Disordered Materials: Glass physics

> 2.7. Introduction, liquids, glasses

> 4.7. Scattering off disordered matter:
> static, elastic and dynamics structure factors

> 9.7. Static structures:
> X-ray scattering, EXAFS, neutrons, data interpretation

> 11.7. Dynamic structures and the glass transition

HELMHOLTZ GEMEINSCHAFT

Hermann Franz
Methoden moderner Röntgenphysik II
July 2013

DESY

Introduction

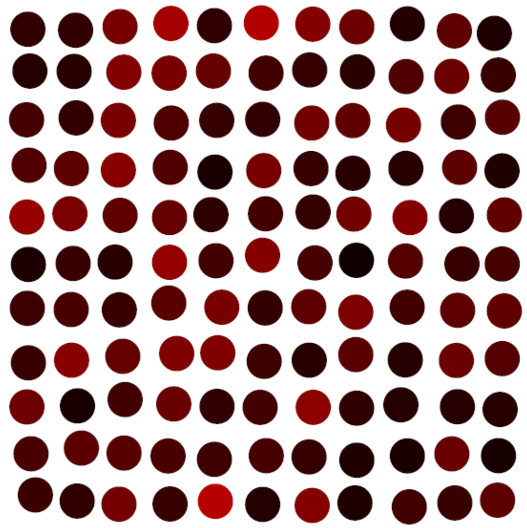
- Systems
- Structure
- Glass transition

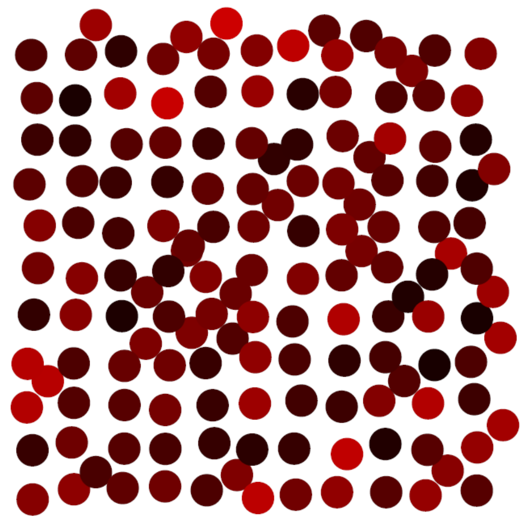
- Metallic glasses
- Mechanical properties
- Applications

Introduction

Glasses are materials with "amorphous structure showing a gradual transition from the liquid to the solid without well defined melting point."

No or only minor changes in the static structure at the transition





Introduction

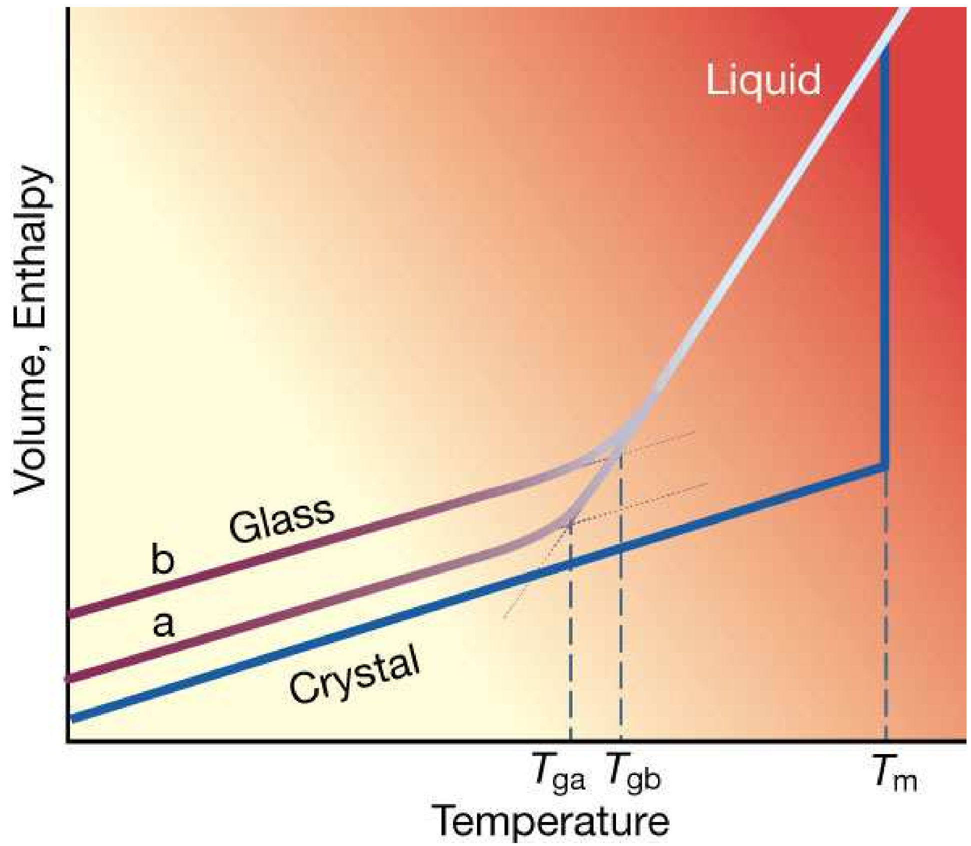
Physical properties change gradually on lowering the temperature

Cross-over depends on cooling/heating rate

i.e. properties depend on thermal history

Glasses are in a frozen in meta-stable state

▶ susceptible to crystallization



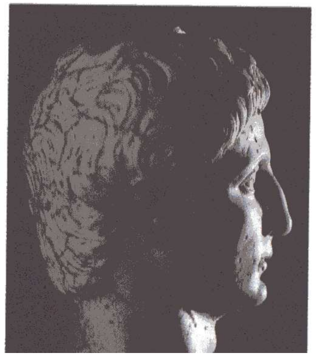
History

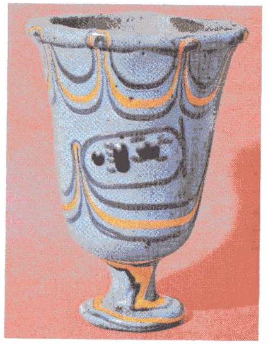
Art of glass making known since

ca 3000 b.c.

Earliest records in Egypt and Mesopotamia, later many records in Rome

Sacophagus of Tut Ench Amun





Glas 2): Becher aus dem Grab Thutmosis' III.; Höhe 8,5 cm, um 1450 v. Chr. (München, Staatliche Sammlung Ägyptischer Kunst)

Examples for glasses in everyday life

Traditional glasses

SiO_2, B_2O_3, P_2O_5 based

Window glass

SiO_2 with sodium or potassium

minerals (soda, potash)

Glasses for art work

doped with variety

of elements

Industrial glasses

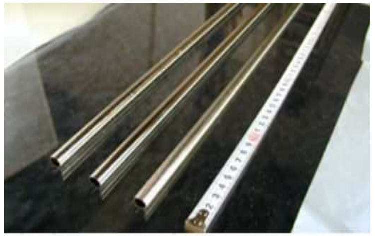
Polymers

Plastic materials: PE, PMMA, PS…..

SMO (small organic molecules)

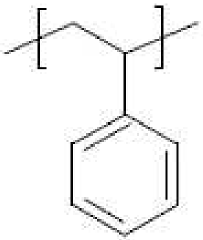
Glycerol, OTP, salol, squalane, ……

Metallic glasses

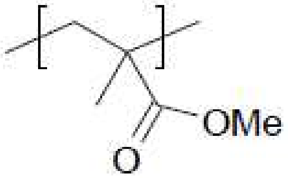


Examples for typical glass formers

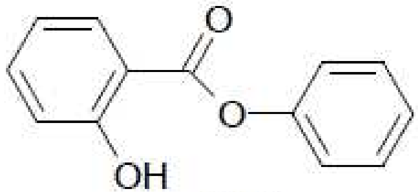
SiO_2	B_2O_3	$Ca_{0\cdot38}K_{0\cdot62}(NO_2)_{1\cdot38}$	$CH_3CH_2CH_2OH$
"Fused Silica"	Boratglas	"CKN"	n-Propanol



