Fragility of Glass-Forming Liquids

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CA Angell, W Sichina

Thermodynamics of the glass transition: empirical aspects

*Ann. NY Acad. Sci.*

**279** (1976) 53.
Fragility of the liquid

Data on metallic glasses of different compositions and after various annealing treatments. The critical value of Poisson’s ratio, $\nu_{\text{crit}} = 0.31-0.32$.

The better the glass-forming ability, the more likely to be brittle!

An inverse correlation of fragility of the liquid with fragility of the glass!

GN Greaves, AL Greer, RS Lakes, T Rouxel: Poisson’s ratio and modern materials
Fragility: \[ m = \left( \frac{d \log_{10} \eta}{d \left( \frac{T_g}{T} \right)} \right) \bigg|_{T=T_g} \]
“Fragile” liquids … have structures which degrade rapidly on increase of temperature above the glass transition


Liquids can be fragile because, in contrast with other condensed phases, their structures can change so much without destroying the integrity of the phase

CA Angell: this Symposium Volume, page 21.
Oxford English Dictionary

Fragility:
first recorded in English (from the French) in 1398, meaning moral weakness —
“bi humayne fragilyte … thou trespas ayenst the commaundement of almyghty god”

Fragile:
First recorded in English in 1513, meaning liable to err or fall into sin —
“More lyke an angell..Than a fragyll mayde, of sensuall appetyte … A wanton prynce, folowynge sensualyte And his fragyll appetyte.”
• The nature of the liquid:
  – structure, heterogeneity, relaxations, dynamics
  – dependence on $T$ and $V (P)$
  – fragile-to-strong transitions

• Energy and entropy:
  – atomic/molecular interactions
  – energy landscapes
  – Adam-Gibbs model
  – relationships between kinetic and thermodynamic aspects

• How are the liquid and the glass related?
  – correlations of liquid properties with glass properties
  – e.g. with elastic properties notably Poisson’s ratio
  – liquid stability relative to the crystalline state

• Experimental techniques (physical and simulation), new directions
• Correlations
Elastic shear strain limit of metallic glasses

**Scopigno correlation** — between the kinetic fragility of the liquid and the vibrational properties of the glass (specifically the $\alpha$ parameter in the non-ergodicity factor)

Correlations across and within glass-forming systems

- oxides and silicates
- polymers
- chalcogenides
- organics, molecular liquids
- ionics
- bio: carbohydrates, proteins (and their folding)
- metallic alloys
- water

We will focus on some practical aspects of FRAGILITY … … for machines, memory, and survival!
Unachievable shapes for metals?

Hollow, thin, seamless, complex parts —

[courtesy: Jan Schroers, Yale]
Microformability of BMGs

• of interest for micro- & nano-imprinting of surfaces

AFM and SEM images of a patterned (100) Si die and a Pt-based BMG imprinted with the die (10 MPa, 550 K, 300 s)

Nanomoulding with amorphous metals

Controlling metallic glass moulding on scales smaller than 100 nm

Pt-based BMG

The world’s smallest motor
Chalcogenide glass-forming compositions

Ternary phase change diagram showing composition of phase-change alloys used in different types of commercialized optical data media.

Chalcogenide (e.g. Ge$_2$Sb$_2$Te$_5$) thin film, 20 nm thick, in a CD-RW

- data marks written by laser-melting: rapid cooling gives a glass
- reading is by laser, exploiting contrast in reflectivity $\sim$ 20 \% $R(\lambda)$
PC-RAM

- example of Intel, STMicroelectronics 128 Mb μTrench cell architecture memory introduced to market in 2008

1T/1R cell structure
Die: 7 mm x 5 mm,
Unit cell die: 0.22 x 0.44 μm²
Capacity: 128 Mbits
Reset: 400 μA, ~ 2V, 100 ns
Set: 250 μA, ~ 1.5V, 100 ns
Read: 20 μA, ~ 0.2 V
Technology: 90nm CMOS

Programming of memory devices (schematic)

Crystallization during the SET pulse occurs in the supercooled liquid, and is $10^{16}$ to $10^{17}$ times faster than in the glass at near-ambient temperatures as needed for data retention.
Ultra-fast DSC, Mettler-Toledo Flash DSC 1

1. Ceramic plate
2. Silicon frame
3. Connecting wire
4. Resistance heater
5. Aluminum plate (sample area)
6. Thermocouple
Amorphous GST films, 270 nm thick, RF sputter-deposited onto microscope glass slides, scraped off onto sensor:

Crystal growth from supercooled liquid

\[ U = U_{\text{kin}} \times \left[1 - \exp\left(-\frac{\Delta G}{RT}\right)\right] \]

*Diffusion*-limited growth

\[ U_{\text{kin}}(T) \propto \frac{1}{\eta(T)} \]
\[ \approx \frac{D(T)}{a} \]

Experimental \( U(T) \) for 1,3,5-tri-\( \alpha \)-naphthylbenzene

Ultra-fast DSC extends the measured range of $U(T)$ by nine orders of magnitude!

