EPFL

School of Engineering
Institute of Materials
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Polymer Science 2025/26

Exercise 4 – Solution

1. Let's try to better understand the theory of *free volume*!

At absolute zero ($T = 0$), each segment of a glassy amorphous polymer occupies a volume v_o. As temperature increases, the molecules vibrate and the volume increases, characterized by the thermal expansion coefficient of the glass:

$$V_{\text{glass}} = \alpha_{\text{glass}} v_0 T \quad , \tag{1}$$

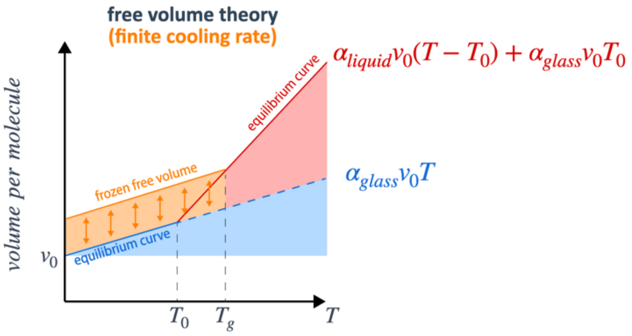
Note: For simplicity, we only consider the temperature-dependent contribution to the volume. The constant segment volume at $T = 0$ (v_0) is ignored, since it cancels when comparing glassy and liquid states.

According to the free volume theory, above a certain onset temperature T_o, “holes” appear that are large enough to allow the displacement of chain segments. Conformational changes become possible and the system enters the liquid (or rubbery) state, characterized by the expansion coefficient α_{liquid}.

Because the glassy state is an out-of-equilibrium state, an average "free volume" v_{fm} is trapped in the glassy state. By definition, this is the excess volume compared to a hypothetically *equilibrated* glass.

a) Show that

$$v_{\text{fm}} = v_0 (T - T_0)\left(\alpha_{\text{liquid}} - \alpha_{\text{glass}}\right) \quad . \tag{2}$$



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

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

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

Therefore, at equilibrium, the excess free volume v_{fm} vanishes at $T = T_o$.

We assume that the probability of finding a hole of size v_o in a given time interval is proportional to exp(-v_o/v_{fm}). Hence, the relaxation time and viscosity are

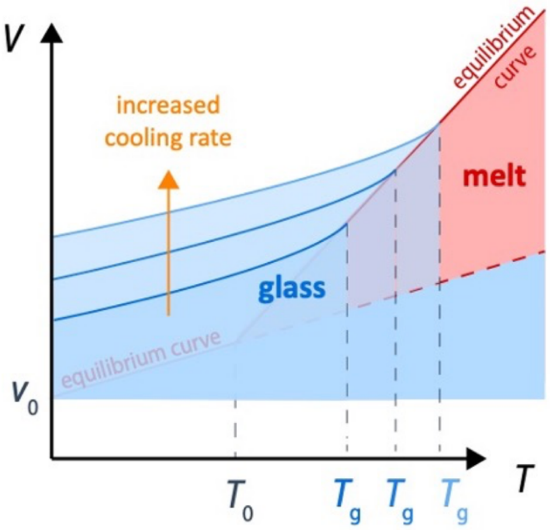
$$\tau = \tau_0 e^{\frac{v_0}{v_{fm}}}, \qquad \eta = \eta_0 e^{\frac{v_0}{v_{fm}}}\,. \tag{3,4}$$

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

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

where $\Delta\alpha > 0$. Thus, when T tends towards T_o, η becomes infinitely large. Physically, the liquid becomes arbitrarily viscous as the available free volume vanishes. Therefore, the very old glass (little free volume above T_o) flows extremely slowly and will not visibly sag under its own weight on human timescales.

c) If we cool at a given rate, conformational rearrangements eventually stop at a temperature $T > T_o$, when the viscosity becomes too high for relaxation on the experimental timescale. This temperature is the *experimental glass transition temperature* T_g. Draw the evolution of the volume as a function of T for several constant cooling rates. Indicate T_g for each cooling rate.



