Web Course
Physical Properties of Glass

1. Properties of Glass Melts
2. Thermal Properties of Glasses

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Melt and Glass Properties

• Viscosity- chapter 9
• Surface Tension- chapter 9
• Thermal Expansion- chapter 10
• Heat Capacity- chapter 11
• Thermal Conductivity- chapter 12
Supplementary References on Viscosity


Why should we care about melt viscosity?

1. Glass Forming Tendency
   a. Nucleation, crystallization, phase separation kinetics

   \[ I_{V}^{HO} = N_{V}^{0} \left( \frac{k \cdot T}{3\pi \cdot a_{0}^{3} \cdot \eta} \right) \exp \left[ -\frac{K \cdot \sigma^{3}}{T \cdot \Delta G_{v}^{2}} \right] \]

2. Melt Fining

   Stoke's Law: \[ V = \frac{d^{2} g (\rho_{b} - \rho_{l})}{12\eta} \]

3. Manufacturing Process Control

4. Annealing Schedules/Permanent Stress

5. What else??
Viscosity Definitions

Viscosity \( \equiv \eta = \frac{Fd}{AV} = \frac{\sigma_0}{\varepsilon} \)

Units: \( \text{dynes} \cdot \text{cm}/(\text{cm}^2 \cdot \text{cm/s}) \)
  = dyne\cdot\text{s/cm}^2 = \text{Poise} \quad \text{or} \quad \text{N}\cdot\text{s/m}^2 = \text{Pa}\cdot\text{s}
  1 \text{ Pa}\cdot\text{s} = 10 \text{ P}
  1 \text{ P} = 1 \text{ dPa}\cdot\text{s}

Newtonian Liquids:

Shear stress \( \sigma \) vs. Time

Strain \( \varepsilon \) vs. Time

\( \varepsilon = \frac{\sigma_0}{\eta} \)
Practical Consequences
Elastic Solid

Newtonian Liquid

Viscoelastic transition

glass
forming
melting

$\eta(T)$ for SLS melt

Temperature (°C)

$\log_{10} \eta$ (poise)
### Table 14
Some Useful Viscosity Reference Values (*approximate only*)

<table>
<thead>
<tr>
<th>Log Viscosity</th>
<th>Log Viscosity</th>
<th>Log Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ASTM Melting Range</strong></td>
<td>1.5-2.5</td>
<td><strong>ASTM Softening Point (S.P.)</strong></td>
</tr>
<tr>
<td><strong>Bottle Vacuum Gathering</strong> (Narrow Neck) 2 to 110 Ounce Weight</td>
<td>2.7-3.8</td>
<td><strong>To Sinter for Porous Body from Powdered Glass</strong></td>
</tr>
<tr>
<td><strong>Heavy Wall Tubing Will Collapse Under Vacuum</strong></td>
<td>3.3</td>
<td><strong>Temperature for Glass to Metal Sealing</strong></td>
</tr>
<tr>
<td><strong>To Heat for Hot Sever or Shear</strong></td>
<td>3.5</td>
<td><strong>ASTM Annealing Range</strong></td>
</tr>
<tr>
<td><strong>To Seal Glass To Glass</strong></td>
<td>3.5</td>
<td><strong>Matching Temperature for Contraction Curves for Glass to Metal Sealing</strong></td>
</tr>
<tr>
<td><strong>Tumbler Vacuum Gathering</strong></td>
<td>3.5</td>
<td><strong>General Limit of Measurement of Viscosity</strong></td>
</tr>
<tr>
<td><strong>Bottle Gob Feeding Range (Wide Mouth) 5 to 16 Ounce Weight</strong></td>
<td>3.7-4.1</td>
<td><strong>The Lowest Temperature at which Stress Relief Can Be Accomplished in a Reasonable (Commercial) Time</strong></td>
</tr>
<tr>
<td><strong>Casting Plate Glass</strong></td>
<td>3.7-3.8</td>
<td><strong>American Softening Point (S.P.)</strong></td>
</tr>
<tr>
<td><strong>To Seal Glass to Metal</strong></td>
<td>3.8</td>
<td><strong>Positive Upper Use Temperature Without Destroying Annealing</strong></td>
</tr>
<tr>
<td><strong>Fourcault Sheet Drawing</strong></td>
<td>4.0-4.4</td>
<td><strong>ASTM Annealing Point (A.P.)</strong></td>
</tr>
<tr>
<td><strong>Begin Updraw Tubing Operation</strong></td>
<td>5.3</td>
<td><strong>Transformation Range</strong></td>
</tr>
<tr>
<td><strong>Begin Downdraw Tubing Operation</strong></td>
<td>5.3</td>
<td><strong>Full Range for General Annealing</strong></td>
</tr>
<tr>
<td><strong>To Flare Glass Tubing or Form a Lip</strong></td>
<td>5.5</td>
<td><strong>Safe Upper Use Temperature of Annealed Glass if Cooled Slowly to Avoid Temporary Cooling Stress</strong></td>
</tr>
<tr>
<td><strong>To Sinter for Solid Body From Powdered Glass</strong></td>
<td>6.0</td>
<td></td>
</tr>
</tbody>
</table>

