"Kristallglas" - a contradiction in terms





Overview of Soft Materials

Polymers	Gels	Colloids	Pastes	Surfactants	Liquid crystals	Glasses
-Synthetic		- Sols				
-Bio-polymers		- Emulsions				
		- Micelles				
Plastics Rubber		Food	Pharmace	uticals	Displays	"Godis"
Fabric		Papermakin	g& pulp			Fibres
		Paint				Windows
						Art
Volvo		ARLA, GB	ASTRA			Karamellkungen
		SIK	SCA, Möl	nlycke		Orrefors
 macroscopically soft not liquids, not solids variety of forms & morphology complex systems, many d.o.f, disorder out of equilibrium structures self assembly interaction energy - entropy balance 				4 Characterist 1) Length scale 2) Time scales 3) Weak intera 4) Self assembl	tics of soft matter es 10-1000 nm of im : processes from 10 ⁻ ctions (kT) ly properties	portant ¹² - 10 ³ s

Glasses

What is a glass?

- Definitions

Glass forming materials

- Classes, characteristic properties, applications

Glass structure

- Order and disorder, characterizing the glass structure

The glass transition

- Manifestations and phenomena

- Theories

Literature on glasses

- Jones chp. 2.4
- J. Jäckle, *Models of the glass transition* Reports on Progress in Physics 49, 171 (1986)
- C. A. Angell, *Formation of Glasses from Liquids and Biopolymers,* Science 267, 1924 (31 March 1995)
- Zachariasen, J. Am. Chem. Soc. 54, 3841 (1932)
- A. Soper in *Local Structure from Diffraction*, p. 59 (1997) (available as E-book at Chalmers lib.)

(articles can be accessed via www.lib.chalmers.se)

What is a glass?

Definition:

A glass is an amorphous solid exhibiting a glass transition

Three criteria:

1) Amorphous - structurally disordered, non-crystalline

- 2) Solid
- 3) Glass transition

1. Amorphous?



- No long range order (unit cells, periodicity etc)
- Short range order (chemical constraints, packing etc.)

2. Solid



Figure 1.6 Schematic sketches of the atomic arrangements in (a) a crystalline solid, (b) an amorphous solid, and (c) a gas.

Snapshot of fluid



Figure 1.7 Sketches of the state of atomic motion (a) in a solid and (b) in a liquid.

Criteria for a solid:

- i) Sustains shear stress without yielding
- ii) Atoms have defined sites
- iii) Atoms exhibit only vibrational motion around "equilibrium" sites

2. Solid



Figure 1.7 Sketches of the state of atomic motion (a) in a solid and (b) in a liquid.

Criteria for a solid:

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Figure 1.5 Glass formation in the gold-silicon system. Two quenches from the liquid state, at two compositions, are indicated. Glasses can be prepared much more readily in quench a than in quench b, since the latter must cross a greater temperature range between T_f and T_g in which it is "at risk" vis-à-vis crystallization. (The T_f curve is from the work of Predel and Bankstahl, 1975; the T_g curve is from the work of Chen and Turnbull, 1968.)

Two ways to form a solid: i) Crystallization at T_m from liquid ii) Glass formation at T_g

To form a glass:

 $\Rightarrow \text{Avoid crystallization at } T_m$ $\Rightarrow \text{ enter into super-cooled liquid}$ $\Rightarrow \text{ cool until } T_g$ Cooling rate is important!

Glass forming materials

- Covalent inorganic systems: SiO₂, B₂O₃, P₂O₅...
- Polymers: polystyrene, PMMA, etc
- Molecules: Ethanol, glycerol, sucrose...
- Metals and alloys: Au_{0.8}Si_{0.2}
- Salts: Ca-K-NO₃, LiCl-H₂O, BeF₂...

Can any material form a glass?

Can any material form a glass?



Figure 1.4 Four methods of forming amorphous solids: (a) slow cooling, (b) moderate quenching, (c) rapid "splat-quenching", and (d) condensation from the gas phase.



Melt spinning of metallic glasses

Yes, if cooled rapidly enough! But rapid is a relative term.

