

Glass transition, exercises

A. Introduction and phenomenology

Exercise 1. Give differences and similarities between 'ordinary' inorganic glass and a polymeric glass like, for example, atactic polystyrene.

Exercise 2. Give three essential differences between a glass-rubber transition and a melting first order phase transition, in particular concerning the temperature dependency of volume V , enthalpy H and entropy S around the corresponding transition points.

Exercise 3. Why can, just above the T_g , complete polymer chains not yet move with respect to each other? When are they able to do so?

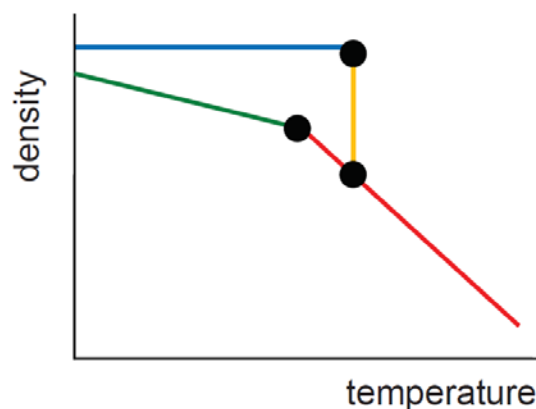
Exercise 4. Why can the glass-rubber transition not be considered as thermodynamic second-order transition?

Exercise 5. If we look at the following series:

PE:	(-CH ₂ -CH ₂ -)	$T_g =$	-120 °C
PP:	(-CH ₂ -CH·CH ₃ -)	$T_g =$	-15 °C
PVC:	(-CH ₂ -CH·Cl-)	$T_g =$	+90 °C

a strong rise of the glass-rubber transition temperatures can be seen. Explain the differences in T_g .

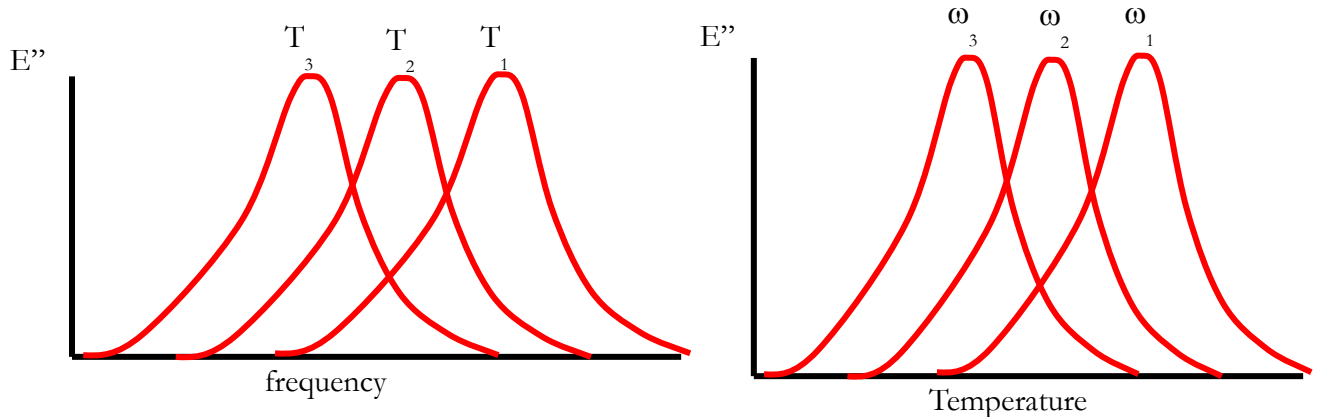
Exercise 6. Consider the diagram in Figure below,



which represents the different phases that we may see in a polymeric material as a function of temperature. Show where we find the liquid, glass, crystal and rubber. Indicate where T_g , T_m and T_k

(Kauzmann temperature) are (approximately) located and describe the relevant molecular motions (which modes of relaxation are constrained, which are free) in each of the phases (i.e. in liquid, in glass, in crystal, in rubber). Also, sketch the behaviour of the modulus as a function of both temperature and time (2 graphs) - using the time-temperature superposition principle to relate one to the other. Make sure you *explain* why your curves look the way they look, give arguments and descriptive reasoning, not formulas in this entire question.

