

# FRUSTRATED STATES OF MATTER – GLASSES

K. Guruswamy

National Chemical Laboratory

# FRUSTRATION – What does it mean?

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Definition from <http://www.merriam-webster.com>

FRUSTRATION:

1. the act of **frustrating**
2. **2 a:** the state or an instance of being **frustrated**  
**2 b:** a deep sense of dissatisfaction arising from unfulfilled needs
- 3: something that **frustrates**

For example:

I'd like to own a Ferrari but I don't

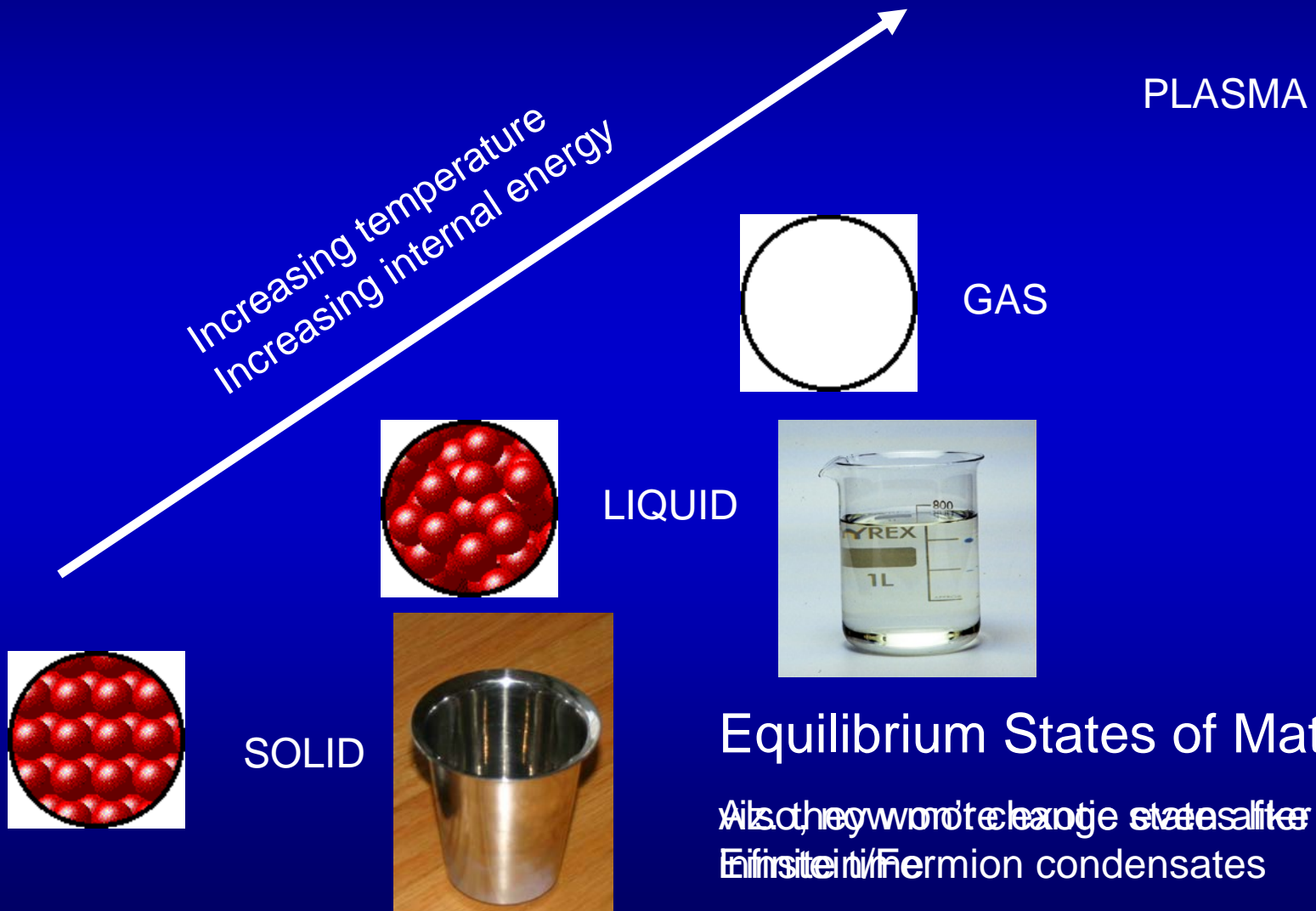
I'd like to be able to bat better than Dhoni but I don't

I'd like world peace, but no one will listen to me

I'd like it if there were no board exams...

I'd like to be at equilibrium

# What are STATES OF MATTER?



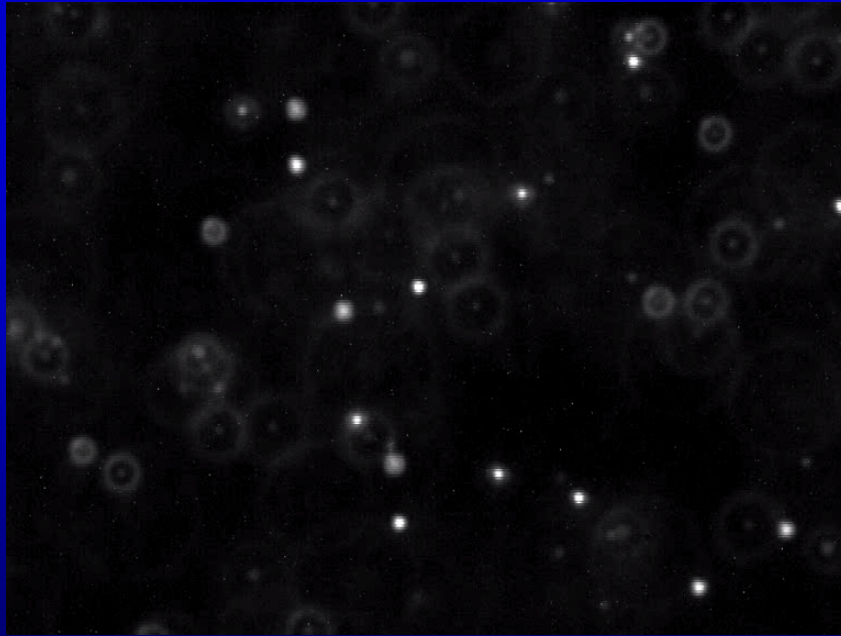
# Temperature

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Temperature – Amount of motional energy for molecules (per degree of freedom)

