GLASS

Glassworking – state-of the-art
Composition – alchemy, chemistry
Vitrification – kinetic theories
Structural studies – entropy
Bulk thermodynamics – classical
Mesoscopic thermodynamics – interfaces
Biothermodynamics – undercooling
Quantum thermodynamics – oscillations

In cooperation with:

Polymers Department, University of Pardubice, New Technology Research Center, West Bohemian University in Pilzen and New York University in Prague
Numerous appearance of glasses and glassy materials

Where it comes from?
We are from the country famous with two truly Czech products: Bohemian glass and Bohemian beer (which is often bottled to glass).

Your question could be WHY?

The answer is simple; there is a tradition of quality as the Czechs just happen to be extremely good in blowing glass and brewing beer. Glass is kind of brittle, and it tends to break whenever there is a foreign invasion or a civil upheaval. Things are easily destroyed, and those made of glass break first. Thanks to our unfortunate strategic location in the center of Europe, Bohemia has been one of the most popular places to invade. Excepting the period of the Hussite movement in the 15th Century (when Czech troops dominated Europe), since most of the invasions were quite influential as several tens of attacks actually took place braking thus lot of glass.
God bless our deeds

we can often help smashing things ourselves
Just during our lifetime we could see Nazi police breaking all glass searching those merely listening to BBC radio.

We can even remember the overseas relatives’ taxes at work when the US Air Forces successfully broke some glass (that Germans could not find in the time of occupation) during bombing raids at the end of the 2nd World War, April 1945.

In 50th, no less harmful were the actions of the communists who transformed some glassworking factories into heavy industry to produce steal throwing thus away all the brittle stocks considered as too luxurious for labor class of camareds.

More realistically, the Red Army tanks did a superb glass-breaking job in the 1968 invasion, too.

In this light everybody would agree that with this kind of practice at replacing broken glass anybody can get good - particularly when having at hand an influential stimulation through the drunken beer as an inspiration for novation.
The existance of the oldest glasswork in the continent, which has been operating without interruption from its foundation in the year 1414 in the little North Bohemian town Chřibská (Lusatian mountains).

1341 foundation of the first Bohemian brewery by King Jan of Luxenburg, which is still in operation in the small town of Domažlice (South Bohemia).

yet earliest treatise on the beer-making ŇDe cerevisia Ň published by the Czech alchemists Hajek in 1585. It is also worth noting that the first printed book emerged in the Bohemia soon after the Gutenbergs discovery of typography and was already printed in the Czech language in Pilzen 1468.
simple glass origin
Glass blowing
Thanks God not all glass was destroyed

The Mosaic of Bohemian Historical Glass
Through history: glass was always regarded to have a magical origin:

just to take plentiful sand and plant ashes and, by submitting them to the transmuting agencies of fire to produce melt which whilst cooling could be shaped into an infinite variety of forms which would solidify into a transparent material with appearance of solid water and which was smooth and cool to the touch, was and still is a magic of the glass workers art
Origin of glass know-how and spreading
The art of processing was passed down from generation to generation but the ancient knowledge has been replaced by the organized scientific research.

"Some glasmakers have three furnaces, other two yet others only one. The glasmaker who have three furnaces, use the first to melt the raw materials, the second to remelt them and the third for cooling the glass vessel and other hot products. The glasmaker often take samples by their blowpipe and at soon as they have ascertained that the glass has attained sufficient clarity, they immerse each blowpipe in the mass, and turning it slowly gather the glass mass. The glass mass sticks to the blowpipe like a soft and sticky syrup and envelope it spherically. He takes as much glass as is sufficient for the making of the intended object, rolls it higher and higher on a marble plate to make it properly homogeneous, and blowing into the blowpipe he inflates it in a bubble form... Then he lifts the pipe, rotating it in a circle round his head and thus protracts the glass, or gives it form by its injection into a hollow copper mould. By repeated heating, blowing, com pressing and extending he forms it according to his will into goblet, vessels or other object. Then he presses it again to the marble, widens its base and bends it inside by the second blowpipe. He cuts its mouth with heart and, if required by the object, adds feet and handles, and even gilds it or paints it with various paints. Finally he deposits it in an oblong clay vessel which is in the third furnace... and lets it cool."

