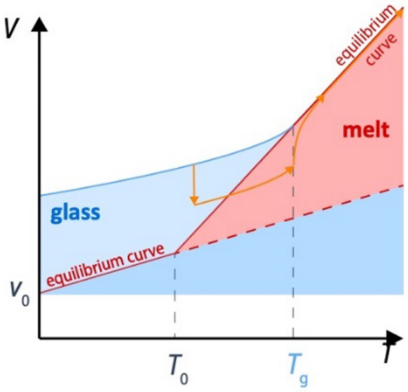


For a given cooling rate, the glass transition, T_g, takes place at a certain critical η (or t), and therefore at a certain critical value of v_{fm}, which increases if the cooling rate is increased (see figure). At temperatures $T < T_g$ the molecules can no longer change position to approach equilibrium, and the coefficient of thermal expansion is that of the glassy state. dv/dT is therefore smaller than in the liquid/rubbery state.

d) In DSC measurements, often a characteristic enthalpy peak is observed at around the glass transition temperature during heating if a faster heating rate is applied compared to the cooling rate of the previous cooling scan (see Slide 131). This enthalpy peak is, however, also observed upon "aging", which is a densification in the glassy state of the material upon resting. Explain this behavior with the help of a schematic illustration of the evolution of the volume (or enthalpy) as a function of the temperature.

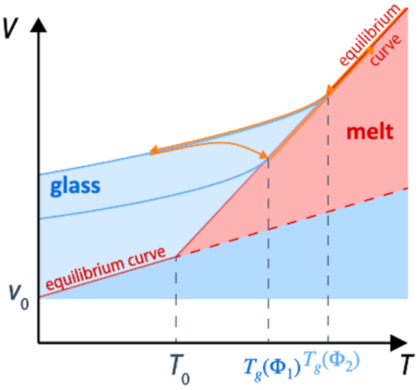
When the rate of a subsequent heating step is faster, we would expect a behavior shown on Slide 131. When we keep, for example, the material at a temperature, T, well below T_g, the volume decreases, which we call "aging" (and if we waited infinitely long it would decrease until $\alpha_g v_0 T$). If we start to heat up at Φ_2 speed now, there will be a sudden increase in volume as soon as the temperature exceeds $T_g(\Phi_2)$, which will now try to quickly regain its equilibrium value.

This explains why an enthalpy peak is often observed during a calorimetry measurement under these conditions (Slide 131, middle). We notice also that we find roughly the same values of T_g (i.e. temperature or dv/dT increases) for a given speed, whether we cool or heat. However, the heating behavior is strongly influenced by the thermal history of the material and therefore it is preferable, if possible, to measure the T_g by cooling from the equilibrium state (which is better reproducible).



e) You cool an amorphous polymer relatively quickly from the rubbery state to a temperature well below the T_g, and you heat it up much more slowly. Schematically show the evolution of the volume as a function of the temperature.

The figure below shows schematically what happens if we cool at a speed Φ_1 and we heat at a speed $\Phi_2 < \Phi_1$ (orange curve). It is assumed that the high free volume which is trapped in the glassy state upon rapid cooling confers some mobility to molecules as soon as you stop cooling or if you start heating more slowly. In this last case, if we start well below $T_g(\Phi_1)$, the volume will therefore decrease compared to the cooling curve when the sample is heated, reaching its equilibrium value when the temperature reaches $T_g(\Phi_2)$.



Reading suggestions:

- Lecture Notes of Chapters 3.1 and 3.2.

(You can download these documents from the Moodle-folder ’Reading Recommendation’.)