– Defines the direction in which heat flows (from hot to cold)

The higher the temperature, molecules jiggle around more



Small particles, each about 1/1000 cm in water at room temperature – observed under a microscope

# Temperature: Brownian motion

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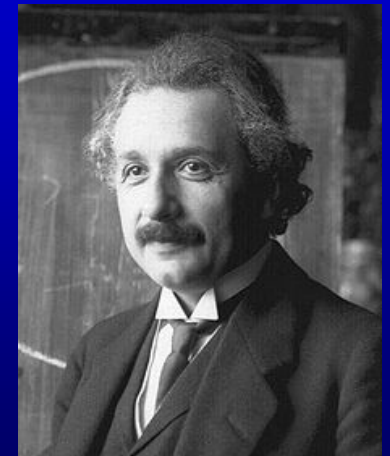
BROWNIAN MOTION – due to water molecules jiggling around and pushing the pollen grains (Robert Brown, Scottish botanist, 1827)



[Brownian motion simulation](#)

In 1905 (his INCREDIBLE year), Einstein explained Brownian motion – how much the particle moves depends on temperature. At higher temperature, higher diffusion.

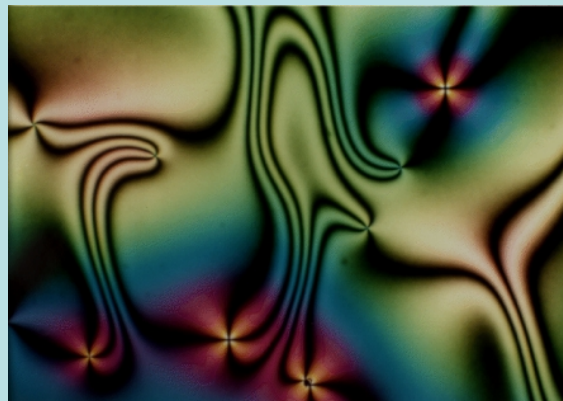
At ABSOLUTE ZERO, all motion ceases:  $0\text{ K} = -273.15^\circ\text{C}$



# Other States of Matter: Between Liquids and Solids

**LIQUID**

LIQUID CRYSTALS



**AMORPHOUS SOLIDS – “GLASSES”**

**FRUSTRATED, OUT-OF-EQUILIBRIUM SYSTEMS**

**viz. they're stuck in a disordered state and don't like it**

**SOLID**

# Glass: Window glass – Amorphous silica

**Glass, Up Close**

Glass is rigid, but the arrangement of molecules and atoms within it is random, like that of a liquid.

**COMPOSITION**  
The building block of window glass is silica, or sand, which forms pyramids of five atoms.

Oxygen  
Silicon

Calcium  
Sodium

**STRUCTURE**  
When molten silica cools, the molecules retain the random order of their liquid state, but form strong bonds like a solid. Some molecules might form symmetrical crystals, but the glass has no overall order or orientation.

**TYPES OF GLASS**  
Typical window glass contains calcium and sodium atoms. Glasses can also be made from polymers.

Window glass

Spot the difference between these  
Quartz

Quartz, a solid, has the same chemical formula as pure silica glass ( $\text{SiO}_2$ ).

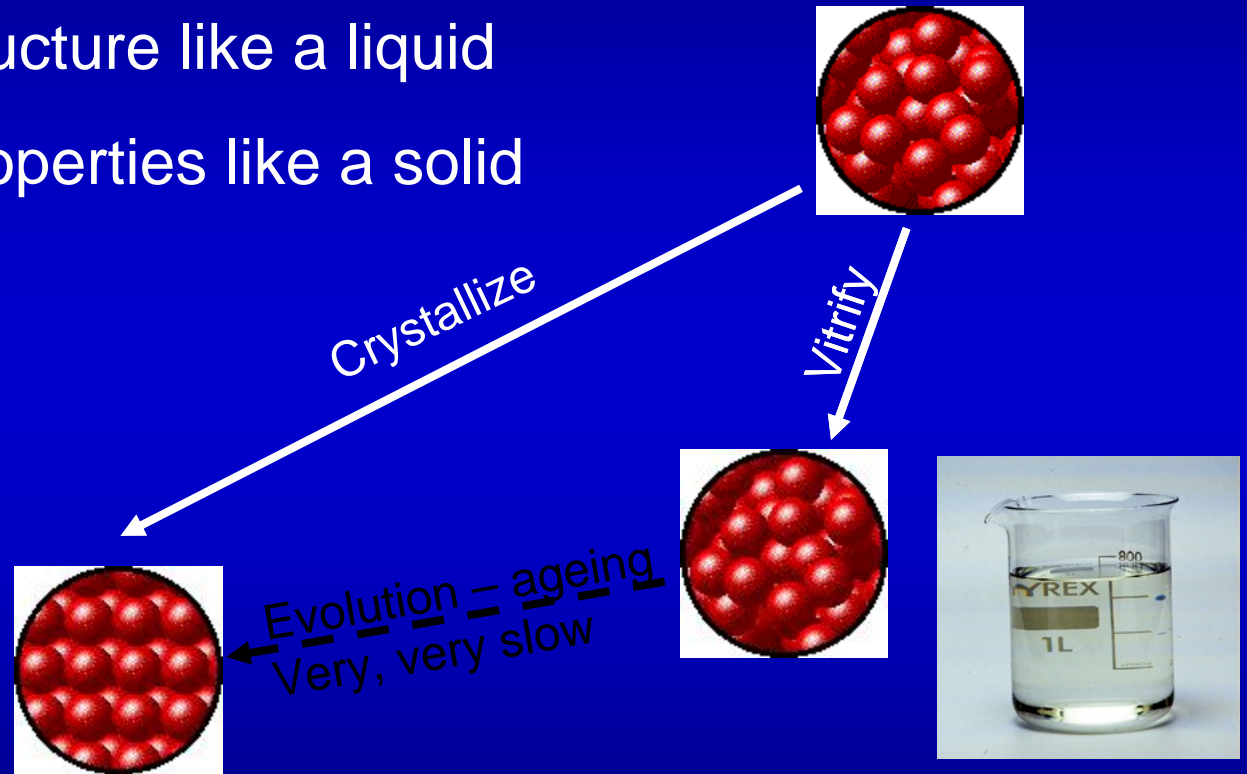
**STRUCTURE**  
The molecules are the same, but they are lined up next to each other in a simple repeating pattern that extends through the material, giving it a crystalline structure.