Exercise 7.



The typical frequency and temperature dependence of the loss modulus is shown at different temperatures and frequencies, respectively. **Left panel:** which temperature T is the highest, which is the lowest? **Right panel:** the same, but for frequencies ω ?

Exercise 8. Calculate the glass-transition temperature T_g of the atactic polystyrene of infinite molar mass M from the following data:

T_g (K)	182	278	354	361	362	369.5	375.5
M (g/mol)	500	1000	4000	5000	6000	10000	20000

Exercise 9. Present briefly the experimental techniques which can be used to differentiate between an amorphous and a semicrystalline polymer. What are the main results indicating full amorphism?

Exercise. 10 (see slide 10 of the lecture 1 for more information)

From the definition of the Gibbs free energy G show that

$$\left(\frac{\partial(G/T)}{\partial(1/T)} \right)_p = H$$

$$\frac{\partial}{\partial T} \left[\left(\frac{\partial(G/T)}{\partial(1/T)} \right)_p \right] = \left(\frac{\partial H}{\partial T} \right)_p = C_p$$

Exercise 11. Describe schematically an experiment by which physical ageing can be recorded.

Exercise 12. (see slide 23 of the lecture 1 for more information)

Show that the logarithmic cooling-rate dependence of the glass-transition temperature observed upon cooling the polymer melts is a simple consequence of the Vogel-Fulcher-Tamman (VFT) equation which provides the temperature dependence of the characteristic chain-relaxation times.

B. Theories and computer simulations

Exercise 1. Show that the Williams –Landel-Ferry (WLF) equation can be produced from the classical free-volume theory.

Exercise 2. The Williams –Landel-Ferry relationship expresses the correlation times, $\tau(T)$, at the temperature T as a function of the temperature gap to the glass transition temperature, $T-T_g$:

$$\log_{10} \frac{\tau(T)}{\tau(T_g)} = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)}$$

a) Define temperature T_∞ at which the WLF relationship diverges. What is the physical meaning of this temperature?

b) For the applications in car headlights the choice has to be made between PS and PMMA whose T_∞ are T_∞ (PS)=55°C and T_∞ (PMMA)=90°C, respectively. Which polymer will you choose? Give physical arguments for your choice.

Exercise 3. Show that the Vogel-Fulcher-Tamman (VFT) equation can be produced from the WLF equation.

Exercise 4. Calculate the temperature dependence of the polymer volume relaxation (ageing) and the correspondent relaxation time in the kinetic theory of the glass transition.

Exercise 5. Obtain the VFT equation from the Adam-Gibbs theory which connects the characteristic chain-relaxation time and the configurational entropy.

Exercise 6. For polymer samples the molecular-weight dependence of the glass transition temperature is nicely approximated by the Fox-Flory equation,

$$T_g(M) = T_g(M_\infty) - \frac{K}{M}$$

Determine the numerical value of K for polybutadiene (PB) samples, using the following Table:

Sample	PB-1	PB-2	PB-3	PB-4	PB-5	PB-6
M , kg/mol	5	10	20	50	100	200
T_g , (C)	-87.6	-85.8	-84.9	-84.4	-84.2	-84.0

and relate K to the free volume available at the chain ends. In your analysis use the typical value for the difference in volumetric thermal expansions between polymer melt and polymer glass, $\alpha_f = \alpha_L - \alpha_g = 4.8 \cdot 10^{-4} \text{ 1/K}$, and typical polymer density 0.9 g/cm^3 .

For polystyrene it has been found that the value of K is much larger. Can you explain why?

Exercise 7. The thermodynamics of the glass transition is experimentally tested by measuring the so-called Prigogine-Defay ratio R

$$R = \frac{\Delta k \Delta C_p}{TV(\Delta\alpha)^2}$$

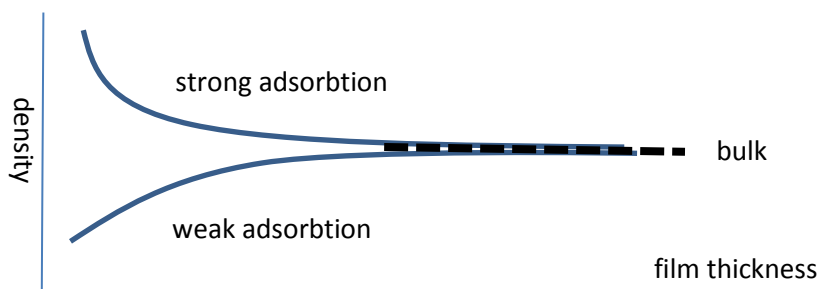
Here Δk , ΔC_p and $\Delta\alpha$ are the differences between the values of the compressibility k , heat capacitance C_p and the thermal expansivity α of two phases (liquid and glass), correspondingly.

