# 1) Introduction to glasses
# 2) Molecular Dynamics

Walter Kob

Université Montpellier
France

DPG Physics School on Computational Physics of Complex and Desirderod Systems

Bad Honnef

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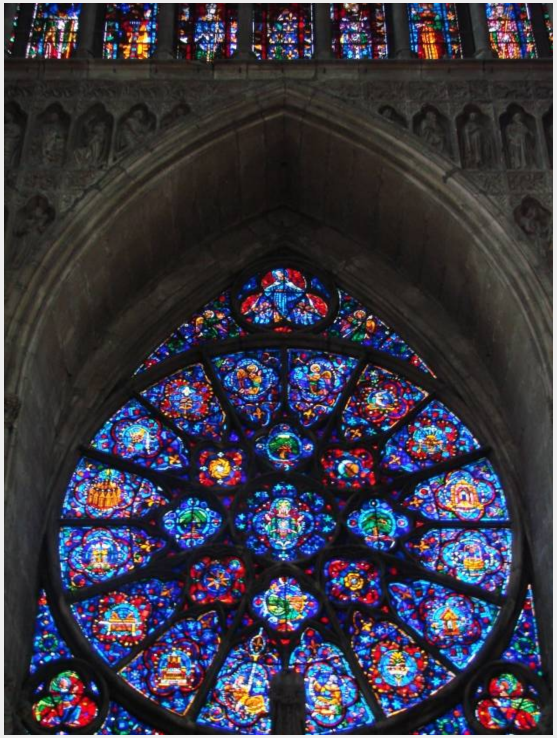
# Part 1: Introduction to glassy systems

- History
- Phenomenology of glassy systems

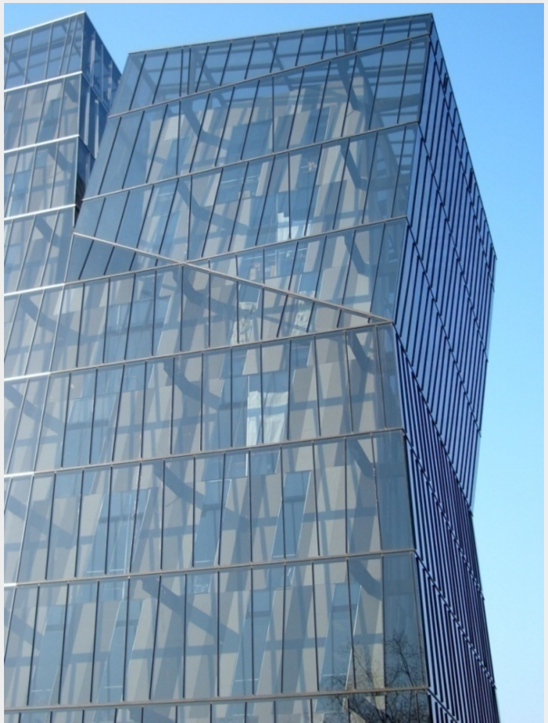
- mainly experimental results

- Nomenclature (often ill-chosen)

# What are glasses?

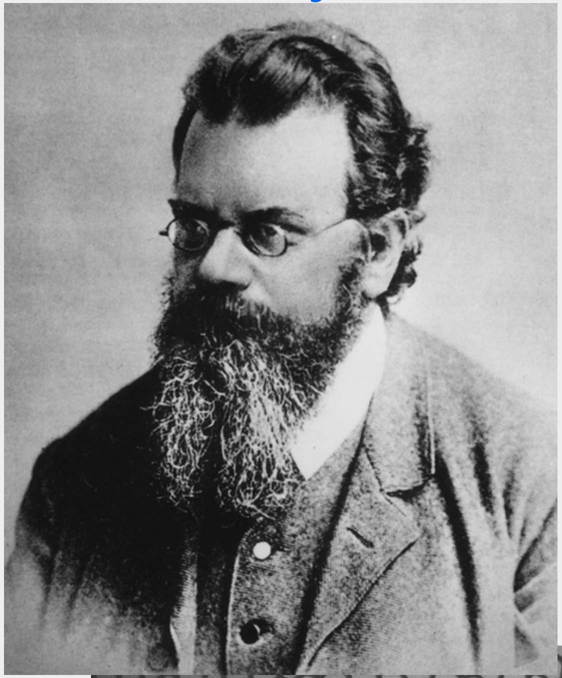


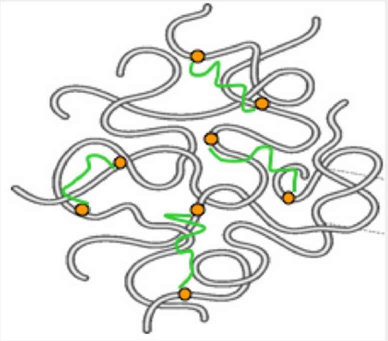
- windows
- mirrors
- vases/containers
- decorative art
- optical fibers
- buildings

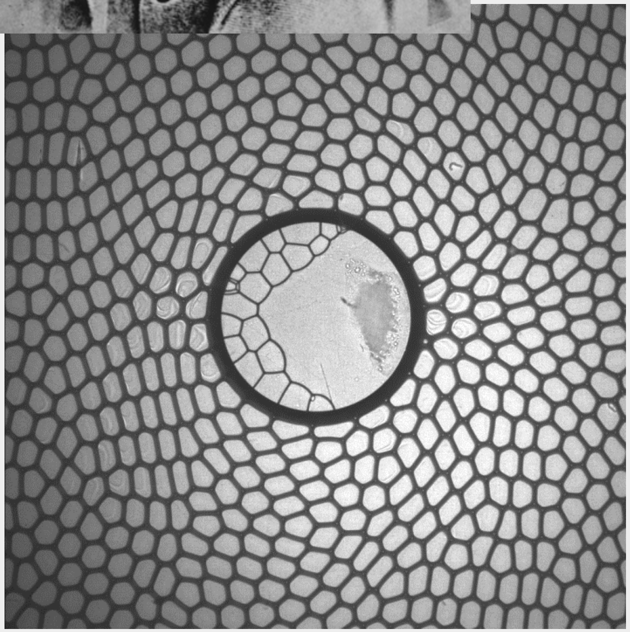


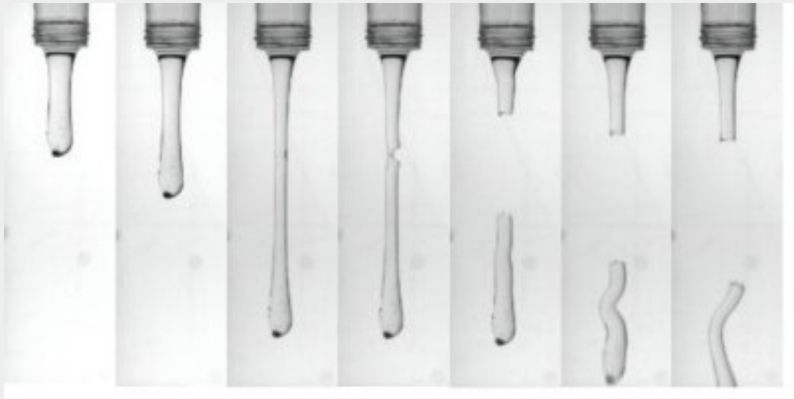
# But also other structurally disordered systems

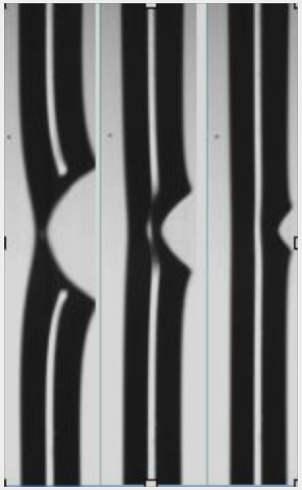
- gels: food, cosmetics, ...
- polymers: plastics, rubber,...
- granular materials: sand, powders,...
- complex fluids: shampoo, paint,...
- foams
- complex proteins









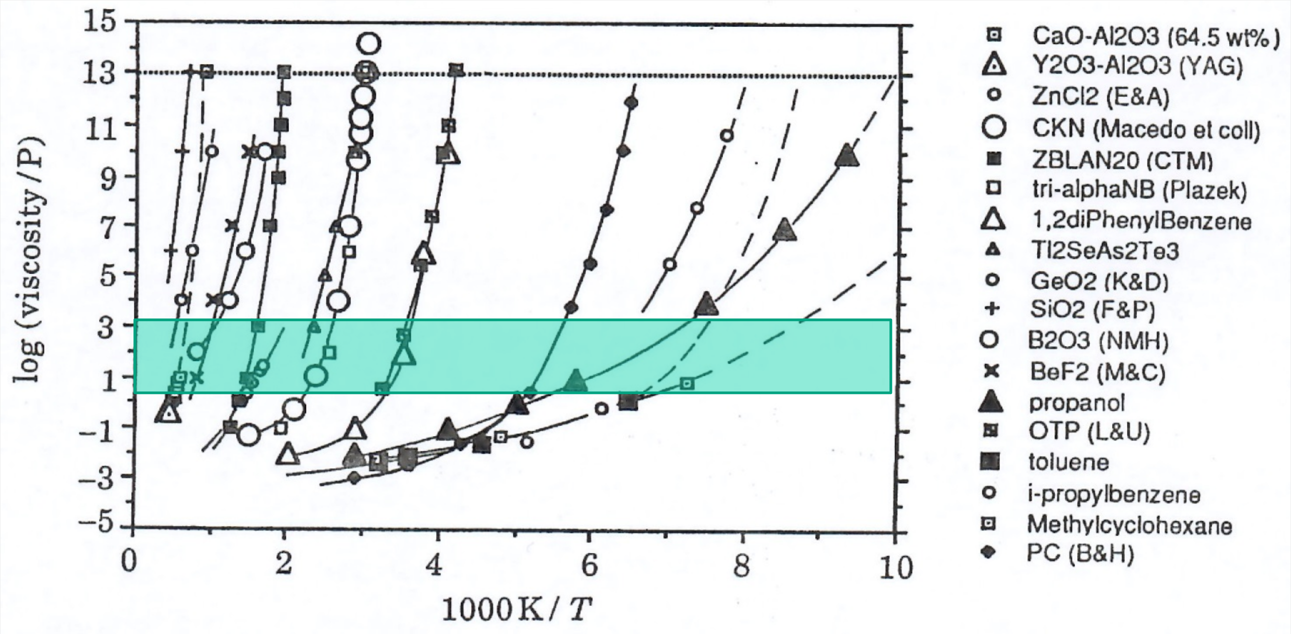


# Supercooled liquids

- Most liquids crystallize if they are cooled below their melting temperature $T_m$
- But some liquids stay in a (metastable) liquid phase even well below $T_m$

⇒ one can study their properties in the supercooled state

- Consider, e.g., the T-dependence of the viscosity $\eta$




- Strong increase of $\eta$ with decreasing T
- Similar results for relaxation times
- NB: slow dynamics has nothing to do with supercooled!!!!

