

# 1. Liquids, solids and ... soft matter

## 1.1 *Viscous and elastic behaviour*

Normal condensed matter comes in two forms - solid and liquid.

Typical “soft condensed matter” seems more difficult to classify:

think of      glue

                soap

                tomato ketchup

                pastes (e.g. cornflour and water)

are they solid or liquid? In some ways they seem to have attributes of both.

More specifically - we define a solid as something that can sustain a shear stress without yielding; a liquid is something that flows in response to a shear stress.

More formally

- for an elastic solid

*an applied shear stress produces a shear strain in response*

The shear strain is proportional to shear stress, and the constant of proportionality is the **shear modulus**.

- for a “Newtonian” liquid

*an applied shear stress produces a flow with a constant shear strain **rate** in response*

The strain rate is proportional to the shear stress, and the constant of proportionality is the **viscosity**.

- many examples of soft-condensed matter respond in much more complicated ways to applied shear strains - non-Newtonian rheology

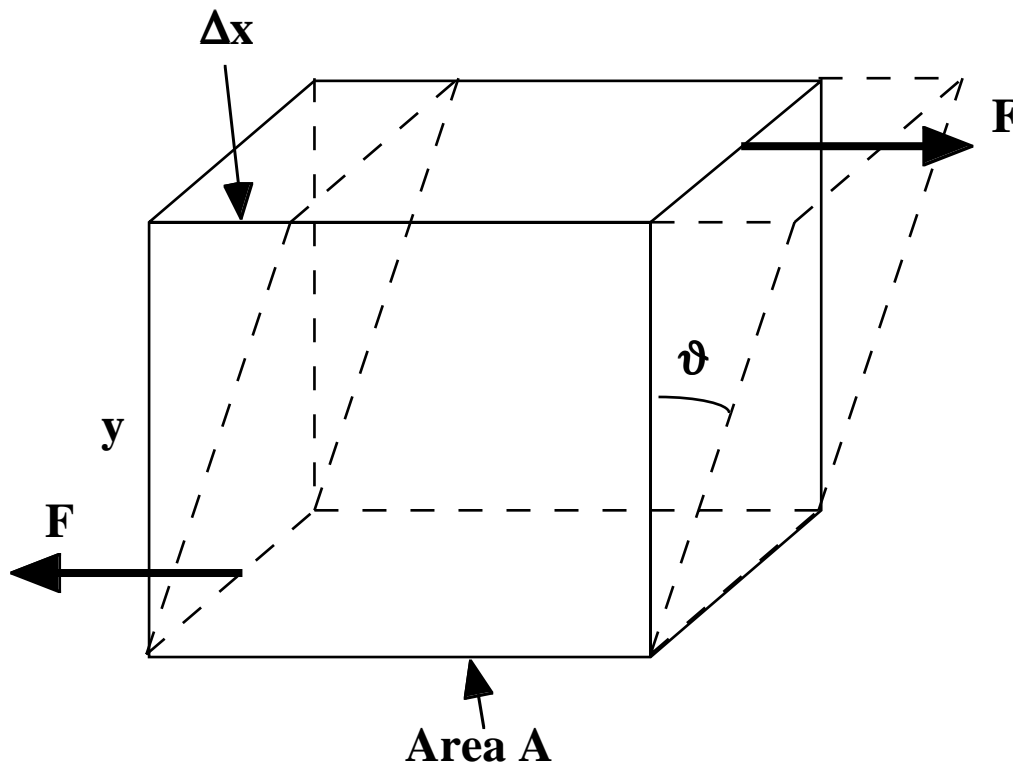
the simplest example is linear viscoelasticity e.g. silly putty

silly putty behaves like a solid on short timescales - but a liquid on larger time scales.

Now we'll talk about this phenomenon in general, but more precise, descriptive terms.

Later in the course we'll get a good idea of how to understand this from the molecular point of view.