Show that for any material which undergoes an apparent thermodynamic second-order phase transition, the Prigogine-Defay ratio R is equal to unity, $R=1$.

Hint: Start with the writing down the full differential for the volume, $V(T,P)$, in the liquid (phase 1) and in the glass (phase 2). The total differential for the volume, as well as the volume itself, are the same in both phases. Similarly, apply the same logics for the total differential of the entropy, $S(T,P)$.

C. Effects of confinement

Exercise 1. The density of the supported polymer film can be thickness-dependent, see the Figure below:



Show that for such a film its glass-transition temperature can be connected with the film thickness H at $T=T_g$ (in film) and the “excess” mass δm due to the confinement as

$$\frac{T_g^{film}}{T_g^{bulk}} = \frac{1 + C_1 \frac{\delta m}{H(T_g^{film})}}{1 + C_2 \frac{\delta m}{H(T_g^{film})}}$$

where constants $C_{1,2}$ do not depend on the film thickness.

Solutions

A. Introduction and phenomenology

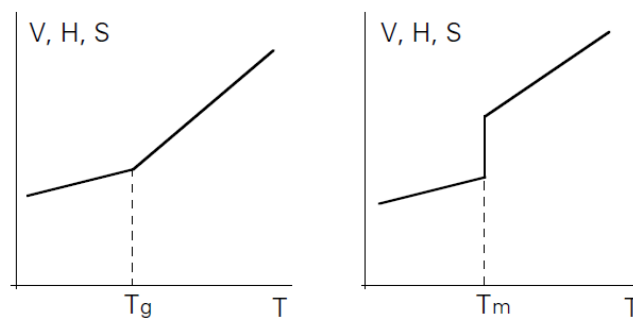
Ex. 1

Similarities: Both are not able to crystallise because of their irregular molecular structure. Both will, therefore, reach the glassy condition upon cooling down from the liquid phase.

Differences: When a low-molecular-weight glass is heated, it will, at its T_g , immediately change into a liquid (though less abrupt as at a real melting point). A polymeric glass, however, first becomes rubbery as a result of chain entanglements. At a higher temperature (T_v) it passes very gradually into the fluid state.

Ex. 2

All three quantities (V , H and S) show an upward jump at T_m upon heating (apart from “pathological” liquids such as water as regards V). At T_g there is, however, no jump, so $\Delta V = 0$, $\Delta H = 0$ and $\Delta S = 0$, but a bend, or a jump in their first derivatives. For V , H and S this means, respectively, jumps in the coefficient of expansion α , in the specific heat c and in the compressibility k .



left panel: glass transition, right panel: phase transition

Ex. 3

Because of the many entanglements a long chain is still fixed at a number of points, so that only parts of the chain (of the order of 50 to 100 links) are free to move. At further temperature increase these entanglements are also loosened, so that the polymer is able to flow.