For a given cooling rate, the glass transition occurs when the viscosity (or relaxation time) reaches a critical value, corresponding to a critical amount of trapped free volume. Faster cooling leaves less time for relaxation, so the effective T_g is higher and the trapped free volume is larger.

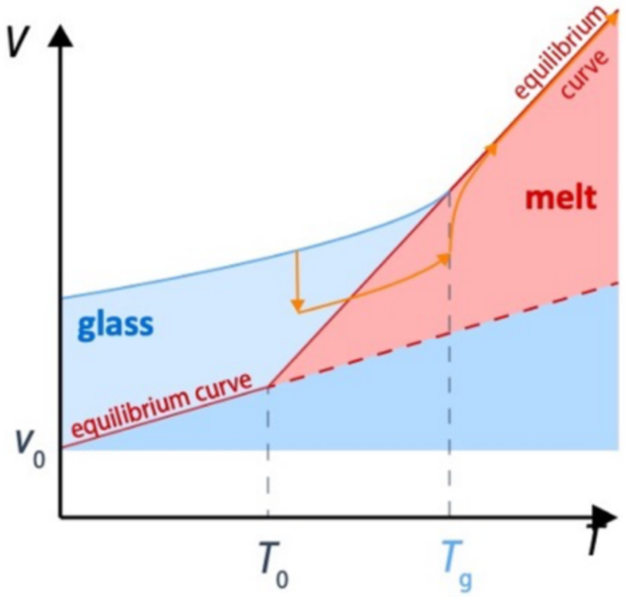
Below T_g, the system can no longer equilibrate. The thermal expansion coefficient reduces to that of the glassy state, so dV/dT is smaller than in the liquid (or rubbery) state.

d) In DSC measurements, a characteristic enthalpy peak is often observed near the glass transition temperature during heating if the heating rate is faster than the cooling rate used in the prior cooling scan (see Slide 147). This enthalpy peak can also appear after physical ageing, i.e. densification of the glassy state when the material rests below T_g. Explain this behavior with the help of a schematic illustration showing the evolution of the specific volume (or enthalpy) as a function of temperature.

If the subsequent heating rate is faster than the cooling rate, the system cannot fully equilibrate during heating. As shown schematically in Slide 131, this leads to a deviation between the equilibrium curve and the actual measured curve, producing an apparent overshoot in enthalpy (or a sudden change in volume) at the glass transition.

Similarly, if the material is kept for a long time at $T < T_g$, structural relaxation continues slowly, leading to densification of the glass (physical ageing). If heating is then applied, the material tries to regain the equilibrium state when reaching T_g, and this relaxation manifests as an enthalpy overshoot in the DSC curve.

Note: while the apparent T_g (onset of dV/dT change) is reproducible for a given rate, the overshoot is highly sensitive to the thermal history. For reliable results, it is therefore preferable to determine T_g during cooling from an equilibrated melt, rather than during heating.

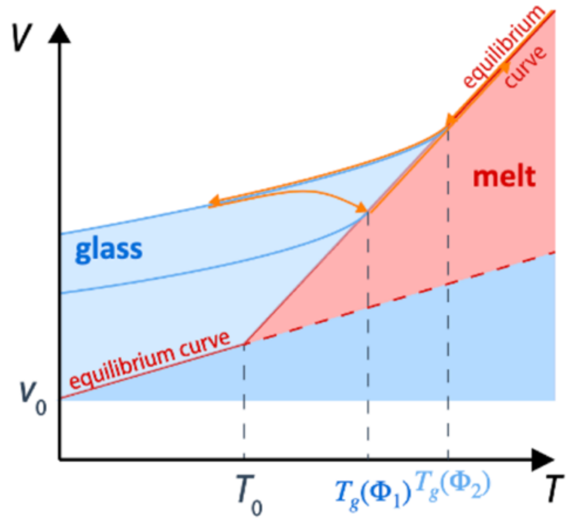


e) An amorphous polymer is cooled relatively quickly from the rubbery state to a temperature well below T_g, and then reheated much more slowly. Schematically show the evolution of the specific volume as a function of the temperature under these conditions.