G. Agricola, De re metallica, 1556
Rich Czech history
Material advancement in the 20th Century

Impact of rational understanding of thermal treatments and material thermal analysis

Eye polymeric lenses

Glass-ceramic implants

Metallic glasses

natural glasses (moldavites)

art glass (Nouveau style)
Structural states of matter (after Trömel [1])

- Glass
  - Long range order
  - Short range order
  - Amorphous
  - Glassy
  - Crystal
  - Opaline
Amorphous opals
Tektite glass
Natural glass
Non-crystalline states can be achieved by certain (seemingly contradictory) methods:

By maintaining already existing disorder (of liquid and/or gas) when preventing phase (ordering) transition when applying an ultrafast heat withdrawal (such as a drastic freeze-in by melt radical undercooling or chemical vapor deposition - VCD) or

by implementing disorder into the previously ordered makeup upon energetically structural disintegration (such as an intensive breakdown by e.g. milling) or

by creation of disordered structure through variously accomplished chemical reactions including low temperature digenetic and biotic processes (such as sol-gel, aqueous amorphisation response creating e.g. natural hyalites and opals).
"The deepest and most interesting unsolved problem in solid state theory is the theory of the nature of glass and of the glass transition."

Philip W. Anderson, Nobel Prize for Physics 1977
Some aspects of Czech glass research
(also initiated by our former studies abroad)

Jaroslav Šesták
Institute of Physics
Academy of Sciences of ČR

Zdeněk Strnad
LASAK - Laboratory for Glass and Ceramic Research

Praha, Czech Republic
Glass tradition - tribute to N.J. Kreidl’s 100 anniversary

Antonín Šesták, director of „Schilling & Knoflíček“ glass cutting factory in Hradec Králové

Celestýn Strnad, owner and developer, glassworking factory in Mnichovo Hradiště

confiscated and nationalized in 1950 both men declassed to helpworkers having struggles to have their sons educated

Sons Jaroslav and Zdeněk, classmates, graduated at the Department of Glass and Ceramics of the Institute of Chemical Technology - MEng. 1962.

1968’s liberalization gave possibility to work abroad

University of Missouri at Rolla, USA, Department of Ceramic Engineering

Professor N. J. Kreidl

University of Sheffield, Turner’s Department of Ceramics, England

Professor R.W. Douglas
The Slovak Glass Society and Czech Glass Society in cooperation with RONA Lednicke Rovne, under the auspices of the International Commission on Glass, organize the Norbert Kreidl Memorial Conference. The conference is dedicated to the 100th birthday anniversary of Prof. Norbert Kreidl. The conference was selected with respect to the close personal ties of Prof. Norbert Kreidl with Lednicke Rovne where he spent part of his fruitful life, as well as his family links with Jan Scheinberger, the founder and original owner of the Rona Company. The conference is dedicated to “Building the Bridges between Glass Science and Glass Technology”, the message of Norbert Kreidl to next generations of glass scientists and technologists. The program commemorating the work and life of Prof. Norbert Kreidl will be the finale part of the conference.

After receiving doctor's degree in physics from Vienna University in 1932, Norbert J. Krejci became interested in a career in the glass industry, i.e., at J. Schneider, Neipper, at the Marzahn Rucklon, Berlin. His life changed dramatically in 1938 when he left with his family to the Czech Republic and joined the firm known in English as B. F. Stokley in the USA starting to work. Making his Basak & Jenkins Co., later after retirement became professor at the Universities of Burgers, Missouri United States, New Zealand (Christchurch, and Antwerp (Yale)). Kreidl's international prominence and activities were longstanding and exceptional. He already participated at the 1st Glass Congress of the International Commission on Glass (ICG) in Venice in 1952. He was the president of ICG in 1955-1958, and he always instilled his students and colleagues by the breadth of his knowledge, his way of thinking in larger contexts and his capitalizing abilities. Previous symposium “Sweden: state-of-the-art of glass science and technology” was held in Trenčín (Glass Industry) in 1994 honoring the 60th birthday of Professor Norbert J. Krejci and was chaired by Wolfgang Hiiemae, Vice-President of the ICG. The proceedings were published as a special issue of Journal of Glass Industry, Trenčín (Glass Industry) 1994 under the editorial of W. Hiiemae and V. Ševčiková.
Initial study guided by Kreidl and Douglas