# Glass – *SUPERCOOLED* liquid – Motions are frozen

## GLASS

Disordered structure like a liquid

Mechanical properties like a solid



Beaker of glass (supercooled liquid) containing a “normal” liquid (water)



# Glass – *SUPERCOOLED* liquid

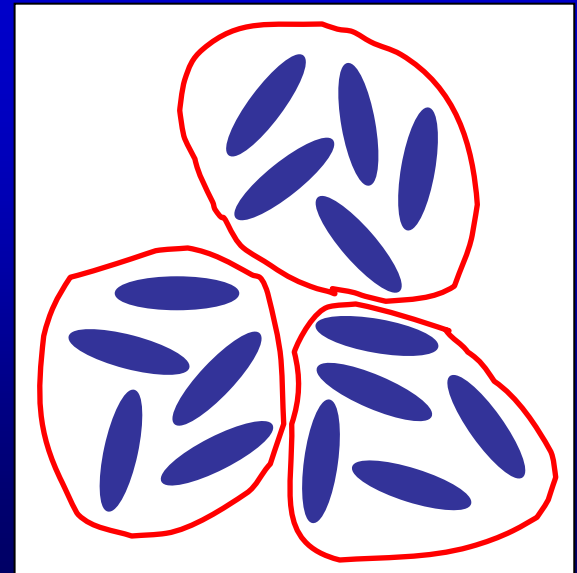
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As the temperature decreases, the atoms/molecules have lesser energy to move around. If the material is cooled very rapidly (*quench*), it is possible to prevent the formation of an ordered crystalline solid (*vitrification*)

On cooling: molecular volume decreases AND free volume (viz. space to wiggle) decreases

If free volume decreases very suddenly (rapid cooling), then no chance to move into a crystalline arrangement – “frozen” glassy system

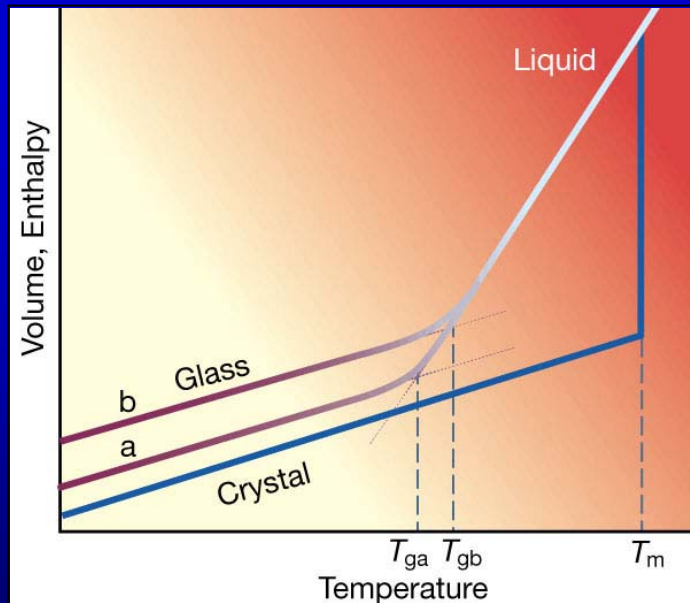
In a glass, motions have to be co-operative  
viz. you cannot move unless everyone around  
you cooperates and moves  
We all know that cooperation is difficult  
Flow becomes very sluggish



# Glass

“Glasses are liquids whose molecules are so tightly packed, and hence are so sluggish, that they cannot relax to equilibrium even over periods of months or years”

Alternate definition of  $T_g$ : temperature at which viscosity =  $10^{13}$  Poise  
= million billion times viscosity of water



Change of specific volume is NOT discontinuous – NOT a first order PHASE TRANSITION (examples of first order transitions : melting, viz. solid to liquid; boiling, viz. liquid to gas)

# Other “glassy” materials

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All polymers:

Polyethylene (plastic bags) – glass transition temperature,  $T_g < -100^\circ\text{C}$