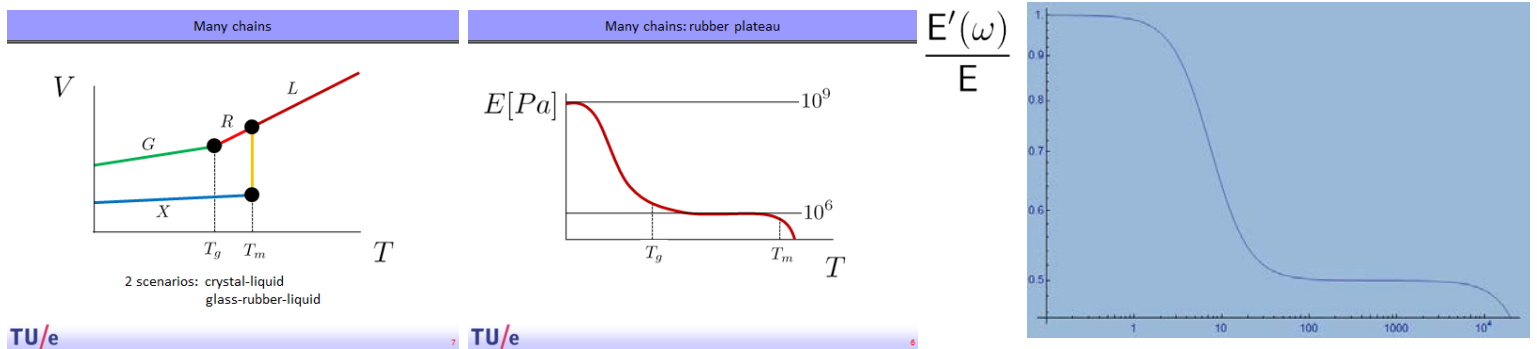
Ex. 4

A thermodynamically defined phase transition is a transition between two equilibrium states. The glassy state is, however, never in thermodynamic equilibrium; it is subjected to volume-retardation (rearrangement of chain segments) up to unimaginably long times. The glass-rubber transition should, therefore, be considered as a freezing-in phenomenon, governed by kinetics.

Ex. 5

The difference between the T_g 's of PP and PE is caused by the much greater chain stiffness of PP as a result of the hindered rotation round the C-C bonds in the main chain; the CH_3 -groups are in the way. In PVC rotation is hindered in a similar way (the Cl atoms are of about the same size as the methyl groups). The Cl atoms, bound to the main chain, are strong electrical dipoles, and they can exert much larger attraction forces on each other than the methyl groups in PP, which are subjected to the much weaker dispersion forces only.

Ex. 6



The glass:

Low temperature, kT is small compared to all interaction strengths (interchain, intrachain, chain-solvent). We say that the conformational degrees of freedom are frozen in. The chains cannot move about – or it costs a large amount of energy to get them to move. When they do move, it can not be the conformations that change, so the chain interactions must be what is yielding (H bonds, vd Waals). This is why glasses are so hard!

The rubber phase:

Large parts of the polymers are free to move. However, they cannot free themselves of their entanglements in physical timescales. This is referred to as segmental freedom. Its origin lies in the fact that kT becomes of the order of the interaction energies, and the polymers become dynamic. The resulting conformational fluctuations render them deformable and the materials become softer. Entanglements do still prevent them from flowing freely.

The melt:

For high enough temperatures, or low enough chain lengths, the chains acquire in addition to their segmental freedom the freedom to overcome entanglements through reptation. In this phase, interchain interactions (energetic and steric) are no longer important and external deformations (slower than the Rouse time) are accomodated by relative sliding of the polymers. The resulting deformation of the material is non-reversible – no elastic energy is stored and the system becomes a liquid.

Ex. 7

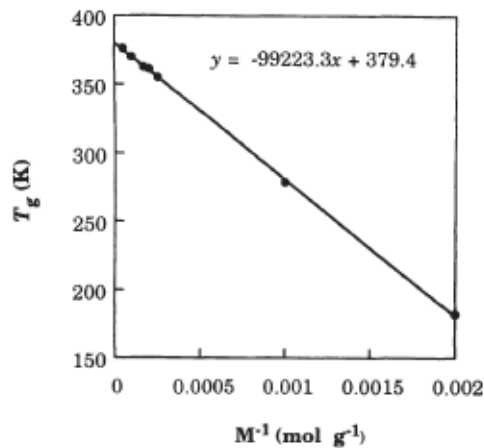
$$T_1 > T_2 > T_3 \quad \omega_1 > \omega_2 > \omega_3$$

Ex. 8

The formula to use is

$$T_g(M) = T_{g,\infty} - \frac{K}{M}$$

By plotting T_g against $1/M$, T_g for *PS* of infinite molecular weight is obtained as the intersection with the T_g axis, which occurs at 379.4 K.