Table 1.1 Quenching techniques and their characteristic rates of cooling

Technique	Cooling rate $(K s^{-1})$	
Annealing	-	
large telescope mirror	10 ⁻⁵	
optical 'glass'	3×10^{-4}	
ordinary 'glass'	$10^{-3} - 10^{-2}$	
Air quenching	1-10	
Liquid quenching	$10^2 - 10^3$	
Chill-block		
splat-cooling	105	
melt-spinning, extraction	$10^{6} - 10^{8}$	
Evaporation, sputtering	10 ⁹ ?	

also computer simulations 10^{12} K/s \Rightarrow Ar-glass

Properties of glasses

- i) isotropic
- ii) no grain boundaries
- iii) no fixed composition-> tuning of properties



- iv) close to ideal strength no dislocations
- v) control the flow properties (viscosity)-> optimise preparation conditions

Technology

Type of Amorphous Solid	Representative Material	Application	Special Properties Used
Oxide glass	(SiO ₂) _{0.8} (Na ₂ O) _{0.2}	Window glass, etc.	Transparency, solidity, formabil- ity as large sheets
Oxide glass	$(SiO_2)_{0.9}(GeO_2)_{0.1}$	Fiber optic waveguides for communications networks	Ultratransparency, purity, forma- bility as uniform fibers
Organic polymer	Polystyrene	Structural materials, ''plas- tics''	Strength, light weight, ease of proc- essing
Chalcogenide glass	Se, As ₂ Se ₃	Xerography	Photoconductivity, formability as large-area films
Amorphous semiconductor	$Te_{0.8}Ge_{0.2}$	Computer-memory elements	Electric-field-induced amorphous ↔ crystalline transformation
Amorphous semiconductor	$Si_{0.9}H_{0.1}$	Solar cells	Photovoltaic optical properties, large- area thin films
Metallic glass	$Fe_{0.8}B_{0.2}$	Transformer cores	Ferromagnetism, low loss, forma- bility as long ribbons

TABLE 1.2 Some examples of applications of amorphous solids

A bio-active glass

Stimulation of Biological Function With Bioactive Glass



Physiologic fluids interact with and gradually erode the bioactive-glass surface.



Erosion of BioGran® particles preferentially creates sheltered recesses in which osteoprogenitor cells attach and differentiate to form osteoblasts.



Each excavated BioGran® particle provides a center for new bone formation.



The glass granules are resorbed and replaced by a framework of bone^{3,5}

Figure 2. Schematic representation of the pathway to bone-tissue formation with bioactive-glass (BG) granules of a narrow size range ($300-355 \mu m$).

(in wt%).*							
Glass		Glass Ceramics (Ceravital)	Glass Ceramics (Cerabone A-W)				
SiO ₂	40-60	40-50	34.0				
Na ₂ O	10-32	5-10					
CaO	10-32	30-35	44.7				
P ₂ O ₅	0-12	10-15	16.2				
CaF ₂	0-18		0.5				
B ₂ O ₃	0-20						
K ₂ O	**	0.5-3.0					
MgO	**	2.5-5.0	4.6				

Table I: Range of Compositions of Bioactive Glasses and Glass Ceramics

*Summarized From References 20 and 48-50.

**Recently the following compositional brackets (in mol%) were considered essential for bone bioactivity to occur in a glass system: <59% SiO₂, 14–30% alkali oxides (Na₂O + K₂O), and 14–30% alkaline earth oxides (MgO + CaO).⁵⁰

MRS Bulletin vol. 23, no. 11 (1998)

A bio-active glass



Figure 1. Micrograph showing two bioactive granules after three months in a periodontal defect; the granules have fully reacted, and the internal reaction layer has been removed leaving a pouch in which bone (red tissue) subsequently formed.

MRS Bulletin vol. 23,no. 11 (1998)

Bulk metallic glasses

Metallic glasses can today be made in bulk configuration



Figure 7. Photo of a commercially cast plate of Vitreloy 1 (V1). The plate was cast by Howmet Corporation, Whitehall, Michigan, using a process developed by Howmet for fabrication of net-shaped bulk-metallic-glass (BMG) components.