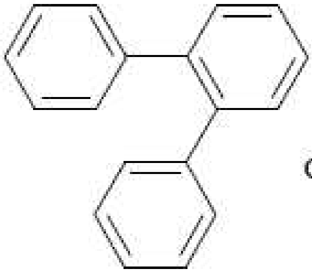
Polystyrol



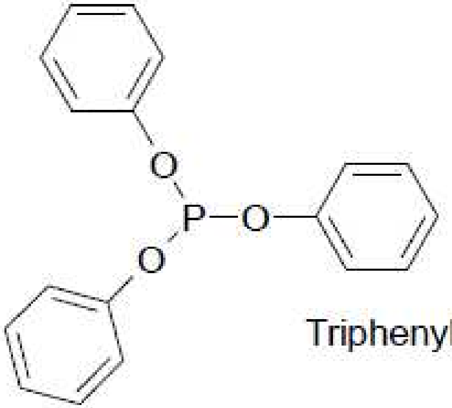
PMMA



Salol

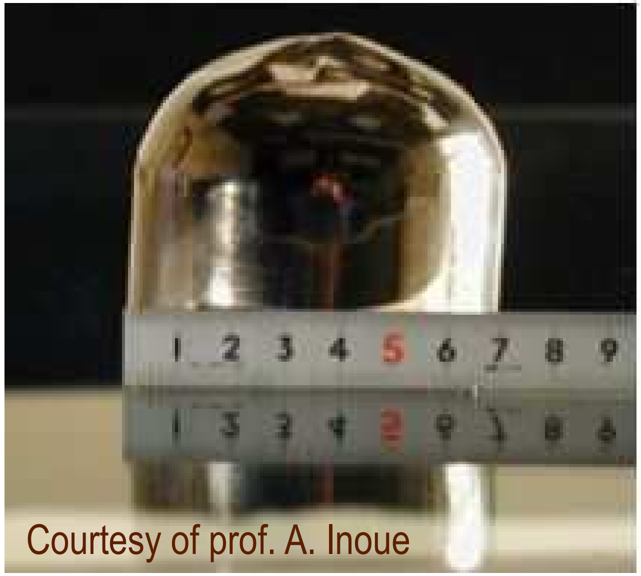


o-Terphenyl



Triphenylphosphit

Bulk Metallic Glasses



Systems

- Historically first alloy AuSi (1960) cooling with 10^6 K/s
- 1969 PdCuSi – only 10^3 K/s needed
- First commercial amorphous alloy, Vitreloy 1 (41.2% Zr, 13.8% Ti, 12.5% Cu, 10% Ni, 22.5% Be)
- Families of alloys
  - Pd based: PdCuNiP
  - Zr based: ZrNi, ZrTiCuNiBe (v4), ZrAlNiCuAg, ZrPd, ZrAlCu, ZrAlCuNiFe
  - La based
  - Fe based: FePCAlBGa
  - Cu based: CuZr, CuTiZr
  - Al based: AlLaNi
  - Ni based: NiZr, NiNbY

  - and many more
- Comparatively simple structure -> ideal model systems

Systems

Table 1
The critical sizes (d_c) and thermal parameters for $Zr_{100-x-y}(Cu_zAg_{1-z})_yAl_x$ ($x = 7$–9 at.%, $y = 42$–50 at.% and $z = 0.75$–0.875) alloys, together with other BMGs reported in Refs. [20,27,28] for comparison

Alloys	Critical size	Amorphous ingots (25 g)	T_g	T_x	T_m	T_l	ΔT_x	T_{rg}	γ
$Zr_{46}Cu_{46}Al_8$	5 mm	No	715	771	978	1163	56	0.615	0.411
$Zr_{47}(Cu_{4/5}Ag_{1/5})_{46}Al_7$	<20 mm	No	704	783	1055	1242	79	0.567	0.402
$Zr_{47}(Cu_{4.5/5.5}Ag_{1/5.5})_{46}Al_7$	<20 mm	Partial	702	782	1056	1123	80	0.625	0.428
$Zr_{47}(Cu_{5/6}Ag_{1/6})_{46}Al_7$	<20 mm	Partial	703	781	1060	1125	78	0.625	0.427
$Zr_{47}(Cu_{6/7}Ag_{1/7})_{46}Al_7$	20 mm	Partial	709	774	1057	1118	65	0.634	0.424
$Zr_{45}(Cu_{4/5}Ag_{1/5})_{48}Al_7$	20 mm	Partial	710	783	1062	1208	73	0.588	0.408
$Zr_{45}(Cu_{4.5/5.5}Ag_{1/5.5})_{48}Al_7$	>20 mm	Yes	711	785	1063	1154	74	0.616	0.421
$Zr_{45}(Cu_{5/6}Ag_{1/6})_{48}Al_7$	>20 mm	Yes	713	786	1061	1159	73	0.615	0.420
$Zr_{43}(Cu_{5/6}Ag_{1/6})_{50}Al_7$	20 mm	No	738	770	1075	1127	32	0.65	0.413
$Zr_{50}(Cu_{4/5}Ag_{1/5})_{42}Al_8$	20 mm	Partial	703	774	1089	1155	71	0.609	0.417
$Zr_{50}(Cu_{5/6}Ag_{1/6})_{42}Al_8$	<20 mm	Partial	701	764	1095	1138	63	0.616	0.415
$Zr_{48}(Cu_{3/4}Ag_{1/4})_{44}Al_8$	20 mm	Partial	706	770	1092	1218	64	0.580	0.400
$Zr_{48}(Cu_{4/5}Ag_{1/5})_{44}Al_8$	>20 mm	Yes	707	762	1090	1132	55	0.625	0.414
$Zr_{48}(Cu_{4.5/5.5}Ag_{1/5.5})_{44}Al_8$	>20 mm	Yes	706	777	1089	1129	71	0.625	0.423
$Zr_{48}(Cu_{5/6}Ag_{1/6})_{44}Al_8$	>20 mm	Yes	705	778	1090	1122	73	0.628	0.426
$Zr_{48}(Cu_{6/7}Ag_{1/7})_{44}Al_8$	>20 mm	Yes	706	778	1089	1127	72	0.626	0.424
$Zr_{48}(Cu_{7/8}Ag_{1/8})_{44}Al_8$	20 mm	Partial	707	779	1095	1127	72	0.627	0.425
$Zr_{46}(Cu_{4/5}Ag_{1/5})_{46}Al_8$	>20 mm	Yes	710	776	1091	1228	66	0.578	0.400
$Zr_{46}(Cu_{4.5/5.5}Ag_{1/5.5})_{46}Al_8$	>20 mm	Yes	703	775	1088	1126	72	0.624	0.424
$Zr_{46}(Cu_{4.5/5.5}Ag_{1/5.5})_{46}Al_8$ ingots	>20 mm	Yes	704	776	1089	1130	72	0.623	0.423
$Zr_{46}(Cu_{5/6}Ag_{1/6})_{46}Al_8$	>20 mm	Partial	710	778	1088	1120	68	0.634	0.425
$Zr_{53}(Cu_{5/6}Ag_{1/6})_{38}Al_9$	20 mm	Partial	711	767	1089	1129	56	0.63	0.417
$Zr_{51}(Cu_{4.5/5.5}Ag_{1/5.5})_{40}Al_9$	20 mm	Partial	703	758	1092	1144	55	0.615	0.410
$Zr_{49}(Cu_{5/6}Ag_{1/6})_{42}Al_9$	20 mm	Partial	708	767	1092	1242	59	0.57	0.393
$Cu_{43}Zr_{43}Al_7Ag_7$ [27]	8 mm	–	722	794	1125	–	72	–	–
$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ [28]	25 mm	–	623	672	932	996	49	0.67	0.415
$Pd_{40}Cu_{30}Ni_{10}P_{20}$ [28]	72 mm	–	575	670	804	840	95	0.72	0.473
$La_{62}Al_{14}Cu_{11.3}Ag_{2.7}Ni_5Co_5$ [20]	>20 mm	–	422	482	642	727	60	0.580	0.419
$La_{65}Al_{14}Cu_{9.2}Ag_{1.8}Ni_5Co_5$ [20]	35 mm	–	419	459	641	687	40	0.610	0.415

"Yes", "partial" and "no" are roughly defined by eyes for ingots having volume fractions of larger than about 80%, 30–80% and less than about 30% for the amorphous component, respectively.