"Supercooled liquids" ⇒ "glassy liquids"

# Strong and fragile glass-formers

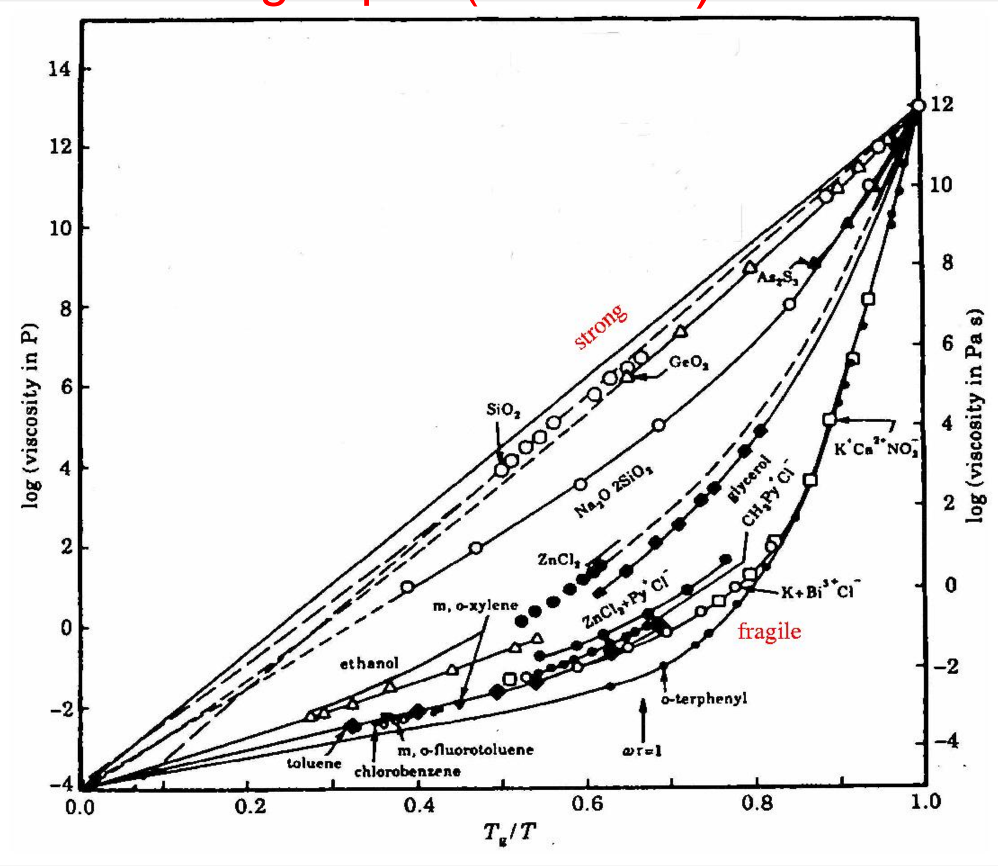
Use the viscosity $\eta$ to define a glass transition temp. $T_g$: $\eta(T_g) = 10^{13}$ Poise

N.B. the value $10^{13}$ Poise is almost completely arbitrary; it was chosen such that the typical relaxation time of the system is on the order of 100 seconds

$\eta = 10^{13}$ Poise $\Leftrightarrow$ very slow flow (a person sinks in by 10cm/year!!)

- make a reduced Arrhenius plot $\log(\eta)$ vs $T_g/T$

Angell-plot (Uhlmann)




- Rescaling did not lead to a master curve $\Rightarrow$ T-dependence is not universal (??)

$\Rightarrow$ **"strong" and "fragile" glass-formers**

**Questions:**

- What is the mechanism for the slowing down?
- Is there one universal mechanism or are there several ones?
- What is the difference between strong and fragile systems?

# More questions

- What is the T-dependence of $\eta$?

Empirically one often (!!!) finds the following dependencies:

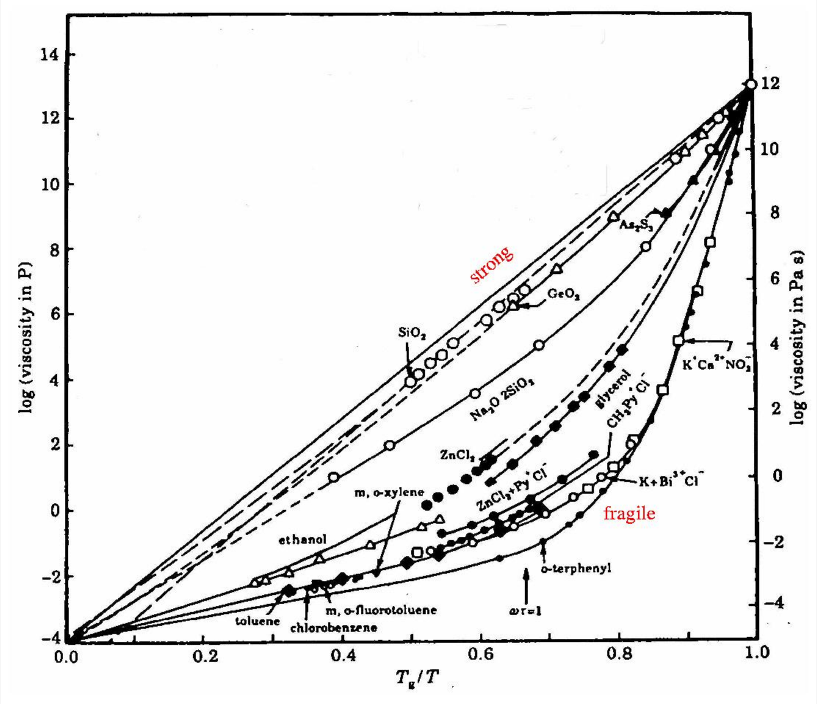
-high T: Arrhenius-law

- intermediate and low T:

  Vogel-Fulcher (-Tammann)- law:

  $$\eta(T) = \eta_0 \exp( A/(T-T_0) )$$

  with the “Vogel temperature” $T_0$




-Sometimes one also finds at low T a cross-over to a different Vogel-Fulcher law (different A and $T_0$)

- Sometimes the low T data is fitted well by the Bässler-law

  $$\eta(T) = \eta_0 \exp( A/T^2 )$$

- Many (>10) other functional forms have been proposed

- Is there a divergence of the relaxation times at a finite T?

Experiments are not able to tell because the glass transition intervenes

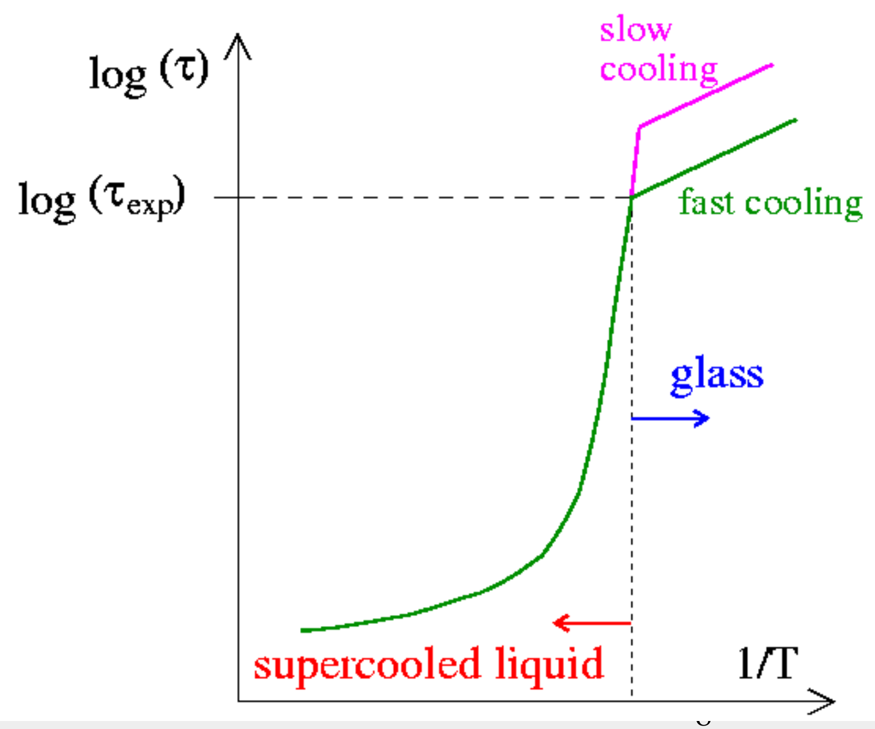
# The glass transition

- If in an experiment (or simulation) one wants to investigate the properties of a system at a given T one first has to bring the system to this temperature (by coupling it to a heat bath)

- If one wants to study the equilibrium dynamics one will have to allow the system to equilibrate and *usually* this takes a time that is comparable with the relaxation time $\tau$ of the system, N.B. $\tau \propto \eta$

- Due to the strong increase of $\tau$ with decreasing T there will exist a temp. T at which the system falls out of equilibrium (because we don't have enough patience) and forms a glass

  ⇒ **the system undergoes a glass transition**

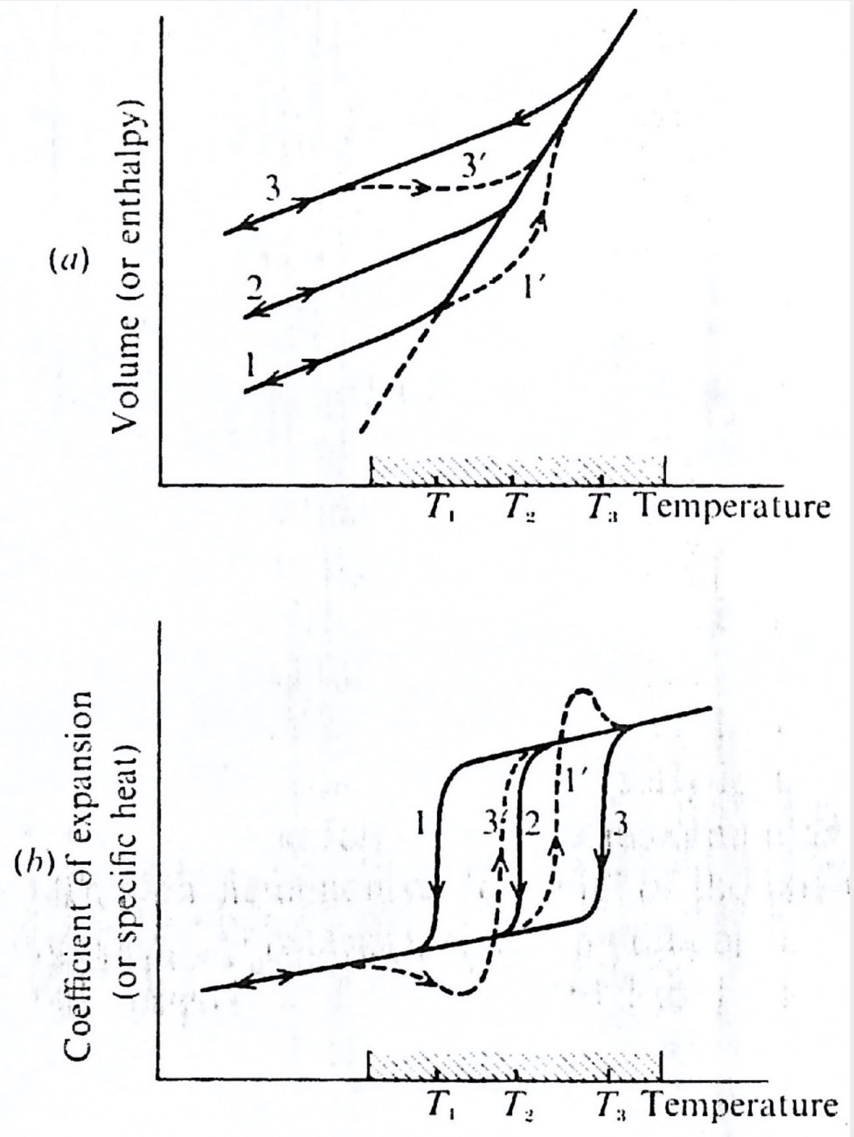



N.B.: 1) the existence of ***this*** glass transition is trivial!