If the polymer is cooled rapidly at rate Φ_1, excess free volume is trapped in the glassy state. When the sample is later heated more slowly at rate $\Phi_2 < \Phi_1$, this excess free volume relaxes progressively during heating.

As a result, the measured volume curve during heating (orange curve) lies below the cooling curve: starting from well below $T_g(\Phi_1)$, the volume decreases compared to the quenched state, approaching the equilibrium value by the time the sample reaches $T_g(\Phi_2)$.

This behavior reflects structural relaxation (physical ageing) of the glass during slow heating, which allows the system to move closer to equilibrium.



2. You saw that the glassy state out-of-equilibrium: no matter how slowly you cool, the free volume will not vanish at $T = T_0$. Therefore, some free volume is always trapped in the glass.

   According to the free volume theory, polymer chain ends contribute an additional free volume θ. Explain, within this framework, how T_g varies with number-average molar mass M_n for a given cooling rate. In your answer, justify the empirical Fox–Flory law (see Slide 158) by expressing the total free volume v_{fm}, as a function of θ, and assuming that the glass transition occurs at the same critical free volume as in the hypothetical case of infinitely long chains without end groups.

Each chain has two end groups, and each end group contributes an additional free volume θ. The number of chain ends per unit volume is:

$$\frac{2\rho N_\mathrm{A}}{M_n} \quad ,$$

where ρ is the density and N_A Avogadro's number. Thus, the free volume in a sample of finite molar mass at its glass transition is:

$$v_\mathrm{fm}(M_n, T) = (\alpha_\mathrm{liquid} - \alpha_\mathrm{glass})v_o(T_\mathrm{g} - T_o) + v_o\frac{2\theta\rho N_\mathrm{A}}{M_n} \quad ,$$

For an infinitely long chain, the contribution of chain ends vanishes, and the glass transition occurs at:

$$v_\mathrm{fm}(M_\infty, T) = (\alpha_\mathrm{liquid} - \alpha_\mathrm{glass})v_o(T_{\mathrm{g}\infty} - T_o) \quad ,$$

If we assume that the glass transition always corresponds to the same critical free volume, we equate the conditions:

$$(\alpha_\mathrm{liquid} - \alpha_\mathrm{glass})v_o(T_{\mathrm{g}\infty} - T_o) = (\alpha_\mathrm{liquid} - \alpha_\mathrm{glass})v_o(T_\mathrm{g} - T_o) + v_o\frac{2\theta\rho N_\mathrm{A}}{M_n} \quad ,$$

which simplifies to:

$$T_\mathrm{g} = T_{\mathrm{g}\infty} - \frac{2\theta\rho N_\mathrm{A}}{(\alpha_\mathrm{liquid} - \alpha_\mathrm{glass})M_n} \quad ,$$

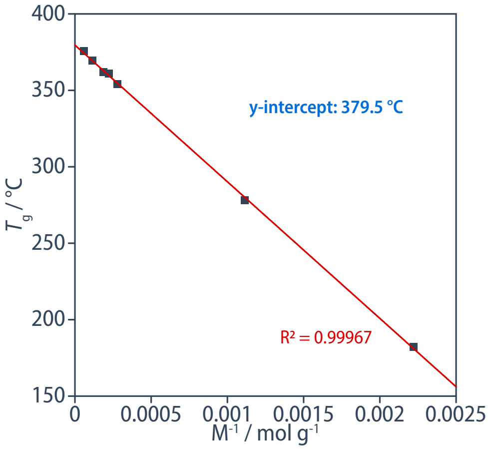
This has the form of the empirical Fox-Flory relation, showing that for a given cooling rate, the glass transition temperature decreases with decreasing molar mass because chain ends increase the effective free volume

Using the following data, determine the glass transition temperature $T_{\mathrm{g}\infty}$ of the polymer at infinite molar mass:

T_g (K)	182	278	354	361	362	369.5	375.5
M_n (Da)	500	1'000	4'000	5'000	6'000	10'000	20'000

Apply the empirical Fox-Flory equation (Slide 158). Convert the given number-average molar masses M_n into their reciprocal values. Plot T_g as a function of $1/M_\mathrm{n}$ and perform a linear regression. The intercept of the regression line at $1/M_\mathrm{n} \rightarrow 0$ yields $T_{\mathrm{g}\infty}$, the glass transition temperature of the polymer of infinite molar mass.