Definition of a shear strain



$$\text{Shear stress} = \frac{F}{A}$$

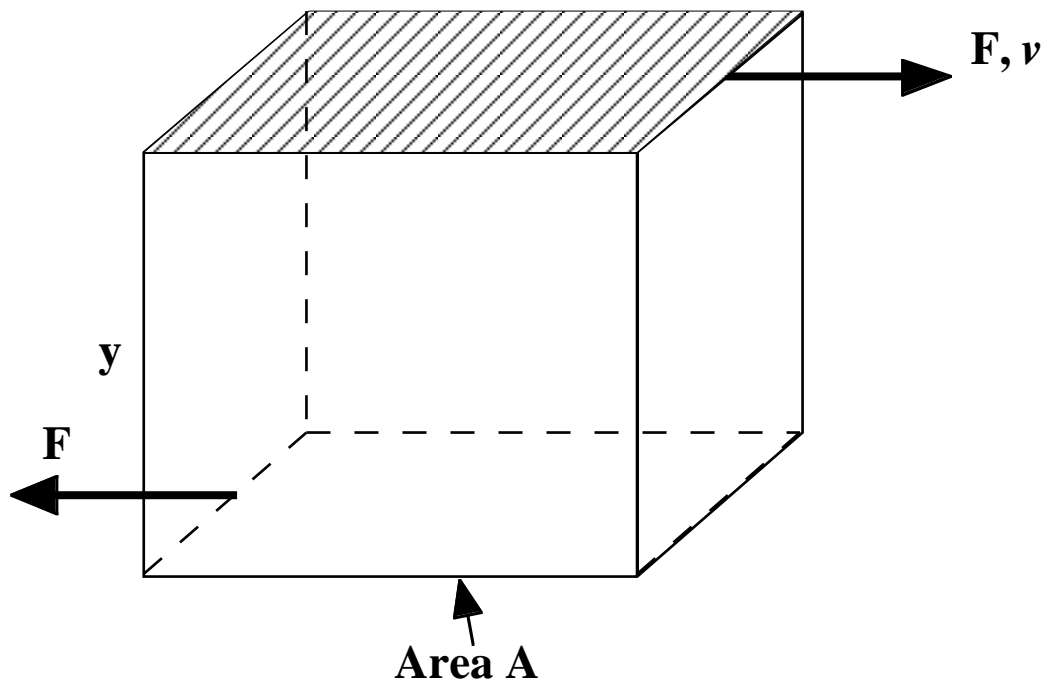
$$\text{Shear strain} = \frac{\Delta x}{y} = \vartheta$$

For elastic solids:

$$\text{Shear stress} \propto \text{Shear Strain}$$

$$\frac{\text{Shear stress}}{\text{Shear strain}} = G \quad \text{Shear modulus}$$

For Newtonian liquids



Imagine exerting the stress with parallel plates. The bottom plate is stationary. The top plate moves with velocity  $v$ .

$$\text{Velocity gradient} = \frac{v}{y}$$

but this is just the same as

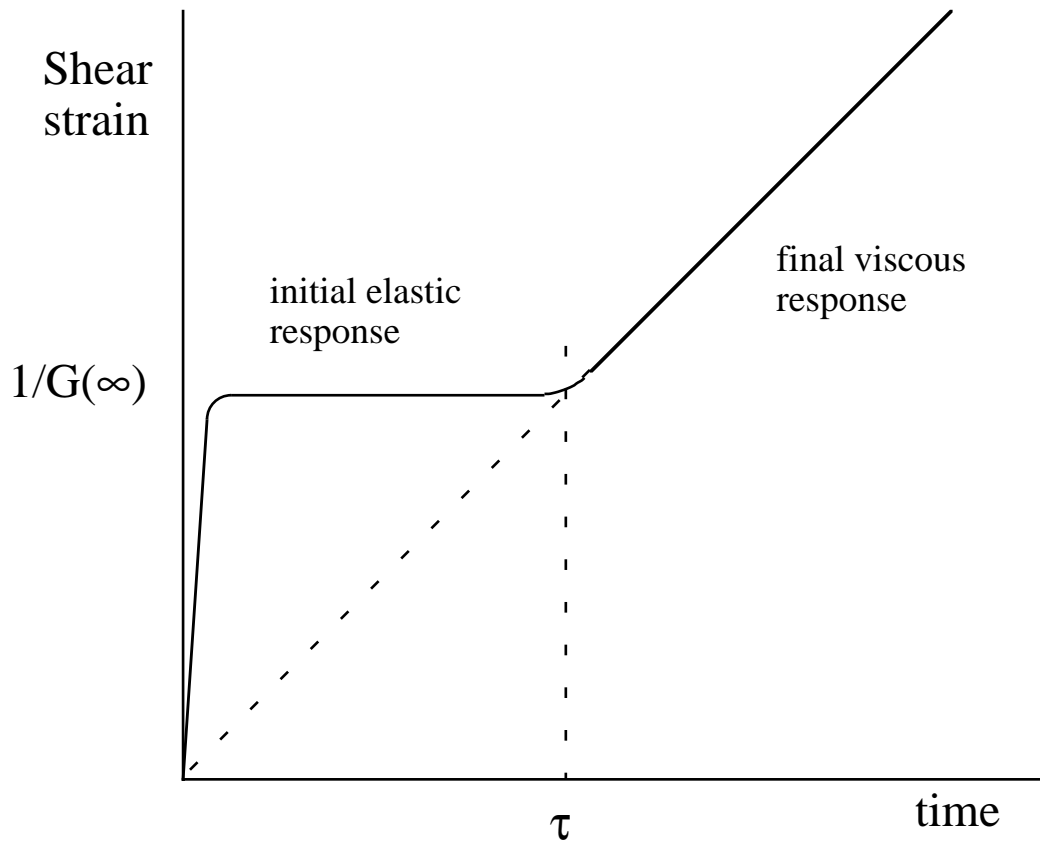
$$\text{Strain rate } \frac{\Delta \dot{x}}{y} = \dot{\vartheta}$$