2) the temperature of this transition depends on $\tau_{exp}$, i.e. the experiment (and observable)

# Cooling rate dependence of $T_g$

To generate a glass one has to cool a liquid to low temperatures until it falls out of equilibrium




- The larger the cooling rate the higher is the glass transition temperature

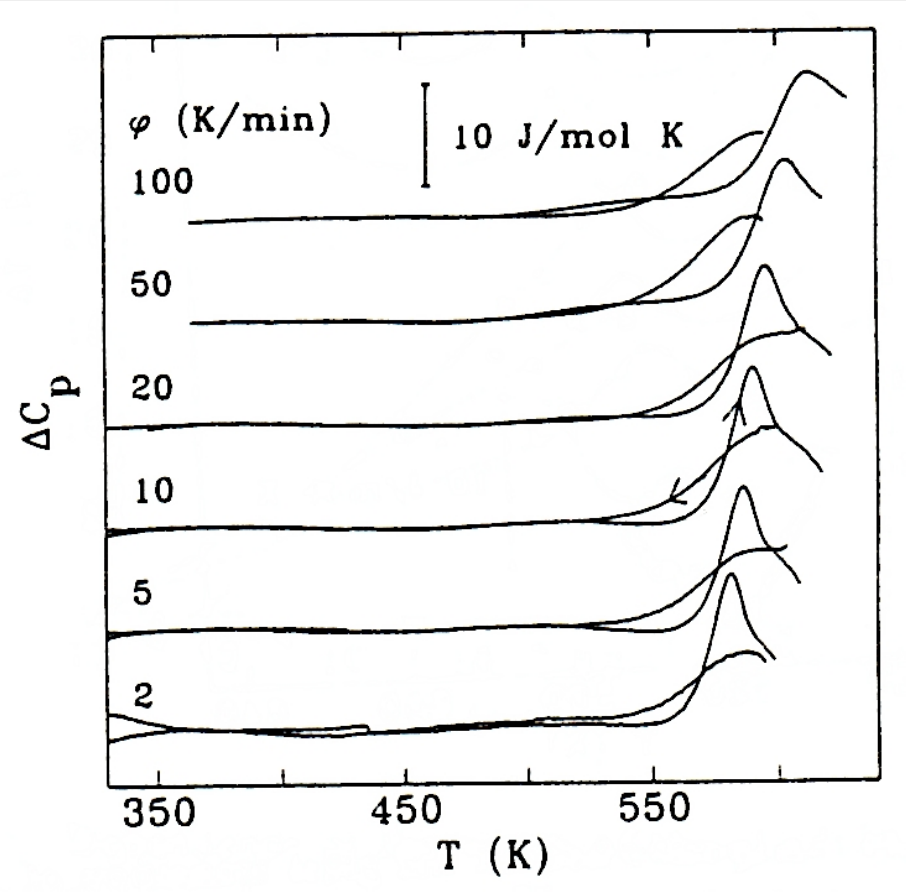
- Upon reheating we find aging effects that are most pronounced close to the glass transition temperature

- These effects are even more pronounced in the derivatives

NB: All these effects are easily understood by recalling that the glass transition and the resulting glass depends on the cooling rate

# Cooling rate dependence of $T_g$: 2

- Cooling rate effects in real experiments




- Dependence of specific heat on cooling rate in $Pd_{40}Ni_{40}P_{19}Si_1$

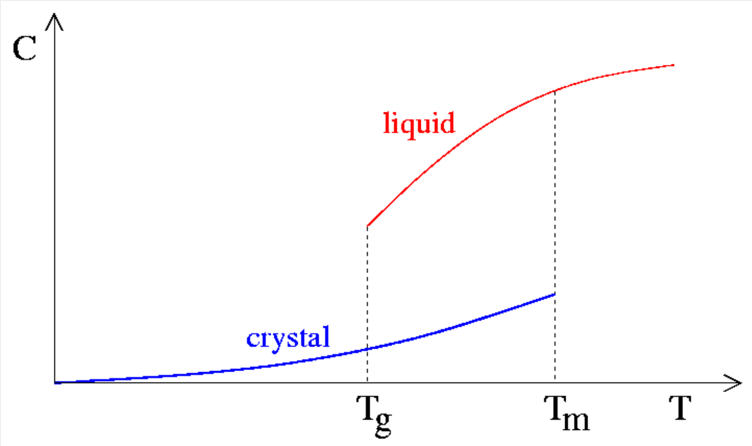
(heating rate = cooling rate)

Brüning and Samwer PRB **46**, 11318 (1992)

NB: In order to see a change in $T_g$ one needs a *large* change in cooling rate since
i) the relaxation time $\tau(T)$ is a very strong function of T and
ii) $\tau(T_g) \propto \varphi^{-1}$

# The Kauzmann temperature

- Typical T-dependence of the specific heat




- For all liquids the specific heat is higher than the one of the corresponding crystal:
  Reason: in a supercooled liquid there are not only vibrational excitations but also translational degrees of freedom
- In the glass c(T) is similar to the one of the corresponding crystal (vibrational excitations are quite similar)

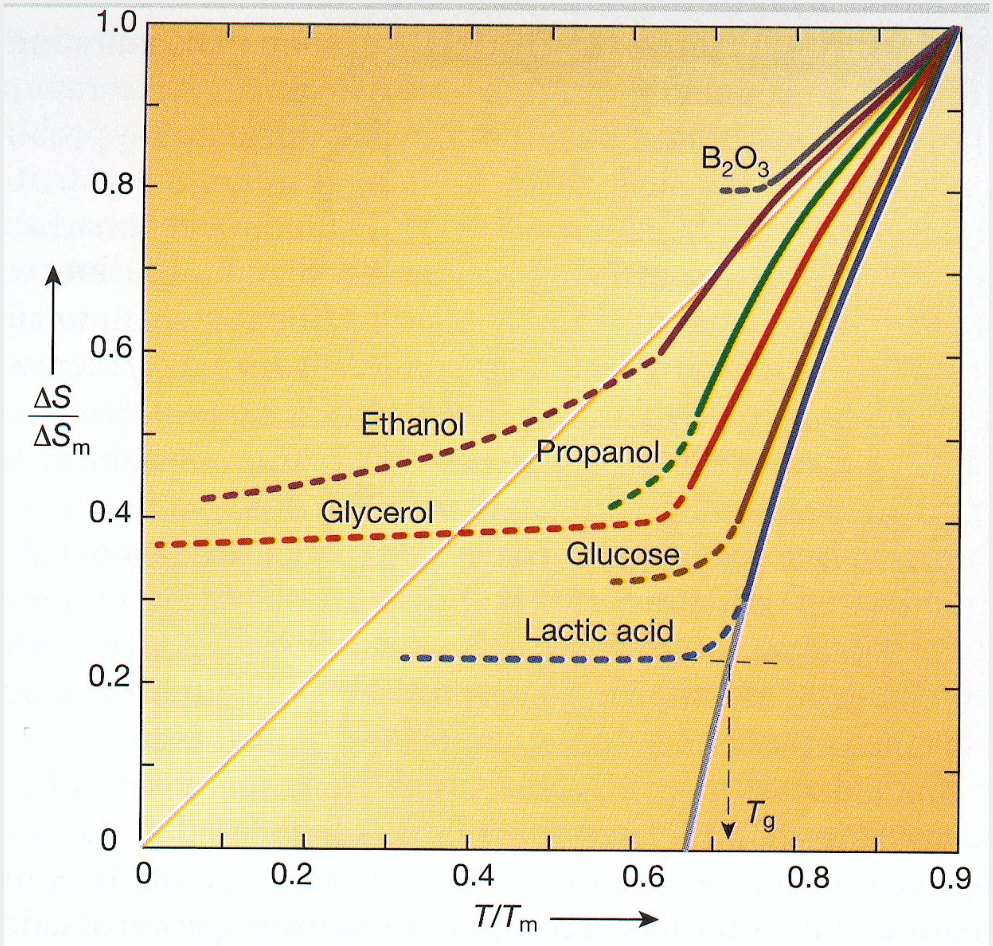
- Kauzmann (1948) used the temperature dependence of the specific heat to calculate the entropy of the system for $T < T_m$

$$s_\alpha(T_m) = s_\alpha(T) + \int_T^{T_m} \frac{c_\alpha}{T} dT \quad \alpha \in \{\text{liquid, crystal}\}$$

- Since $c_{liquid} > c_{crystal}$ the entropy of the liquid decreases faster (with decreasing T) than the one of the crystal

# The Kauzmann temperature: 2

- Calculate the difference $\Delta s(T) = s_{liquid} - s_{crystal}$ and normalize it by $\Delta s_m$, its value at the melting temperature




- Solid lines: equilibrium data
  dashed lines: data in the glass
- Above $T_g$ difference depends strongly on T and a reasonable extrapolation seems to predict that $\Delta s(T)$ vanishes at a temperature $T_K$, the Kauzmann temperature
- Implication: below $T_K$ the entropy of the liquid is smaller than the one of the crystal! ⇒ "Kauzmann paradox"

⇒ Boltzmann: $s = k_B \log(\Omega)$ ⇒ $s=0 \Leftrightarrow \Omega = 1$ ⇒ below $T_K$ there is only **one** (ideal!) glass state

# Glass transition temperatures

So far we have three glass transition temperatures:

- $T_g$ from $\eta(T_g) = 10^{13}$ Poise
  is an intrinsic (= equilibrium) temperature but arbitrary
- $T_{kinetic}$ from falling out of equilibrium
  depends on experiment (cooling rate, ...) but is important to characterize the glass; attempts to make this more systematic: Tool, Narayaswamy, Moynihan, … "fictive temperature"
- $T_K$ from the extrapolation of the entropy (Kauzmann temperature)
  is an intrinsic temperature but can be obtained only by extrapolations (see later)