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Melt properties-8
## Important Manufacturing Viscosities

<table>
<thead>
<tr>
<th>Name</th>
<th>( \eta ) (Pa·s)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting pt (( T_m ))</td>
<td>( 10^1 )</td>
<td></td>
</tr>
<tr>
<td>Melting range</td>
<td>( 10^{0.5-10^{1.5}} )</td>
<td>Melting, fining</td>
</tr>
<tr>
<td>Working pt (( T_w ))</td>
<td>( 10^3 )</td>
<td></td>
</tr>
<tr>
<td>Working range</td>
<td>( 10^{2-10^6} )</td>
<td>Forming</td>
</tr>
<tr>
<td>Liquidus temp (( T_l ))</td>
<td>( \sim 10^4 )</td>
<td>No crystallization for ( T&gt;T_l )</td>
</tr>
<tr>
<td>Flow point</td>
<td>( 10^4 )</td>
<td></td>
</tr>
<tr>
<td>Softening point (( T_{Lit} ))</td>
<td>( 10^{6.6} )</td>
<td>Littleton, flow under own weight</td>
</tr>
<tr>
<td>Crystallization temp (( T_x ))</td>
<td>( \sim 10^7 )</td>
<td>No crystallization for ( T&lt;T_x )</td>
</tr>
<tr>
<td>Deformation temp (( T_d ))</td>
<td>( 10^{10-10^{11}} )</td>
<td>Dilatometric: expansion compensated by viscous flow</td>
</tr>
<tr>
<td>Glass transition (( T_g ))</td>
<td>( 10^{11-10^{12}} )</td>
<td></td>
</tr>
<tr>
<td>Annealing pt (( T_{ap} ))</td>
<td>( 10^{12} )</td>
<td>Internal stresses relieved &lt;15 min</td>
</tr>
<tr>
<td>Strain pt (( T_{sp} ))</td>
<td>( 10^{13.5} )</td>
<td>Internal stresses relieved &lt;15 hrs</td>
</tr>
</tbody>
</table>
**Defined Viscosities**

<table>
<thead>
<tr>
<th></th>
<th>log Pa·s</th>
<th>log P</th>
</tr>
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<tbody>
<tr>
<td>Working Pt</td>
<td>$10^3$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>Littleton</td>
<td>$10^{6.6}$</td>
<td>$10^{7.6}$</td>
</tr>
<tr>
<td>Softening Pt</td>
<td>$10^{12}$</td>
<td>$10^{13}$</td>
</tr>
<tr>
<td>Annealing Pt</td>
<td>$10^{13}$</td>
<td>$10^{13}$</td>
</tr>
<tr>
<td>Strain Pt</td>
<td>$10^{13.5}$</td>
<td>$10^{14.5}$</td>
</tr>
</tbody>
</table>

**FIGURE 5.21**  Viscosity $\eta$ versus temperature for a typical soda-lime-silicate glass.

$\eta(T)$ for SLS melt
Viscosity Classifications

• Working Range: Temperatures (ΔT) between ‘working point’ and ‘softening point’
  – Long glasses: large ΔT (shallow η(T) curves)
  – Short glasses: small ΔT (steep η(T) curves)
  – Hard glasses: Working range at greater temperatures than for S-L-S glass
    • Borosilicates, aluminosilicates, oxynitrides, silica, etc.
    • Sometimes defined as CTE<6x10⁻⁶/°C
  – Soft glasses: Working range at lower temperatures than for S-L-S glass
    • Soda-lime silicate, Pb-silicates
    • Sometimes defined as CTE>6x10⁻⁶/°C
From Seward and Varshneya (2001)