Newton's law of viscosity says

$$\begin{array}{ccc} \frac{F}{A} & = & \eta \frac{v}{y} \\ \uparrow & & \uparrow \\ \text{Shear stress} & & \text{Shear strain} \end{array}$$

## 1.2 Viscoelasticity

Now what happens in a viscoelastic liquid? Apply an instantaneous unit shear stress at time  $t = 0$ .



The initial response is *elastic*, characterised by

$G(\infty)$ , the high frequency shear modulus

at some characteristic relaxation time  $\tau$  we cross over to viscous behaviour.

viscosity =  $\eta$

From the diagram, at long times the viscosity is given by the stress/strain rate,

$$\text{strain rate} \sim \frac{1}{G(\infty)\tau}$$

So we find

$$\eta \sim G(\infty)\tau$$

[In passing “ $\sim$ ” means scales as

is of the order of

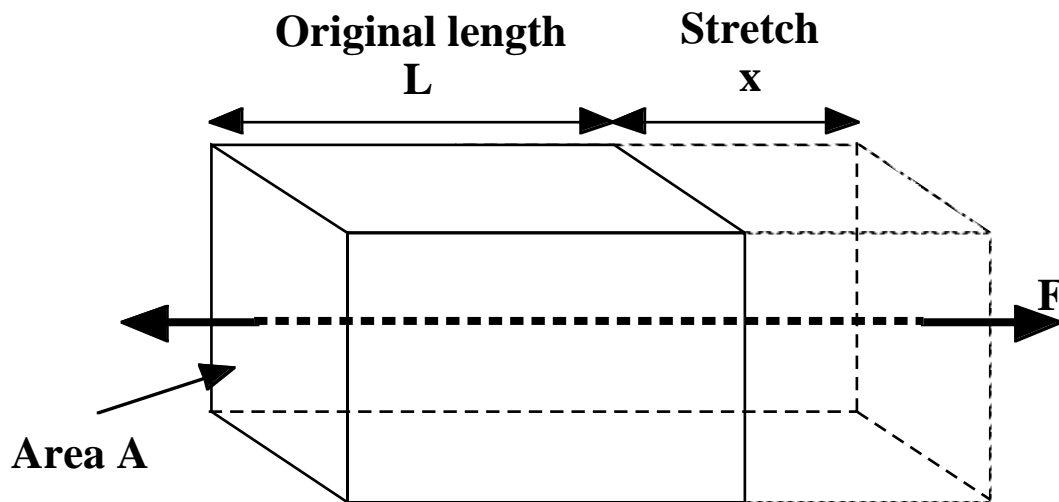
- like  $\approx$  (approximately equal) only less so!]

We can use this argument to gain more insight into what's special about soft condensed matter.

### 1.3 Calculating the modulus from first principles

Where do these quantities come from, in microscopic terms?

Remember how you can use the idea of intermolecular forces to calculate the elastic properties of solids from first principles: you did this for the Young modulus in PHY204.