Rubber (in tyres, rubber bands) –  $T_g = -72^\circ\text{C}$

PET (soft drink/water bottles) –  $T_g = 70^\circ\text{C}$

Polycarbonate (20 liter water bottles) –  $T_g = 145^\circ\text{C}$

Polystyrene (styrofoam) –  $T_g = 100^\circ\text{C}$

Polymethylmethacrylate (Plexiglass) –  $T_g = 105^\circ\text{C}$

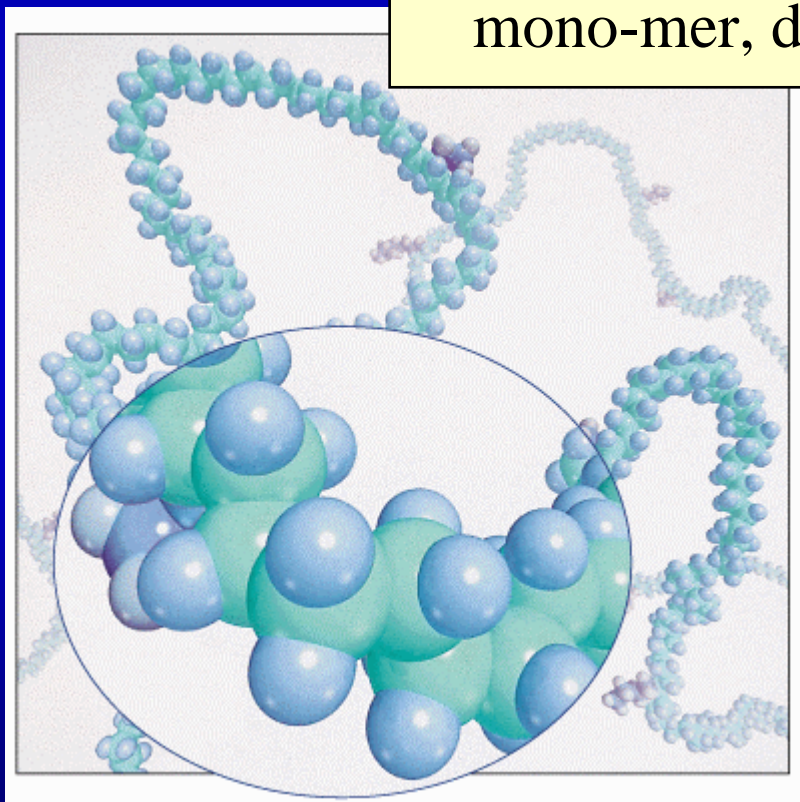
Form glasses on cooling relatively slowly

Silica (soda-lime glass) –  $T_g = 520$  to  $600^\circ\text{C}$

Even water and metals can be vitrified – “splat” cooling at million  $^\circ\text{C}/\text{min}$

# What is a polymer?

Long molecules made up of repeating units  
mono-mer, di-mer, tri-mer ..... poly-mer



Staudinger

1953 Nobel Prize  
to Staudinger for  
*macromolecular*  
hypothesis

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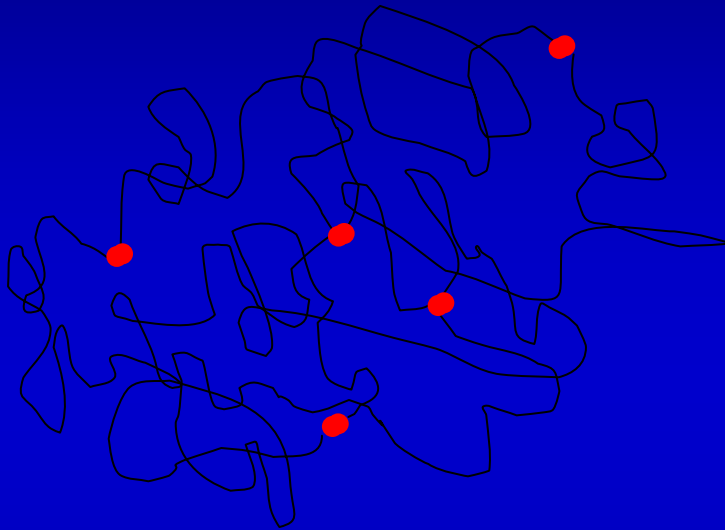
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# Change in properties at the glass transition

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Rubber bands: polyisoprene (natural rubber)



Red balls (chemical crosslinks) connected by “springs” when the molecules are able to wiggle

Stretchy, elastic material

$T_g = -72$  to  $-75^\circ\text{C}$

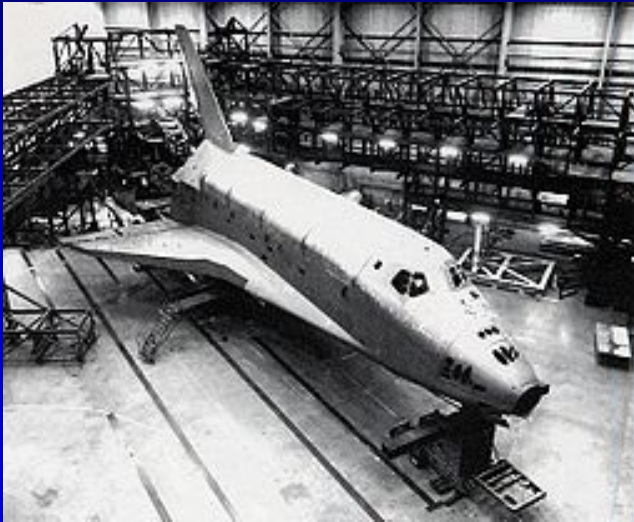
LET US DO AN EXPERIMENT

What happens to the properties of a rubber-band when we cool it to really, really cold temperatures (liquid nitrogen,  $-196^\circ\text{C}$ )?

OK, that was interesting, but why should anyone care?