Corning Codes:
8363: High PbO radiation shield
0010: Pb-silicate tube
7070: Borosilicate
0080: SLS lamp glass
7740: Pyrex
1720: Alkaline-earth boro-aluminosilicate

FIGURE 6.2 Viscosity versus temperature for some commercial glasses designated by glass codes (see Tables 6.1 and 6.2). (Courtesy of Corning Incorporated.)
## Measurement of Viscosity

<table>
<thead>
<tr>
<th>Range</th>
<th>Method</th>
<th>Viscosity Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting</td>
<td>Falling Sphere/Bubble Rise</td>
<td>$\eta &lt; 10^4$ Pa-s</td>
</tr>
<tr>
<td></td>
<td>Margules Rotating Cylinder</td>
<td>$\eta &lt; 10^6$ Pa-s</td>
</tr>
<tr>
<td>Softening and</td>
<td>Parallel Plate</td>
<td>$10^5$ Pa-s$&lt;\eta&lt;10^9$ Pa-s</td>
</tr>
<tr>
<td>Annealing</td>
<td>Penetration Viscometer</td>
<td>$10^5$ Pa-s$&lt;\eta&lt;10^9$ Pa-s</td>
</tr>
<tr>
<td></td>
<td>Fiber Elongation</td>
<td>$10^5$ Pa-s$&lt;\eta&lt;10^{15.5}$ Pa-s</td>
</tr>
<tr>
<td></td>
<td>Beam Bending</td>
<td>$10^7$ Pa-s$&lt;\eta&lt;10^{12}$ Pa-s</td>
</tr>
<tr>
<td></td>
<td>Disappearance of Stress</td>
<td>$10^{11}$ Pa-s$&lt;\eta&lt;10^{14}$ Pa-s</td>
</tr>
</tbody>
</table>
Rotating Spindle: 10-10^6 Pa·s

( ASTM C965-96 )

\[
\eta = \frac{1}{4\pi \cdot L} \left( \frac{1}{r^2} - \frac{1}{R^2} \right) \left( \frac{T}{\omega} \right)
\]

- \( T = \) torque
- \( \omega = \) rotational velocity
Littleton Softening Point: $10^{6.6}$ Pa·s
(fiber elongation- ASTM C338-93)

$$\eta = \frac{L \cdot F}{3A \cdot (dL/dt)}$$

Applied Stress = $F/A$
Elongation rate = $dL/dt$

Balance of gravitational force (density) and surface tension
Annealing/Strain Points: $10^{12}$, $10^{13.5}$ Pa·s
(fiber elongation: ASTM-C336-69)

dL/dt = $2.5 \times 10^{-6}$ l/d²
at $10^{12}$ Pa·s (anneal pt)
Strain pt elongation rate is
0.0316 x annealing pt
elongation rate (1.5 log units)
Beam Bending: $10^8$-$10^{13}$ Pa-s

$$\eta = \frac{g \cdot L^3}{2.4 I_c \cdot V} \left( \frac{M + A \cdot L \cdot \rho}{1.6} \right)$$

V=deflection rate
Orton Instruments to Determine the Viscosity as a Function of Temperature

- Annealing and Strain Points
  - Model SP-2A-DAS
  - or
  - Model SP-5A-DAS

- Littleton Softening Point
  - Model SP-1A-DAS

- Glass Transition Point
  - Model DIL 2010 STD

- Liquidus Point
  - Model GTF-MD Series

- Molten Glass Viscosities
  - Model SP-4A Series
The temperature dependence of viscosity
Consider the ‘activated’ motion of a hole under the action of a shearing stress.
Jump frequency ($\nu_0$), no shear:
- Same l-r as r-l
- Depends on barrier energy and probability of finding suitable hole as neighbor ($P_h$)

$$
\nu_0 = \left[ \frac{k_B T}{\hbar} \right] \exp \left[ -\frac{\Delta G_0}{k_B T} \right] \cdot P_h
$$

