Viscosity of glass-forming liquids

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Outline

- Background and motivation
- Viscosity models
- Iso-structural viscosity
- Non-Newtonian flow
- Fragile-to-strong transition
Background and motivation
About flow

Heraclitus:
"everything is in a state of flux".

Confucius (孔夫子) stood by a river:
"Everything flows like this, without ceasing, day and night".

Deborah:
"Everything flows if you wait long enough, even the mountains".
Flow is everywhere!
Flow is remarkable, but sometimes dangerous!
How to judge whether a substance is liquid or solid?

A fundamental number of rheology: Deborah number (De)

\[ De = \frac{\tau}{t} \]

If \( \tau < t \), a substance is a liquid, otherwise, a solid!
Some liquids flow easily, some not. How to quantify this?

Measure **Viscosity** by viscometers:

- Concentric Cylinder
- Parallel-Plate Compression
- Capillary
- Beam Bending
- Fiber Elongation
- Sphere penetration
- Melt containerless levitation

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Viscosity is a crucial quantity of glass technology.
Viscosity determines

- Melting conditions
- Fining behaviour
- Working ranges
- Annealing range
- Upper temperature of use
- Devitrification rate
- Glass forming window
- Glass fiber drawing window

Every step of industrial glass formation depends critically on the viscosity.

The glass product relaxation depends on the nonequilibrium viscosity of the glass, which is a function of composition, temperature, and thermal history.
Viscosity is a key quantity of glass science. It provides information on:
- Glass dynamics
- Transport properties
- Glass structure
- Liquid fragility
- Thermodynamics
- Geology
- Crystallization

...
Viscosity of a melt varies with

- Temperature
- Time
- Deformation rate
- Pressure
- Composition
- Hydroxyl
- Crystallization
- Phase separation
- Inclusions
- .......
The non-Arrhenian behavior of liquids is described by liquid fragility.

It is quantified by the kinetic liquid fragility index $m$.

$$m = \frac{d \log \eta}{d(T_g / T)} \bigg|_{T=T_g}$$

- It is defined as the rate of the viscosity or relaxation liquid at $T_g$ upon cooling.
- It is an important dynamic parameter of glass-forming liquids.
Connection between fragility index ($m$) and heat capacity jump ($\Delta C_p$) in glass

\[
\Delta C_p = \frac{A}{T_g} \left( \frac{m}{m_0} - 1 \right)
\]

Viscosity models
Vogel-Fulcher-Tamman (VFT) Model

\[ \eta = \eta_\infty \exp\left( \frac{A'}{T-T_0} \right) \]

where \( \eta_\infty \) is the high temperature limit of viscosity, and \( A \) and \( T_0 \) are constants. Or

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

\( T_0 = T_k \)? This is a debating problem.

Adam-Gibbs (AG) Model (Entropy model)

\[ \eta = \eta_\infty \exp \left( \frac{B'}{TS_c(T)} \right) \]

where \( \eta_\infty \) is the high temperature limit of viscosity, \( B \) is constant, and \( S_c(T) \) is the configurational entropy as a function of temperature:

\[ S_c(T) = \Delta C_p \ln \left( \frac{T}{T_K} \right) \]

This is a problem too.

Avramov-Milchev (AM) Model

\[ \log \eta = \log \eta_\infty + B_{AM} \left( \frac{T_g}{T} \right)^F \]

where \( \eta_\infty \) is the high temperature limit of viscosity, \( B_{AM} \) constant, and \( T_g \) the glass transition temperature, and \( F \) is a measure of liquid fragility.

\( F = m/B_{AM} \), where \( m \) is the Angell fragility index

Angell-Rao (AR) model

\[ \log \eta = \log \eta_\infty + A \exp \left( \frac{B}{T} - C \right) \]

This 4-parameters model with fits the data excellently and bears physical meaning.

Angell and Rao, JCP (1972)
Other models

- Free volume model
- Doremus model
- Shoving model
- Sanditov model
- Parabolic model
- ........