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Some common glasses

Borosilicate Glass - Pyrex composition: $80SiO_2 + \sim 10B_2O_3 + \sim 2Al_2O_3 + \sim 5Na_2O$

Lab-glass, kitchen ware, optical lenses ... High chemical stability



Some common glasses

Lead-glass - crystal

- Composition: 15 30 PbO + \sim 70 SiO₂ + \sim 5 (Na₂O, K₂O)
- Exclusive glasses, arttglass ..
- Lower T_g
- High index of refraction 1.8-2 (windowglass \approx 1.5)
- High density



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The glass transition

- Manifestations and phenomena

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Glass structure

"It must be frankly admitted that we know practically nothing about the atomic arrangement in glasses."

Zachariasen 1932



What is the nature of the glassy state? Molecules in a glass are arranged much like those in liquids but are more tightly packed. Where and why does liquid end and glass begin?

Science 1st July, 2005

Different types of disorder



a) Topological disorder: no translational periodicity

b) Orientational disorder:Random orientation of molecules or spins

c) Substitutional disorder:Types of atoms randomlydistributed, e.g. metal alloys

d) Vibrational disorder: Random motion around an equilibrium site

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Crystals







Fig. 2.17 Illustration of the structure of ice, a hydrogen-bonded tetrahedral network of oxyge atoms.



Perfect crystal:

- Atomic/molecular positions uniquely defined
- Translational periodicity

Crystals



Fig. 2.17 Illustration of the structure of ice, a hydrogen-bonded tetrahedral network of oxygen atoms.

Disorder also in crystals:

- Orientational disorder glassy crystals
- Rotational disorder plastic crystals
- Interstitials
- Vacancies

Amorphous



Figure 1.6 Schematic sketches of the atomic arrangements in (a) a crystalline solid, (b) an amorphous solid, and (c) a gas.



- No long range order (unit cells, periodicity etc)
- Not random arrangement chemical constraints, ionic interactions, packing etc.
 ⇒ short range order (SRO)
- Packing/ordering of SRO units
 ⇒ intermediate range order
- r >> SRO isotropic medium ρ_0 average density

Types of glass structure



SiO₂, B₂O₃...



Ca-K-NO₃...



- Network glasses covalently bonded systems
- Polymeric glasses 1-D networks + crosslinks
- Ionic glasses charge balance
- Metal glasses random packing of hard spheres
- Molecular glasses packing of molecules (van der Waals interactions)
- Hydrogen bonded glasses molecular network

Types of glass structure



SiO₂, B₂O₃...







- Network glasses
- Polymeric glasses
- Ionic glasses
- Metal glasses
- Molecular glasses
- Hydrogen bonded glasses





 \Rightarrow very different structural types

Types of glass structure



SiO₂, B₂O₃...





- Network glasses
- Polymeric glasses
- Ionic glasses
- Metal glasses
- Molecular glasses
- Hydrogen bonded glasses

Ca-K-NO₃...



 \Rightarrow very different structural types

Can we find common structural features and descriptions?

Short range order (SRO)



Coordinating structure

Order within the first coordination shell (r<5 Å):

- bond lengths, r_{AB}
- coordination numbers, N_{AB}
- bond angles, Θ_{ABA}

SRO due to:

- chemical/charge ordering
- directional bonding
- packing & geometry

Short range order (SRO)



Disorder?

Relative orientation of coordinating structures

Order within the first coordination shell (r<5 Å):

- bond lengths, r_{AB}
- coordination numbers, N_{AB}
- bond angles, Θ_{ABA}

SRO due to:

- chemical/charge ordering
- directional bonding
- packing & geometry

Intermediate range order



r - characteristic length scale of IRO

Intermediate range order (IRO):

- ordering ≈5-30 Å
- superstructures \Rightarrow result of steric hindrance
- correlations between structural units, e.g. polymer chains
- frozen in density fluctuations

Network glasses



Covalently bonded systems:

Continuous Random Network SiO₂, B_2O_3



Modified Random Network network former+ modifier

Figure 5.2 Schematic drawing of a 2-dimensional structure for a soda – lime – silicate glass. A fourth oxygen would be located above each silicon in the 3-dimensional structure

Continuous Random Network

Zachariasen J. Am. Chem, Soc. 54, 3841 (1932)



- Same coordinating structures
 in the glass as in the crystal
 ⇒ same SRO
- Nearest neighbour distances are constant
- No dangling bonds
- Disorder introduced in ϕ distribution in dihedral angles

Modified Random Network



Fig. 3.41 Modified CRN model of network modifier-containing (oxide) glasses. The channels through the structure containing the modifier ions are clearly apparent (Greaves 1985).