Ex. 9

The main technique is wide-angle X-ray scattering (WAXS). The X-ray scattering pattern from an amorphous polymer is diffuse and liquid-like, whereas for a semicrystalline polymer the diffraction pattern also shows a number of sharp Bragg reflections. A preliminary, less exact assessment can be made by visual examination - the amorphous polymer is transparent, whereas crystalline polymers are opaque. Differential scanning calorimetry is another useful tool. An amorphous polymer displays only a glass transition, whereas a crystalline polymer shows a melting peak.

Ex. 10

$$G = U - TS + PV$$

$$G/T = H/T - S$$

$$\frac{\partial}{\partial(1/T)} \left(\frac{G}{T} \right)_p = H + \frac{1}{T} \left(\frac{\partial H}{\partial(1/T)} \right)_p - \left[\frac{\partial S}{\partial(1/T)} \right]_p$$

$$dH = TdS + Vdp$$

$$\left(\frac{\partial H}{\partial(1/T)} \right)_p = T \left(\frac{\partial S}{\partial(1/T)} \right)_p$$

and the two terms in the equation above cancel each other.

$$dH = TdS + Vdp$$

$$\left(\frac{\partial H}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p = C_p$$

Ex. 11

The experiment can be carried out in a dilatometer measuring the volume or in a differential scanning calorimeter recording changes in the enthalpy. Start at a temperature (T_1) well above T_g . Cool the sample at a constant rate to a temperature below T_g . Stop the cooling at a certain temperature (T_2) and hold the sample at that temperature while recording volume and enthalpy changes. The process may be so slow that the resolution of the DSC apparatus is not sufficient. In that case, the integrated evolved enthalpy between the starting time and a selected interruption time t can be measured by taking the difference between the integrated enthalpies in heating scans

between T_2 and T_1 for the sample after ageing during the time period t and for a sample that has not been aged at T_2 .

Ex. 12

Follow the steps as explained in the lecture.

B. Theories and computer simulations

Ex. 1

Either from the Doolittle equation, or from the free-volume approach we have

$$D \sim \eta^{-1} \sim \exp\left(-\frac{bv_0}{v_f}\right)$$

here v_0 – occupied volume per molecule

v_f – free volume per molecule.

Let us introduce the fractional free volume, $f = v_f / (v_f + v_0)$. Close to the glass transition, $v_0 \gg v_f$, and fractional free volume $f \sim v_f/v_0$

$$\ln \frac{\eta(T)}{\eta(T_g)} = \frac{b}{f} - \frac{b}{f_g}$$

Assumption made in WLF: $f = f_g + \Delta\alpha_p(T - T_g)$. Here $\Delta\alpha_p$ is the difference between thermal expansions of liquid and glass.

$$\log_{10} \frac{\eta(T)}{\eta(T_g)} = \frac{\ln \frac{\eta(T)}{\eta(T_g)}}{\ln 10} = \frac{b}{2.303} \left(\frac{1}{f} - \frac{1}{f_g} \right) = \frac{-b}{2.303} \left(\frac{\Delta\alpha_p(T - T_g)}{ff_g} \right)$$

$$\log_{10} \frac{\eta(T)}{\eta(T_g)} = \frac{-b}{2.303} \left(\frac{\Delta\alpha_p(T - T_g)}{f_g^2 + \Delta\alpha_p(T - T_g)f_g} \right) = \frac{-b}{2.303f_g} \left(\frac{(T - T_g)}{\frac{f_g}{\Delta\alpha_p} + (T - T_g)} \right)$$

$$\log_{10} \frac{\eta(T)}{\eta(T_g)} = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)}$$

and the connection between free-volume parameters is simple,

$$C_1 = \frac{b}{2.303f_g}$$

$$C_2 = \frac{f_g}{\Delta\alpha_p}$$

Ex. 2

a) $T_\infty = T_g - C_2^g$, it is the lowest temperature at which the main chain motions involved in the glass transition at an infinitely low frequency (or an infinitely long time) would occur.

b) Having higher T_∞ , PMMA will not develop any deformation (resulting from glass transition motions) during a long time exposure to heat and, therefore, it can be used for these applications.