See recent reviews:
Derivation of our new model (MYEGA)

\[ \log \eta = \log \eta_\infty + \frac{K}{T} \exp\left(\frac{C}{T}\right) \]

\[ \log \eta = \log \eta_\infty + \frac{B_3}{T S_c} \]

The configurational entropy

\[ S_c = fNk \ln \Omega \]

Topological degrees of freedom
A simple two-state system

Mauro, Yue, Ellison, Gupta, Allan, PNAS 106 (2009) 19780
The viscosity-temperature relation for most liquids can be described by VFT and AM models, even better by MYEGA:

\[ \eta \sim T \]

relation for oxide, ionic and molecular liquids

\[ \log \eta = \log \eta_\infty + \frac{B}{T} \exp\left(\frac{C}{T}\right) \]
The new model is physically reasonable. (Fitting results based on 1000 glasses)

New model:
• $S_c$ converges at $T=\infty$
• $S_c = 0$ at $T=0$
• $\log \eta_\infty$: the narrowest distribution
• $\log \eta_\infty = -3$: A universal value?
The new model shows stronger ability to predict low $T$ viscosity data from high $T$ viscosity data than the other 3-parameter models.
Is there a universal log $\eta_\infty$ value?
Results on 946 Corning compositions

It is about -3!

$T_{g,\text{vis}}$ (from viscosity) and $T_{g,DSC}$ (from DSC)

$T_{g,\text{vis}}, 10\text{K/min} = T_{\log \eta=12}$

Practical use of the MYEGA

\[ \log \eta = \log \eta_\infty + \frac{B}{T} \exp\left( \frac{C}{T} \right) \]

\[ m = \frac{d \log \eta}{d (T_g / T)} \bigg|_{T=T_g} \]

\[ \log \eta = \log \eta_\infty + \left( \log \eta_{T_g} - \log \eta_\infty \right) \frac{T_g}{T} \exp \left[ \frac{m}{\log \eta_{T_g} - \log \eta_\infty - 1} \left( \frac{T_g}{T} - 1 \right) \right] \]

**For inorganic systems**

\[ \eta_\infty \approx 10^{-3} \text{ Pa s} \]

\[ \eta_{T_g} \approx 10^{12} \text{ Pa s} \]

\[ \log \eta = -3 + 15 \frac{T_g}{T} \exp \left[ \left( \frac{m}{15} - 1 \right) \left( \frac{T_g}{T} - 1 \right) \right] \]

Now, only two parameters, \( m \) and \( T_g \), remain. Meaning: the entire \( \log \eta \sim T \) relation can be estimated just by DSC!
Be careful with the difference between $m_{\text{vis}}$ and $m_{\text{DSC}}$

- $m_{\text{vis}} > m_{\text{DSC}}$
- $m_{\text{vis}} - m_{\text{DSC}}$ due to Arrhenian approximation of non-Arrhenius behavior
- $m_{\text{vis}} - m_{\text{DSC}}$ increases as fragility increases

A model:

$$m_{\text{vis}} - m_0 = (m_{\text{DSC}} - m_0)[1 + f(m_{\text{DSC}} - m_0)]$$

$$m_{\text{vis}} = 1.289(m_{\text{DSC}} - m_0) + m_0$$

The entire viscosity-temperature curve can be determined by DSC!

\[ \log \eta = -3 + 15 \frac{T_g}{T} \exp \left[ \left( \frac{m}{15} - 1 \right) \left( \frac{T_g}{T} - 1 \right) \right] \]

Example

Based on the facts:
- \( T_g \) and \( m_{DSC} \) are measurable by DSC
- \( m_{DSC} \) can be converted to \( m_{vis} \).
- \( \log_{10} \eta_{\infty} = -3 \)
- \( T_g \) corresponds to \( 10^{12} \) Pa s

Advantages of the DSC method:
- It is simpler.
- Takes much less time than viscometry technique.
- Uses smaller samples.
- Measure both good and poor glass forming systems.
Derivation of VFT from MYEGA

\[ \log \eta(T) = \log \eta_\infty + \frac{C}{T} \exp\left(\frac{K}{T}\right) \]

\[ = \log \eta_\infty + \frac{C}{T \exp(-K/T)} \]

• In the high temperature limit, \(-K/T\) can be expanded in a Taylor series:

\[ \log \eta(T) \approx \log \eta_\infty + \frac{C}{T \left(1 - \frac{K}{T}\right)} \]

\[ = \log \eta_\infty + \frac{C}{T - K} \]

Divergent at a finite $T$?