# The Challenger Space Shuttle mission (1986)

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# Feynman's explanation for the Challenger disaster

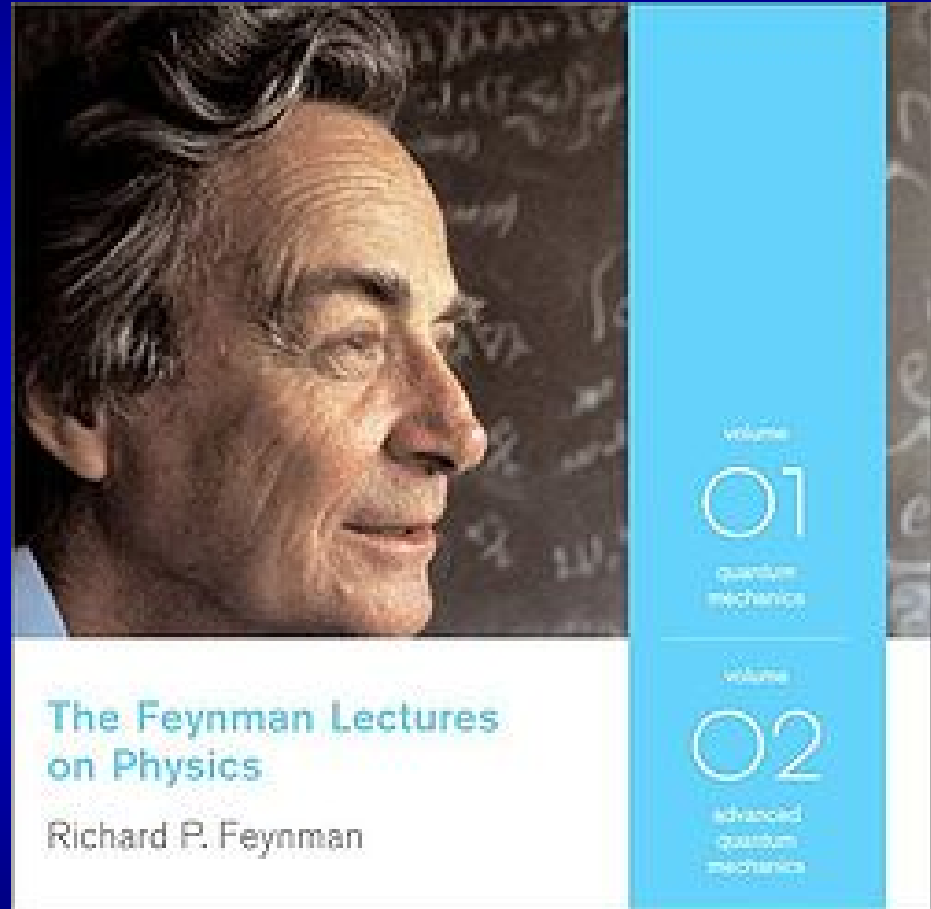
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Richard Feynman

Professor at Caltech

Nobel Prize (Physics, 1965)  
for quantum electrodynamics

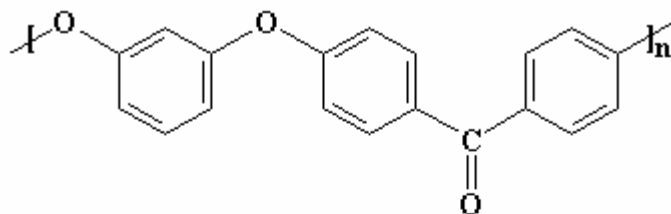




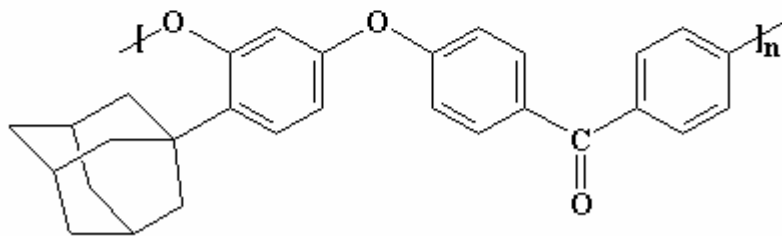
# Polymers: Manipulating the glass transition

If we change polymer structure – can change the molecular bulkiness (and therefore, the mobility). Thus can get the properties that we need. That is always useful!

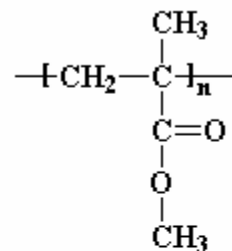
Need a good polymer chemist to make these molecular changes...



This poly(ether ketone) has a  $T_g$  of 119 °C

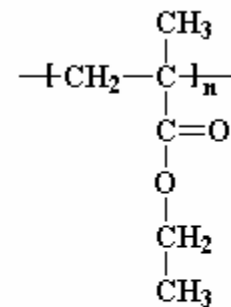


This poly(ether ketone) has a  $T_g$  of 225 °C



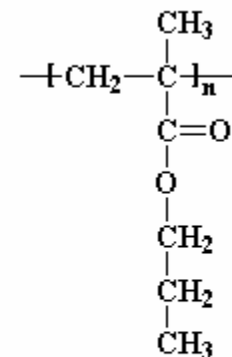
Poly(methyl methacrylate)

$T_g = 100-120$  °C



Poly(ethyl methacrylate)

$T_g = 65$  °C



Poly(propyl methacrylate)

$T_g = 35$  °C

# Polymers: “Softening” using additives

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PVC = polyvinylchloride

The same polymer is used for hard pipes...