Ex. 3

VFT equation:

$$\eta(T) \sim \tau \sim \tau_0 \exp\left(\frac{B'}{T - T_0}\right)$$

$$\eta(T_g) \sim \tau_0 \exp\left(\frac{B'}{T_g - T_0}\right)$$

$$\log_{10} \frac{\eta(T)}{\eta(T_g)} = \frac{\ln \frac{\eta(T)}{\eta(T_g)}}{2.303} = \frac{B(T_g - T)}{(T - T_0)(T_g - T_0)}$$

where $B=B'/2.303$. To connect VFT parameters with those in WLF equation we have to solve

$$\frac{B(T_g - T)}{(T - T_0)(T_g - T_0)} = -\frac{C_1(T - T_g)}{C_2 + (T - T_g)}$$

The solution is

$$C_2 = T_g - T_0$$

$$B' = 2.303C_1C_2$$

Ex. 4

In the variant of the kinetic theory explained in the lecture two states 1 and 2 are separated by the barrier $U_1=U_2+\Delta E$. The probabilities of forward $1 \rightarrow 2$ and backward $2 \rightarrow 1$ transitions are

$$w_{12} \sim e^{-\frac{U_1}{k_B T}}$$

$$w_{21} \sim e^{-\frac{U_2}{k_B T}}$$

The population j_2 of the “excited” state 2 is changing with time,

$$\frac{dj_2}{dt} = -j_2 w_{21} + j_1 w_{12}$$

In equilibrium

$$j_1^{eq} w_{12} = j_2^{eq} w_{21}$$

and at any time $j_1 + j_2 = j = const$. This normalization gives

$$j_1 = j_2^{eq} \left(1 + \frac{w_{21}}{w_{12}}\right) - j_2$$

$$\frac{dj_2}{dt} = -j_2(w_{21} + w_{12}) + j_2^{eq}(w_{12} + w_{21}) = -\frac{1}{\tau}(j_2 - j_2^{eq})$$

$$\tau = \frac{1}{w_{12} + w_{21}}$$

$$\tau = \frac{1}{\exp\left(\frac{-U_1}{kT}\right) + \exp\left(\frac{-U_2}{kT}\right)} \sim \exp\left(\frac{-U_2}{kT}\right) \frac{1}{1 + \exp(-\Delta E / kT)}$$

$$V - V_{eq} \sim j_2 - j_{eq}$$

Ex. 5

From Adam-Gibbs theory it follows that

$$\tau \sim \exp\left(\frac{C}{S_c T}\right)$$

S_c vanishes at the Kauzmann temperature T_K , this implies that τ diverges at T_K . If we assume

$$S_c \sim \left(1 - \frac{T_K}{T}\right)$$

then we have

$$\tau \sim \exp\left(\frac{C}{T - T_K}\right)$$

and the VFT equation is recovered at $T_0 = T_K$.

Ex. 6

For polymer with infinite molecular weight

$$\frac{v_f(T, M_\infty)}{v(T)} = \frac{v_f(T_g)}{v(T_g)} + \alpha_f [T - T_g(M_\infty)]$$

For polymer with molecular weight M

$$\frac{v_f(T, M)}{v(T)} = \frac{v_f(T_g)}{v(T_g)} + \alpha_f [T - T_g(M)]$$

Therefore

$$\frac{v_f(T, M) - v_f(T, M_\infty)}{v(T)} = \alpha_f [T_g(M_\infty) - T_g(M)]$$

The increase of free volume between the two polymer samples may be assigned to the chain ends that facilitate conformational changes. If an additional free volume θ_f is associate with each chain

end, $\frac{v_f(T, M) - v_f(T, M_\infty)}{v(T)}$ is equal to $2\theta_f N_A$ (in molar units, that is why Avogadro number). The

sample volume $v = M/\rho$ (again in molar units), we have

$$\frac{v_f(T, M) - v_f(T, M_\infty)}{v(T)} = \frac{2\rho N_A \theta_f}{M \alpha_f}$$

and, finally,

$$T_g(M) = T_g(M_\infty) - \frac{2\rho N_A \theta_f}{M \alpha_f}$$

The glass transition temperature for PB is lower as that for PS, the effect of molecular weight is weaker. Such a result, which is quite general, originates from the fact that the more flexible PB chains are less sensitive to the additional free volume provided by the chain ends.

Ex. 7.