Other studies of crystallization of amorphous GST:

GW Burr, P Tchoulfian, T Topuria, C Nyffeler, K Virwani, A Padilla, RM Shelby, M Eskandari, B Jackson, B-S Lee

“Observation and modeling of polycrystalline grain formation in Ge$_2$Sb$_2$Te$_5$”

Non-Arrhenius crystallization kinetics in PCM devices

PCM structures with GST

Thermal annealing at $T < 250^\circ C$ gives a high activation energy ($Q \approx 2$ eV)

At higher temperatures the activation energy is much lower

Crystal growth: decoupling from viscosity

**Ediger**

\[ U = U_{\text{kin}} \left[ 1 - \exp \left( -\frac{\Delta G}{RT} \right) \right] \]

\[ U_{\text{kin}} \propto \eta^{-\xi} \]

\[ \xi = 1 \text{ no decoupling} \]

\[ \xi \leq 1, \text{ the value of decoupling parameter } \xi \text{ is smaller for larger decoupling} \]

**Zanotto**

Breakdown in Stokes-Einstein equation

\[ \eta = \frac{k_B T}{3 \pi a D} \quad (U_{\text{kin}} = D/a) \]

\[ 1.1 - 1.25 T_g \]

General picture of decoupling (empirical relation)

just above $T_g$, the crystal growth rate is much faster than would be predicted from the viscosity

Molecular-dynamics simulations of supercooled liquid GeTe: — breakdown of the Stokes-Einstein relation

Supercooled liquid GeTe has a high fragility: $m = 104$ to $111$ (uncertainty in $T_g$)

At low temperature, $\eta$ is some $10^3 \times$ greater than would be predicted from the average $D$

Comparison of crystal-growth rates in supercooled liquids

Comparison of crystal-growth rates in supercooled liquids lies:

- between pure metals and glass-forming alloys
- between diffusion-limited and collision-limited growth

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Molecular-dynamics simulations of the freezing of pure metals

Two regimes:

High-temperature ($T > T_g$)
- thermally activated
- maximum in $U$ above $T_g$

Low-temperature ($T < T_g$)
- athermal (very low activation energy)

$T_g$ is in just the same range for GST

Y Ashkenazy, RS Averback: ”Kinetic stages in the crystallization of deeply undercooled body-centered-cubic and face-centered-cubic metals”
Can pure metals form true glasses?

• generally considered that pure metals cannot form glasses
• metallic liquids have low viscosity
• metallic crystal structures are simple and easily formed
• amorphous metals can be formed by quench condensation (vapour deposition onto substrates) but they soon crystallize on heating:

Crystallization of quench-condensed amorphous metals:
Many studies, including:


Crystallization of quench-condensed amorphous metals:

• semi-metals (Bi & Ga) do form amorphous deposits at 4.2 K, but..
• .. their crystallization temperatures are very low (14–25 K)
• crystallization temperatures are higher for thinner films
• amorphous Bi, 6 nm thick has $T_x$ as high as 42 K
• ccp metals don’t form amorphous films at all, without some alloying/impurities
• amorphous Fe crystallizes as low as 3.3 K, but..
• .. can be stabilized up to 300 K by impurities

These results have been taken to mean that, even if a glassy pure metal could be formed by ultra-rapid quenching, it would have very limited stability, BUT ....
Electrohydrodynamic atomization of liquid pure metals in vacuum

• gives droplets 2 nm to 100 μm in diameter
• radiative cooling, containerless solidification
• a 60 μm droplet would encounter only 1 gas molecule in critical cooling range
• crystal nucleation is difficult (no substrate, clean, small volume)
• some partially or fully glassy spheres were found for a wide range of elements: Co, Fe, Ge, Mo, Nb, Ni, Ta, Ti, V, W, Zr


• spheres of Fe have a 50:50 chance of being glassy for ~ 30 nm diam
• for 30 nm Co spheres, the critical cooling rate for glass formation $\approx 10^7$ K s$^{-1}$
Suggested reduced glass-transition temperatures, 
\[ T_{rg} = T_g / T_m \]

Suggested \( T_g \) for Ni is 732 K

From MD for liquid Ni, Rodriguez & Soler suggest \( T_g \approx 750 \) K


MD simulations of the quenching of 30 nm droplets (10^6 atoms) of liquid pure Cu onto a solid amorphous Cu-Zr substrate:

— quenching at 10^{12} to 10^{13} K s^{-1} gives fully glassy deposits, stable to >600 K

Can pure metals form true glasses?