Favorable conditions for glass formation

Couple of empirical rules in literature

However up to now still empirical (trail and error) development

- **Three or more alloy components**
- **Very different atomic radii**
- **Negative heat of mixing**
- **Low eutectic**
- **Competing crystalline phases**

Applications

Transformers

low thermal losses

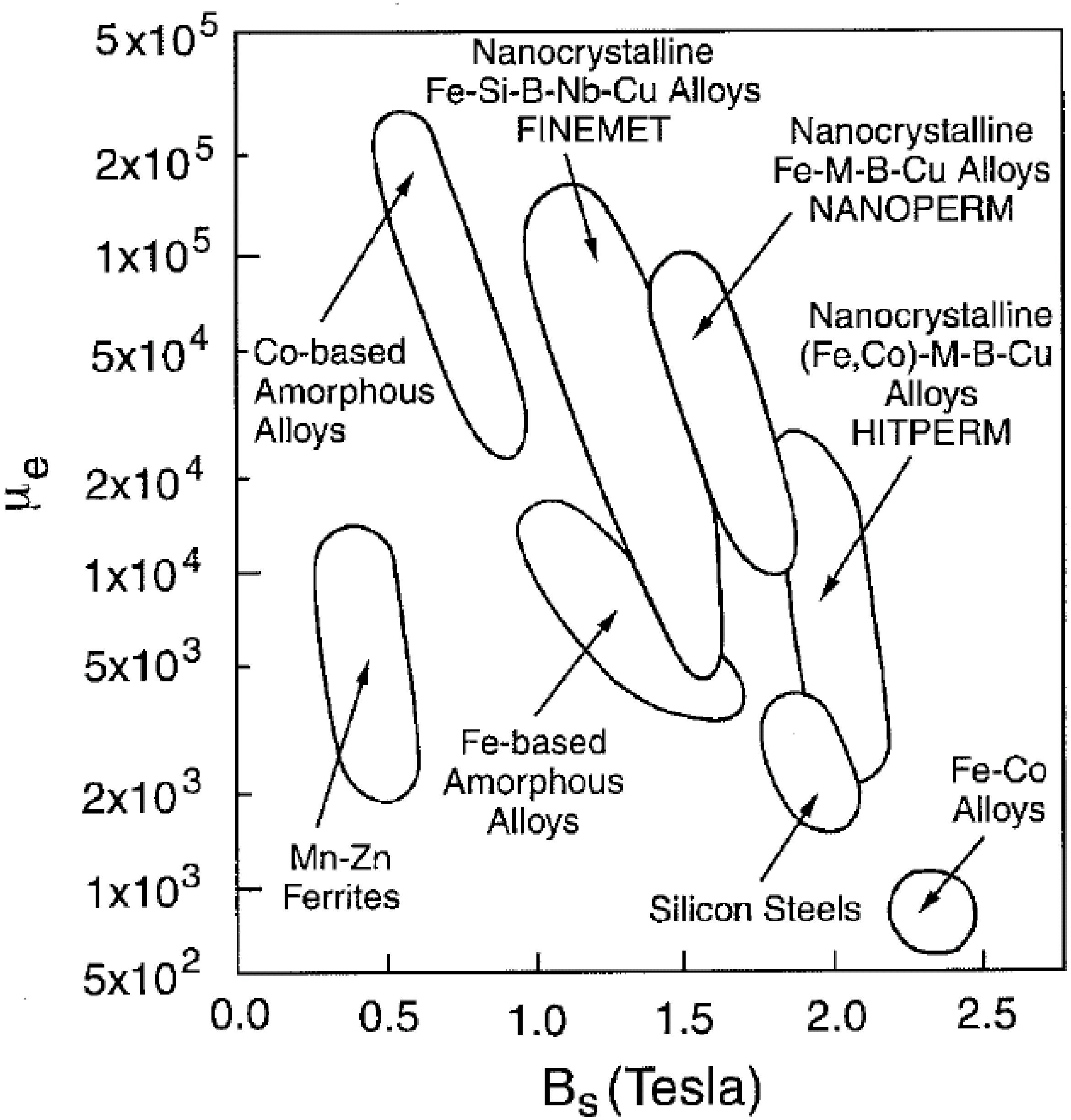
Light weight compounds in space crafts

high specific strength

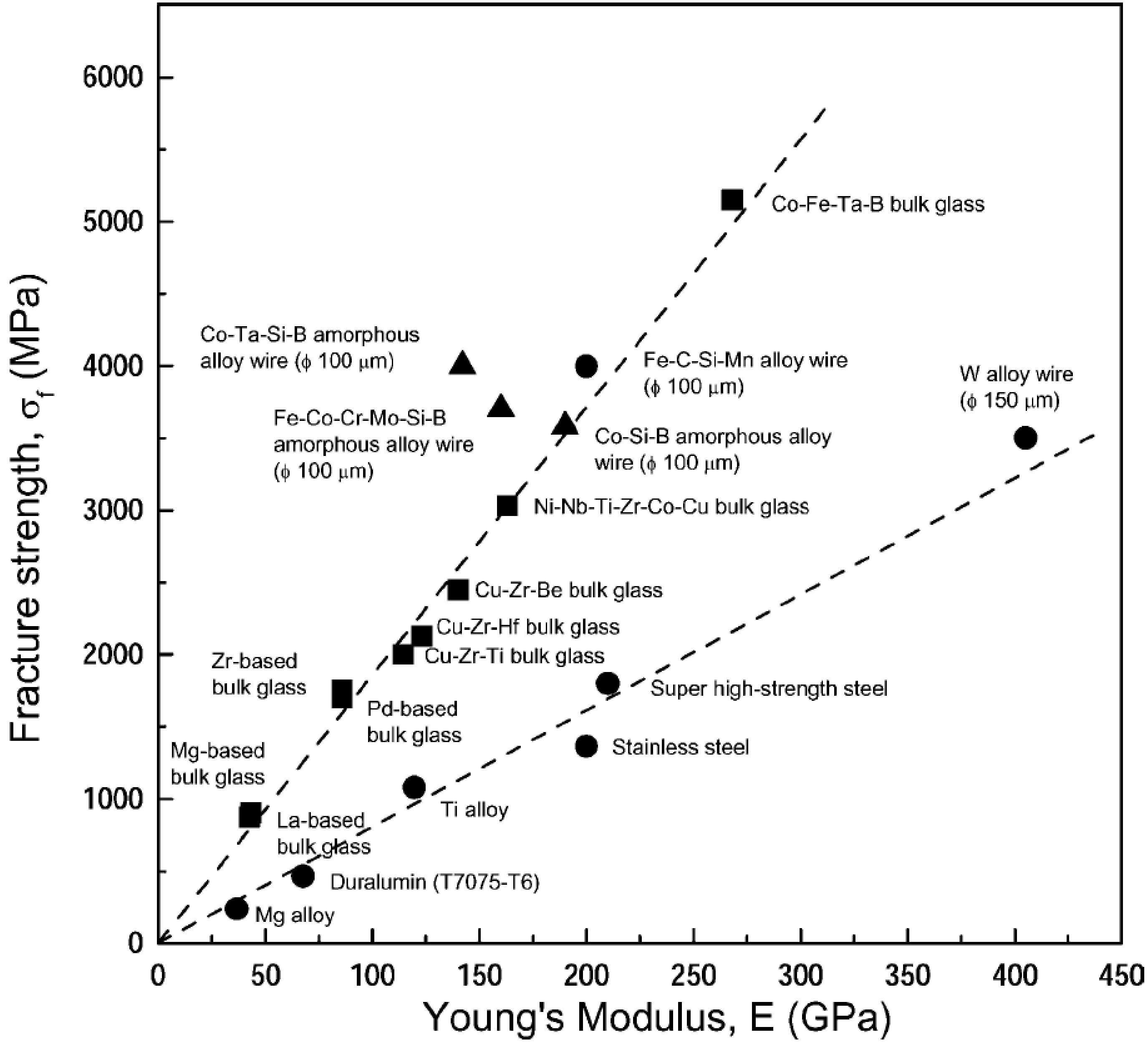
Surface coating

very hard thin films

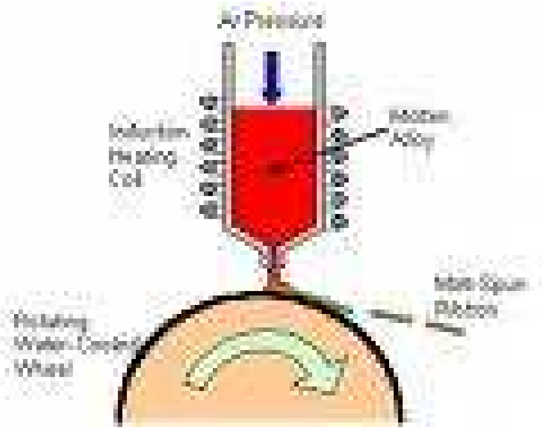
Magnetic properties

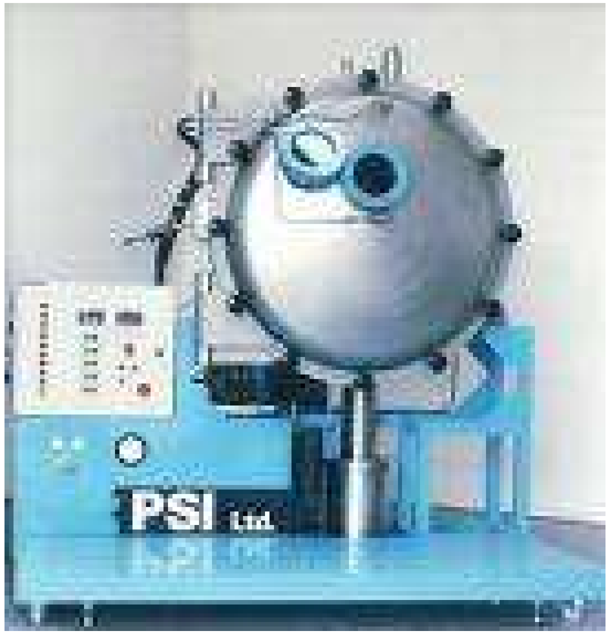


High strength



Sample preparation - melt spinning





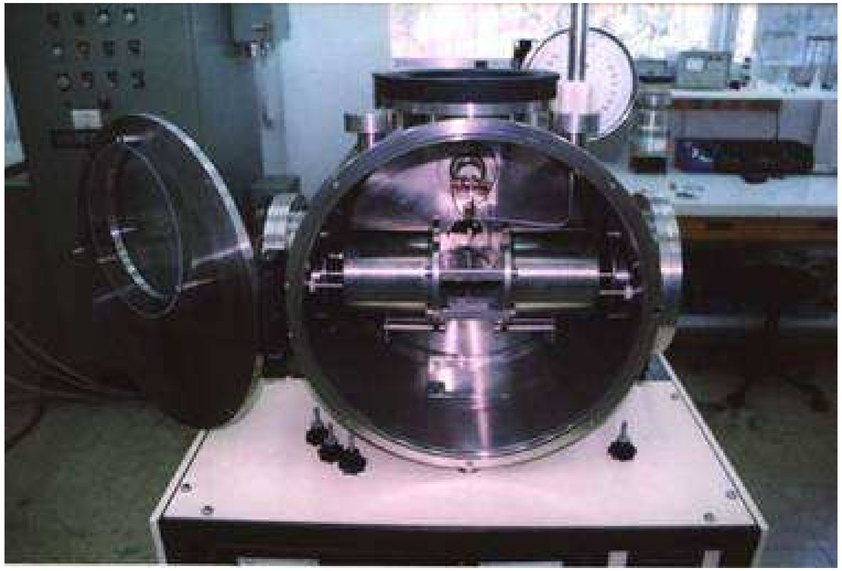
Rather wide spread

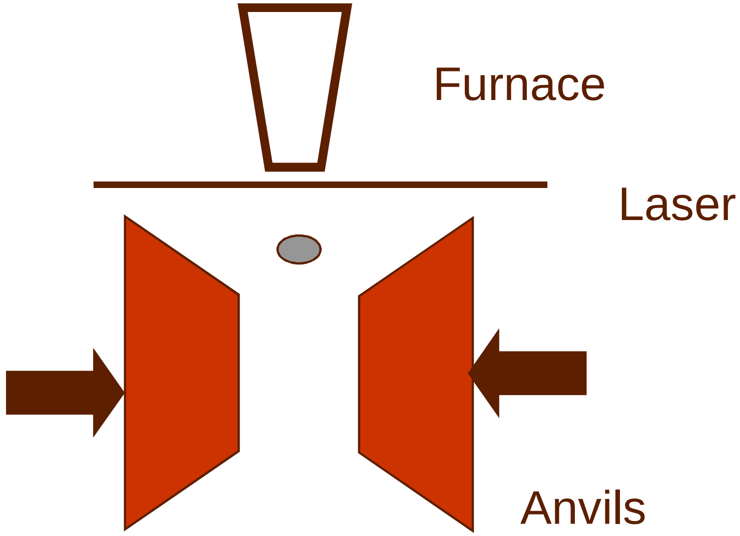
Cooling rate up to 10^5 K/s

Production of large quantities

However only thin films (couple of 10 μm)

Sample preparation - splat cooling





Rather wide spread

Cooling rate up to 10^6 K/s

Production of small quantities

Only thin disks (couple of 10 μm)