**Rolla 1969/70**
Study of $\text{Fe}_2\text{O}_3$-rich oxide ($\text{B}_2\text{O}_3$-based) glasses

Sheffield 1970/71
Crystallization study of window glasses
$\text{CaO- Na}_2\text{O-SiO}_2$

**crystallization**

**crystallization boundary**

J.Therm.Anal. 5(1973)669
previously by P.C.Schultz,

Phys.Chem.Glass. 14(1973)33
adding $\text{P}_2\text{O}_5$ - L.L.Hench etal,
J.Biomed.Mater. 2(1971)117

equal limits of cryst. & bioactivity

Šesták

Strnad
superparamagnetic glass and glassceramics
J.Am.Cer.Soc. 55(1972)537

concept of bridging and nonbridging oxygen
Proc. IX ICG, Praha 1977, p.399

quenched glass of FeBiO$_3$
and Fe$_{0.5}$Mn$_{0.5}$BiO$_3$ with curious sperimagnetic behavior

Activation energies of glass crystallization by DTA

thermodynamics of glass separation
J.Amer.Cer.Soc. 61(1978)283

ZnO-Al$_2$O$_3$-SiO$_2$ low dilatation glasses: Silikaty/Ceramics 20(1976)225

kitchen glassware and cooktop panels from „Nukryst“, Res.report VUSU-SU Teplice 1978, former Czechoslovakia
Appearance of various micro-view of glasses

Hypo-crystalline:
- Non-crystalline
- Para-crystalline
- Nano-crystalline
- Plastic-crystals

Biological glasses
Glass Transitions

Solids

△Cp ≈ 11 J/(K mol)
(per mobile "bead")

△S_{fusion} = n△S_c + △S_o + △S_p
(n = number of "beads")

First Order Transitions

Glass
LC Glass
PC Glass
CD Glass
Crystal
Condensed Crystal
Plastic Crystal
Liquid Crystal
Liquid
Gas

△S in J/(K mol)
△S_c = 7-12 conformational per "bead"
△S_o = 20-50 orientational per molecule
△S_p = 7-14 positional per molecule

Connects to all phases above.
To the melt, with: △S_e ≈ 100
$T_g = T_K$

Ideální sklo
Fiktivní teplota $T_f$ – charakterizuje strukturu

(4. Q. Tool)
The Arrhenius and VFT equations for the viscosity \( \eta \) are:

- **Arrhenius**: \( \eta = \eta_0 \exp\left(\frac{E}{RT}\right) \)
- **VFT**: \( \eta = \eta_0 \cdot \exp\left[\frac{B}{(T - T_0)}\right] \)

The diagram shows the comparison between strong and fragile materials, with different symbols representing various compositions.
Schematic picture for liquid-like (and also glassy structures) composed of variously bonded blocks illustrating the degree of possible coupling.
Schematic representation of the amplitude increase (pictured on vertical axis) of a non-linear oscillator causing the serial displacements of neighboring particles on the account of total expansion of the sample volume.
CROSSOVER temperature, $T_{cr}$, for polymers from the experimental course of relaxation modulus (depicted on the vertical axis) in the main intermediary zone. The graph provides the typical track of relaxation modulus for an ordinary polymer – polystyrene.
Kinetic approach

T-T-T diagrams

Formation of new phase (1→2)

- NUCLEATION-GROWTH

- Original: melt
- Nucleation
- Growth
- Solidified

Rate of homogeneous nucleation

\[ I \sim K(t) \exp(-\beta) \]

- Kinetic coefficient
  - Decreasing with \( \Delta T \)
- Thermodynamic coefficient
  - Increasing with \( \Delta T \)

- Surface tension \( \beta / \Delta C^2 \)

Fraction transformed (degree of crystallization)
extrapolation) to metastability (yet thermodynamically loyal) regions. Faster cooling, however, forces the system to enter ‘kinetic status’, controlled by the rates of transport processes so that whole boundary (thick lines, new shadowed PD) are shifted away from the originally equilibrium pattern (thin lines). Finally, at the extreme temperature changes (bottom PD), the entire state is relocated to the highly non-equilibrium condition, where the material set-up cannot match the transport processes, so that a kind of forcefully immobilized (‘frozen’ amorphous) state is established, where the actual phase boundary are missing (or being featureless, shaded),and the region is factually characterized by glass transformation. The right-hand column depicts the system behavior under the experimental observation of a given property (normalized within 0 a 1) where thin straight lines represent the development of equilibrium background (balanced conditions – where vertical lines stand for invariant and sloping lines for variant processes). The thick s-shaped curves endure for the practically measured trace, i.e., for the actually observed ‘kinetic’ curve.
Repetitive structures