From the definitions of compressibility $\left(\frac{\partial V}{\partial p}\right)_T = -kV$ and expansivity $\left(\frac{\partial V}{\partial T}\right)_p = \alpha V$, we have for the full differential of pressure

$$dV_l(T, p) = \alpha_l V_l dT - k_l V_l dp = dV_g(T, p) = \alpha_g V_g dT - k_g V_g dp$$

Regrouping, and because $V_l = V_g$ at the transition, we can write

$$\left(\frac{dT}{dp}\right)_{tr} = \frac{\Delta k}{\Delta \alpha}$$

where Δ stands for the difference between the corresponding values in the liquid and in the glass phases. Similarly, for the entropy, we write

$$dS_l(T, P) = \frac{C_{p,l}}{T} dT + \left(\frac{\partial S_l}{\partial p}\right)_T dp = dS_g(T, P) = \frac{C_{p,g}}{T} dT + \left(\frac{\partial S_g}{\partial p}\right)_T dp$$

$$\left(\frac{\partial S}{\partial p}\right)_T = \frac{\partial}{\partial p} \left[- \left(\frac{\partial G}{\partial T}\right)_p \right]_T = - \frac{\partial}{\partial T} \left[\left(\frac{\partial G}{\partial p}\right)_T \right]_p = - \left(\frac{\partial V}{\partial T}\right)_p = -\alpha V,$$

and

$$dS_l(T, P) = \frac{C_{p,l}}{T} dT - \alpha_l V_l dp = dS_g(T, P) = \frac{C_{p,g}}{T} dT - \alpha_g V_g dp$$

Again, regrouping terms and noting that $S_g = S_l$ and $V_l = V_g$ at the transition

$$\left(\frac{dT}{dp}\right)_{tr} = \frac{\Delta\alpha VT}{\Delta C_p}$$

Combining everything,

$$R = \frac{\Delta k \Delta C_p}{TV(\Delta\alpha)^2} = 1$$

C. Effects of confinement

Ex. 1

For both glass and melt in the bulk state we can write down the following linear (in T) equations

$$\rho_g(T) = \rho_g^0 + \left(\frac{d\rho}{dT}\right)_g T$$

$$\rho_m(T) = \rho_m^0 + \left(\frac{d\rho}{dT}\right)_m T$$

at $T=T_g$ both densities (of glass and melt) are equal, $\rho_g = \rho_m$, and

$$T_g = -\frac{\rho_g^0 - \rho_m^0}{\left(\frac{d\rho}{dT}\right)_g - \left(\frac{d\rho}{dT}\right)_m}$$

For the film (symbols with planks will be used) the similar expression can be easily produced,

$$\bar{T}_g = -\frac{\bar{\rho}_g^0 - \bar{\rho}_m^0}{\left(\frac{d\bar{\rho}}{dT}\right)_g - \left(\frac{d\bar{\rho}}{dT}\right)_m}$$

The ratio is

$$\frac{\bar{T}_g}{T_g} = \frac{\bar{\rho}_g^0 - \bar{\rho}_m^0}{\rho_g^0 - \rho_m^0} \frac{\left(\frac{d\rho}{dT}\right)_g - \left(\frac{d\rho}{dT}\right)_m}{\left(\frac{d\bar{\rho}}{dT}\right)_g - \left(\frac{d\bar{\rho}}{dT}\right)_m}$$

Let us introduce $\delta\rho = \bar{\rho} - \rho$, the change of the density due to confinement. Then

$$\frac{\bar{\rho}_g^0 - \bar{\rho}_m^0}{\rho_g^0 - \rho_m^0} = 1 + \frac{\delta\rho_g^0 - \delta\rho_m^0}{\rho_g^0 - \rho_m^0}$$

$$\frac{\left(\frac{d\rho}{dT}\right)_g - \left(\frac{d\rho}{dT}\right)_m}{\left(\frac{d\bar{\rho}}{dT}\right)_g - \left(\frac{d\bar{\rho}}{dT}\right)_m} = \frac{1}{1 + \frac{\left(\frac{d\delta\rho}{dT}\right)_g - \left(\frac{d\delta\rho}{dT}\right)_m}{\left(\frac{d\rho}{dT}\right)_g - \left(\frac{d\rho}{dT}\right)_m}}$$