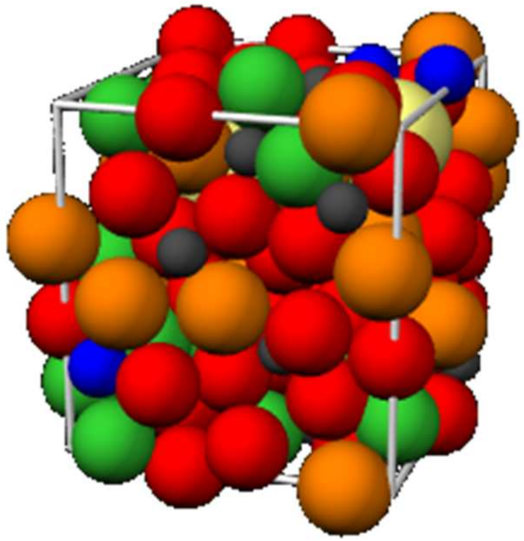
Sample preparation - mold casting

Cooling rate up to 100 K/s

Production of "large", bulk samples

Flexible shapes

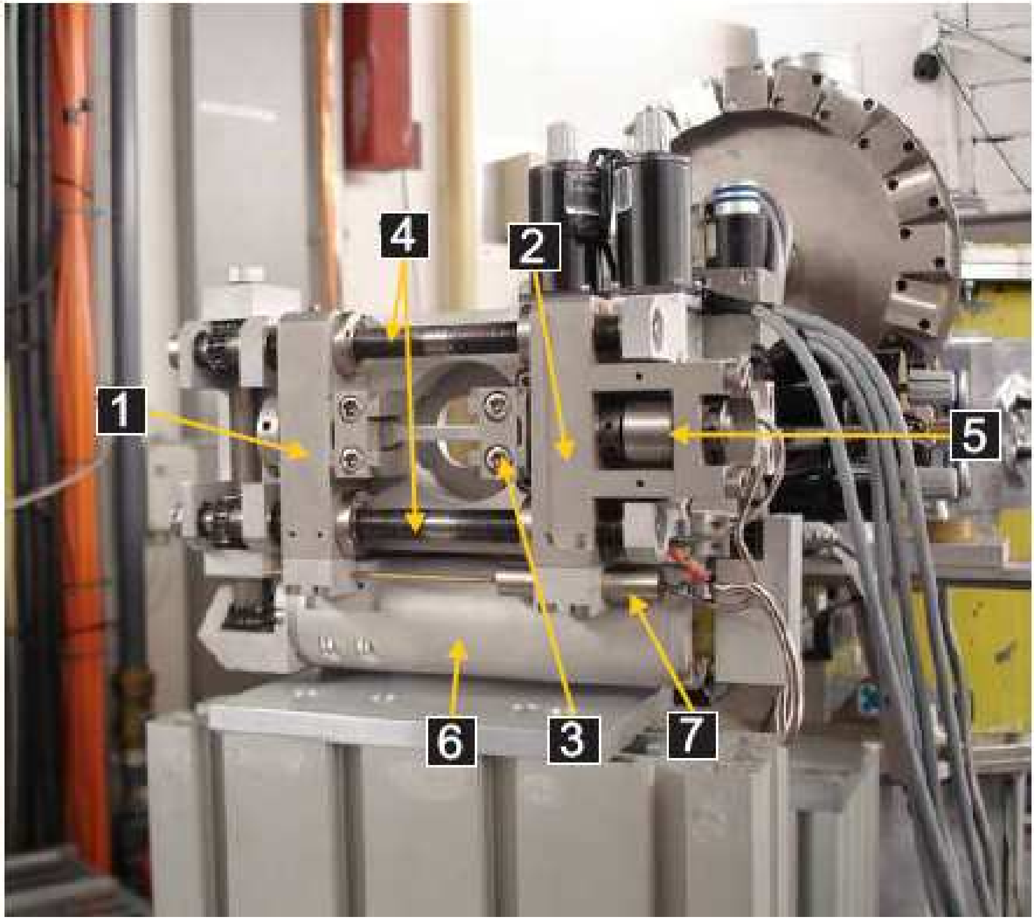
Structure vs. macroscopic properties



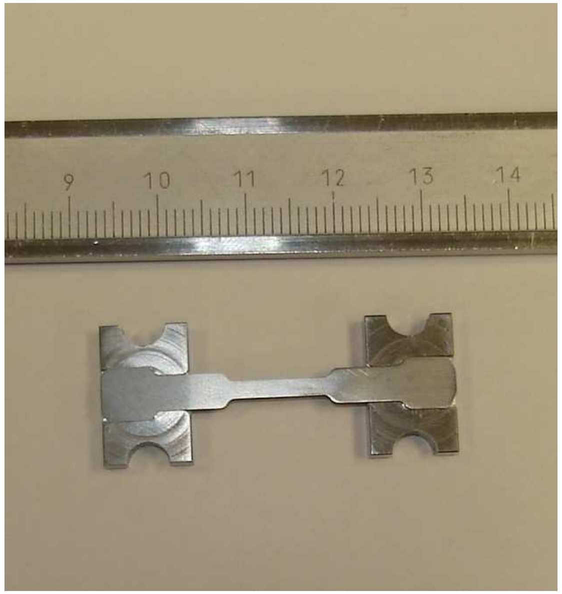
Understanding relation between the structure and macroscopic properties is important for improving performance of existing and crucial for designing novel materials

In-situ tensile experiments

Tensile/compression module



[1] - rear yoke, [2] - front yoke, [3] - clamping, [4] - leading screws, [5] -load cell, [6] - motor, [7] - displacement gauge

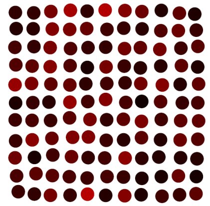


$Zr_{64.13}Cu_{15.75}Ni_{10.12}Al_{10}$

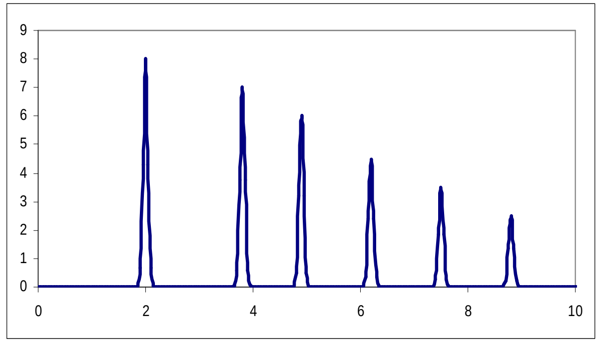
Y. H. Liu, G. Wang, R. J. Wang, D. Q. Zhao, M. X. Pan, and W. H. Wang, Science **315**, 1385 2007.

Reminder:

Scattering amplitude from a crystal

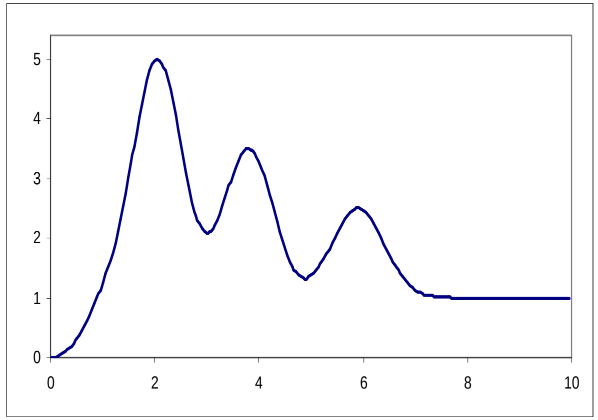


$$F^{crystal}(Q) = \underbrace{\sum_{r_j} F_j^{mol}(Q)\exp(i\mathbf{Q}\mathbf{r}_j)}_{\text{unit cell structure factor}} \bullet \underbrace{\sum_{R_n}\exp(i\mathbf{Q}\mathbf{R}_n)}_{\text{lattice sum}}$$



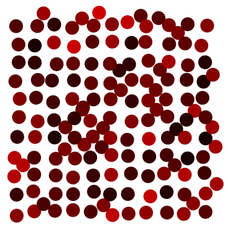
leading to reciprocal lattice

$$\mathbf{G} \bullet \mathbf{R}_n = 2\pi\,(hn_1 + kn_2 + ln_3)$$



As there is no lattice in amorphous structures we have to treat the whole sample like a molecule

$$F^{mol}(Q) = \sum_{r_j} f_j(Q)\exp(i\mathbf{Q}\mathbf{r}_j)$$



With the sum running over all atoms in the illuminated volume

Structure by X-rays - temperature dependence

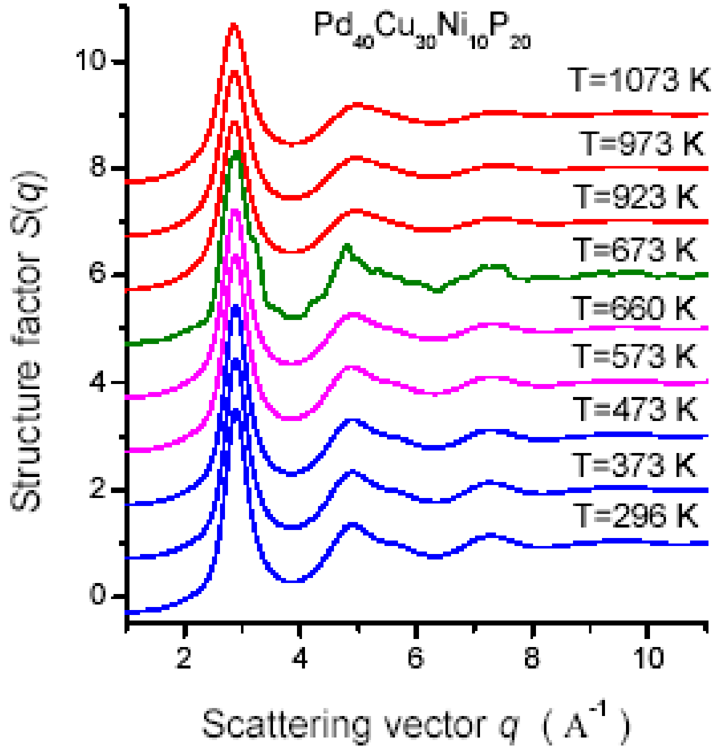


Fig.1: Structure factor $S_T(q)$ of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ at different temperatures