Other important ones:

- Onset temperature $T_0$ : Temperature at which the system starts to become sluggish (see later)
- $T_c$ critical temperature of mode-coupling theory (intrinsic temperature at which the mechanism for the relaxation dynamics changes )

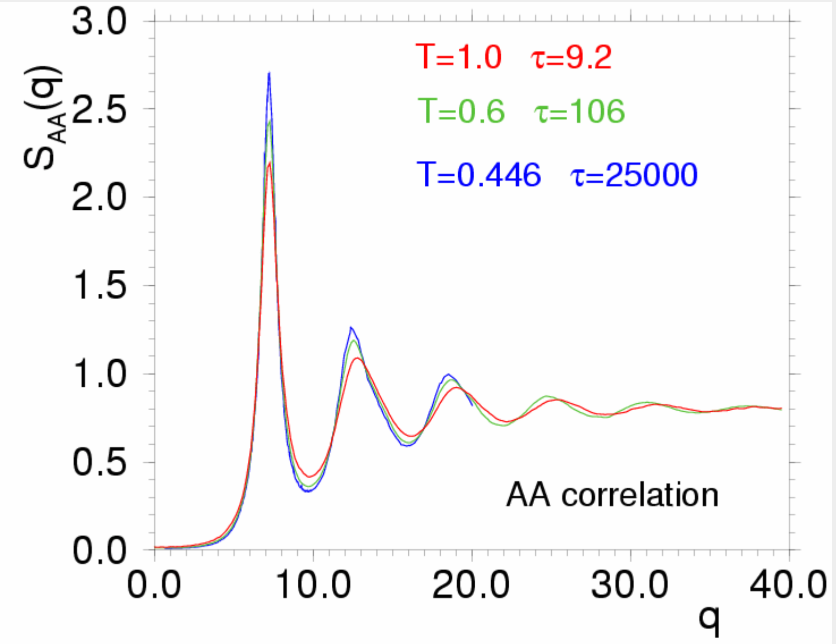
# And static quantities?

So far we have considered only dynamic quantities; do static quantities also show a strong T-dependence?

Look, e.g. at the static structure factor S(q):

$$S(q) = N^{-1} \sum_k \sum_j \langle \exp(i\, \mathbf{q} \cdot (\mathbf{r}_k - \mathbf{r}_j)) \rangle$$

S(q) can be measured in light or neutron scattering experiments




- Compared with the dynamic quantities, S(q) shows only a very weak T-dependence
- Similar results for *most* other static quantities that have been investigated so far (however, spin glasses show a divergent length scale, and since recent times also structural glasses show a pronounced T-dependence in certain static observables!)

# Time dependent correlation functions

So far: T-dependence of macroscopic quantities; what is the dynamics of the system on the microscopic level? $\Rightarrow$ study time correlation functions

- consider an observable A(t) [density at a given point in space, magnetization, velocity of particle #351, …] and an observable B(t)

- calculate the time correlation function

$$\phi_{AB}(t, t') = \langle A(t)\, B(t') \rangle$$

where $\langle \ldots \rangle$ is the canonical average

In equilibrium we have time translation invariance and hence:

$$\phi_{AB}(t, t') = \langle A(t)\, B(t') \rangle = \langle A(t-t')\, B(0) \rangle = \phi_{AB}(t-t')$$

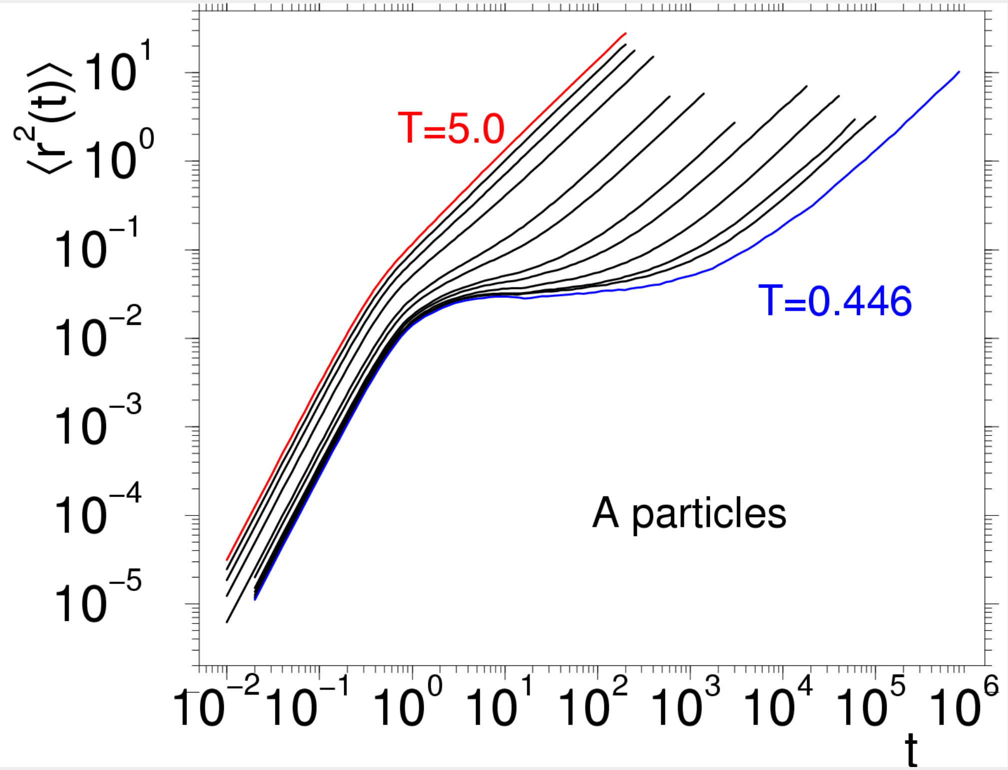
special case: A = B: $\Rightarrow$ autocorrelation function of observable A

# Time dependent correlation functions 2

- Mean squared displacement is defined as

$$\langle r^2(t)\rangle = \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2\rangle$$

## T- and t-dependence of MSD in a L-J system

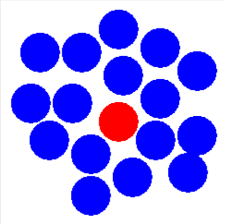



- short t: ballistic regime

$$r_i(t)=r_i(0)+v_i(0)t+\ldots$$

$$\Rightarrow \langle r^2(t)\rangle \propto t^2$$

- long t: diffusive regime $\langle r^2(t)\rangle \propto t$
- intermediate times at low T: cage effect

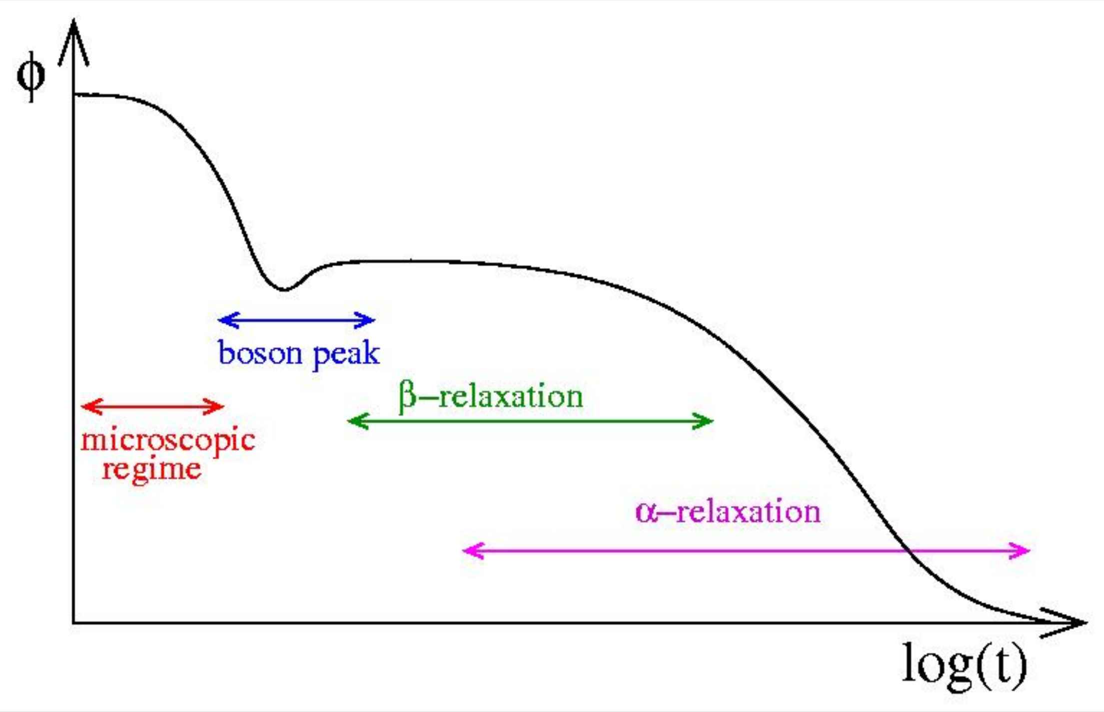


- with decreasing T the dynamics slows down quickly since the length of the plateau increases; ⇒ in order to understand the slowing down one must understand the breaking up of the cage

# Time dependent correlation functions 3

What is the typical time dependence of a correlation function for a system with glassy dynamics?

N.B.: We are interested in **glass-forming systems**. Therefore we **need a logarithmic time axis**.