...and for the soft skin on dolls

Changing the glass transition changes the flexibility and softness

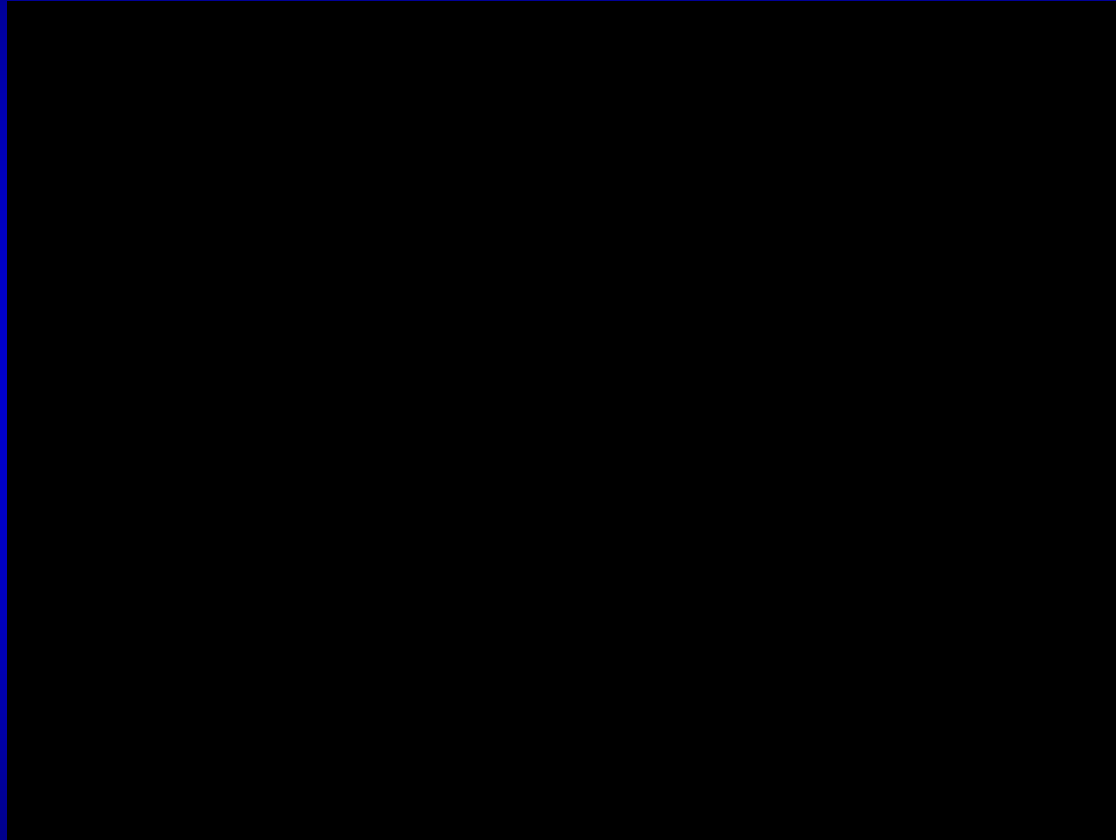
Done here using small additive molecules that “lubricate” flow by creating free volume

Plasticizers: Also responsible for “new car” smell



# “Glassy” versions of materials other than polymers

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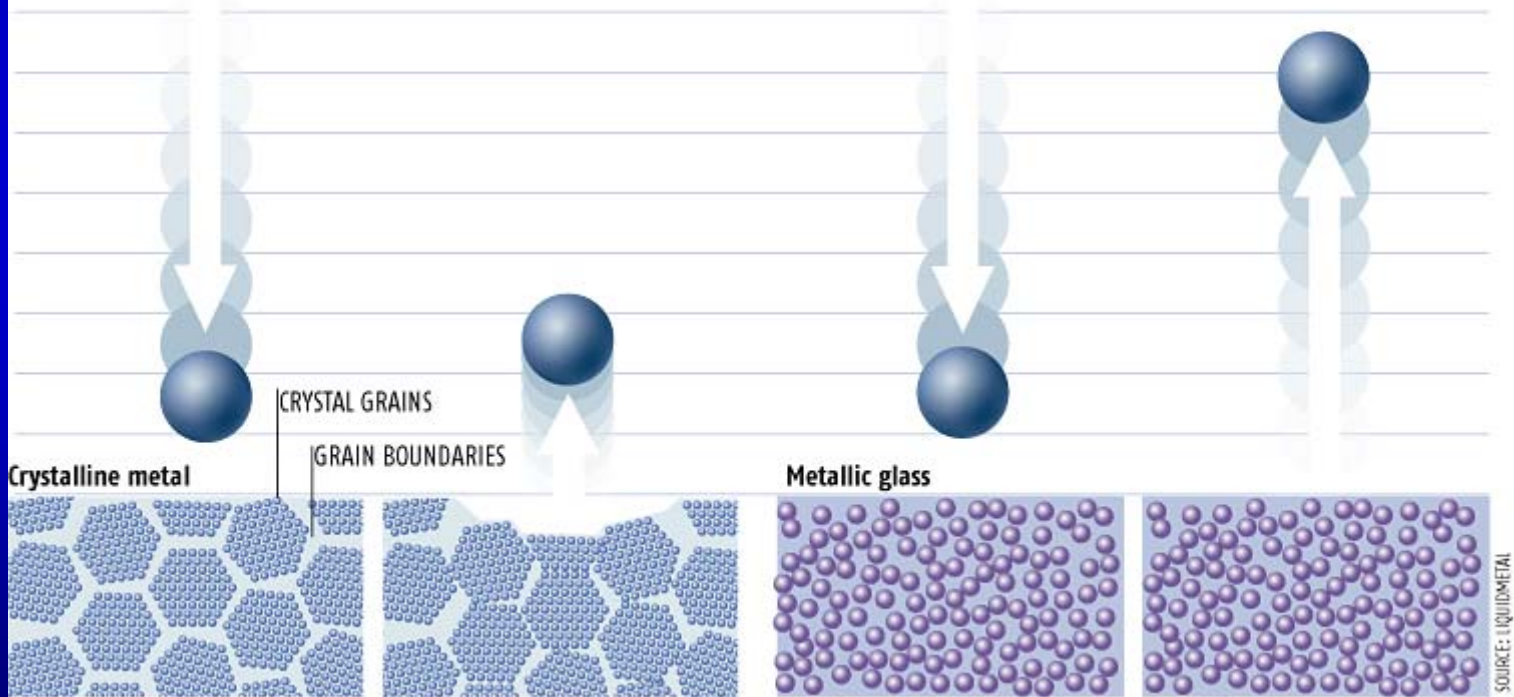
# Glassy Liquid Metal™ - Complex alloys of Zr, Ti, Ni, Cu, Be