M g/mol	M^{-1} mol/g	T_g °C
500	0.002	182
1000	0.001	278
4000	2.5E-4	354
5000	2E-4	361
6000	1.66667E-4	362
10000	1E-4	369.5
20000	5E-5	375.5



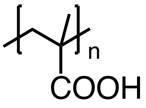
3. Show the qualitative shape of the elastic modulus $E(T)$ of an amorphous polymer as a function of temperature. Indicate the correct orders of magnitude of E in the different characteristic regimes. Also describe influence of the strain rate on the curve. Finally, sketch the corresponding $E(T)$ for a "small molecule".

   Refer to the schematic diagram from Slide 148 and be sure to indicate the correct modulus values.

   - **glassy state (below T_g): $E \approx 10^9$ Pa**
   - **transition (glass-rubber transition region): strong drop in modulus; the width and position of this transition depend strongly on the strain rate. Faster strain rates shift the apparent transition to higher temperature.**
   - **rubbery plateau (above T_g, for high-molar-mass polymers): $E \approx 10^6$ Pa**
   - **terminal viscous flow (well above T_g): $E \rightarrow 0$ Pa**

   For small molecules (very low molar mass), the rubbery plateau does not exist. Instead, the system transitions directly from the glassy state into the liquid state at T_g, where the modulus drops effectively to zero (unless crystallization occurs above T_g.

4. Name each polymer below and order them by expected glass transition temperature T_g (highest → lowest). Explain your ranking briefly.



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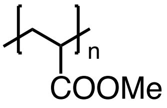

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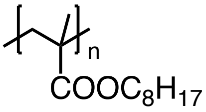

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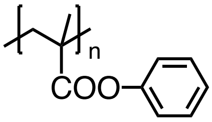

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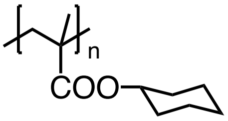

5

- **α-substitution (as in case of methacrylates) generally rigidifies the backbone relative to acrylates (raises T_g), because the backbone carbon bears an additional side group that hinders rotation.**
- **bulky/rigid side groups (cyclohexyl, phenyl) increase T_g by steric hindrance.**
- **hydrogen bonding (–COOH) can produce the largest increase in T_g.**
- **long flexible side chains (*n*-octyl) act as plasticizers and reduce T_g, sometimes overcompensating the backbone substitution effect.**

1: poly(methacrylic acid): $T_g \approx 228$ °C (hydrogen-bonding)

2: poly(methyl acrylate): $T_g \approx 10$ °C

3: poly(*n*-octyl methacrylate): $T_g \approx -20$ °C (flexible substituent)

4: poly(phenyl methacrylate): $T_g \approx 54$ °C (bulky substituent)

5: poly(cyclohexyl methacrylate): $T_g \approx 104$ °C (very bulky and rigid substituent)

5. You receive two samples of polystyrene. The supplier informs you that sample #1 can crystallize while #2 cannot. Is this possible? Explain your reasoning.

Polystyrene (PS) is a vinyl polymer and can exist in different tacticities:

- **atactic PS: most common commercial form with random stereochemistry along the chain. It cannot crystallize, so it is fully amorphous and transparent.**
- **isotactic PS: all substituents oriented on the same side. This regularity allows crystallization (via a helical chain conformation).**
- **syndiotactic PS: alternating substituent orientation. This is also a regular chain configuration that permits crystallization via a different helical conformation.**

Thus, depending on the tacticity, PS may be either amorphous (atactic) or semi-crystalline (isotactic or syndiotactic).

A practical check is a DSC measurement: atactic PS only shows a glass transition at ~100 °C, while semi-crystalline PS shows an additional melting endotherm at higher temperature (~270 °C).

Additionally, crystalline lamellae in semi-crystalline PS scatter visible light strongly, making isotactic and syndiotactic PS usually opaque, different from the transparent atactic PS.