Various regimes

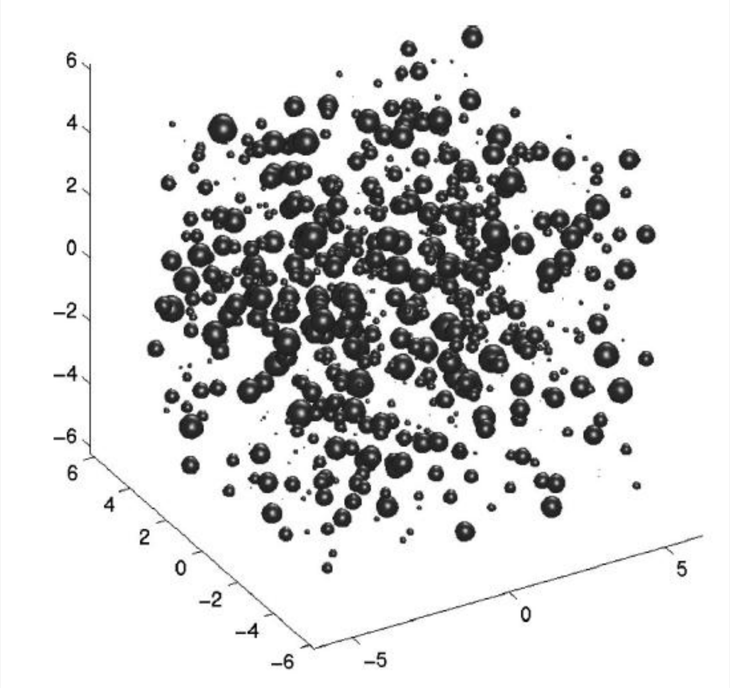
- microscopic regime
  short times; ballistic motion; vibrations
- boson peak
  low frequency vibrations
- $\beta$-relaxation regime
  intermediate times; correlator depends only weakly on time (cage effect)
- $\alpha$-relaxation regime
  long times; correlator decays to zero in a non-exponential way (=particles leave cage)

Kohlrausch-Williams-Watts function: $\phi(t) = A \exp(-(t/\tau)^{\beta})$ with $\beta \leq 1$

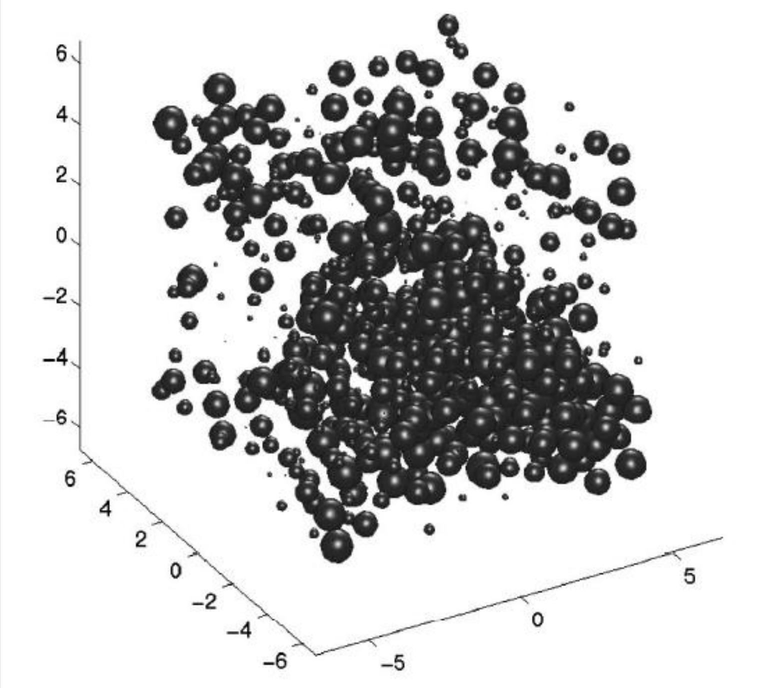
# Origin of stretched exponential $\phi(t) = A \exp(-(t/\tau)^{\beta})$ with $\beta \leq 1$

Dynamical heterogeneities: Become very prominent if the temperature is lowered; size of dynamically correlated regions increases

Example: Particles in a binary Lennard-Jones mixture that relax on intermediate time scales faster than average (Berthier 2004)



High T



Low T

$\Rightarrow$ growing *dynamical* length scale

# Correlation functions in the frequency domain

- Many experimental techniques do not give information in the time domain but only in the frequency domain (spectroscopy)

$\Rightarrow$ what one measures is $\phi'(\omega)$ and $\phi''(\omega)$, the real and imaginary part of the time-Fourier transform of a time correlation function $\phi(t)$

or

$\chi'(\omega)$ and $\chi''(\omega)$, the real and imaginary part of the dynamic susceptibility

- important connection between $\phi''(\omega)$ and $\chi''(\omega)$ (valid for systems in equilibrium!):

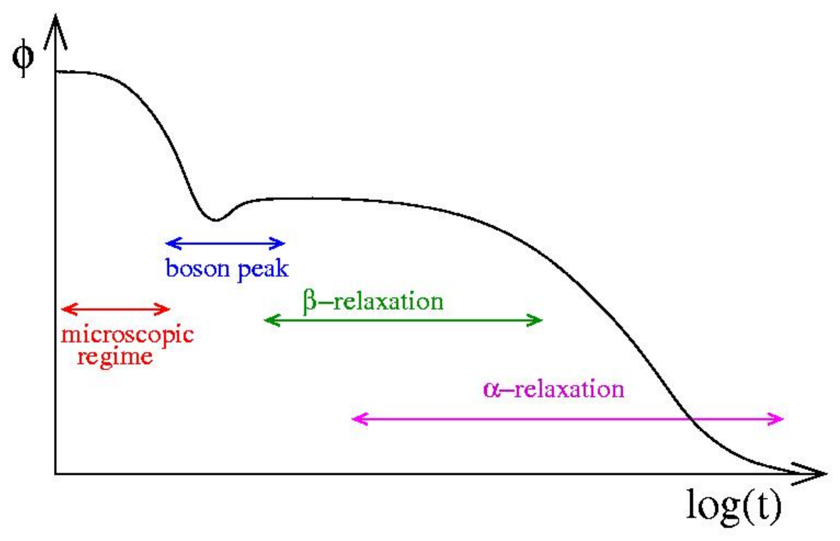
$$\chi''(\omega) = \phi''(\omega)\, \omega/(k_B T)$$

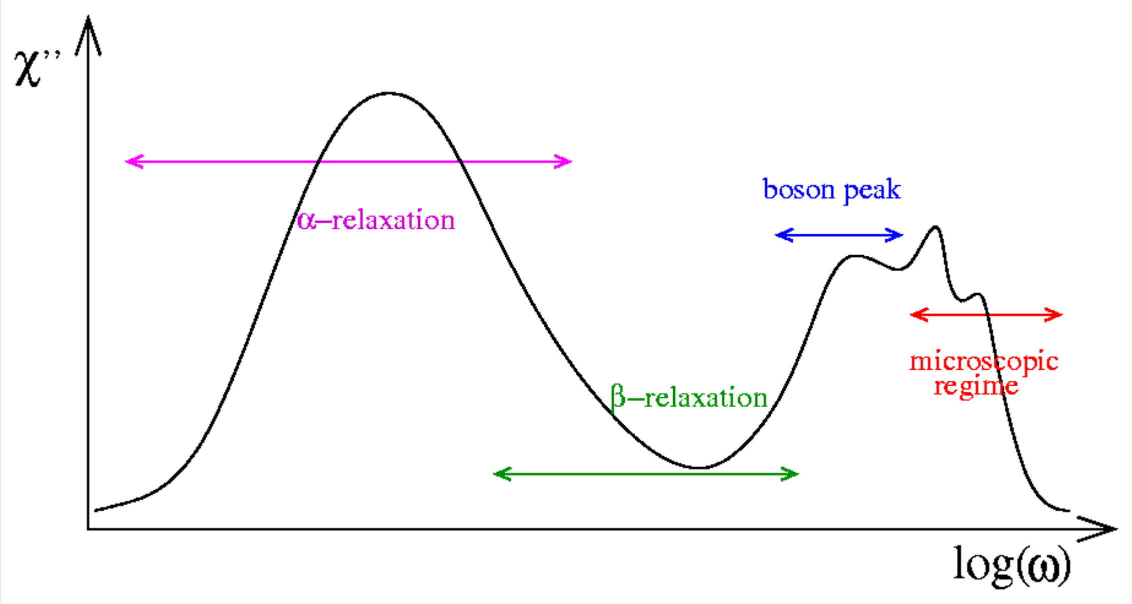
# Correlation functions in the frequency domain 2

- $\phi''(\omega)$: imaginary part of the time-Fourier transform of a time correlation function

  $\chi''(\omega)$: imaginary part of the dynamic susceptibility

$$\chi''(\omega) = \phi''(\omega)\, \omega/(k_B T)$$

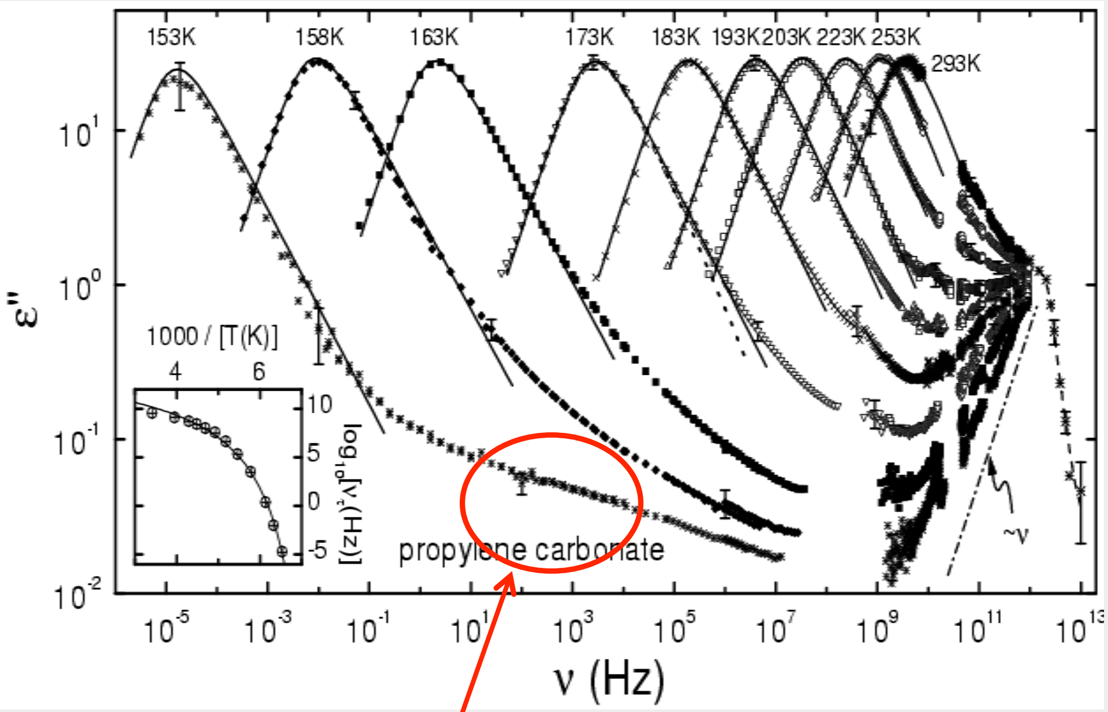



- various peaks correspond to the different processes seen in the time domain

# Correlation functions in the frequency domain 3: Real data

- One of the best techniques to probe the system in a large frequency and temperature range is dielectric measurements