## BOUNCING BACK

Metals with a glassy, or amorphous, structure can be far stronger and springier than normal metals

Drop a metal ball onto a normal metal and the grains shift along grain boundaries, absorbing the energy of the bounce and creating a dent

Drop a metal ball onto a metallic glass and it bounces back up



# Liquid Metal™ - Applications

## CURRENT APPLICATIONS



Industrial Coatings



Defense Applications



Electronic Casings



Medical Devices



Sporting Goods and  
Leisure Products



Space Projects



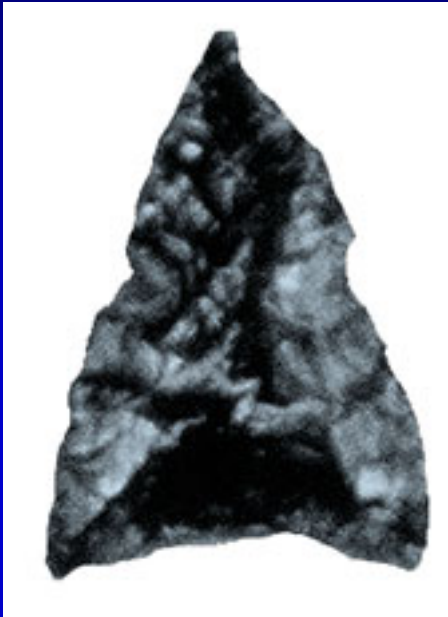
Fine Jewelry



Hinge Applications

# Glassy materials used by Stone Age “Engineers”

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Obsidian – glassy materials from cooled volcanic lava

Glassy, no crystals > Can be sharpened to a very fine edge

Used in the Stone Age to make arrowheads



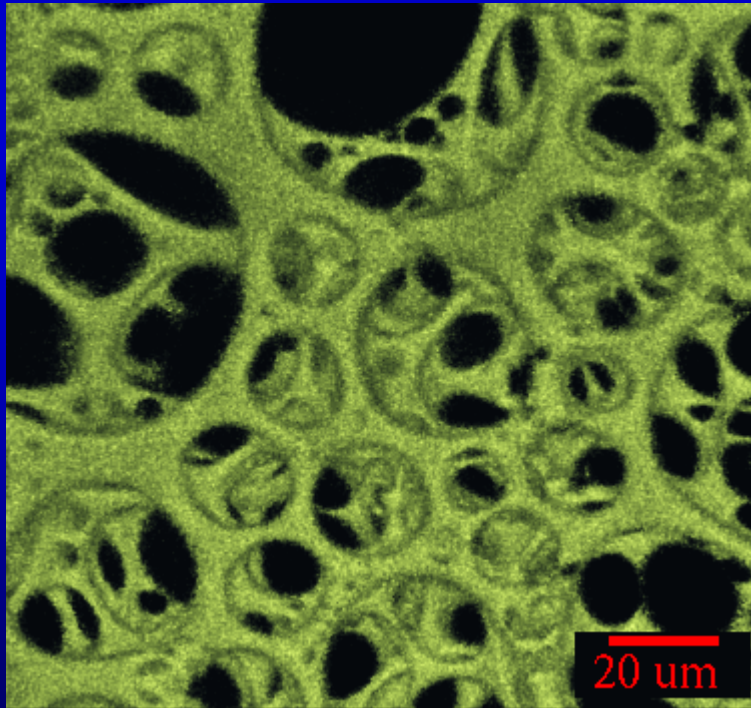
Obsidian is used to make some surgical scalpels today

# Glasses in foods too! (not just metals and plastics)

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The taste/texture of many foods depends on the structure

Foods are often in the glassy state – for example, curd, mayonnaise, and tasty foams such as ice cream



Confocal microscopy image of mayonnaise – a glassy colloidal emulsion

# How does the transition from liquid to glass happen?

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Wikipedia's list of major unresolved problems in physics includes:

## Amorphous solids

What is the nature of the phase transition between a fluid or regular solid and a glassy phase? What are the physical processes giving rise to the general properties of glasses?

Philip W Anderson (1975 Nobel prize winner in Physics, from Princeton University) said in 1995 that: "The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition. This could be the next breakthrough in the coming decade."

In 2008, there is still no consensus on the route to the glass transition.