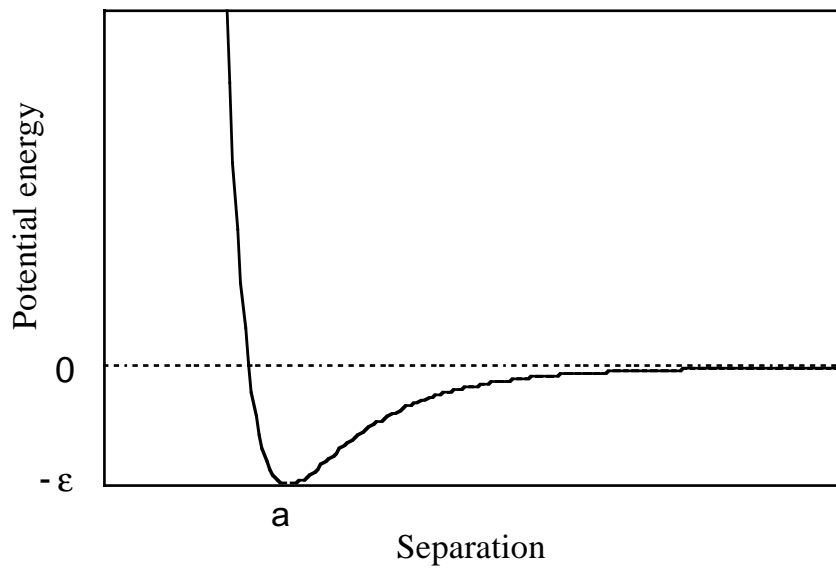


$$\text{Stress} = \frac{F}{A} \qquad \text{Strain} = \frac{x}{L}$$

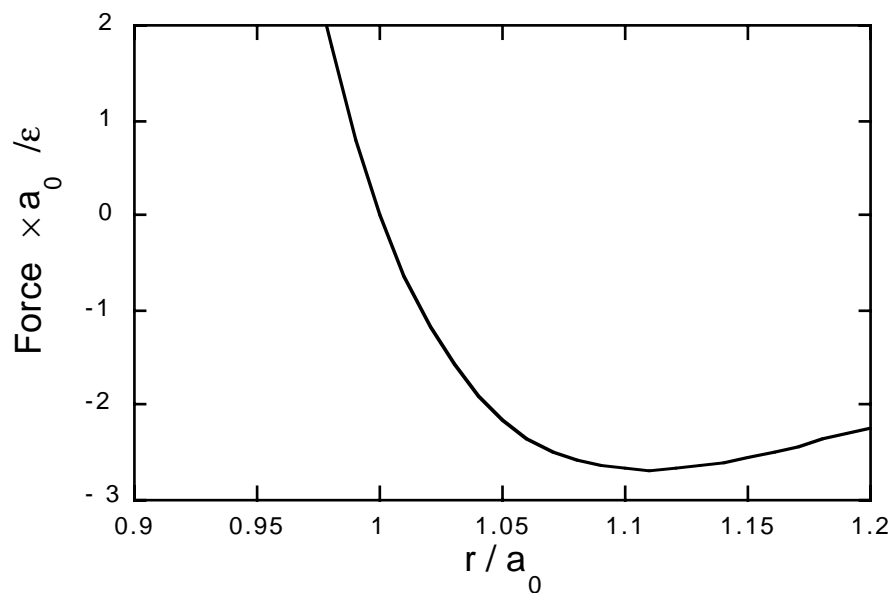
$$\frac{\text{Stress}}{\text{Strain}} = Y \quad \text{Youngs modulus}$$

Youngs modulus is related to the intermolecular potentials.

Curves of potential vs separation.



If we plot the force, we find that close to the equilibrium point  $a_0$  the curve is linear, hence Hookes law.



For a cubic lattice there would 1 bond in area  $a_0^2$ .

If each bond is deformed by  $\Delta a_0$

$$\text{Force} = \left. \frac{d^2 u}{dr^2} \right|_{a_0} \Delta a_0 \text{ in each bond}$$

$$\text{Stress} = \left. \frac{d^2 u}{dr^2} \right|_{a_0} \frac{\Delta a_0}{a_0^2}$$

$$\text{Strain} = \frac{\Delta a_0}{a_0} \text{ so } \frac{\text{Stress}}{\text{Strain}} = \frac{1}{a_0} \left. \frac{d^2 u}{dr^2} \right|_{a_0} = Y$$

How is this related to the shear modulus  $G$ ?