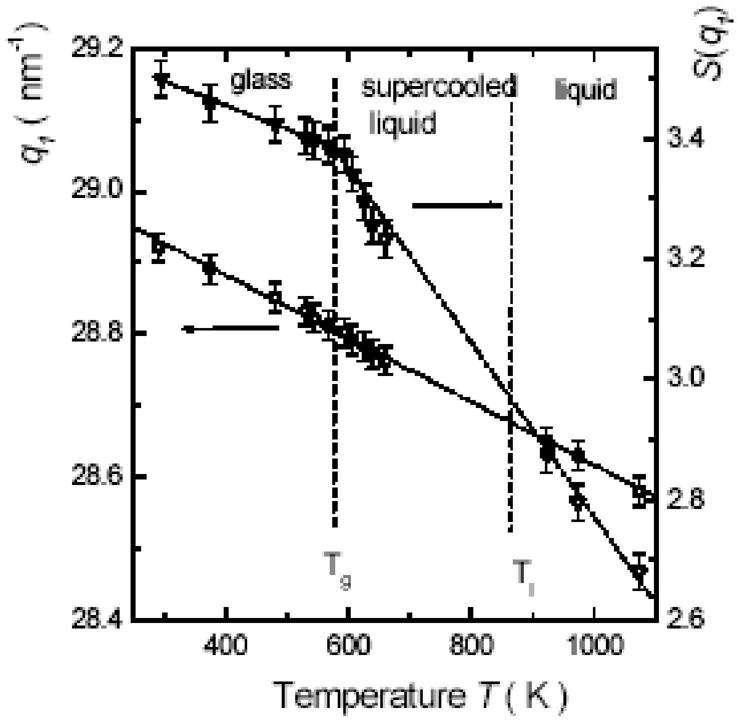
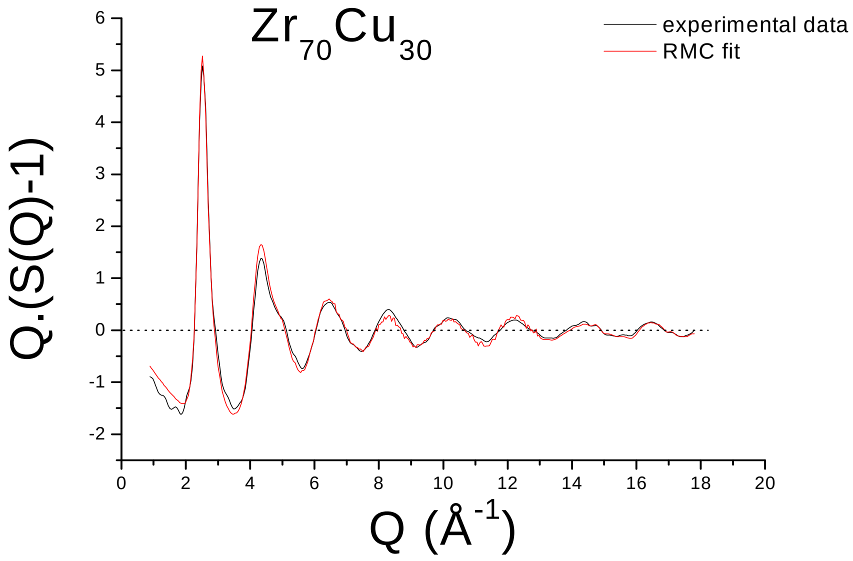
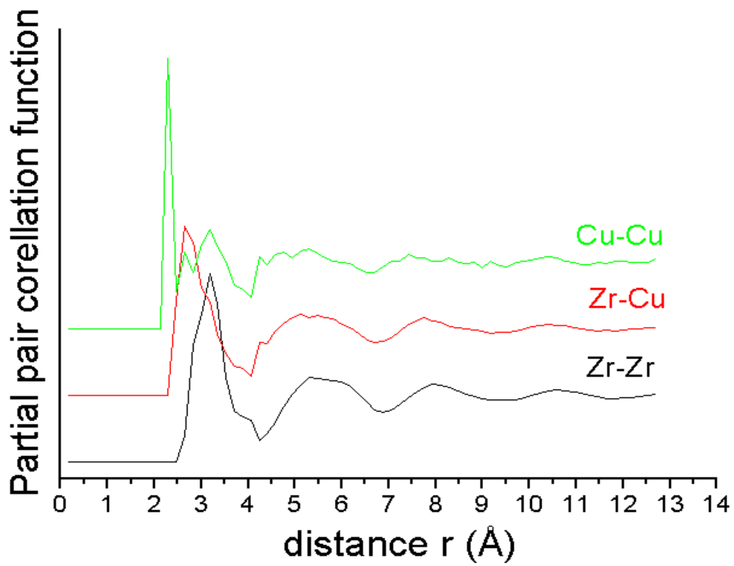
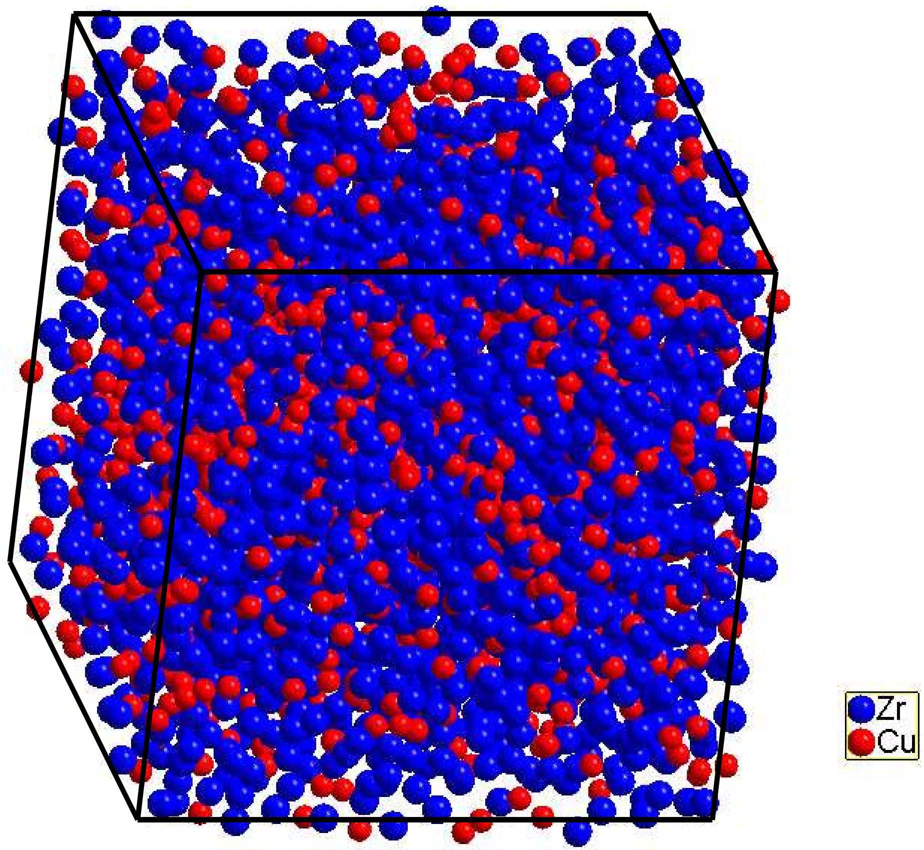


Fig.2: Position q_1 and height $S(q_1)$ of the first maximum of the structure factor $S_T(q)$ vs temperature

N. Mattern et al APL 2003


$Zr_{70}Cu_{30}$
experimental data
RMC fit
Q.(S(Q)-1)
Q (Å^{-1})
6
5
4
3
2
1
0
-1
-2
0
2
4
6
8
10
12
14
16
18
20


Partial pair corellation function
Cu-Cu
Zr-Cu
Zr-Zr
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
distance r (Å)


Zr
Cu

The glass transition temperature T_g

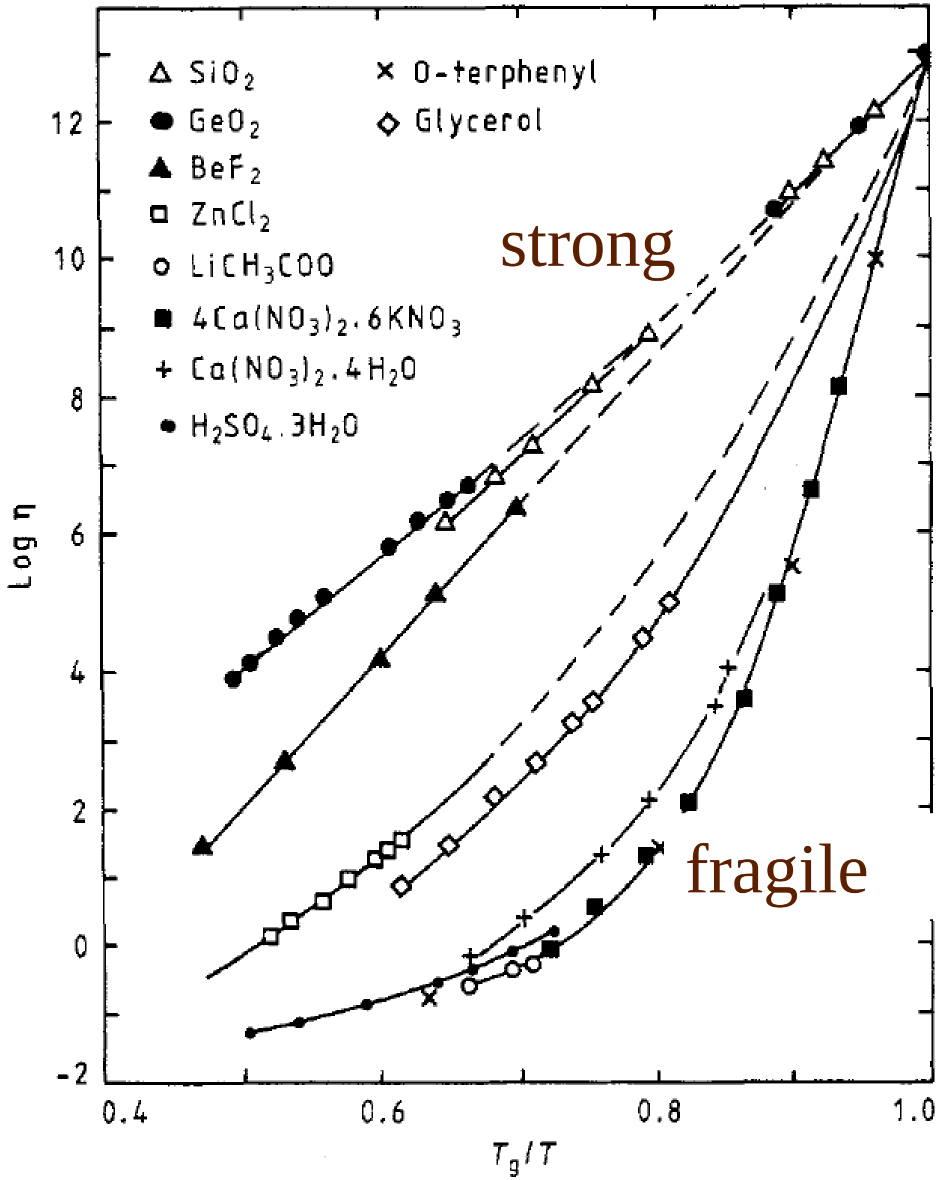
What is glass (solid) ?

