In the following, examples from the progress of relaxation research in glass will be shown in order to illustrate what relaxation is about. It is neither a comprehensive picture of the history of relaxation research nor a balanced assessment of the contributions of all individuals involved.

To illustrate glass properties, references will be made to different companies. These references have been picked arbitrarily for educational reasons, copyright issues etc., not to provide a balanced view of the achievements of different companies.

Despite its careful preparation, the manuscript may contain errors.

Dr. Ulrich Fotheringham
Observation 1a (before 1912!):
Glass, if heated to high temperatures and cooled down rapidly, shows birefringence like Calcite:

In contrast to the permanent birefringence of Calcite, the birefringence in glass is stress-induced. Otto Schott found that it will relax if the sample is held for 24h at a minimum temperature which depends on the composition:

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12,0</td>
<td>2,5</td>
<td>8,5</td>
<td>2,0</td>
<td>—</td>
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<tr>
<td>Br₂O₅</td>
<td>71,95</td>
<td>66,9</td>
<td>69,34</td>
<td>67,3</td>
<td>43,83</td>
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<td>SiO₂</td>
<td>5,0</td>
<td>—</td>
<td>2,5</td>
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<tr>
<td>Al₂O₃</td>
<td>11,0</td>
<td>6,0</td>
<td>9,0</td>
<td>14,0</td>
<td>0,5</td>
</tr>
<tr>
<td>Na₂O</td>
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<td>10,5</td>
<td>—</td>
<td>8,0</td>
</tr>
<tr>
<td>K₂O</td>
<td>—</td>
<td>5,1</td>
<td>—</td>
<td>7,0</td>
<td>—</td>
</tr>
<tr>
<td>CaO</td>
<td>—</td>
<td>—</td>
<td>2,3</td>
<td>7,0</td>
<td>—</td>
</tr>
<tr>
<td>ZnO</td>
<td>—</td>
<td>3,0</td>
<td>—</td>
<td>—</td>
<td>47,3</td>
</tr>
<tr>
<td>PbO</td>
<td>—</td>
<td>0,4</td>
<td>0,3</td>
<td>—</td>
<td>0,3</td>
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<tr>
<td>As₂O₅</td>
<td>—</td>
<td>0,05</td>
<td>0,1</td>
<td>0,06</td>
<td>0,2</td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>—</td>
<td>—</td>
<td>0,2</td>
<td>—</td>
<td>0,07</td>
</tr>
<tr>
<td>Relaxation temperature</td>
<td>100,00</td>
<td>100,00</td>
<td>100,00</td>
<td>100,00</td>
<td>100,00</td>
</tr>
</tbody>
</table>

(calcite birefringence picture from Carl Zeiss AG, information on polarisation microscopy)

(Left: from Zschimmer, Chemische Technologie des Glases, Jena, 1913; Right: Abbe-Diagram with optical glasses from Schott AG, from Internet)
Observation 1b (before 1912!):
Similarly, Schott’s coworker Zschimmer measured relaxation times of stressed cubes (by a rapid quench from a high temperature) at different temperatures:

<table>
<thead>
<tr>
<th>Kühl-temperatur</th>
<th>Kron O 4417</th>
<th>Entspannungszeiten für</th>
<th>Flint O 4551</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gehärtet bei 510 °</td>
<td></td>
<td>Gehärtet bei 510 °</td>
</tr>
<tr>
<td>520 °</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>470</td>
<td>—</td>
<td>40 min.</td>
<td>—</td>
</tr>
<tr>
<td>465</td>
<td>—</td>
<td>12 min.</td>
<td>—</td>
</tr>
<tr>
<td>460</td>
<td>1 h</td>
<td>13 min.</td>
<td>5 min. 50 sec.</td>
</tr>
<tr>
<td>455</td>
<td>2 h</td>
<td>45 min.</td>
<td>6 min. 6 sec.</td>
</tr>
<tr>
<td>440</td>
<td>10 h</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>430</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>415</td>
<td>4 d 2 h</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>410</td>
<td>4 d 15 h</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>395</td>
<td>—</td>
<td>18 d</td>
<td>—</td>
</tr>
<tr>
<td>360</td>
<td>—</td>
<td>45 min.</td>
<td>—</td>
</tr>
</tbody>
</table>

The interpretation was: The rapid quench leads to the freezing of deformations $\varepsilon$. This causes stress $\sigma$ (M elastic modulus):

\[
\sigma = M \cdot \varepsilon
\]

At high temperatures, the stress will relax via viscous flow. If one assumes stress relaxation to be proportional to the remaining stress, one arrives at Maxwell’s relaxation law ($\tau$: relaxation time):

\[
\sigma = \sigma_0 \cdot e^{-t/\tau}
\]

(from Zschimmer, Chemische Technologie des Glases, Jena, 1913)
Observation 1c (1875 and 1877!):
Hardening of glass. De Bastie found that by a very rapid quench such as by diving a hot glass plate into water, glass can be hardened. Having loads fall from rising heights onto glass plates, Luynes found the following significant increase in toughness:

In Zschimmer´s book, this is explained this way: The rapid quench makes the surfaces become rigid quickly which causes intermediary stress between the surfaces and the core. As the core remains soft for some time, these stresses relax. When the core glass stiffens itself, however, it acts like a contracting spring. At the end, there will be permanent compression in the surface and permanent tension in the core.