Applied shear biases potential energy function
- $V_a$ is atom volume
- Forward jump frequency ($\nu_+$) exceeds reverse ($\nu_-$)

$$
\nu_+ = \nu_0 \exp \left[ \frac{\sigma_{yx} V_a}{2 k_B T} \right] \\
\nu_- = \nu_0 \exp \left[ -\frac{\sigma_{yx} V_a}{2 k_B T} \right]
$$
The net ‘forward velocity’ is
\[
(v_{Bx} - v_{Ax}) = (\nu_+ - \nu_-) \delta x
\]
\[
\partial v / \partial y = (\nu_+ - \nu_-) \delta x / \delta y \approx (\nu_+ - \nu_-)
\]
\[
\partial v / \partial y = 2 \nu_0 \sinh(\sigma_{yx} V_a / 2 k_B T) \approx \nu_0 \sigma_{yx} V_a / k_B T
\]
Shear strain rate is \( \dot{\epsilon}_{xy} = \partial v / \partial y \),
\[
\eta = \sigma_{yx} / [\nu_0 \sigma_{yx} V_a / k_B T] = [h / V_a \exp(\Delta G_0 / k_B T)] P_h^{-1}
\]
Consider the energy required to create a hole \( \Delta E_h \), then \( P_h \) can be described by
\[
P_h = \exp[-\Delta E_h / k_B T]
\]
Substituting \( P_h \) into the viscosity equation,
\[
\eta = [h / V_a] \exp(\Delta G_0 + \Delta E_h / k_B T)
\]
Simplifying as an Arrhenius equation:
\[
\eta = \eta_0 \exp(\Delta H_\eta / RT)
\]
Most glass-forming liquids are non-Arrhenius

\[ \log \eta = A + \frac{B}{T - T_0} \]

Melt Fragility

Log (viscosity in poise) vs. $\frac{T_g}{T}$


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Melt properties-24
Why the non-Arrhenius temperature-dependence?

1. Energy for hole formation ($\Delta E_h$) is low at high temperatures
   - $\Delta H_\eta$ is greater at lower temperatures
2. Free-volume increases with temperature
3. Configurational entropy increases with temperature (Adam-Gibbs description)
What accounts for viscous flow in a silicate melt?

What has to happen for flow to occur?
What happens at the molecular-level that affects viscosity?

At the short timescales, ‘melt structures’ are similar to ‘glass structures’…. 

- **Raman spectroscopy**- probing structure on timescales $10^{-12}$-10$^{-14}$ s
- Si-O stretching/bending modes remain dominate from room temperature into the melt
- Some evidence for some melt speciation reactions: $2Q^3 \leftrightarrow Q^2 + Q^4$
NMR provides structural information about glasses

Maekawa et al. 1991

Fig. 2. Proportions of Q species in lithium silicate glasses. $\Delta E/kT = 1$; $\Delta E/kT = 2$. The numbers indicate experimental values of $n_i$, $i = 0-4$. Data from Raman and NMR studies.
Chemical exchange in melts: silicate species and viscous flow

- NMR exchange frequencies (kHz range) are comparable to the timescales for viscous flow in silicate melts
- The ‘lifetimes’ for Si-O bonds in a melt can be determined and compared with timescales associated with viscous flow
- At high temperatures, the $Q^3$-$Q^4$ exchange (Si-O bond rupture) is fast compared to the experimental time frame.

Figure 18. Static (i.e. non-MAS) $^{29}$Si spectra of K$_2$Si$_4$O$_9$ glass and liquid (left) and multi-site exchange simulations (right). Temperatures: (a) 697°C; (b) 774°C; (c) 800°C; (d) 847°C; (e) 997°C. Exchange frequencies, in kHz: (f) 2; (g) 10; (h) 25; (i) 50; (j) 500. $Q^4$ and $Q^3$ static CSA patterns are labeled in the lowest temperature spectrum. [Used by permission of the editor of Journal of the American Chemical Society, from Farnan and Stebbins (1990a), Fig. 5, p. 36.]
NMR exchange and viscosity timescales coincide

1. Maxwell relationship: $\eta = \tau_{\text{shear}} \cdot G_\infty$
2. Assume that $\tau_{\text{shear}} \approx \tau_{\text{ex}}$
3. Calculate diffusivity (D) from $\tau_{\text{ex}}$: $D = \frac{d^2}{6\tau}$, d is ‘jump distance’
4. Calculate viscosity from $\eta = k_B T/(dD)$
Stebbins model for viscous flow

Si-O bond-rupture through Q³-Q⁴ site exchange
- Conversion of one bridging oxygen to a nonbridging oxygen
- ‘Diffusion’ of modifying cation from one silicate unit to another

- Creation of an SiO₅ transitional site?