What is liquid ?

There are also complex fluids

- **Emulsions**
- **Colloids**
- **Gels**
- **Ketchup, honey, starch, ………**

The glass transition temperature T_g



$$\eta = \exp\left(-\frac{E_0}{k(T-T_0)}\right)$$

VFT law

transition temperature T_0

Very strong variation of η / τ with temperature

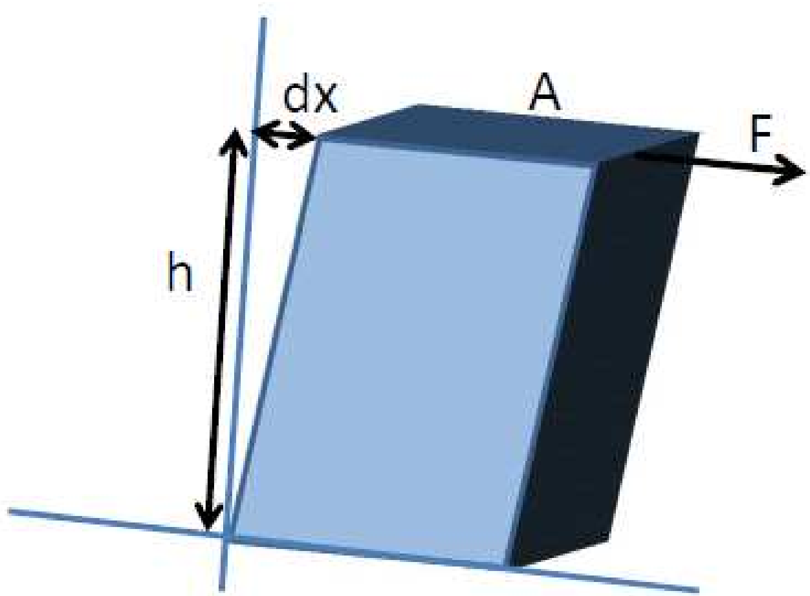
T_g determined by state of the experimental technique