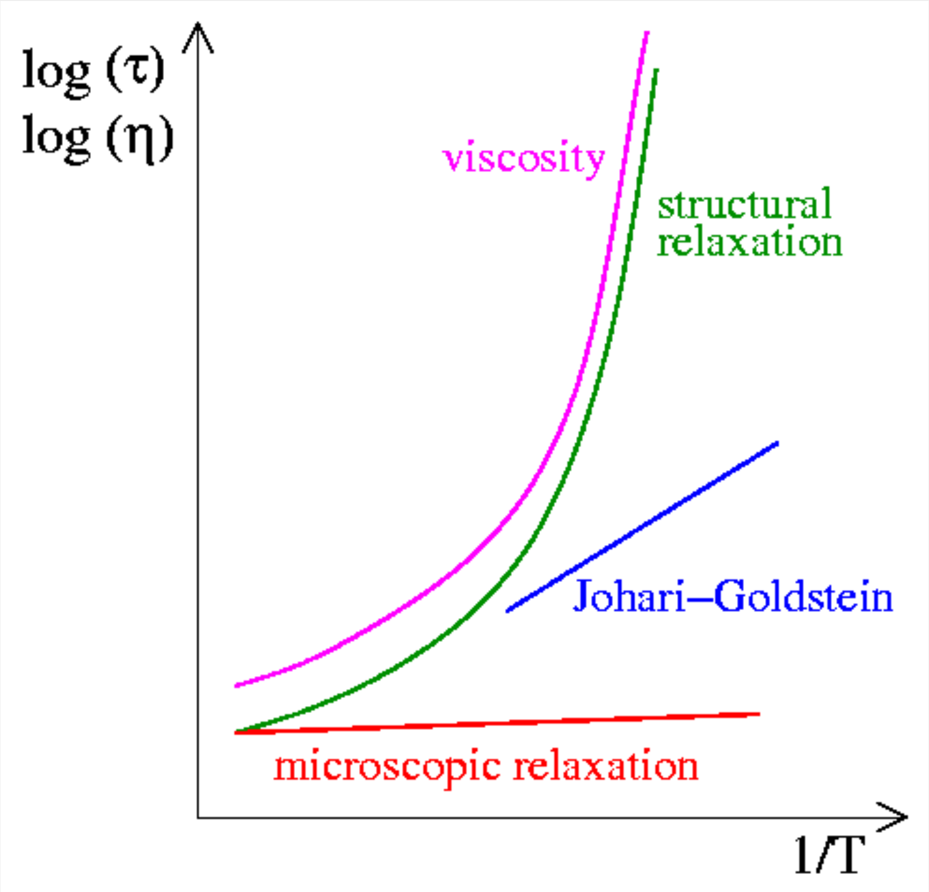



Lunkenheimer *et al.* (2001)

- Problem: what exactly is measured??

Johari-Goldstein peak

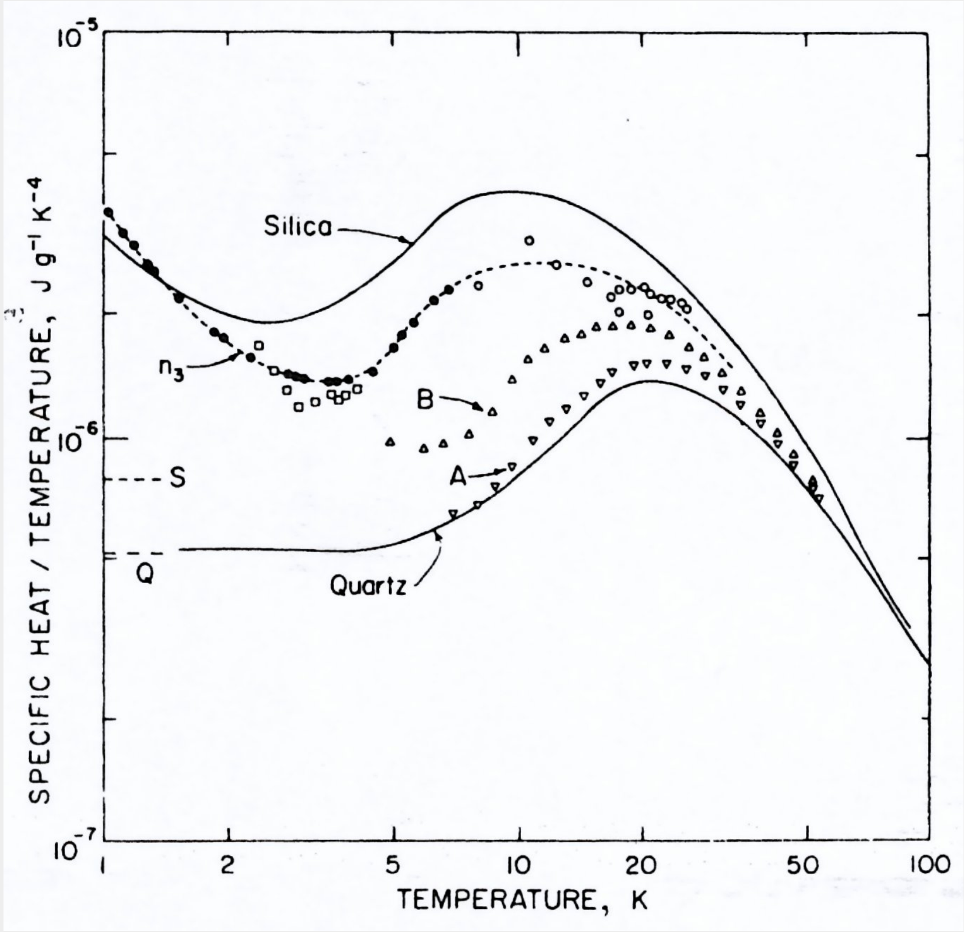
# T-dependence of characteristic times




- viscosity and microscopic relaxation times
  - strong T-dependence
  - unclear whether or not they have the same T-dependence
- microscopic relaxation
  - weak T dependence ( $\propto T^{-0.5}$)
- Johari-Goldstein peak
  - Arrhenius law
- Conductivity: often Arrhenius

# Properties of the glass

- For a crystal the specific heat at low T is proportional to $T^3$ (Debye)
  ⇒ a plot of $C/T^3$ gives a plateau
  (N.B. peak at higher T stems from optical vibrations)




- In a glass there are three anomalies:

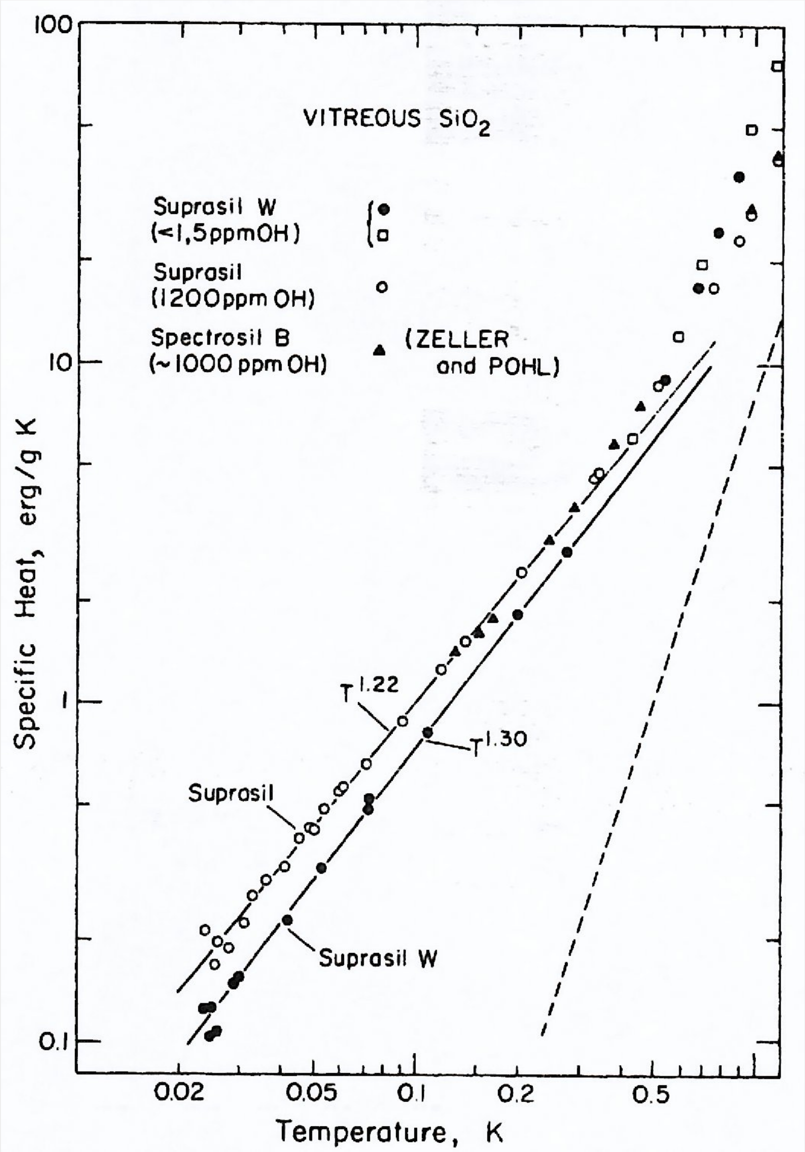
1) the specific heat is increased with respect to the one of the crystal

2) there is a peak at relatively low T
⇒ there exist excitations that are quite soft; nature of the excitations is not quite clear (Boson peak); intensity is correlated with fragility

3) at very low T there is a strong increase of C

# Specific heat at low T

- For a crystal the specific heat at low T is proportional to $T^3$

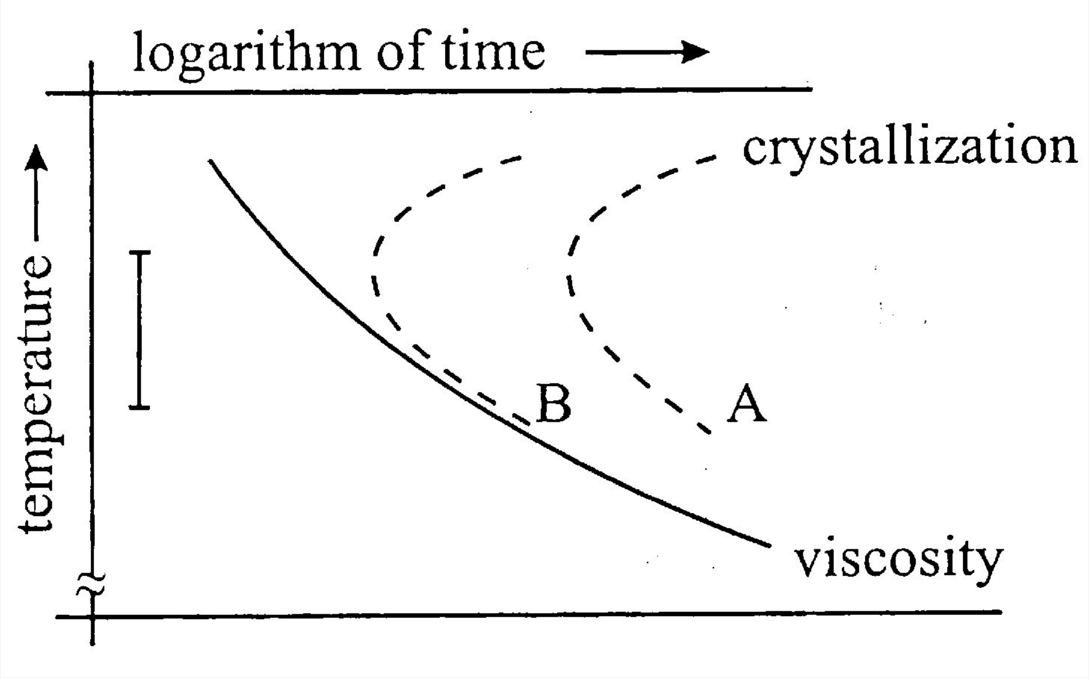



- In glasses C shows an increase $\propto T^{\alpha}$ with $0.8 < \alpha < 1.4$
- Phenomenological explanation: two-level systems, i. e. atoms/or a group of atoms that oscillate between two local minima; under certain assumptions on the distribution of the asymmetry and the barrier height one is able to reproduce the fractional power-law; the real mechanism is, however, not really known

N.B. the density of the TLS is estimated to be $\approx 10^{-6}$ per atom!