It turns out that classical continuum mechanics relates the Young modulus, the shear modulus and *Poisson's ratio*  $\sigma$  :

$$G = \frac{Y}{2(1 + \sigma)}$$

Poisson's ratio for isotropic materials falls between the limits of 0 and 1/2 (taking the latter value for a material that is *incompressible* ).

As dimensional analysis indicates, moduli are essentially *energy densities* (see exercise 1).

**Weak bonds -> floppy materials**

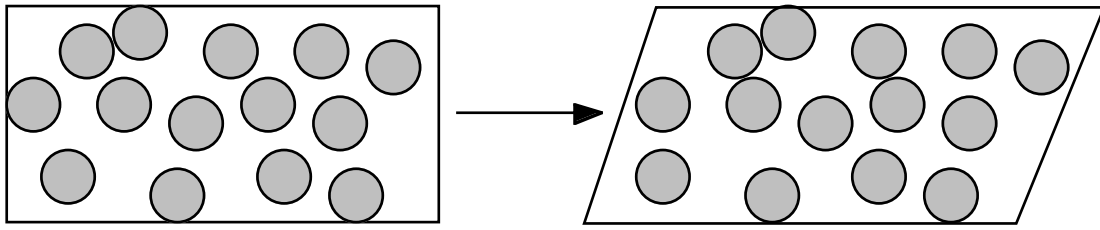
**Strong bonds -> stiff materials**

### ***1.4 Relaxation times***

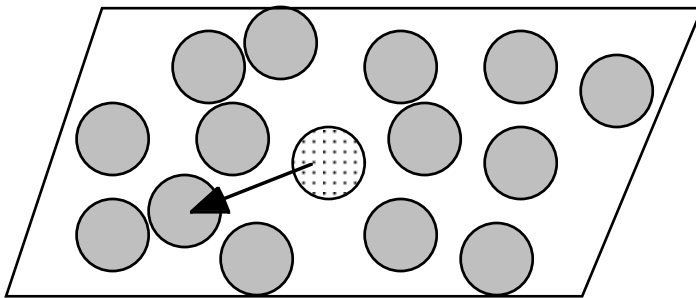
What happens microscopically when we try to shear a liquid?

Initial response - motion of molecules within their potential wells, without change of relative position.





After some time, molecules will be able to overcome the potential barrier preventing them from moving out of their relative positions - this time is the *relaxation time*.



The relaxation time is the time after which the stress *relaxes*.

For simple liquids, we might imagine that this time was determined by an “Arrhenius process”:

to jump out of its “cage”, a molecule has to overcome a potential barrier of height  $\epsilon$ .

If it vibrates in its potential well with a frequency  $\nu$  (the *attempt frequency*) every time it hits the barrier, there's a probability  $\exp(-\epsilon/kT)$  of crossing it.

We expect the relaxation time to look like

$$\tau^{-1} \approx \nu \exp\left(-\epsilon/kT\right)$$

How big is the *activation energy*  $\epsilon$ ?

An upper limit is the latent heat of vaporisation per molecule -  $\epsilon'$ .

In fact, it turns out that  $\epsilon \approx 0.4 \epsilon'$

### ***1.7 Viscosities in liquids - our simple picture***

To summarise, we have

$$\eta \sim G(\infty)\tau$$

where  $G(\infty)$  is related to the bond energy per unit volume (a guess at its order of magnitude would be  $kT/a^3$ )