Potential energy

initial

transitional

final

oxygen • silicon • alkali
NMR evidence for transitional sites ‘frozen into’ quenched glass structures

**Figure 12.** $^{29}$Si MAS spectra for Cs$_2$Si$_4$O$_9$ and Na$_2$Si$_4$O$_9$ glasses, with vertical scale expanded greatly to show $[5]$Si peak. Note that this feature is more intense in the fast-quenched sample (higher fictive temperature). The steep slope to the left is the side of the SiO$_4$ peak; that to the right is the side of the spinning sideband. [Used by permission of the editor of Journal of Non-Crystalline Solids, from Stebbins and McMillan (1993), Fig. 3, p. 120.]
Effects of composition on viscosity

Viscosity is determined by

• Molecular attractive forces, especially associated with glass-forming oxides
  – Si-O vs. Ge-O

• Number of non-bridging oxygens in structure
  – Alkali oxide additions reduce viscosity
  – Water (-OH) and fluorine reduce viscosity

• Coordination number of the cation
Figure 9-7. Variation of log (viscosity) vs. $10,000/T$ for simple glass-forming oxides. (After R. H. Doremus, Glass Science, Fig. 2, p. 105. Wiley & Sons, New York, 1973. Reproduced with permission of the publishers.)
Reminder: Effect of Modifier Additions on Silicate Glass Networks

\[
\begin{align*}
\text{B}_0 + R_2O & \rightarrow 2\text{NBO} \\
2\text{Q}^4 + R_2O & \rightarrow 2\text{Q}^3
\end{align*}
\]
Increasing the modifier content reduces viscosity

- Water is a particularly effective flux

Na-K-Zn-Al-silicate
(Wu, JNCS, 41 381, 1980)
The effect of water on \( T_g \) (\( \eta \approx 10^{12} \text{ Pa} \cdot \text{s} \)) of silicate glasses

The effects of modifier content on melt viscosity

Isokom temperatures for mixed alkali melts

Nemilov (1969)

Log $\eta$ (Poise)

| Mol % Na$_2$O (X) | X Na$_2$O $\cdot$ (20-X) K$_2$O $\cdot$ 80 SiO$_2$ |
---|---|
8  | |
10 | |
12 | |
16 | |
Reminder: Effect of Alumina Additions on Silicate Glass Networks

\[
\begin{align*}
\text{O} & \quad \text{Si} \quad \text{O}^- \quad \text{O} \\
\text{R}^+ & \quad \text{} \\
\text{O} & \quad \text{Si} \quad \text{O} \\
\end{align*}
\]

\[1/2\text{Al}_2\text{O}_3 \text{ for } 1/2\text{R}_2\text{O}\]

\[
\begin{align*}
\text{O} & \quad \text{Si} \quad \text{O} \quad \text{Al} \quad \text{O} \\
\text{R}^+ & \quad \text{} \\
\text{O} & \quad \text{Si} \quad \text{O} \\
\end{align*}
\]
Viscosity of alkali alumino-silicate melts is greatest when $\text{Al/Na} \approx 1$—fully cross-linked networks....

Fig. 2. Measured viscosities along the 50 mol%, 67 mol%, and 75 mol% $\text{SiO}_2$ isopleths at 1596°C. The accuracy of the compositional analyses and the precision of the viscosity measurements are both smaller than the size of the symbols.
Reminder: Effect of Alkali Addition on Borate Glass Networks

\[ \frac{[O]}{[B]} = 1.5 \]

\[ \frac{[O]}{[B]} = 2.0 \]  
\[ \text{[O]/[B]=2.5} \]

\[ \frac{[O]}{[B]} = 3.0 \]
Alkali borate melt viscosity

2BØ₃ + Na₂O → 2(BØ₄⁻Na⁺)

2(BØ₄⁻Na⁺) + Na₂O → 2(BØO₂²⁻·2Na⁺)

Note the loss of the ‘borate anomaly’ effect at high temperatures (low viscosity)
38.6Li$_2$O·61.4B$_2$O$_3$ glass and melt

Raman spectra indicate that the BØ$_2$O$^-$ triangles replace BØ$_4$ tetrahedra in the melt.

**Fig. 3.** Raman spectra for the 6LB2 glass from room temperature to 1359 K. The glass transition temperature ($T_g$) is indicated.