Using 20-million year-old amber, Zhao, et al. provided an implication against the existence of the divergence at a finite $T$.


Iso-structural viscosity or non-equilibrium viscosity
Comparison between the measured $\eta_{iso}$ data and the $\eta_{iso}$ data calculated from models

Data from Mazurin (1982)
$\log \eta (\eta \text{ in Pa s})$

$\frac{1}{T} (10^{-4} \text{ K}^{-1})$

Window glass

$T_f = 0.96 T_g$

$T_g$
Non-Newtonian flow
(Shear rate dependence of viscosity)
(Shear thinning)
Non-Newtonian shear flow of glass-forming liquids (soda lime silicate vs Li-Na metaphosphate)

\[ \eta_0 = 10^9 \text{ Pa s} \]

\[ \sigma = \eta_{\infty} + (\eta_0 - \eta_{\infty}) \dot{\varepsilon}_g \left(1 - \exp\left(-\frac{\dot{\varepsilon}}{\dot{\varepsilon}_g}\right)\right) \]

\[ \frac{\eta}{\eta_0} = \frac{\eta_{\infty}}{\eta_0} + \left(1 - \frac{\eta_{\infty}}{\eta_0}\right) \frac{\dot{\varepsilon}_g}{\dot{\varepsilon}} \left[1 - \exp\left(-\frac{\dot{\varepsilon}}{\dot{\varepsilon}_g}\right)\right] \]

It is attributed to orientation of structural units.

Fragile-to-strong transition
(An abnormal liquid dynamic behaviour)
A normal liquid – a window glass!
A normal liquid – a window glass!

\[
\log \eta = -3 + 15 \frac{T_g}{T} \exp \left[ \frac{m}{15} \left( \frac{T_g}{T} - 1 \right) \right]
\]
An abnormal case – a metallic liquid!

La$_{55}$Al$_{25}$Ni$_{15}$Cu$_{5}$
An abnormal case – a metallic liquid!
Its dynamics cannot be described by a 3-parameters model.

\[
\log \eta = -3 + 15 \frac{T_g}{T} \exp \left[ \left( \frac{m}{15} - 1 \right) \left( \frac{T_g}{T} - 1 \right) \right]
\]

La\(_{55}\)Al\(_{25}\)Ni\(_{15}\)Cu\(_5\)

SD: 0.181
\(\log \eta_{inf} = -13.2\)

SD: 0.48
\(\log \eta_{inf} = -7.5\)
We recall a famous liquid – water, which shows an abnormal dynamic behaviour to – fragile-to-strong transition

More metallic liquids similar to water, which exhibits Fragile-to-Strong (F-S) Transition

The data of these liquids cannot be described by a single model.

The extent of the F-S transition can be determined by:

\[ f = \frac{m'}{m} \]

- \( f > 1 \): F-S transition
- \( f = 1 \): no F-S transition
- \( f < 1 \): never seen (unphysical?)

Zhang, Hu, Yue and Mauro, JCP (2010)
The calculated $f$ values for different MGFLs