and  $\tau$  takes the value  $10^{-12}$  -  $10^{-10}$  s for simple liquids

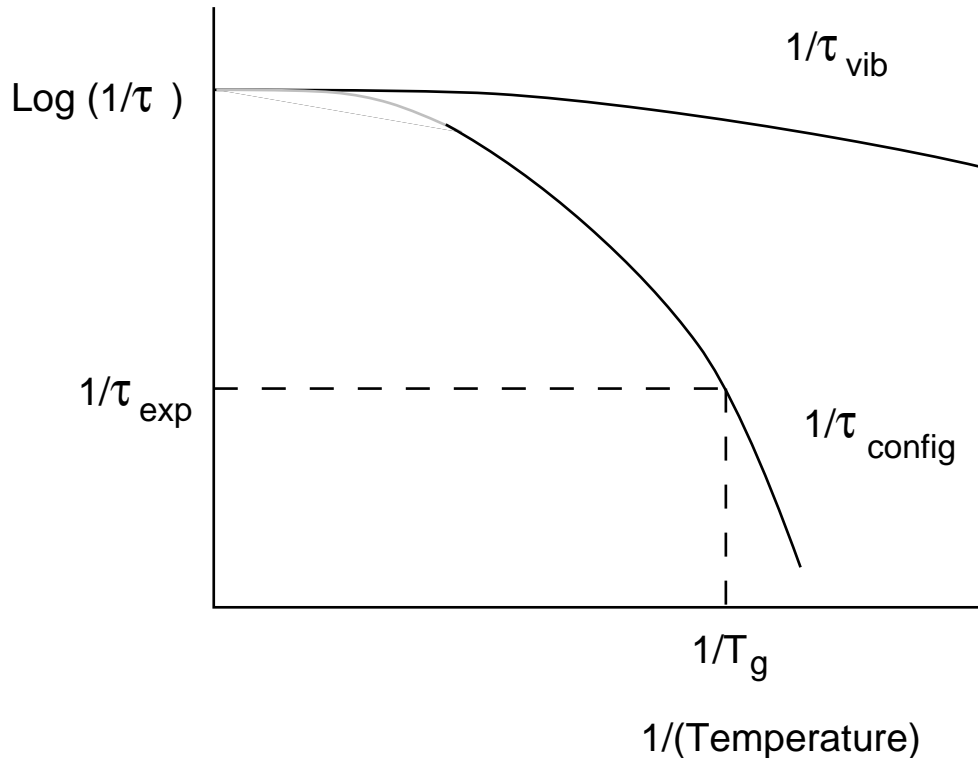
The temperature dependence of viscosity is dominated by the exponential dependence on the activation energy:

$$\eta \sim \frac{G(\infty)}{\nu} \exp\left(\frac{\epsilon}{kT}\right)$$

with  $\epsilon \approx 0.4 \epsilon'$ .

## 1.6 Relaxation times of glass forming liquids

Many liquids (all liquids?) don't have relaxation times that vary in an Arrhenius way - their relaxation times look like this:



In glass forming liquids the vibrational relaxation time  $\tau_{\text{vib}}$  becomes decoupled from the configurational relaxation time  $\tau_{\text{config}}$ . The relaxation time appears to diverge at a finite temperature  $T_0$ .

Because  $G(\infty)$  does not vary much with temperature, the viscosity also seems to diverge, following an empirical law known as the Vogel-Fulcher law:

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

Here  $\eta_0$  and  $B$  are constants, and  $T_0$ , the temperature at which the viscosity formally becomes infinite, is usually found to be about  $50^\circ$  below the experimental glass transition temperature.

In practise, as the temperature is lowered, we reach a state at which the relaxation time becomes comparable with the timescale of the experiment. When this happens, the system falls out of equilibrium with respect to

configurational degrees of freedom. This marks the onset of the experimental glass transition. When a liquid goes through a glass transition, it forms a *glass*.

### ***1.7 Glasses and the glass transition***

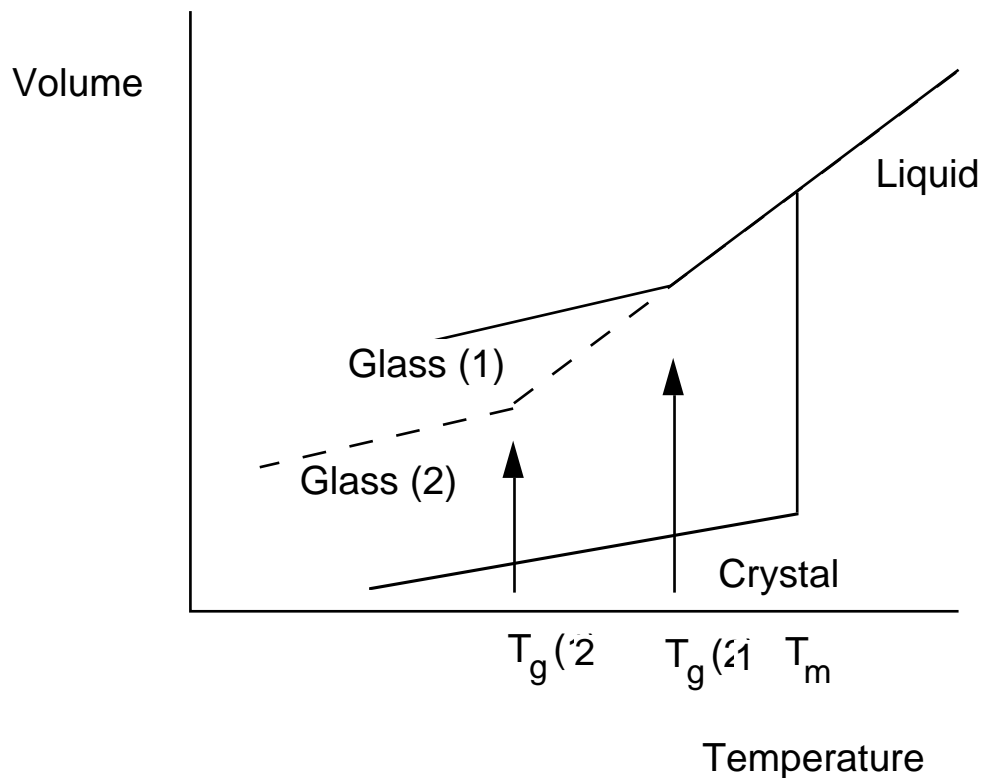
What is a glass? The conventional definition is that it is a *supercooled liquid*.