Viscosity and T_g

$$\frac{F}{A} = \eta * \frac{dv}{dy}$$

Shear stress

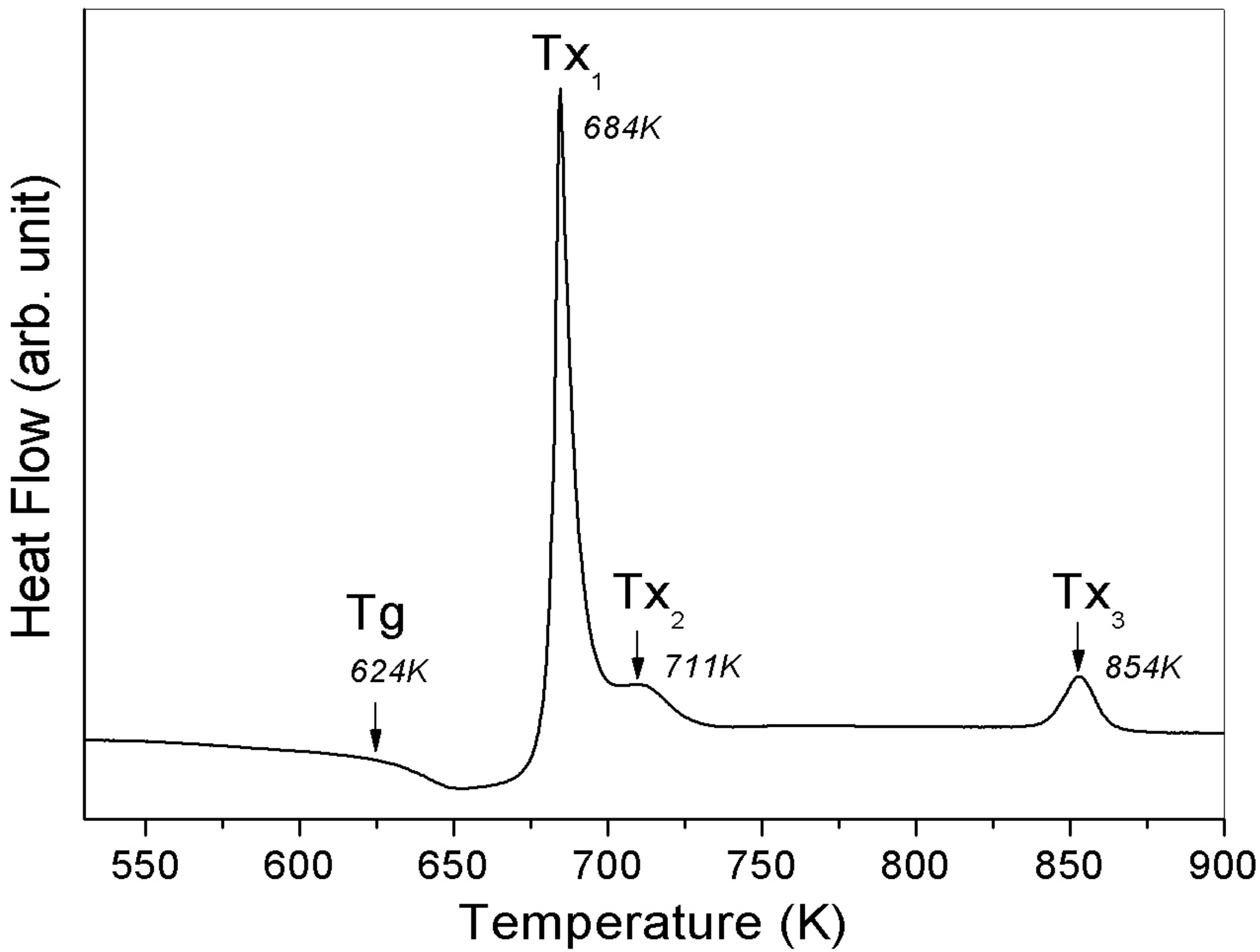
Shear rate



$$\eta \cong G * t_r$$

Viscosity and share modulus are connected by a characteristic relaxation time

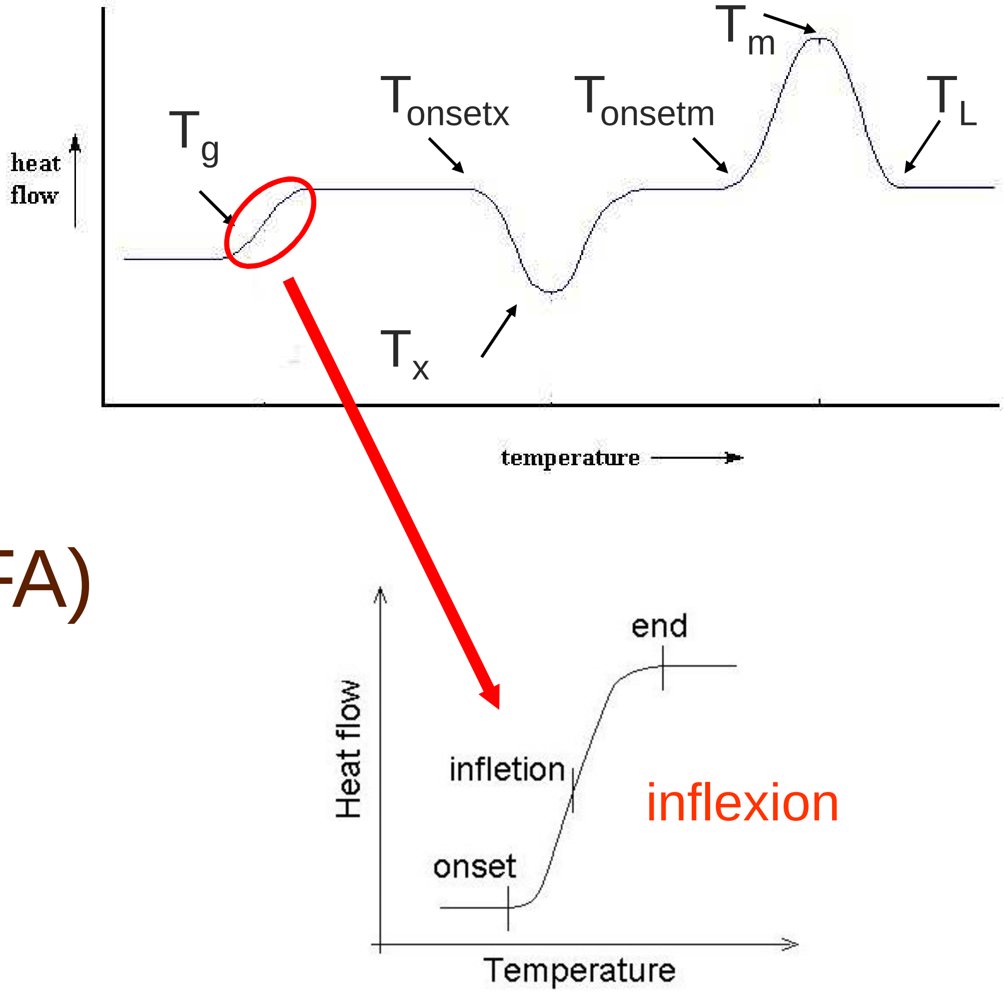
Differential Scanning Calorimetry (DSC)



Differential Scanning Calorimetry

Supercooled liquid region:

$$\Delta T = T_{onsetx} - T_g$$



Glass forming ability (GFA)

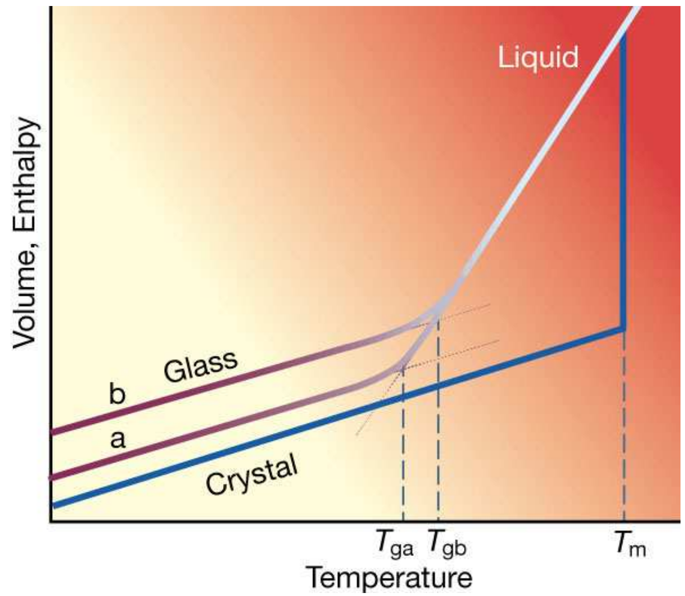
$$\Delta T$$

$$T_{rg} = T_g / T_m$$

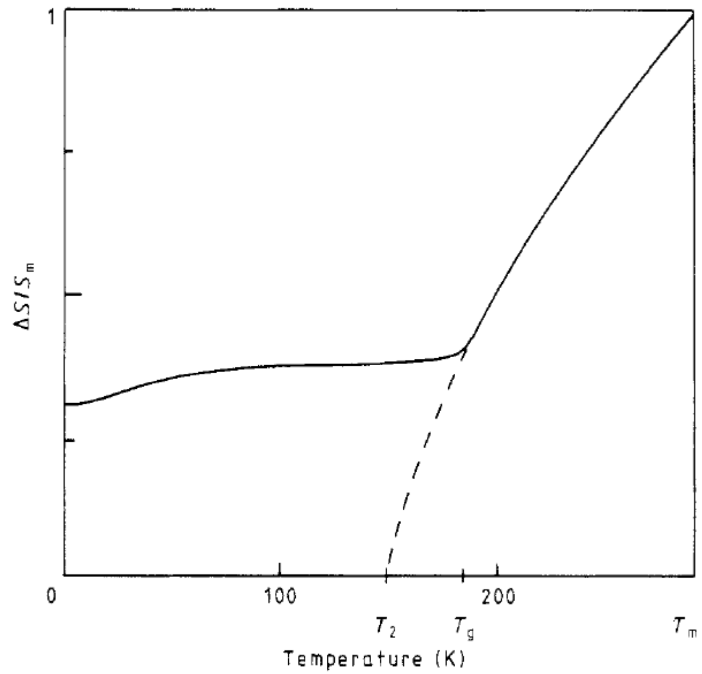