<table>
<thead>
<tr>
<th>Composition</th>
<th>$m'$</th>
<th>$m$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd$<em>{55}$Al$</em>{25}$Co$_{20}$</td>
<td>113</td>
<td>25</td>
<td>4.5</td>
</tr>
<tr>
<td>Gd$<em>{55}$Al$</em>{25}$Ni$<em>{10}$Co$</em>{10}$</td>
<td>133</td>
<td>25</td>
<td>5.3</td>
</tr>
<tr>
<td>Pr$<em>{55}$Ni$</em>{25}$Al$_{20}$</td>
<td>156</td>
<td>19</td>
<td>8.2</td>
</tr>
<tr>
<td>Sm$<em>{55}$Al$</em>{25}$Co$<em>{10}$Ni$</em>{10}$</td>
<td>130</td>
<td>37</td>
<td>3.5</td>
</tr>
<tr>
<td>Sm$<em>{50}$Al$</em>{30}$Co$_{20}$</td>
<td>136</td>
<td>29</td>
<td>4.7</td>
</tr>
<tr>
<td>Sm$<em>{55}$Al$</em>{25}$Co$<em>{10}$Cu$</em>{10}$</td>
<td>114</td>
<td>27</td>
<td>4.2</td>
</tr>
<tr>
<td>La$<em>{55}$Al$</em>{25}$Ni$_{20}$</td>
<td>127</td>
<td>40</td>
<td>3.2</td>
</tr>
<tr>
<td>La$<em>{55}$Al$</em>{25}$Ni$<em>{15}$Cu$</em>{5}$</td>
<td>130</td>
<td>34</td>
<td>3.8</td>
</tr>
<tr>
<td>La$<em>{55}$Al$</em>{25}$Ni$<em>{5}$Cu$</em>{15}$</td>
<td>134</td>
<td>40</td>
<td>3.4</td>
</tr>
<tr>
<td>Al$<em>{87}$Co$</em>{8}$Ce$_{5}$</td>
<td>114</td>
<td>34</td>
<td>3.3</td>
</tr>
<tr>
<td>Ce$<em>{55}$Al$</em>{45}$</td>
<td>127</td>
<td>32</td>
<td>4.0</td>
</tr>
<tr>
<td>Water</td>
<td>98</td>
<td>22</td>
<td>4.5</td>
</tr>
</tbody>
</table>

The factor $f$ confirms the existence of the F-S transition in the investigated MGFLs.
Question:

Is there a model that can describe the abnormal liquid dynamic behaviour?
Yes! But, to do so, the MYEGA has been generalized to the form:

\[
\log \eta = \log \eta_\infty + \frac{1}{T} \left[ W_1 \exp\left(-\frac{C_1}{T}\right) + W_2 \exp\left(-\frac{C_2}{T}\right) \right]
\]

Fragile term \quad \text{Strong term}

\( C_1 \) and \( C_2 \): two constraint onsets. 
\( W_1 \) and \( W_2 \): normalized weighting factors.
If \( C_1 = C_2 \), the equation reduces to that for normal liquids.

Zhang, Hu, Yue, Mauro, JCP (2010)
Two “phases” co-exists in the F-S crossover regime: Strong and fragile phases

Fragile phase (LDA):
- higher $T_g$
- higher activation enthalpy
- higher entropy
- lower density

Strong phase (HDA):
- lower $T_g$, i.e., actual $T_g$ of the mixed liquid
- lower activation enthalpy
- lower entropy
- higher density

The fragile phase is cooled, the F-S transition intervenes, mitigating the sharp increase in viscosity with decreasing $T$. 
Non-montonic structural response to sub-$T_g$ annealing measured by x-ray scattering

Annealing dependence of the structural unit size

Critical temperature for the dramatic decreases in $R_c$: $T_c \sim$ around $1.3T_g$
Schematic scenario of the structural evolution during fragile-to-strong transition

Containerless aerodynamic levitation (ADL) melting to avoid heterogeneous nucleation

Melting of Al₂O₃

- Extend the supercooled region
- Measure viscosity
- In-situ structural characterization

\[ \eta = \frac{3M}{20\pi R} \Gamma \]

Forced oscillation and decay
Fragile-to-strong transition in aluminates

\[ \log \eta = -3 + 15 \frac{T_g}{T} \exp \left[ \left( \frac{m}{15} - 1 \right) \left( \frac{T_g}{T} - 1 \right) \right] \]

Fitted with (MYEGA)
The data can be described by the generalized MYEGA

\[
\log \eta = \log \eta_0 + \frac{1}{T} \left[ W_1 \exp \left( \frac{-C_1}{T} \right) + W_2 \exp \left( \frac{-C_2}{T} \right) \right] 
\]

\[
T_{f-s} = \frac{C_1 - C_2}{\ln W_1 - \ln W_2}
\]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \log \eta_0 \ (\text{Pa s}) )</td>
<td>-2.039</td>
</tr>
<tr>
<td>( W_1 )</td>
<td>0.018</td>
</tr>
<tr>
<td>( C_1 )</td>
<td>7324</td>
</tr>
<tr>
<td>( W_2 )</td>
<td>1.68E-4</td>
</tr>
<tr>
<td>( C_2 )</td>
<td>1407</td>
</tr>
</tbody>
</table>
I would like to all my co-authors and collaborators.
Thank you for your attention!