Solutions to Soft Matter exercise 1: Introduction

1. Viscosity:

Water can form H-bonds, acetone cannot form H-bonds and only undergoes VdW-interactions.

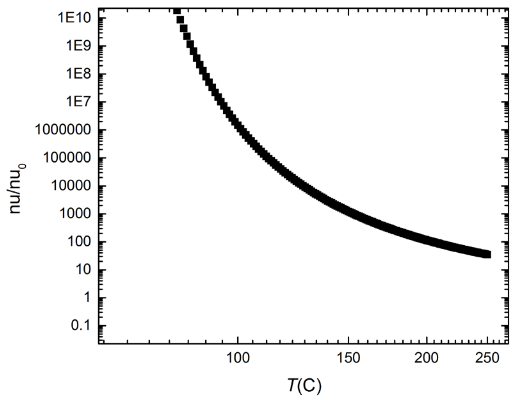
2. Non-Newtonian fluids

Non-Newtonian fluids are fluids whose viscosity is a function of the shear rate. An example of a fluid that shows shear thickening behavior (the viscosity increases with increasing shear rate) is corn starch in water.
Examples of fluids that show shear thinning behavior (the viscosity decreases with increasing shear rate) are ketchup, whipped cream, or blood.

A shear-rate dependent change in viscosity can occur if the fluid consists of different components and the interactions between these components (intermolecular or intra-particle forces) change if exposed to shear. This behavior must be taken into account for example if these fluids (or melts) are processed through extrusion.

3. Temperature dependence of the viscosity of poly(styrene):

a. Using the Vogel Furcher law, $\frac{\eta}{\eta_0} = \exp\left(\frac{B}{T-T_0}\right)$, one finds



At 80°C

$$\frac{\eta_{80°C}}{\eta_0} = exp\left(\frac{710}{353-323}\right) = 1.9 \times 10^{10}$$

At 100°C

$$\frac{\eta_{100°C}}{\eta_0} = exp\left(\frac{710}{373-323}\right) = 1.47 \times 10^{6}$$

At 120°C

$$\frac{\eta_{120°C}}{\eta_0} = exp\left(\frac{710}{393-323}\right) = 2.54 \times 10^{4}$$

At 140°C

$$\frac{\eta_{140°C}}{\eta_0} = exp\left(\frac{710}{413-323}\right) = 2.67 \times 10^3$$

Hence

$F_1 = \frac{\eta_{80°C}}{\eta_{100°C}} = 1.3\times 10^4$ and

$F_2 = \frac{\eta_{120°C}}{\eta_{140°C}} = 9.5$

Hence, at low temperatures, the changes in viscosity are much more pronounced. Poly(styrene) (PS) has a glass transition temperature, T_g, around 100°C. Changes of the viscosity with temperatures below the glass transition temperature, where PS is an undercooled glass are much more pronounced than above T_g, where PS is a liquid. Therefore $F_1 >> F_2$.

b. Factors to consider:

- glass transition temperature
- thermal decomposition temperature
- heating/cooling rate
- temperature-dependent viscosity
- feature size
- production costs

The processing temperature depends on the shape of the piece to be processed. If very fine structures need to be cast, the viscosity of poly(styrene) should be relatively low; this requires temperatures significantly above the glass transition temperature.

In general, the processing temperature is a trade-off between minimizing processing costs and thus the processing temperature and reaching a viscosity of the melt, suitable for the process.

4. Temperature dependence of the viscosity for glass-forming liquids

a. The glass transition temperature is no material property because it depends on the heating and cooling rates. If the temperature-dependent viscosity follows the Vogel Furcher law, it can be described as

$$\frac{\eta}{\eta_0} = \exp\left(\frac{B}{T-T_0}\right)$$

The viscosity is related to the shear modulus, G_0, and the shear rate, τ, which is related to the experimental time scale as

$$\eta = G_0\tau$$

With G_0 being a constant we find,

$$\frac{\tau}{\tau_0} = \exp\left(\frac{B}{T-T_0}\right)$$

To determine the temperature-dependent viscosity, we must determine τ_0.

$$\tau_0 = \tau \exp\left(-\frac{B}{T-T_0}\right) = 1000s \times \exp\left(-\frac{710K}{(101.4+273)K-(50+273)K}\right) = 0.001s$$

$$T = \frac{B}{\ln\left(\frac{\tau}{\tau_0}\right)} + T_0$$

At T_g: $\tau_{exp} = \tau_{conf}$
using

$$T = \frac{B}{\ln\left(\frac{\tau}{\tau_0}\right)} + T_0$$

we find
for $\tau_{conf} = 10\ s$, T_g = 127 °C
for $\tau_{conf} = 100\ s$, T_g = 112 °C
for $\tau_{conf} = 10^6\ s$, T_g = 84 °C
Hence, T_g decreases with increasing τ_{conf}

b. (i) For $T_g = T_0$+50°C=100 °C:

$$\tau = \tau_0 \exp\left(\frac{B}{T-T_0}\right) = 0.001s \times \exp\left(\frac{710K}{50K}\right) = 1472s = 24.5\min$$