Breaking up of network, creation of non-bridging oxygens (NBO)

Modifier added to network former to introduce desired properties:

 Mechanical, magnetic, electrical, viscosity, bio comp., colour,...

*Na*₂*O*, *CaO*, *Er*₂*O*₃, *Li*₂*O*

Modified Random Network



Modifier oxide breaks up the network (but SRO of PO_4 unit is preserved)



Modifier cations provide ionic bridges between network segments

Example Phosphate glasses:

- P_2O_5 - network former



Metaphosphate composition: $M_x^+(PO_3)_x$ Polymer-like chain structure (1D-network)

Characterising the glass structure



Pair distribution function, g(r):

Probability of finding an atom a distance r away taking any atom as origin

g(r) is a 1-dimensional representation of a 3D structure

Pair distribution function



Pair distribution function, g(r):

- Probability of finding an atom a distance r away taking any atom as origin
- *g(r)* is a 1-dimensional representation of a 3D structure
- Discrete function in a crystal, continuous function in a glass

Radial distribution function



Radial density function $\rho(r)$: the average number of atoms a distance r away taking any atom as origin. $\rho(r) = \rho_0 g(r)$

Radial distribution function: $J(r)=4\pi r^2 r(r)$ *J(r)* used to quantitatively determine structural parameters:

- position of a peak \Rightarrow bond-length, r_{ij}
- area under a peak \Rightarrow coordination number, N_{ij}
- bond angel within a coordinating structure can be calculated from the relative peak distance



Experimental investigations

Diffraction techniques:

- *x-ray* λ≈0.5-5 Å
- neutron λ≈0.5-5 Å
- electron $\lambda < 1 \text{ Å}$

Vibrational spectroscopy

- infra-red
- Raman
- neutron

Element specific:

- Nuclear magnetic resonance (NMR)
- Extended x-ray absorption spectroscopy (EXAFS)
- Mössbaur (Fe, Sn, ..)

Computational

- Molecular dynamics (MD)
- reverse Monte Carlo (RMC)

Determining the glass structure



Diffraction pattern for

- a crystal

- a glass

no sharp peaks

S(Q) - static structure factor

Determining the glass structure



Information on real space structure - F.T. S(Q)



$$g(r) = \frac{1}{(2\pi)^3 \rho_0} \int (S(Q) - 1) \frac{\sin Qr}{Qr} 4\pi Q^2 dr + 1$$

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i)

ii)



Figure 1.5 Glass formation in the gold-silicon system. Two quenches from the liquid state, at two compositions, are indicated. Glasses can be prepared much more readily in quench *a* than in quench *b*, since the latter must cross a greater temperature range between T_f and T_g in which it is "at risk" vis-à-vis crystallization. (The T_f curve is from the work of Predel and Bankstahl, 1975; the T_g curve is from the work of Chen and Turnbull, 1968.)

- $T > T_m$ normal liquid $T_m < T < T_g$ - super cooled liquid $T < T_g$ - glass
 - Why does the glass form?
 - What happends at Tg?
- iii) Dynamics in the super cooled liquid?

What goes on in the liquid?



Relaxation in simple liquid

Potential to escape from local neighbourhood - ε

Thermally activated process - Boltzman distribution of probability

$$\Rightarrow \qquad \tau^{-1} \sim \nu e^{-\frac{\varepsilon}{k_B T}}$$



v - vibrational frequency



Figure 1.1 The two general cooling paths by which an assembly of atoms can condense into the solid state. Route ① is the path to the crystalline state; route ② is the rapid-quench path to the amorphous solid state.