(from Zschimmer, Chemische Technologie des Glases, Jena, 1913)
Understanding Observations 1a-c, Part 1:

1. Stress relaxation: discovered and made use of > 100 years ago (hardening!).
2. Today we know that there are different stress relaxation mechanisms in glass.
3. Most important mechanism is shear stress relaxation which was discovered investigating fluids by James Clerk Maxwell in 1866. Maxwell considers certain materials to be viscoelastic which may be symbolized by combining a spring and a dashpot:

![Diagram of a spring and a dashpot](image)

If the material is sheared, stress will result (elongation of the spring) which may be permanent (hardening) but will relax via viscous flow (dashpot) at high temperatures.

4. Maxwell relaxation time ($\tau$: shear viscosity, $G$: shear modulus):

$$\tau = \eta / G$$

Plausibility: $\tau$ increases with $\eta$: o.k.
$\tau$ decreases with $G$: the higher the modulus, the smaller the deformation for a given stress level and therefore the smaller the path to be covered by viscous
Melting, casting, pressing, drawing, sagging: Maxwell’s relaxation time is extremely short. What is true in the transformation range? Why is it called such and used for stress relaxation? See next slide.
Some exercises:

1. Assume that the relaxation observed follows Maxwell´s law. Assume that the times given by Zschimmer mean that birefrigence has decreased to 1% of its original value. What are the Maxwell relaxation times at 470°C and at 520°C for the flint glass quenched from 600°C?

2. Consider the solder glass at ca. 380°C. Assume that Young´s modulus E is 48 GPa and that Poisson´s ratio $\nu$ is 0.2. Calculate the shear modulus $G$:

$$G = \frac{E}{2 \cdot (1 + \nu)}$$

Calculate Maxwell´s relaxation time at 380°C. Go back by 1 slide and guess why the temperature region around 380°C is called transformation range.

3. (Optional:) Assume that the temperature dependence of a Maxwell relaxation time is of the Arrhenius type, i.e.

$$\tau = \tau_0 \cdot e^{\frac{H}{R \cdot T}}$$

with $T$ being the temperature in Kelvin. What is the activation enthalpy $H$ for Zschimmer´s flint glass if $R = 8.3145 \text{ J/(mol·K)}$ is the gas constant?
Observation 2a (1870-1890!):
Glass dimensions depend on thermal history which means that one and the same piece of glass may have different dimensions at the same temperature, depending on prior thermal treatment. The first systematic study of this effect has been carried out considering glass thermometers.

Any increase of the volume of the storage vessel at the bottom will make the fluid (in many cases: mercury) column in the capillary indicate a lower temperature than the actual one (ice point depression) and vice versa (ice point increase).

There are two such effects: one in the transformation range and one in the vicinity of room temperature.
Observation 2b (1870-1890!):
Weber compared the depression after boiling which may be observed in ordinary glass and special thermometer glass. He found

1. Boiling increases the specific volume (decreases the density) of glass
2. Held at room temperature for several months, the specific volumes decreases again
3. The size of the effect is big if there are mixed alkalis in the composition
4. The cooperation of Weber and Schott led to the development of essentially single-alkali thermometer glasses.

(from Zschimmer, Chemische Technologie des Glases, Jena, 1913)
Observation 2c (1870-1890!):
In the 19th century (and still today!), glass thermometers were used up to several hundred degrees Celsius.

So ice point and boiling point positions of a thermometer from thermometer glass 16Ⅲ were checked after exposure to temperatures around the range (400°C-410°C) for which significant stress relaxation within 24h had been observed.

A significant decrease of the specific volume was found compared to the original state resulting from rapid cooling at the end of the manufacturing process.

(from Zschimmer, Chemische Technologie des Glases, Jena, 1913)
Understanding Observations 2a-c, Part 1 (1900-1930):
Arthur Q. Tool, Franz Simon, Gustav Tammann and others investigated the drastic changes of properties like thermal expansion or specific heat in the glass transformation range.

This has raised the idea of a glass transition temperature $T_G$.

Considering dilatometric curves $T_G$ has been defined as the position of the bent between low-temperature and high-temperature branch.

$T_G$ is seen as transition point between the (high T) supercooled liquid where physical and chemical readjustments happen (with calorimetric & dilatometric fingerprints) and the (low T) glass where they are frozen (not completely, see zero point depression).

Understanding Observations 2a-c, Part 2 (1930-1950):
As the above physical and chemical readjustments are necessary for reaching thermal equilibrium, glass is identified as a non-equilibrium material (with respect to the metastable equilibrium of a supercooled liquid).

Tool introduced fictive temperature $T_f$ to characterize the non-equilibrium state by the temperature where, if exposed to it, the glass would be in equilibrium with its environment without physical or chemical adjustment (“structural relaxation”).

