Fragility and Thermodynamics in Complex Glass-Formers

Daniele Cangialosi
Ángel Alegría
Juan Colmenero

University of the Basque Country
CSIC-CFM
Fundación Donostia International Physics Center (D.I.P.C.)

9 October 2008
Fragility in glass-forming systems

liquids cooled down below the melting temperature undergoes a rapid increase of the viscosity and the structural relaxation time that eventually leads to structural arrest.

The steepness of the relaxation time variation is normally named “fragility”.

Steepness index:

\[ m = \frac{d \ln \tau(T)}{d \left( \frac{T_g}{T} \right)} \bigg|_{T=T_g} \]

“Fragile” liquid \( \rightarrow \) Large \( m \)

“Strong” liquid \( \rightarrow \) Small \( m \)
Fragility vs. other properties

- Stretching exponent;
- Boson peak;
- Non-ergodicity factor;
- Mechanical properties;
- Thermodynamics.
Fragility vs. other properties

- Stretching exponent;
- Boson peak;
- Non-ergodicity factor;
- Mechanical properties;
- Thermodynamics.
**Connection fragility-thermodynamics: state of the art**

AG relation:

\[ \tau = \tau_0 \exp \left( \frac{C}{T S_c} \right) \]

\( F_{1/2} \) related to steepness of relaxation time variation

\( F_{3/4} \) related to steepness of configurational entropy variation

Connection fragility-thermodynamics: state of the art


fragility vs. the specific heat jump at $T_g$

NO correlation for polymeric and non-polymeric glass-formers
Connection fragility-thermodynamics from the AG equation

- Connection between fragility and thermodynamics from the AG equation:

\[ \tau = \tau_0 \exp \left( \frac{\Delta \mu_s^*}{k_B T S_c} \right) = \tau_0 \exp \left( \frac{C}{T S_c} \right) \]

- Normalized fragility:

\[ m_A = \frac{d \left[ \ln \left( \frac{\tau(T)}{\tau_0} \right) / \ln \left( \frac{\tau(T_g)}{\tau_0} \right) \right]}{d \left( \frac{T_g}{T} \right)} \bigg|_{T=T_g} \]

- Configurational properties replaced by excess properties (experimentally accessible);

- Not the same but proportional;

- The specific heat jump at \( T_g \) as in previous approaches + \( S_{ex}(T_g) \)

Connection fragility-thermodynamics from the AG equation

\[ m_A = 1 + \frac{\Delta c_p(T_g)}{S_{ex}(T_g)} \]

\[ m_A = 40 \frac{\Delta c_p(T_g)}{S_{ex}(T_m)} \]

- Analogous to the correlation recently proposed;*
- Verified for a large number of LMWGF

Data for glass-forming polymers

\[ m_A = 1 + \frac{\Delta c_p(T_g)}{S_{ex}(T_g)} \]

- Structural relaxation times from dielectric spectroscopy;
- Thermodynamics data:
  - for polymers: extensive work of Wünderlich and Pyda;*
  - BCDE and DBP: our data and melting data from NIST database.

* B. Wünderlich and M. Pyda, ATHAS database, http://web.utk.edu/~athas/ and references therein

Verification of the fragility relation

- The fragility relation verified ONLY for some polymers;
- It fails for others and for LMWGF: DBP and BCDE;
Comparison with other approaches

Same deviation of other fragility relations for some glass-forming polymers


Comparison with other approaches

Deviation only for polymer-like systems
**Vogel temperature vs. Kauzmann temperature**

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

\[ T_0 \quad \Rightarrow \quad \tau \rightarrow \infty \]

\[ \tau = \tau_0 \exp \left( \frac{C}{T S_{ex}} \right) \]

\[ T_K \quad \Rightarrow \quad S_{ex} = 0 \]

\[ T_0 = T_K \]