In the liquid the viscosity, η , or relaxation time, τ , follows Arrhenius dependence:

$$\eta = \frac{G_0}{v} \exp\left(\frac{\varepsilon}{kT}\right), \ \tau \propto v \exp\left(-\frac{\varepsilon}{kT}\right)$$

at
$$T_m \tau \approx 10^{-12}$$
 s

In super cooled liquid, relaxation processes are slowed down:

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right), \ \tau = \tau_0 \exp\left(-\frac{D}{T - T_0}\right)$$

the Vogel-Fulcher-Tamman (VFT) equation



T_g practically defined as: T≈10²-10³ s, η≈10¹³ poise (1 poise=0.1 Ns/m²) At 300 K (RT): H₂O: η≈0.8·10⁻² poise Glycerol: η≈1.3·10¹ poise In super cooled liquid, relaxation processes are slowed down:

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right), \ \tau = \tau_0 \exp\left(-\frac{D}{T - T_0}\right)$$

Dramatic temperature behaviour, at T_g $\tau \approx 10^2$ -10³ s, $\eta \approx 10^{13}$ poise

Below T_g relaxations are so slow that the material is a solid \Rightarrow the liquid structure is frozen in!



Fig. 3. Variations of the viscosity with temperature, plotted in Arrhenius form, for a variety of liquid different types with different calorimetric glass transition temperatures. The T_g value is roughly temperature at which the viscosity reaches 10^{13} P except for fragile molecular liquids, where T_g fall viscosities up to four orders of magnitude lower. Dashed lines are interpolations between T_g and lowest temperature data point. Source of data are given in earlier publications (17, 36, 59) and indicated here by authors' initials; ZBLAN20, [ZrF₄]_{0.53}[BaF₂]_{0.20}[LaF₃]_{0.04}[AlF₃]_{0.03}[NaF]_{0.20}.

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i) V(T) - continuous at T_g

 T_g is found at the kink in the V(T) curve.

a result of difference of thermal expansion in liquid and in solid



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i) V(T) - continuous at T_g

 T_g is found at the kink in the V(T) curve.

a result of difference of thermal expansion in liquid and in solid

ii) Thermal expansion coefficient $\alpha(T)$ is discontinuous at T_g



Figure 1.8 The specific heat of the crystalline, amorphous, and liquid forms of As_2S_3 , a covalent material which is a prototypical glass former (after Blachnik and Hoppe, 1979).

- i) V(T) continuous at T_g
- ii) $\alpha(T)$ discontinuous at T_g
- iii) $C_P(T)$ discontinuous at T_g

most common way to experimentally measure T_g



Figure 10. Specific heat C_p against reduced temperature T/T_g in the vicinity of the glass transition temperature T_g for different glass forming liquids. Note that for SiO₂ and BeF₂ a jump in C_p at T_g is not discernible (from Brawer 1983).

- i) V(T) continuous at T_g
- ii) $\alpha(T)$ discontinuous at T_g
- iii) $C_P(T)$ discontinuous at T_g
- most common way to experimentally measure T_g
- size of step in C_P(T)
 depends on actual material



Figure 1.2 Volume-versus-temperature cooling curves for an organic material in the neighborhood of the glass transition. V(T) is shown for two greatly different cooling rates, as is the coefficient of thermal expansion $\alpha(T)$ for the fast-cooling curve (0.02 hr). The break in V(T), and the corresponding step in $\alpha(T)$, signal the occurrence of the liquid-glass transition (after Kovacs, Hutchinson, and Aklonis, 1977).

- i) V(T) continuous at T_g
- ii) $\alpha(T)$ discontinuous at T_g
- iii) $C_P(T)$ discontinuous at T_g

iv) T_g is cooling rate dependent high dT/dt -> lower T_g



Figure 11. Cooling-rate dependence of the glass transition in a borosilicate glass as observed in the density curves. Cooling rates for curves B, C and D are 1, 2 and 10 K h^{-1} , respectively. Curve A corresponds to the equilibrium liquid (from Ritland 1954).



Figure 12. Glass transition temperature T_g as function of cooling rate. T_g is determined by projecting the glass densities horizontally on the equilibrium curve A in figure 11. In this example, the T_g values can equally be interpreted as fictive glass temperatures T_f (see below; from Ritland 1954).

i) V(T) - continuous at T_g ii) $\alpha(T)$ discontinuous at T_g iii) $C_P(T)$ - discontinuous at T_g iv) T_g is cooling rate dependent high dT/dt -> lower T_g weak dependence~ ln(dT/dt)