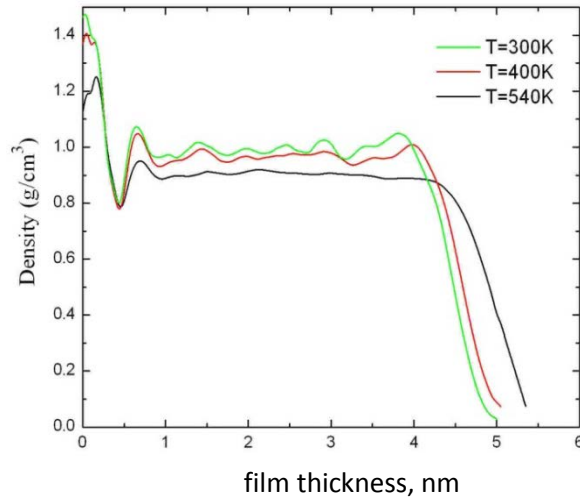
and, finally, for the ratio of two glass transition temperatures,

$$\frac{\bar{T}_g}{T_g} = \frac{1 + \frac{\delta\rho_g^0 - \delta\rho_m^0}{\rho_g^0 - \rho_m^0}}{1 + \frac{\left(\frac{d\delta\rho}{dT}\right)_g - \left(\frac{d\delta\rho}{dT}\right)_m}{\left(\frac{d\rho}{dT}\right)_g - \left(\frac{d\rho}{dT}\right)_m}}$$

We will use the fact that indeed, due to confinement, this excess density is non-zero, it can be both positive and negative, depending on the interaction strength with the support. Let us divide the film into three layers:

- the substrate layer close to the substrate;
- the middle layer in the film middle part;
- and the surface layer close to the film free interface.

It is obvious that in the film middle the density should be close to that in a bulk, and the differences can occur because of the mass re-distribution between the substrate and the surface layers. So, the film density is stratified.



For film density

$$\bar{\rho} = \frac{1}{H} \sum_{i=1}^3 h_i \rho_i, \quad \rho_{mid} \approx \rho_{bulk}$$

$$\delta\rho = \bar{\rho} - \rho = \frac{h_{subst} \delta\rho_{subst} + h_{surf} \delta\rho_{surf}}{H} = \frac{\delta m}{H}$$

The “excess” mass can, in principle, depend on T and H. Let us assume that it is NOT T-dependent.

$$\delta\rho_g^0 - \delta\rho_m^0 = \delta m \left[\left(\frac{1}{H} \right)_g^0 - \left(\frac{1}{H} \right)_m^0 \right]$$

$$\frac{d}{dT} (\delta\rho_g^0 - \delta\rho_m^0) = -\frac{\delta m}{H(\bar{T}_g)} \left[\frac{\left(\frac{dH}{dT} \right)_{T=\bar{T}_g}^{glass}}{H_{T=\bar{T}_g}} - \frac{\left(\frac{dH}{dT} \right)_{T=\bar{T}_g}^{melt}}{H_{T=\bar{T}_g}} \right]$$

$$\frac{d}{dT} (\delta\rho_g^0 - \delta\rho_m^0) = -\frac{\delta m}{H(\bar{T}_g)} \left[\bar{\alpha}_{g,T=\bar{T}_g} - \bar{\alpha}_{m,T=\bar{T}_g} \right]$$

here α are film thermal expansion coefficients in glassy and in the melt states. Substitution into the equation for $\frac{\bar{T}_g}{T_g}$ gives

$$\frac{\bar{T}_g}{T_g} = \frac{1 + C_1 \frac{\delta m}{H(\bar{T}_g)}}{1 + C_2 \frac{\delta m}{H(\bar{T}_g)}}$$

$$C_1 = \frac{\left[\left(\frac{1}{H} \right)_g^0 - \left(\frac{1}{H} \right)_m^0 \right] H(\bar{T}_g)}{\rho_g^0 - \rho_m^0}$$

$$C_2 = \frac{1}{\rho(T_g)} \frac{\bar{\alpha}_{g,T=\bar{T}_g} - \bar{\alpha}_{m,T=\bar{T}_g}}{\alpha_{g,T=T_g} - \alpha_{m,T=T_g}}$$