Above transformation range: $T_f \approx T$ (instantaneous structural relaxation)

$$\Delta l/l = \alpha_{\text{glass}} \Delta T + \alpha_{\text{structural}} \Delta T_f = (\alpha_{\text{glass}} + \alpha_{\text{structural}}) \Delta T$$

$$\Delta h = c_{p,\text{glass}} \Delta T + c_{p,\text{structural}} \Delta T_f = (c_{p,\text{glass}} + c_{p,\text{structural}}) \Delta T$$

Below transformation range: $T_f \approx \text{const.}$ (no structural relaxation at all)

$$\Delta l/l = \alpha_{\text{glass}} \Delta T$$

$$\Delta h = c_{p,\text{glass}} \Delta T$$

$l$: length, $h$: specific enthalpy. If temperature changes above transformation range, there is a 2nd contribution to thermal expansion / specific heat $\propto \Delta T_f$. Below: none.

Questions left:
1. What happens in the transformation range?
2. Remark: room temperature effects (ice point depression) not included.
Understanding Observations 2a-c, Part 3 (1930-1950):
In the transformation range, there is a gradual deviation from equilibrium during cooling and a gradual return to equilibrium during heating. In contrast to a single-point transition at a certain $T_G$, Tool’s fictive temperature allows for that.

Different glass densities resulting from different cooling rates were explained this way: the slower a glass is cooled, the longer there is time to stay in equilibrium with the environment, the lower the resulting $T_f$ and specific volume are:

\[
\Delta T_f \propto \frac{\Delta V}{V} = -\frac{\Delta \rho}{\rho}
\]

Fig. 2.2 Volume change during the cooling process of a melt forming: (1) a crystal structure; (2) a glass structure.

Understanding Observations 2a-c, Part 4 (1930-1950):
To describe fictive temperature kinetics in a quantitative way, Arthur Q. Tool introduced the following equation:

\[
\frac{dT_f}{dt} = \frac{T - T_f}{\tau} = \frac{T - T_f}{\tau_0 \cdot e^{\frac{H}{R \cdot T}}}
\]

The Arrhenius-type temperature dependence of the structural relaxation time \( \tau \) had been inspired by the Arrhenius-type temperature dependence of the viscosity over small temperature ranges (for broader temperature ranges, the VFT equation is used). \( \tau \) is called structural relaxation time.

For an isothermal hold, \( T_f \) becomes:

\[
T_f(t) = T + (T_f(0) - T) \cdot e^{-\frac{t}{\tau}}
\]

Further phenomenon (refractive index, 1950-1960; optional):

For a linear cooling rate $\beta$, one may write:

$$\frac{dT_f}{dt} = \frac{dT_f}{dT} \cdot \frac{dT}{dt} = \frac{dT_f}{dT} \cdot \beta = \frac{T - T_f}{H} \Rightarrow \frac{dT_f}{dT} = \frac{T - T_f}{\tau_0 \cdot e^{\frac{H}{RT}}}$$

So the transition from $T_f \approx T$ (high $T$) to $T_f \approx \text{const.}$ (low $T$) is expected at a temperature $T$ where $\beta \cdot \tau_0 \cdot e^{\frac{H}{RT}}$ reaches a certain value. This temperature will be the resulting $T_f$.

From this, one gets a relation between the resulting $T_f$'s of different coolings:

$$\frac{H}{\beta_1 \cdot \tau_0 \cdot e^{\frac{H}{RT}, \text{resulting }, 1}} = \frac{H}{\beta_2 \cdot \tau_0 \cdot e^{\frac{H}{RT}, \text{resulting }, 2}} \Rightarrow \frac{1}{T_f, \text{resulting }, 1} - \frac{1}{T_f, \text{resulting }, 2} = \ln\left(\frac{\beta_2}{\beta_1}\right)$$

Lillie and Ritland concluded for the refractive index $n$ (linearly dependent on $T_f$):

$$\frac{n_1 - n_2}{n_1 \cdot n_2} = m \cdot \ln\left(\frac{\beta_2}{\beta_1}\right)$$

$m$ is a constant.

Some exercises:

1. Make a screen-shot of the slides and mark $T_G$ in the dilatometric measurement on BK7® (Understanding …, Part 1). Make a rough determination of $\alpha_{\text{glass}}$ and $\alpha_{\text{structural}}$.

2. What is the fictive temperature at the beginning of the isothermal hold of BK7® (Understanding …, Part 4)? What will be its value when the isothermal hold is long enough?

3. Assume that the isothermal hold has approximately come to an end in the experiment. Can you calculate $\alpha_{\text{structural}}$ then? Compare with the value found above. And what is the structural relaxation time in the isothermal hold?

4. (Difficult!) Show where the path of the isothermal hold of BK7® might be in a drawing like the one in “Understanding, …, Part 3”.

5. (Optional:) Calculate “m” for SF56 (Further phenomenon; $n(\text{SF56}) = \text{ca. 1.8}$).