# Colloidal glasses – the JAMMED state

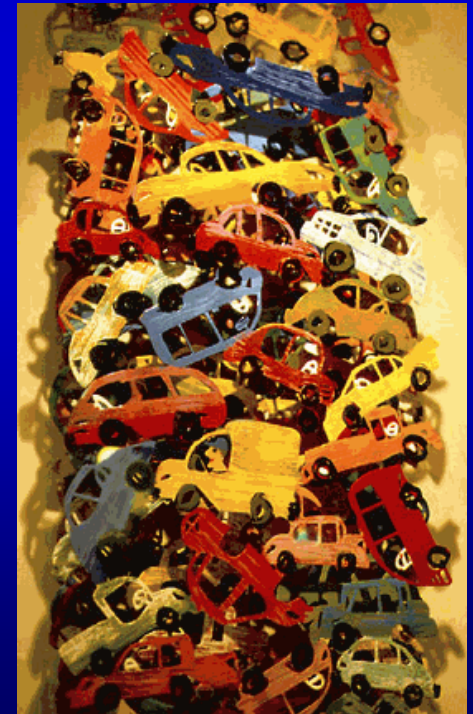
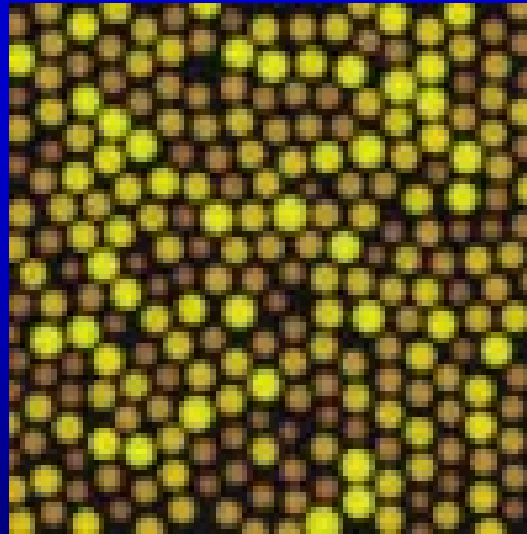
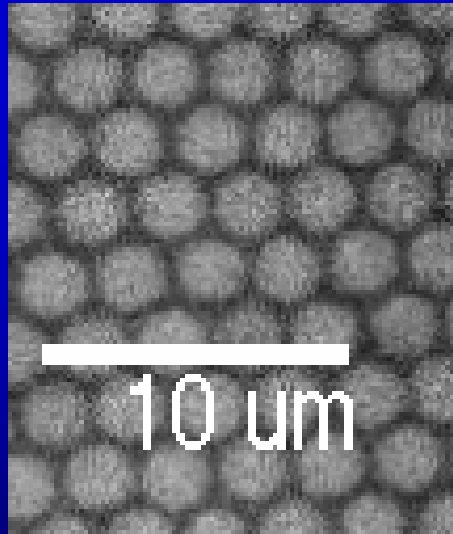
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One of the problems with molecular glasses is the difficulty in seeing the details of what the molecules are doing

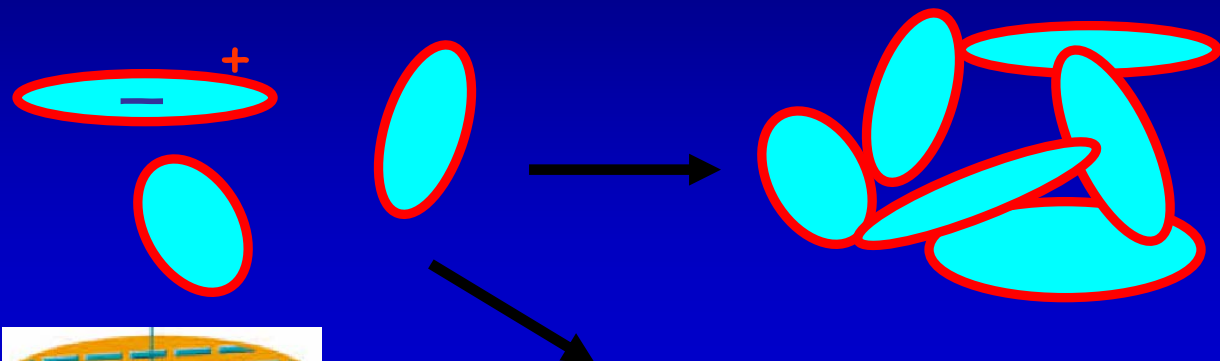
Model systems: Colloidal glasses

Jamming – can't organize into crystals if there are too many particles

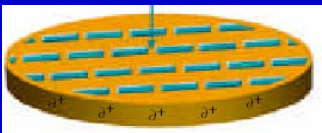
Also, colloidal gels important in their own right, in foods, for example



# Work in my laboratory: Colloidal nano-plates

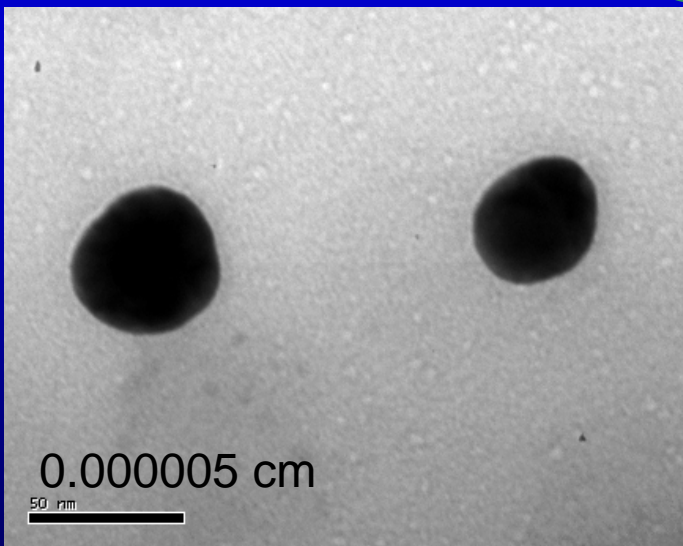


Gelation: driven by edge-face attraction to form house-of-cards



o-modification

Edge-edge attraction and edge-face repulsion



Can we prevent these plates from getting stuck to each other and *frustrated*?

Can we get a liquid crystal phase with the plates all pointing in the same direction on average?

# SUMMARY

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There is still a lot of work that needs to be done, both in molecular glasses and colloidal glasses

Glassy states found almost everywhere

Very important to understand this state of matter – we're not there yet...

THANK YOU FOR YOUR ATTENTION