Cormier et al., JACerS, 89 13 (2006)
Raman spectra indicate that the BØ₂O⁻ triangles replace BØ₄⁻ tetrahedra in the melt:

\[ \text{BØ}_4^- \text{Li}^+ \leftrightarrow \text{BØ}_2\text{O}^- \text{Li}^+ \]

Note that B-O bonds are broken, and that such configurational changes will contribute to changes in heat capacity.…

Fig. 4. Ratio of the relative area for the two high-frequency bands of the Raman spectra for the LB2 sample. The temperatures of glass transition and melting are indicated. The line is a guide for the eye.

Cormier et al., JACerS, 89 13 (2006)
### Effects of composition on viscosity

<table>
<thead>
<tr>
<th>Component</th>
<th>Effect on Viscosity</th>
<th>Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High Temp</td>
<td>Low Temp</td>
</tr>
<tr>
<td>Alkali oxide</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Alkaline earths</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>PbO</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>OH⁻/F⁻</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Modifications to soda-lime silicate melt viscosity, after Beerkens, 1997.
Viscosity dependence on temperature and composition

- Vogel-Fulcher-Tamman (VFT) Equation
  \[ \log \eta = A + \frac{B}{T - T_0} \]

- Lakatos Method*: empirical additivitiy factors
  \[ A = -2.4550 + \sum a_i \cdot p_i \]
  \[ B = 5736.4 + \sum b_i \cdot p_i \]
  \[ T_0 = 198.1 + \sum t_i \cdot p_i \]
  For S-L-S melts, \( T \, (^{\circ}C) \) and \( \eta \, (Pa \cdot s) \), \( p_i \) (mole fraction oxide per mole \( SiO_2 \))

*T. Lakatos, et al., *Glass Technology*, 13 88 (1972)
Lakatos additivity parameters (after Beerkens, 1997)

<table>
<thead>
<tr>
<th></th>
<th>ai</th>
<th>bi</th>
<th>ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na\textsubscript{2}O</td>
<td>+1.4788</td>
<td>-6039.7</td>
<td>-25.07</td>
</tr>
<tr>
<td>K\textsubscript{2}O</td>
<td>-0.8350</td>
<td>-1439.6</td>
<td>-321.0</td>
</tr>
<tr>
<td>MgO</td>
<td>-5.4936</td>
<td>+6285.3</td>
<td>-384.0</td>
</tr>
<tr>
<td>CaO</td>
<td>-1.6030</td>
<td>-3919.3</td>
<td>+544.3</td>
</tr>
<tr>
<td>B\textsubscript{2}O\textsubscript{3}</td>
<td>-15.880</td>
<td>+7272.1</td>
<td>+521.4</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>+1.5183</td>
<td>+2253.4</td>
<td>+294.4</td>
</tr>
<tr>
<td>PbO</td>
<td>+1.3058</td>
<td>-5880.0</td>
<td>-275.5</td>
</tr>
</tbody>
</table>

Valid for the log(viscosity) range 1-12 Pa·s
Not all liquids exhibit Newtonian viscosity behavior

- Bingham Plastic
- Pseudoplastic (decreasing $\eta$)
- Newtonian (constant $\eta$)
- Dilatant (increasing $\eta$)
Non-Newtonian Viscosity

Shear thinning—decreasing effective viscosity with increasing deformation rates
• fiber drawing
• press-and-blow

Greater problem at higher temperatures

Figure 4. Normalized non-Newtonian viscosity as a function of normalized deformation rate for glass melts H, I and J at three Newtonian viscosities.

Yue & Brückner
Non-Newtonian Viscosity

\[ \eta / \eta_0 = 1 / \left[ 1 + \left( \dot{\varepsilon}_{xy} \right) \eta_0 / \sigma_\infty \right] \]

- \( \eta_0 \) is Newtonian viscosity
- \( \sigma_\infty \) is the cohesive shear strength

Cohesive strength increases with viscosity

- Viscosity becomes nonlinear at high shearing rates
- Shear stress builds up if stress relaxation rate is sufficiently low
- If shear stress $> \sigma_\infty$, then ‘liquid fracture’ can occur

Consequences of Non-Newtonian Viscosity

• High-speed glass processing
  – Fiber attenuation
  – Container processing
• Source for glass inhomogeneities
  – Induced phase separation or crystallization in high shear regions
Deformation, stress relaxation, and crystallization of lithium silicate glass fibers below the glass transition temperature

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- Fibers heated below $T_x$
- Stress in ‘bent’ regions reduces ‘effective’ viscosity
- Examine differences in crystallization behavior

*Corresponding author.