Quantum impact: $K m \lambda u = h$

co-centric patterns of some natural formations and Liesegang’s rings of silver chromate crystallites

directionally solidified dielectric eutectic of PbCl$_2$-AgCl

ornamentally casing work of micro-organisms based on calcite structures, oscillations as natural phenomena
Metallic glasses surprise the 20th Century
Casting of metallic glasses

The detailed view of the single roll technique with two alternatives of the molten sample draws (shadow). Left, simple layer deposition by injecting molten stream against the rotation coolant surface the deposited ribbon leaves the roll after its full solidification (dotted). Right, a more advanced deposition through the kneading-like system enabling to form more fixed and thicker ribbons, possible of preparing streamer with multiple compositional layers.

Crystallization on non- and nano- crystalline alloys

Fe75Si15B10 and Fe74Cu1Nb3Si13B9
Some examples of the melt quenching instruments (used in the laboratory of Institute po Physics during eighties): Left - belt running device where the molten drop was let falling in between a modified twin-roller quenching machine, here improved by inserted filament - infinitesimal running metallic ribbon. This adjustment helped to assure prolonged contact of the quenched sample melt onto the cooling substrate (thus avoiding supplementary crystallization of glass after its taking away from the simple wheels' linear contact). Middle - a sloped or slanted plate of metallic (usually copper) coolant enabling a simple dropping the melt to slip onto the surface or splat quenching if the melt layer is pressed in between an added cover block. Right - on instrument for continuous casting the melt onto the outside of a rotating drum, which is customarily called 'single roll technique' and which is common for the preparation of metallic ribbons.
Effect of bulk/surface treatment
Hypothetical T-T-T diagram (left) suggested for the rapidly quenched HTSC in the YBaCu-O and BiCaSrCu-O systems (expressed in the simplified cation ratios): Initial \( \phi_{\text{crit}} \) Tmelt Precipitating phases \( \Delta T_C \) per TCpercomp. K/s oC A B C D oC oC ‘123’ \( 10^7 \) \( \sim 1400 \) ‘100’ ‘211’ ‘123’ ‘011’ \( \sim 200 \) \( \sim 1000 \) ‘2223’ \( 10^3 \) \( \sim 900 \) ‘001’ ‘2212’ ‘2223’ ‘2021’ \( < 10 \) \( \sim 840 \)

The formation of the superconducting phase ‘C’ precedes likely the polymorphic crystallization where the non-superconducting phase ‘B’ and ‘D’ develop first from the low- and/or noncrystallized matrix latter re-reacting to form the desired superconducting phase ‘C’. Indisposition of the system to provide directly the phase ‘C’ on mere quenching is exploited for a trick needed to prepare technically applicable HTSC in two-step melting and cooling (right diagram) without achieving the total melting. As shown by shaded area the first sharp melting assures certain leftover of fine unmelted particles of \( Y_2O_3 \) (which later serve as vital pinning canters) while the second broad melting and controlled cooling provides the required peritectic formation of superconducting phases and alignment of its microcrystallites.
Transition region responsible for glass earliest occurrence.

- **Cryosorption**
- **HK**
- **Temperature**
- **Heat Flow**
- **Exothermic**
- **Crystallisation**
- **Cross-Linking** (other cure)
- **Oxidation**
- **Glass Transition**
- **Melting**

**DTA/DSC measurements**
Phenomenological description of vitrification, transformation and crystallization of glasses on basis of DTA measurements

Actual case of ZnO-Al₂O₃-SiO₂ crystallization

Analysis of the DTA peak positioning
Crystallographic representation of short-, middle- and long-range order
Self-developed apparatus for laser melting and quenching

Glass vitrification, transformation, and crystallization
Preservation of Plant Biodiversity