(ii) For $T_g = T_0$+10°C=60 °C:

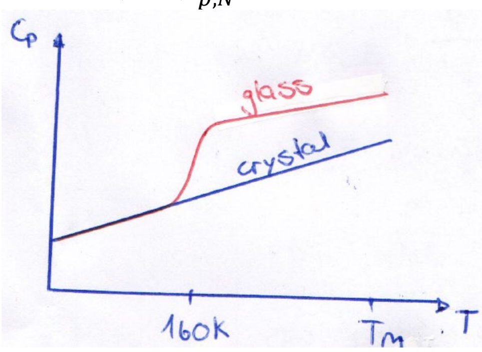
$$\tau = \tau_0 \exp\left(\frac{B}{T-T_0}\right) = 0.001s \times \exp\left(\frac{710K}{10K}\right) = 6.8\times10^{27}s$$

This is experimentally not possible.

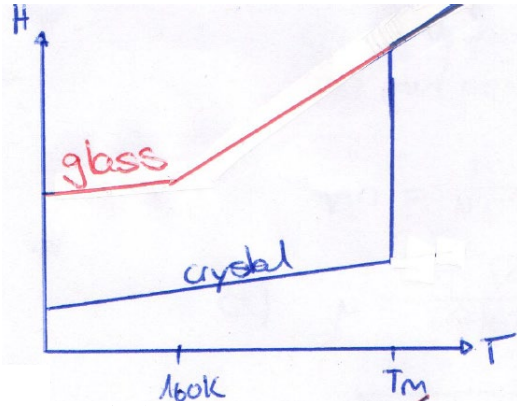
5. Glass transition

a. Glass transition resembles a 2. order phase transition. However, it is no real phase transition because the temperature, where this transition occurs depends on the heating rate. In the following examples, the changes in C_p, H, and S as a function of temperature for a glass are indicated in red those for a crystal in blue.

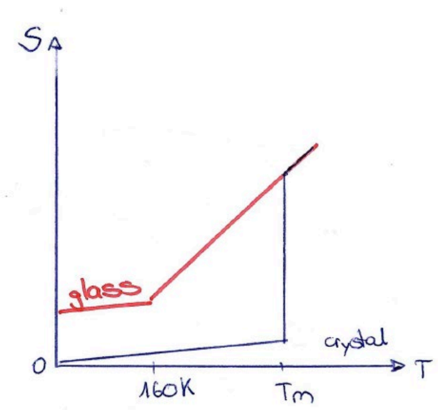
$$-\frac{C_p}{T} = \left(\frac{\partial^2 G}{\partial T^2}\right)_{p,N}$$



$H = G + TS$



$-S_p = \left(\frac{\partial G}{\partial T}\right)_{p,N}$



b. The heat capacity is related to the degree of freedom atoms/molecules have (vibrational/rotational/translational degrees of freedom). In crystals, usually atoms/molecules essentially only have vibrational degrees of freedom. In glasses atoms/molecules often also have some rotational or even translational degrees of freedom. As a result, they have more possibilities to store energy such that their specific heat capacity is higher.

c. Entropy is a measure of disorder. The disorder is much higher in glasses than in crystals. Crystals have, by definition, a long-range order.

d. T_g is defined we the temperature where $\tau_{conf} = \tau_{exp}$. As the cooling rate increases, τ_{exp} decreases such that τ_{conf} must also decrease. This is the case if the temperature is increased because the vibrational frequency and mobility of atoms and molecules increases with increasing temperature. Hence, with increasing cooling rate, T_g increases.

6. Elasticity

The Young's modulus is determined as $E = \frac{\sigma}{\varepsilon}$. To determine the stress, σ, we use

$\sigma = \frac{F}{A}$ where

$$A_{final} = \frac{A_{initial}}{1.5} = \frac{0.4mm^2}{1.5} = 0.267mm^2$$

hence

$$\sigma = \frac{F}{A} = \frac{10N}{0.267 \times 10^{-6} m^2} = 37.5MPa$$

and

$$E = \frac{\sigma}{\varepsilon} = \frac{3.75 \times 10^7 Pa}{0.5} = 75MPa$$