**Figure 1** Schematic diagram of the glass fibers in a refractory block for heat treatment. Length of the glass fiber: 120 mm. Diameter of the glass fiber: 150 μm.
Figure 4: Scanning electron microscope pictures of the (a) stressed and (b) un-stressed (straight) LS$_{1.6}$ glass fibers after heating at 410°C for 12 h. (c) and (d) are the enlarged view of the outer and inner part of stressed fiber at locations shown in (a). No crystallization is observed on the heat treated straight fiber (b).
Another example

- Melts prepared in micro-gravity have greater glass-forming tendencies than melts on earth at comparable quench rates
  - Hypothesis*: gravity-driven fluid-flow increases overall strain rate within melt
    - Reduced ‘local’ viscosity through shear thinning
    - Increased ‘local’ crystallization rates

An Analysis of the Differences in the Glass Forming Tendency of Melts on Earth and in a Low - Gravity Environment

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*BAE Systems, Marshall Space Flight Center, National Aeronautics and Space Administration, Huntsville, AL 35812, USA.

Calculated for LS$_2$ melts at 1400°C and a 5°C temperature gradient

Normalized acceleration due to gravity

Fig. 6 : Maximum system wall shear stress and maximum system strain as a function of g level.

Normalized acceleration due to gravity

Shear-thinning behavior is reduced when gravitational effects are reduced.

Fig. 7: Superimposition of calculated strain rate from present study on experimental measurements of viscosity as a function of strain rate.
Phase separation affects viscosity

Figure 11: Viscosity change in Pyrex due to phase separation. Period (a) is dominated by spinodal decomposition. Period (b) is dominated by coarsening[92].
Crystallization affects viscosity
- Example: crystallizable sealing glass


**Figure 12.** Parallel plate viscometer data for frit glasses.
Viscosity Summary

• Viscosity is the most important melt property
  – Critical for processing, from melting through annealing
• Compositional dependence can be understood in terms of melt/glass structure
  – Stronger networks = greater viscosity
    • Fraction of NBO’s on silicate tetrahedra
    • Aluminosilicate networks
    • Borate ‘anomaly’- tetrahedral sites
  – Viscosity is sensitive to changes in melt structure
• Temperature dependence is non-Arrhenian
  – VFT equation is a useful empirical description
  – Fragile/strong classification can be related to configurational changes
• Shear-thinning has processing consequences
Glass formation is ‘crystallization avoidance’

\[ \dot{T}_c \approx \frac{AT_m^2}{\eta(\text{at } 0.77T_m)} \cdot \exp(-0.212B) \cdot \left[ 1 - \exp\left( -\frac{0.3\Delta H}{RT_m} \right) \right]^{3/4} \]

- **Kinetic barrier**
- **Nucleation barrier**
- **Free energy driving force**

Reduce critical cooling rate to improve glass formation

- Lower \( T_m \)
- Increase \( \eta \) at \( T_m \)

If \( T_g \) (\( \eta = 10^{13} \text{ P} \)) is near \( T_m \), then \( \eta(T_m) \) will be high

Glass formation expected when \( T_g/T_m > 2/3 \)

<table>
<thead>
<tr>
<th></th>
<th>( T_m )(°C)</th>
<th>( \eta(T_m) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeF(_2)</td>
<td>540</td>
<td>&gt;10^6 P</td>
</tr>
<tr>
<td>B(_2)O(_3)</td>
<td>460</td>
<td>10^5 P</td>
</tr>
<tr>
<td>GeO(_2)</td>
<td>1150</td>
<td>10^7 P</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>1710</td>
<td>10^7 P</td>
</tr>
<tr>
<td>LiCl</td>
<td>613</td>
<td>0.02 P</td>
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<tr>
<td>Zn</td>
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<td>0.03</td>
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<tr>
<td>Fe</td>
<td>1535</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Good glass formers

Poor glass formers
Eutectic compositions are good glass-formers


W. Vogel, *Chemistry of Glass*, 1985

$T_g / T_{liq}$ is a maximum (~0.7) at the eutectic

$\Delta T_g \sim 30^\circ C$

$\Delta T_{liq} \sim 800^\circ C$