# But sometimes it happens…

- So far: ideal situation in which the liquid did not crystallize at all; but in reality most systems will crystallize sooner or later



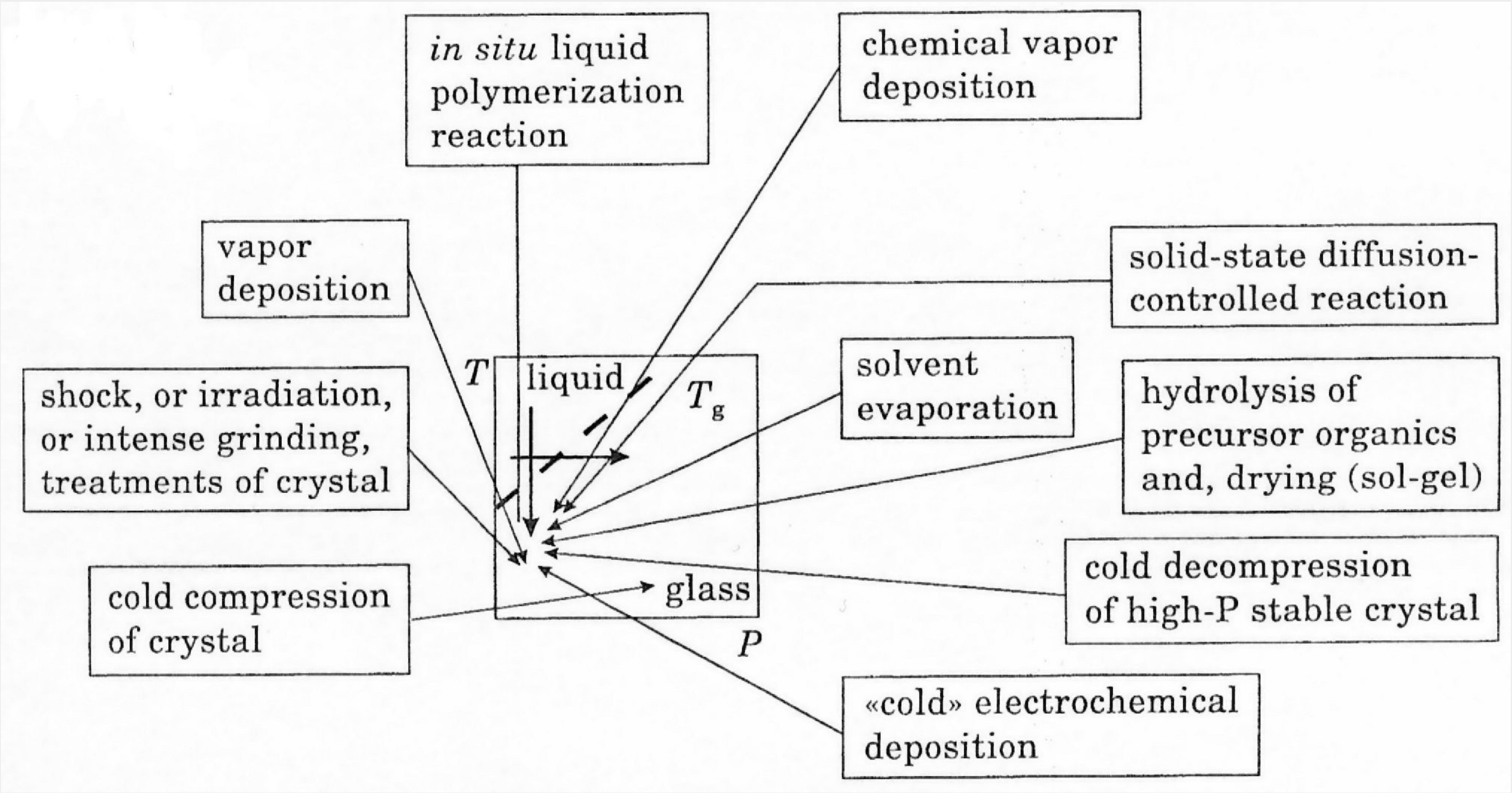

Time-Temperature-Transformation plot

- A bit below the melting temperature the system is stable for a very long time
- With decreasing T the driving force for crystallization increases
- With decreasing T the dynamics slows down and hence the critical nuclei cannot form or grow

⇒ there exists a dangerous T-range in which (sometimes) the liquid cannot be studied

# How to produce a glass?

- So far: the slowing down of the dynamics was due to a decrease of temperature; is this the only way to produce a glass?




N.B.: glasses obtained in different ways are usually not equivalent, even if their macroscopic properties (density, composition, temperature,…) are the same

⇒ **properties depend strongly on history**

# Frequent features of disordered materials

Glassy materials show many (but not necessarily all!) of the following features:

- strong slowing down of the dynamics upon a modest change of some external parameter (temperature, pressure, magnetic field,…)

- a transition to a non-ergodic phase

- no obvious presence of long range order

- stretching of time correlation functions

- some sort of frustration

- complex time dependence of correlation functions

- …

⇒ at low T these systems will show aging, i.e. their properties will depend on time

# Examples of glassy systems

- oxide glasses: windows, bottles, optical fibers,…
- polymers: plastic bags, spectacles, boxes, gels,…
- paint: colloidal particles in a solution of water, polymers, and more
- metallic glasses: $Ni_{24}Zr_{76}$ etc.: *thin* ribbons (few μm) because of large cooling rates ($10^6$ K/s); used in transformer cores because of good magnetic properties
  Since 1993: bulk metallic glasses Zr-Ti-Ni-Cu-Be alloys; cooling rates 1K/s; very good mechanical properties; used in high strength materials, golf clubs (see http:// www.liquidmetalgolf.com), etc.
- food: caramel, mayonnaise,…
- foams
- granular materials: sand, flour, …
- spin glasses: magnetic impurities in a noble metal, i.e. Au-0.5%Mn; $Eu_{1-x}Sr_xS$
- domain growth in a system with impurities
- biological systems: large proteins that have to fold; commissions; …
- abstract optimization problems: traveling salesman problem, k-sat problem, …
- …

# Various models/theories for the glass transition

- Continuous Random Network (Zachariasen)
- Adam-Gibbs (Adam, Gibbs)
- Excitation/defect mediated dynamics (Chandler, Garrahan)
- Ensembles of histories (Chandler)
- Free volume theory (Cohen, Turnbull, Grest)
- Frustrated domains/avoided criticality (Kivelson, Tarjus)
- Gibbs-DiMarzio theory (Gibbs, DiMarzio)
- Mode-coupling theory (comes in various flavors) (Götze, Sjögren)
- Random first order theory (Kirkpatrick,Thirumalai, Wolynes)
- Rigidity percolation (Philips, Thorpe)
- Shoving model (Dyre)
- Trap model (Bouchaud)
- ...

# Things I didn't mention

- Aging dynamics below $T_g$: Is very complex and not very well understood; can one introduce an effective temperature to describe this nonequilibrium state? (see L.F. Cugliandolo, Lecture Notes Les Houches 2003)
- Dynamical heterogeneities: how does the relaxation dynamics depend on the particle/region considered? (see R. Richert, J. Phys.: CM **14**, R703 (2002))
- Driven glassy systems: Driving a system (shearing, stirring,...) is similar to impose an external temperature to it; what are the resulting properties?
- Transport phenomena in disordered systems: Ion conducting glasses; mixed alkali effect; electrophoresis
- Fracture of glasses: Highly complex phenomenon due to the disorder and slow intrinsic time scales
- ...

# References

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- A. K. Varshneya, Fundamentals of Inorganic Glasses (Soc. Glass Tech., 2006)

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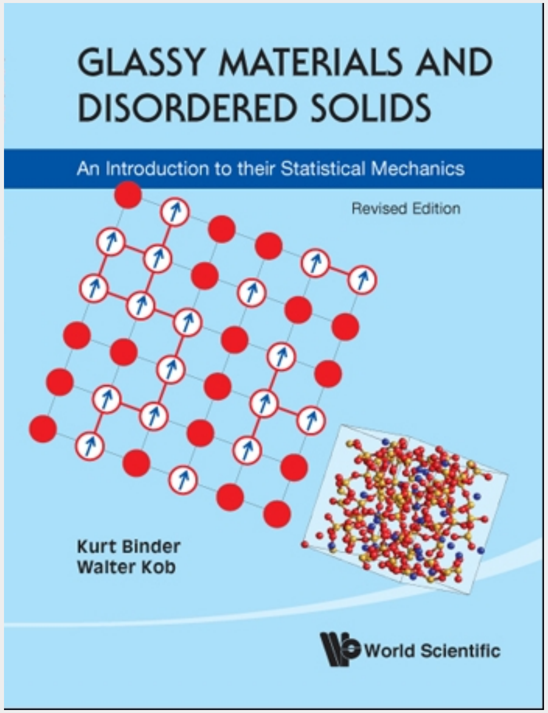


# A brief history of glass

- Prehistoric times: obsidian was used to make knives, arrow tips etc.