Fig. 3. Variations of the viscosity with temperature, plotted in Arrhenius form, for a variety of liquid different types with different calorimetric glass transition temperatures. The T_g value is roughly temperature at which the viscosity reaches 10^{13} P except for fragile molecular liquids, where T_g fall viscosities up to four orders of magnitude lower. Dashed lines are interpolations between T_g and lowest temperature data point. Source of data are given in earlier publications (*17, 36, 59*) and indicated here by authors' initials; ZBLAN20, [ZrF_4]_{0.53}[BaF_2]_{0.20}[LaF_3]_{0.04}[AlF_3]_{0.03}[NaF]_{0.20}.

i) V(T) - continuous at T_g
ii) α(T) discontinuous at T_g
iii) C_P(T) - discontinuous at T_g
iv) T_g is cooling rate dependent
v) Viscosity, η, obeys VFT

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right)$$

 η goes from 10⁻³-10¹³ poise in small temperature interval typically T_g/T_m≈0.8



Fig. 4. Arrhenius plots of the viscosity data scaled by values of T_g from Fig. 3 and other sources showing the "strong-fragile" pattern of liquid behavior on which the liquid's classification of the same name is based. As shown in the insert, the jump in C_p at T_g is generally large for the fragile liquids and small for strong liquids, although there are a number of exceptions, particularly when hydrogen bonding is present. [From (36)]

Fragility is important for processing

- i) V(T) continuous at T_g
- ii) $\alpha(T)$ discontinuous at T_g
- iii) $C_P(T)$ discontinuous at T_g
- iv) T_q is cooling rate dependent
- v) Viscosity, η , obeys VFT
- vi) Strong-fragile classification

$$\eta = \eta_0 \exp\left(\frac{DI_0}{T - T_0}\right)$$

D ⇒ ∞ Arrhenius behavior all materials extrapolate to η ≈10⁻⁴ Poise at T-> ∞



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i) V(T) - continuous at T_g ii) $\alpha(T)$ discontinuous at T_g iii) $C_P(T)$ - discontinuous at T_g iv) T_g is cooling rate dependent v) Viscosity, η , obeys VFT vi) Strong-fragile classification

A theory for the glass transition needs to explain all this!



Figure 1.1 The two general cooling paths by which an assembly of atoms can condense into the solid state. Route ① is the path to the crystalline state; route ② is the rapid-quench path to the amorphous solid state.

Crystallization is a 1:st order phase transition:

 $V = \left(\frac{\partial G}{\partial P}\right)_T$ is discontinuous

Glass transition:

 $C_P = T\left(\frac{\partial S}{\partial T}\right)_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)$ is discontinuous

- ⇒ 2:nd order thermodynamic phase transition, but...
- i) T_g cooling rate dependent \Rightarrow kinetic effects
- i) Non-equilibrium conditions



Figure 1.8 The specific heat of the crystalline, amorphous, and liquid forms of As_2S_3 , a covalent material which is a prototypical glass former (after Blachnik and Hoppe, 1979).

Entropy:

$$C_P = T \left(\frac{\partial S}{\partial T}\right)_P$$

Excess entropy in super-cooled liquid compared to crystal:

 $\Delta S = S_{scl} - S_c$



Figure 1.10 The excess entropy of a glass-forming liquid in the region between T_f and T_g , showing the extrapolation to zero excess entropy at a temperature near T_g (Angell and Sichina, 1976).

Extrapolated part of the Δ S-curve can in theory be accessed by a slower cooling rate (kinetic effect).

Excess entropy in super-cooled liquid compared to crystal:

 $\Delta S(T) = S_{scl}(T) - S_c(T)$

Extrapolation gives $\Delta S=0$ at a finite temperature T_0

 ΔS <0 not physical

Entropy crisis or *Kauzmans paradox*



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Excess entropy in super-cooled liquid compared to crystal: $\Delta S(T)=S_{scl}(T)-S_c(T)$

Extrapolation gives $\Delta S=0$ at a finite temperature T_0

i) A phase-transition is expected around T_0

ii)
$$T_0$$
 very close to VFT- T_0
 $\eta = \eta_0 \exp\left(\frac{DT_0}{T - T_0}\right)$

 \Rightarrow T₀ an ideal T_g? Is there kinetically masked thermodynamic phase transition?