Verified for the vast majority of low-molecular weight glass-formers.*

**Vogel temperature vs. Kauzmann temperature**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_v$ (K)</th>
<th>$T_k$ (K)</th>
<th>$T_0$ (K)</th>
<th>$S_{ex}(T_0)$ (J/molK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-PP</td>
<td>270</td>
<td>174.5</td>
<td>174</td>
<td>0±1.1</td>
</tr>
<tr>
<td>LDPE</td>
<td>237</td>
<td>149</td>
<td>160</td>
<td>1±0.3</td>
</tr>
<tr>
<td>cis-PI</td>
<td>200</td>
<td>166.5</td>
<td>162</td>
<td>-0.9±2.6</td>
</tr>
<tr>
<td>PVC</td>
<td>354</td>
<td>308</td>
<td>317</td>
<td>0.38±0.2</td>
</tr>
<tr>
<td>PDMS</td>
<td>146</td>
<td>130.5</td>
<td>130</td>
<td>0±0.05</td>
</tr>
<tr>
<td>PS</td>
<td>373</td>
<td>278</td>
<td>324</td>
<td>6.7±0.3</td>
</tr>
<tr>
<td>PEN</td>
<td>390</td>
<td>326</td>
<td>358</td>
<td>9.1±0.4</td>
</tr>
<tr>
<td>PET</td>
<td>342</td>
<td>269</td>
<td>308</td>
<td>14.0±0.3</td>
</tr>
<tr>
<td>a-PMMA</td>
<td>378</td>
<td>263.5</td>
<td>334</td>
<td>10.7±1.8</td>
</tr>
<tr>
<td>PC</td>
<td>420</td>
<td>292</td>
<td>373</td>
<td>21.7±1.4</td>
</tr>
<tr>
<td>PEEK</td>
<td>419</td>
<td>324</td>
<td>398.5</td>
<td>22.5±0.7</td>
</tr>
<tr>
<td>PA 6,6</td>
<td>323</td>
<td>196</td>
<td>290</td>
<td>64.0±6.8</td>
</tr>
<tr>
<td>PVME</td>
<td>244</td>
<td>166.5</td>
<td>205</td>
<td>8±0.5</td>
</tr>
<tr>
<td>BCDE</td>
<td>239</td>
<td>146</td>
<td>188.5</td>
<td>26±2</td>
</tr>
<tr>
<td>DBP</td>
<td>177.5</td>
<td>126</td>
<td>147</td>
<td>25 ±2</td>
</tr>
</tbody>
</table>

- $T_0 = T_k$ also for those polymer verifying the fragility relation;
- $T_0 > T_k$ for the other polymers and DBP and BCDE;
- Presence of $S_{ex}(T_0)$ unrelated to the $\alpha$ process.
**Structure and $\alpha$ relaxation**

- Fragility: ONLY related to the $\alpha$ process vs. properties: related to the overall structure;

- **ONLY** $S_{ex,\alpha}$ related to the $\alpha$ process should be taken into account:

\[
m_A = \frac{\Delta c_p(T_g)}{S_{ex}(T_g)}
\]

\[
m_A = 1 + \frac{\Delta c_p(T_g)}{S_{ex,\alpha}(T_g)}
\]

- **$S_{ex,\alpha}$** obtained subtracting the contribution from non-$\alpha$ related processes. At a first approximation equal to $S_{ex}(T_0)$. 
New fragility relation

\[ m_A = 1 + \frac{\Delta c_p(T_g)}{S_{ex,\alpha}(T_g)} = 1 + \frac{\Delta c_p(T_g)}{S_{ex,tot}(T_g) - S_{ex}(T_0)} \]
New fragility relation

\[ m_A = 1 + \frac{\Delta c_p(T_g)}{S_{ex,\alpha}(T_g)} = 1 + \frac{\Delta c_p(T_g)}{S_{ex,\text{tot}}(T_g) - S_{ex}(T_0)} \]

- fragility relation reestablished!
- Employment of \( S_{ex}(T_0) \) for the fragility relation, defined at \( T_g \), not trivial;
- non-\( \alpha \) related contribution is temperature independent;
Glass-formers possessing a non-$\alpha$ related $S_{ex}$ present complicated rather chemical structure:

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>PC</td>
<td>PEN</td>
<td>PEEK</td>
<td>PA 6,6</td>
</tr>
</tbody>
</table>
| \[
\text{PS: } \left(-\text{CH}_2\text{CH}_2-\right)_n
\] | \[
\text{PC: } \left(-\text{CH}_3-\text{C}-\text{O-}\right)_n
\] | \[
\text{PEN: } \left(-\text{OCH}_2\text{CH}_2\text{O-}\text{C}-\right)_n
\] | \[
\text{PEEK: } \left(-\text{O}-\text{CH}_2-\text{O}\right)_n
\] | \[
\text{PA 6,6: } \left(-\text{NH}_2-\text{(CH}_2)_4\text{CH}_2\text{NH-}\text{C}-\text{CH}_2-\text{(CH}_2)_2\text{CH}_2-\text{C}\right)_n
\] |
| PET | DBP | PMMA | BCDE |   |
| \[
\text{PET: } \left(-\text{OCH}_2\text{CH}_2\text{O-}\text{C}-\right)_n
\] | \[
\text{DBP: } \text{CH}_3
\] | \[
\text{PMMA: } \left(-\text{CH}_2-\text{C}-\text{CH}_3\text{O}-\text{C}\right)_x
\] | \[
\text{BCDE: } \text{OCH}_3
\] |   |
**Role of internal degrees of freedom**

Motions related to internal degrees of freedom detectable through standard spectroscopic techniques (non-JG secondary relaxations)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td><img src="image" alt="PS Structure" /></td>
</tr>
<tr>
<td>PEN</td>
<td><img src="image" alt="PEN Structure" /></td>
</tr>
<tr>
<td>PET</td>
<td><img src="image" alt="PET Structure" /></td>
</tr>
<tr>
<td>PMMA</td>
<td><img src="image" alt="PMMA Structure" /></td>
</tr>
<tr>
<td>PC</td>
<td><img src="image" alt="PC Structure" /></td>
</tr>
<tr>
<td>PEEK</td>
<td><img src="image" alt="PEEK Structure" /></td>
</tr>
<tr>
<td>PA 6,6</td>
<td><img src="image" alt="PA 6,6 Structure" /></td>
</tr>
<tr>
<td>DBP</td>
<td><img src="image" alt="DBP Structure" /></td>
</tr>
<tr>
<td>BCDE</td>
<td><img src="image" alt="BCDE Structure" /></td>
</tr>
</tbody>
</table>
Polystyrene secondary relaxation

- No detectable secondary relaxation for low molecular weight PS;

- Role of secondary relaxation compatible with the deviation from the correlation between fragility and $V_f/V_t$.*

• No specific heat jump at the temperature where secondary relaxation shows up at the same time-scale of the DSC experiment;
• Result compatible with a temperature independent contribution $S_{ex}$ from secondary relaxations.
• Geometry of motion independent of temperature.
• Entropy of motion between two non equivalent positions:

$$S = k \ln 2 = 5.8 \text{Jmol}^{-1} \text{K}^{-1}$$

Uncorrected thermodynamic fragility vs. non-ergodicity factor

\[ m_T = 1 + \frac{\Delta c_p \left( T_g \right)}{S_{\text{ex_tot}} \left( T_g \right)} \]

\[ \alpha = \lim_{q \to 0} \frac{d \log f_q \left( T \right)}{d \left( T/T_g \right)} \bigg|_{T \to 0} \]

\( \alpha \) needs correction too!

...collaboration with T. Scopigno, S. Capaccioli and G.C. Ruocco
Summary and Conclusions

- The fragility has been related to thermodynamics starting from the AG relation;

- A positive relation was found only for polymers with simple monomeric structure (also vast majority of LMWGF);

- The relation clearly fails for other polymers, and BCDE and DBP;

- The role of non-$\alpha$ process related relaxations (possibly secondary relaxations) has been highlighted to explain this discrepancy;

- Any correlation between fragility and structure must be taken into account the contribution to the structure on non-$\alpha$ process related relaxations.