Seed Plants

Vegetatively Propagated Plants

Cryopreservation

Slow Cooling

Fast Cooling Vitrification

Cryoprotectants

Dehydration

J. Zámečník
Research Institute of Corp Production, Prague

The Aim

Attempt for a thermodynamic description

Biothermodynamics
Appearance of biological glasses under natural conditions

So far unknown behavior of water not fully understood yet

- seeds
- pollen
- buds
- "resurrection plants"

Water frozen in plants as a bio-glass

Curiosity: icosahedral and dodecahedral pentagonal-like symmetry of water incommensurable with hexagonal ice
The 'strategy of being in the glassy state', is exploited by plants in the nature to withstand unfavourable conditions of surrounding environment. Plant pollen flying in the air has a potential to be in glassy state keeping its viability after stigma pollination. Dormant poplar twigs can survive the low temperatures in glassy state in mid winter. It is possible to add other examples of glassy state occurrence in plant species in the nature.

The knowledge of conditions at which the glass is induced in plants can help to control the glassy status during cryopreservation of plant germplasm. Thermal analysis is of a favourite use in the study of thermal behaviour of both under cooling and re-heating, particularly curious about the determination and concentration-temperature dependences of glass $T_g$. 
Some Temperature Natural Milestones

- 0 0 °C freezing point
- -20 -21,8 °C eutectic point NaCl + H₂O
- -40 -38,1 °C water supercooling point
- -60 conventional use of solid CO₂
- -80 -88,7 °C lowest temper. detected on the Earth
- -100
- -120 -130 °C vapour phase of liquid nitrogen
- -140 -139 °C termodyn. glass transition of water
Life on the Earth depends on the unusual structure and anomalous nature of liquid water.

Water as ‘fluid glass’ thanks to its uniqueness of molecular orbitals and dimerization

(other similar oxides are gases: H₂S, H₃N, HF, H₃B)

WHY ?

Hydrogen (Van der Walls) bonds make possible the formation of polymeric liquid exhibiting important anomalies:

- High melting and boiling points
- Irregular density (max. at 4 C)
- Solid ice lighter (more voluminous) than liquid water
- Large specific and latent heats
- Penetrating and intensive solvating capability
- High solution capacity
It is clear that life on the Earth depends on the unusual structure and anomalous nature of liquid water.

It may help to explain the curiosity why warmer water freezes more rapidly than cold water. It is because the cold water at the temperature near freezing is densely packed with these icosahedras, for the ice incommensurable nuclei, which are thus capable of easier and thus deeper undercooling.

The water at higher temperatures gradually disintegrate such icosahedras possessing thus a greater number of smaller fragments, which can survive rapid cooling being more easily compatible with the highly symmetrical configuration of ice.
Water pentamers

Expanded structure (ES)

Collapsed structure (CS)

$\Delta H$ is $+$ve
$\Delta S$ is $+$ve
$\Delta V$ is $-$ve
PŘED 720 MILÍ ROKY

DNES
It is clear that life on the Earth is sustained and threatened by the unusual properties of solid ice

- Ice flows on the water surface (cover preserves life underneath, decrease heat flow as thermal insulate)
- Ice has various structural and morphological forms (snow flakes, which defend icing of the Earth surface)
- Solidification is associated with the volume increase – dangerous to enclosed volumes (vessels, living sells)
- Water penetrates everywhere (wetting, humidity)
Glass transition during dehydration up to recovery

Relative Humidity (%)

Glass Transition (°C)

y = 0.0655x - 66.187

R² = 0.0212
Phase diagrams of a hydrocarbon-water system: explanation

- Glass transition of mixture
- Thickening/dehydration
- Liquids lines
- Super-saturated solution
- Glass regions
- Ice and frozen semicryst. solution
- Low temperat. transit. of semicryst. mixture
- Glassy water below -110 C
- Glass transition of mixture
- Eutectic
- Safe

Figure 1: Schematic phase diagram of a hydrocarbon water system. (Tg: glass transition of the homogeneous mixture; Tlw: liquidus line of the water rich phase; Tls: liquidus line of the hydrocarbon rich phase; Te: eutectic point; T1: glass transition of the “maximally freeze concentrated solution”; T2: low temperature transition of semi-crystalline mixture.)
Celebration of the new book publication at the new technology Research Center at Pilsen West Bohemian University
Thank you for your attention!
and welcome to visit golden Prague

Fractal wonder of snow
and glassiness of water