and many others

Kautzmann paradoxon

Glass transition at T_K when entropy of the amorphous is lower than in the corresponding crystal

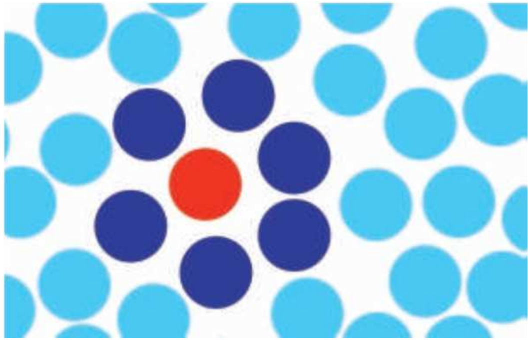


All real systems fall out of equilibrium before



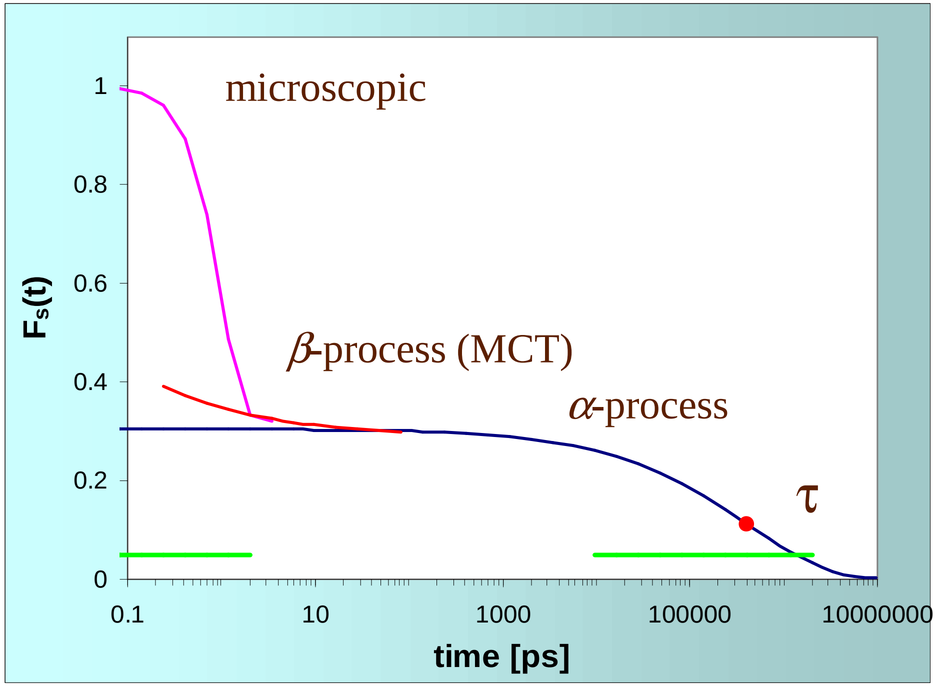
Dynamics in real disordered solids

- microscopic process: rather harmonic in most glasses



- cage (β)- process: intermediate times

α- process: long range diffusion, very strong T-dependence, stretched exponential $f_q \exp(-(t/\tau)^\beta)$



glass transition T_c: α and β process merge