•Oldest man-made glasses date from 3000 BC (Mesopotamia); $Na_2O$-$CaO$-$SiO_2$; melting of sand and addition of sea plants

Egyptian perl, XII cent. BC

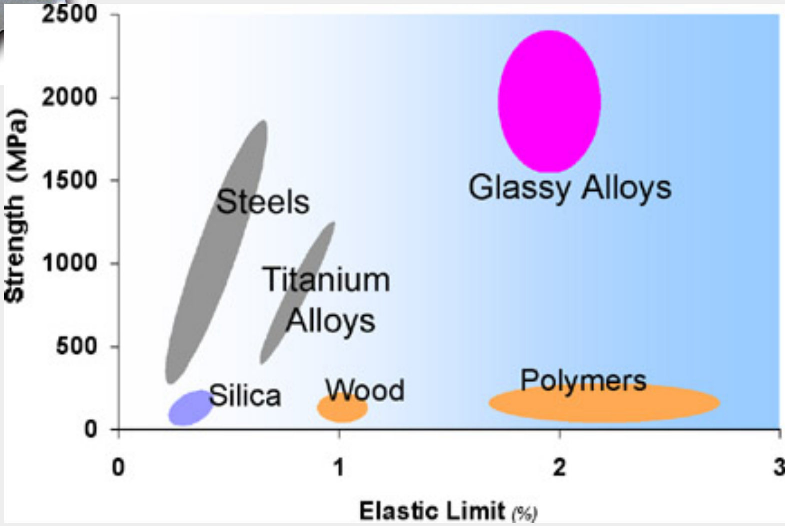
•Invention of glass blowing in Phoenicia (today Lebanon) around 50 BC

pitcher, Italy, 2 cent. AC

# History of glasses: cont.

- 17th century
  - large mirrors (Versailles)

- 20th century
  - float-glass
  - polymers
  - metallic glasses
  - spin glasses
  - foams
  - granular materials
  - colloidal systems
  - …

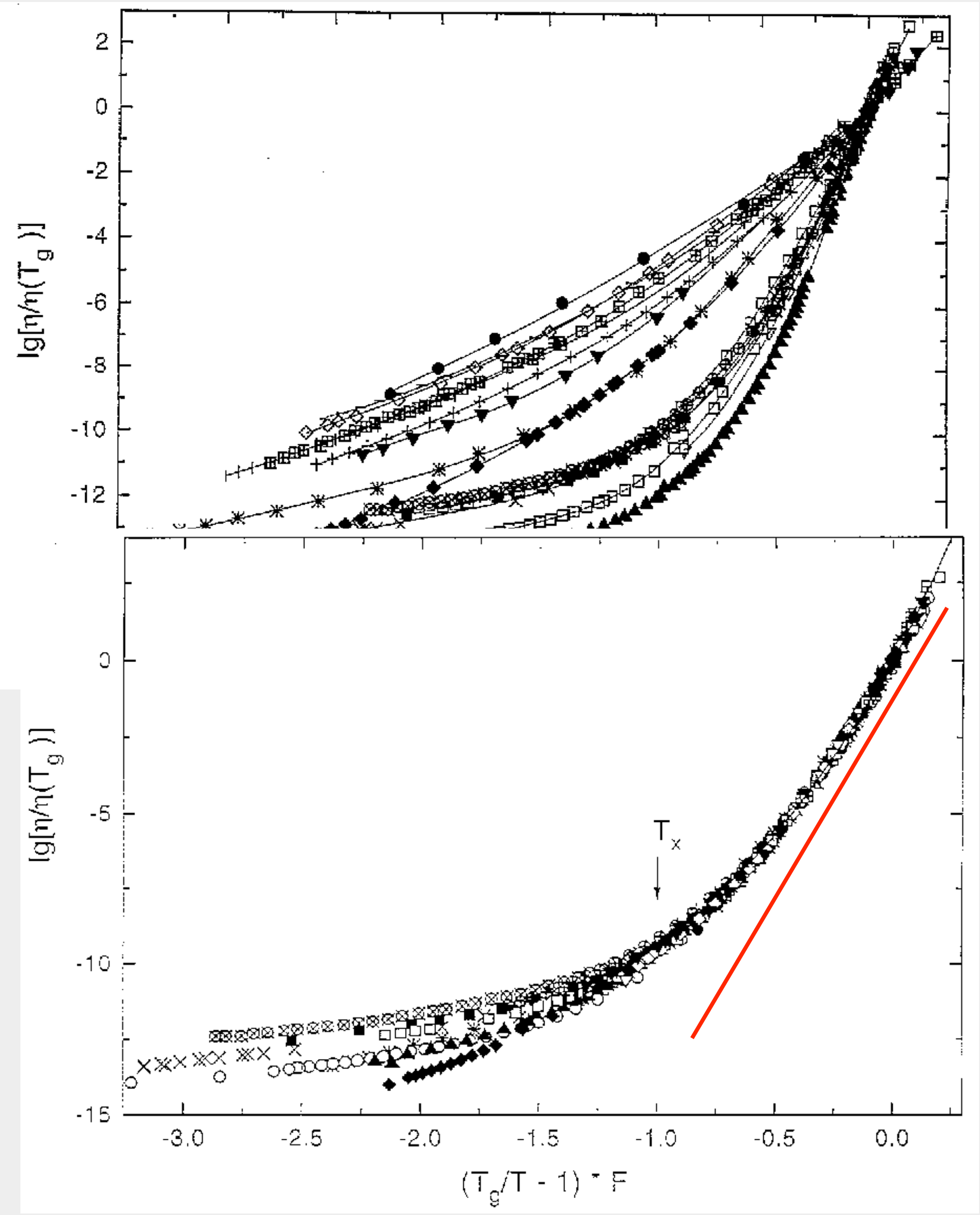



- All these materials have certain properties in common that are considered to be “typical“ for glassy systems

- To understand/define these properties we consider one important class of glass-forming systems: **liquids**

# Strong and fragile glass-formers?

- Is there really a fundamental difference between strong and fragile glass-formers?



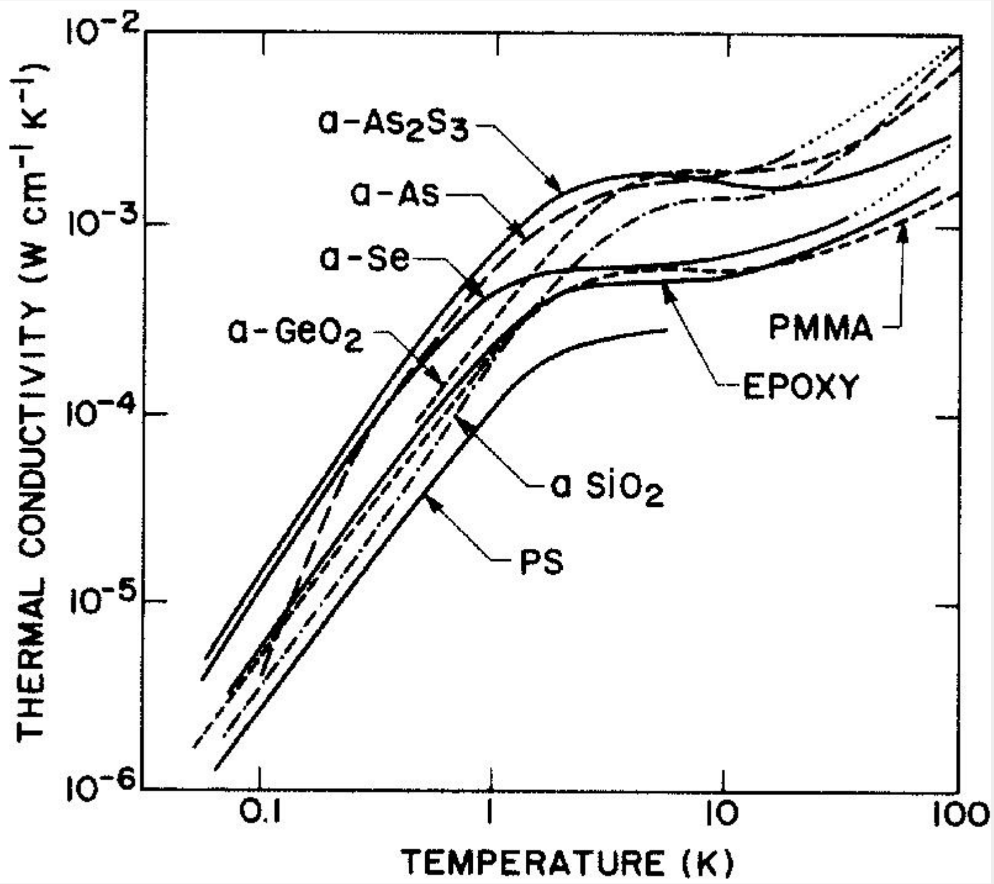

Scale T-axis such that the slope of the different curves at $T_g$ is the same

Rössler, Hess, and Dingwell (1998):

Not really! Perhaps???

# A related anomaly

• Recall: C shows at around 10 K a broad peak whose existence is related to the presence of soft excitations (Boson peak)




• the thermal conductivity shows between 1-10 K a plateau

⇒ phonons with this energy do not propagate anymore because they are scattered by the disorder

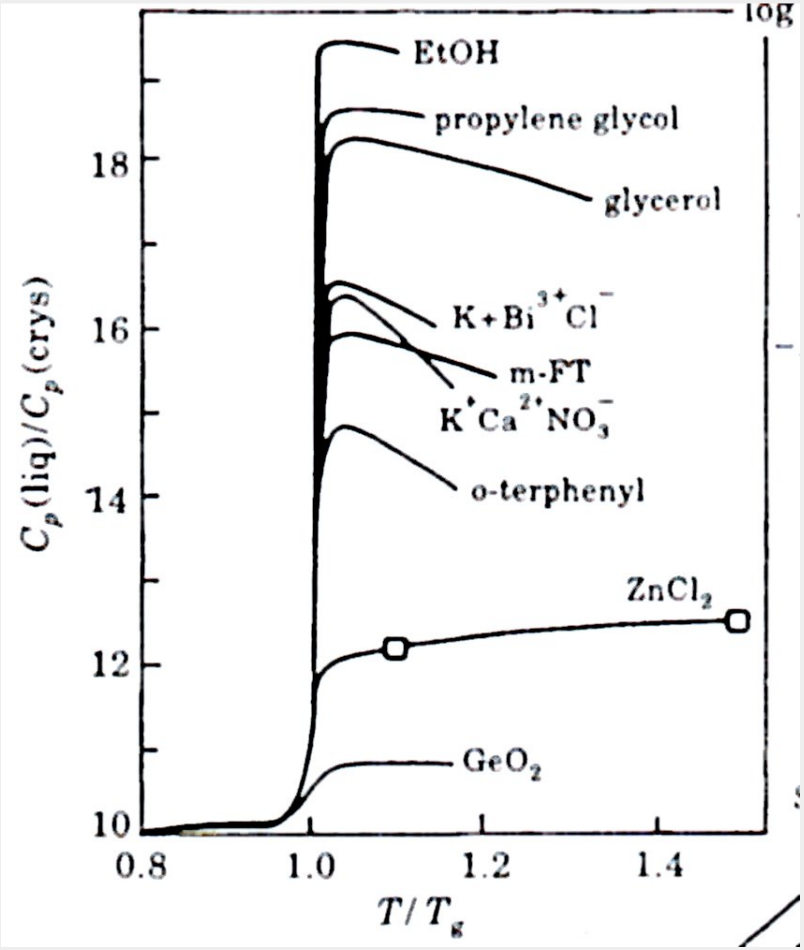
Since the anomaly occurs in the same T-range as the one of the Boson peak, it is believed that they have a common origin

# Close to the glass transition

• Recall: At the glass transition the system falls out of equilibrium since the translational degrees of freedom cannot relax anymore

⇒ these degrees of freedom do not contribute anymore to the specific heat

⇒ drop in $C_p$ (or $C_V$) at the glass transition; is used in experiments to obtain $T_g$




How does this drop depend on the fragility?

• trend: the more fragile the system, the larger is the drop

• for fragile systems the curve above $T_g$ (i.e. the equilibrium values) tend to decrease with increasing T