How can these results on formation of stable glasses be reconciled with the results on quench-condensed films?
Ultrastable glasses from *in silico* vapour deposition

Sadanand Singh¹, M. D. Ediger² and Juan J. de Pablo¹,³,Ａ *

Glasses are generally prepared by cooling from the liquid phase, and their properties depend on their thermal history. Recent experiments indicate that glasses prepared by vapour deposition onto a substrate can exhibit remarkable stability, and might correspond to equilibrium states that could hitherto be reached only by glasses aged for thousands of years. Here we create ultrastable glasses by means of a computer-simulation process that mimics physical vapour deposition. These stable glasses have, far below the conventional glass-transition temperature, the properties expected for the equilibrium supercooled liquid state, and optimal stability is attained when deposition occurs at the Kauzmann temperature. We also show that the glasses’ extraordinary stability is associated with distinct str and the relative lack of irregular polyhedra.

binamy mixture of LJ particles

potential energy

Plastic deformation of metallic glass
$\text{Zr}_{55}\text{Al}_{10}\text{Cu}_{30}\text{Ni}_{5}$

- shot-peening at room temp. → AMORPHIZATION
- shot-peening at 77 K → CRYSTALLIZATION

**Bulk Metallic Glasses**

- **multicomponent** compositions aid glass formation
- the critical cooling rate is low (~1 K s\(^{-1}\))
- glasses can be **formed in bulk** (maximum diameters mm up to a few cm)
Comparison of crystal-growth rates in supercooled liquids

PHASE-CHANGE MATERIALS

Fast transformers

The pronounced temperature dependence of crystal-growth speed in phase-change materials not only rationalizes their favourable characteristics for non-volatile memory applications, but also suggests a profound new insight into their fundamental properties.

Matthias Wuttig and Martin Salinga

Unravelling the mysteries of chocolate making, comprehending the formation of amethyst geodes, or producing advanced steels requires an understanding of the relevant crystallization phenomena. Phase-change materials pose a similar challenge. They can be rapidly and reversibly switched between the amorphous and crystalline states, which is accompanied by a significant change of their optical and electrical properties. This renders these materials suitable for optical and electronic data-storage applications that require the structural transformation to occur extremely rapidly once the material is heated to sufficiently high temperatures. In a study of the crystallization dynamics at ultrahigh heating rates, reported in *Nature Materials*, Jiri Orava and colleagues now provide a new insight into our understanding of these fast transformations in phase-change materials that make them so attractive for memory devices.

Figure 1 | Crystal-growth speeds. In comparison to the behaviour of Si (ref. 10) and SiO₂ (ref. 11), which show a temperature-independent activation energy for crystal growth, phase-change materials such as Ge₂Sb₂Te₅ show a very different, fragile behaviour. The red squares, circles and diamonds show results from earlier experiments at lower temperatures.


Although these experiments have demonstrated that crystallization indeed can be completed within a few nanoseconds, they have not been able to provide an explanation for why this occurs. But now, in a collaborative effort with colleagues, they have developed a novel experimental approach that provides a glimpse into the underlying dynamics of the process.

“… one can wonder if non-volatile memories employing phase change materials could also be realized with well-known materials such as Si or GaAs …”

Comparison of crystal-growth rates in supercooled liquids

Range of $T_{\text{max}}/T_m$

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{\text{max}}/T_m$</th>
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<tbody>
<tr>
<td>SiO$_2$</td>
<td>0.97</td>
</tr>
<tr>
<td>OTP</td>
<td>0.95</td>
</tr>
<tr>
<td>Pd-based BMG</td>
<td>0.82</td>
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<tr>
<td>GST</td>
<td>0.76</td>
</tr>
<tr>
<td>Ag</td>
<td>0.62</td>
</tr>
<tr>
<td>Ta</td>
<td>0.55</td>
</tr>
</tbody>
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unpublished collection of data
*Turbellaria* flatworms
— primitive, no respiratory or circulatory systems
Water-Sucrose Diagram

— shows key points about avoiding crystal formation (ice or sugar or salts) in cells

- crystal formation is replaced by formation of a sugar-based glass
- need dehydration and/or cooling
Northern Wood Frog
*Rana sylvatica*

— the only frog found north of the Arctic circle

— when frozen, the frog’s breathing, blood flow and heartbeat stop
Ice formation inside a cell — is fatal

- the salt concentration rises in the remaining cytosol
- water is drawn into the cell by osmosis from the extracellular fluid
- the cell continues to swell and eventually bursts
Ice formation in the extracellular fluid — is beneficial

- the salt concentration rises in the extracellular fluid
- water is drawn from the cell by osmosis from the extracellular fluid
- the cell shrinks and the cytosol is dehydrated into a sugar glass
It is of interest for:

- *Rana sylvatica*
- pharmaceutical industry
- medical science

— to know more about the strength or fragility of liquids forming glasses by dehydration (and glasses into liquids on rehydration)

GM Fahy, DR MacFarlane, CA Angell, HT Meryman:
Vitrification as an approach to cryopreservation,
Best wishes to Austen (angell, not fragyll) on his 80th!

Many happy returns of the day…

Thanks to Austen for stimulating such fruitful fields of research

We look forward to a very successful Fragility Symposium — and also to many happy returns of the event!