Glass transition theories

- Free volume theory (Cohen & Turnbull ≈1960)
- Configurational entropy theory (Adam & Gibbs 1965)
- Mode-coupling theory (Sjögren, Sjölander et al ≈1985)
 Purely dynamic transition controlled by kinetics
- Jamming (Liu & Nagel ≈1998) Unifying glass, gels, colloids and granular materials

Free volume theory



 $\frac{v_f}{v} = f_g + \alpha (T - T_g),$

 v_f and v free and total volume α thermal expansion f_g fractional free volume at T_g

$$\eta = a \exp\left(b\frac{v_f}{v}\right)$$

- Molecular transport made possible by *free volume*, v_f, in the liquid
- Slowing down of dynamics due to decrease in free volume
- VFT can be recovered
- Works well for many van der Waals liquids
 - ... but P-T experiments show a glass transition also under constant *v*_f

Configurational entropy model



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In glass - *S(T) - vibrational contributon*

At T_g : Increase in configurational entropy - $S_{conf}(T)$, i.e. number of accesible configurations increases

Configurations explored by cooperative rearranging regions

Configurational entropy model



Fig. 2.13 The idea of cooperativity in diffusive motion of a molecule in a glass-forming liquid. At high temperatures and low densities (top) a molecule is able to jump to a new position without the necessity for wholesale rearrangement of its neighbours. At lower temperatures and higher densities (bottom), in order for one molecule to be able to make a move (left), some of its neighbours (shown shaded) must move cooperatively to make room (right).

$$\tau^{-1} \propto \upsilon \exp\left(-\frac{z^* \Delta \mu}{kT}\right)$$

 z^* - number of molecules that move $\Delta \mu$ - energy barrier for single molecule movement

Non-arrhenius dependence of τ^1 due to temperature dependence of z^* size of cooperative regions increases with decreasing T, divergence around T_0 (VFT).

...but, the size of the regions is small at T_g and $\tau \approx 10^3$ s and what is the microscopic process?



Fig. 2.8 (a) Instantaneous response of a liquid to an applied stress; the positions of the atoms are distorted without their relative arrangement changing. (b) Relaxation of stress in a strained liquid by the thermally excited escape of an atom (shaded dark) from the 'cage' imposed by neighbouring atoms to another site (shaded light).

Decoupling of vibrational and configurational relaxation times in the super-cooled liquid



Figure 6. Separation of relaxation rates of diffusive $(1/\tau_s)$ and vibrational $(1/\tau_{vib})$ degrees of freedom (schematic).



Fig. 2.8 (a) Instantaneous response of a liquid to an applied stress; the positions of the atoms are distorted without their relative arrangement changing. (b) Relaxation of stress in a strained liquid by the thermally excited escape of an atom (shaded dark) from the 'cage' imposed by neighbouring atoms to another site (shaded light).

In simple liquid the response function to an applied stress is exponential:

$$\phi(t) \propto \exp\left(-\frac{t}{\tau}\right)$$

In super-cooled liquid relaxation functions are non-exponential:

$$\phi(t) \propto \exp\left(-\frac{t}{\tau}\right)^{\beta}$$
, $\beta = 0 - 1$

stretched exponential or Kolrausch-Williams-Watts (KWW) function



Origin of stretched exponential relaxations:

$$\phi(t) \propto \exp\left(-\frac{t}{\tau}\right)^{\beta}$$
, $\beta = 0 - 1$

i) Homogenous scenario:

Stretched behaviour intrinsic due to correlated or cooperative motions, hierarchical processes

i) Heterogenous scenario:

Distribution of environments - summation of exponentials



Fig. 7. The different types of molecular motions in a liquid and a glass(36). The data are for 17.2 mole% chlorobenzene-cis-decalin solution. In addition to the vibrational modes, there are two types of molecular processes, known as secondary and main relaxations. T_g is the glass transition temperature.

Secondary relaxations, β :

- Fast process decouples from the structural relaxation close to T_{g}
- Persist in the glassy state
- Local molecular motion (non-diffusive)
- Important for energy dissipation in glasses, e.g. strength of *plexiglass*



Relaxation processes in glasses & glass forming liquids span an enormous time range:

10⁻¹²-10³ s (or THz-mHz)

 \Rightarrow experimentally demanding!