- a liquid which has been cooled down fast enough that before it has a chance to crystallise (if it can) the relaxation time has increased to greater than experimental time scales.
- its microscopic state is disordered like a liquid, with no crystalline structure
- its macroscopic properties are like a solid - it is *rigid* i.e. with a finite shear modulus.

So is a glass simply a liquid with a very high shear viscosity?

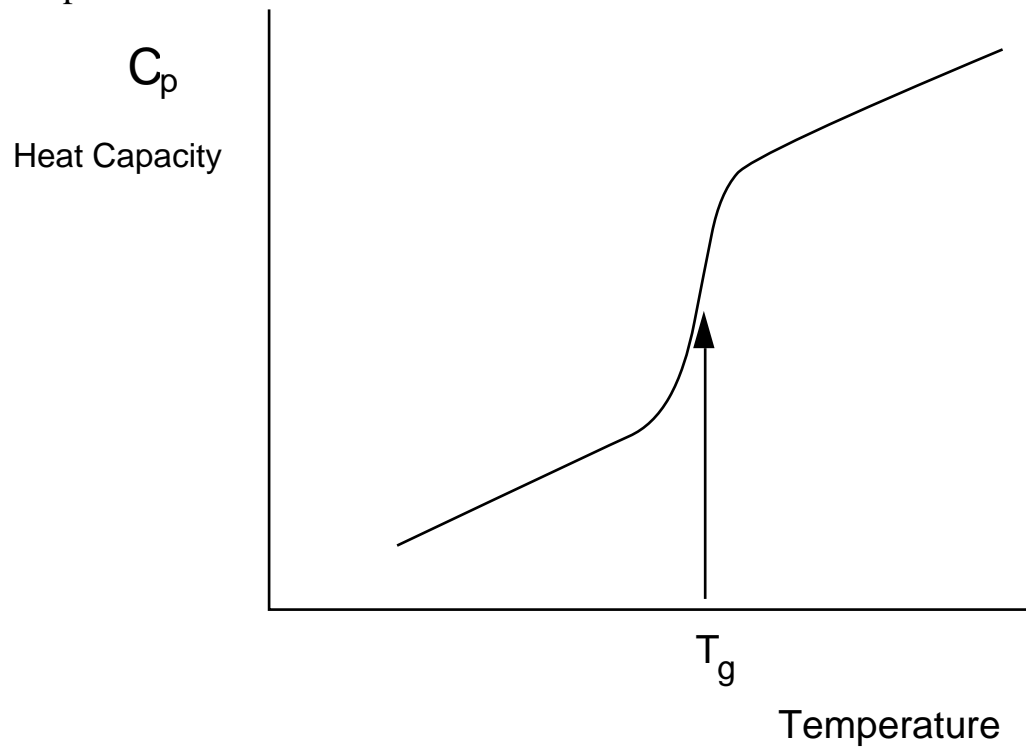
No - there's more to it than this - there is a definite transition between a glass and a liquid that occurs at a definite temperature - *the glass transition*.

The glass transition is a thermodynamic transition in the sense that it is marked by discontinuities in thermodynamic quantities, but it is not a phase transition.



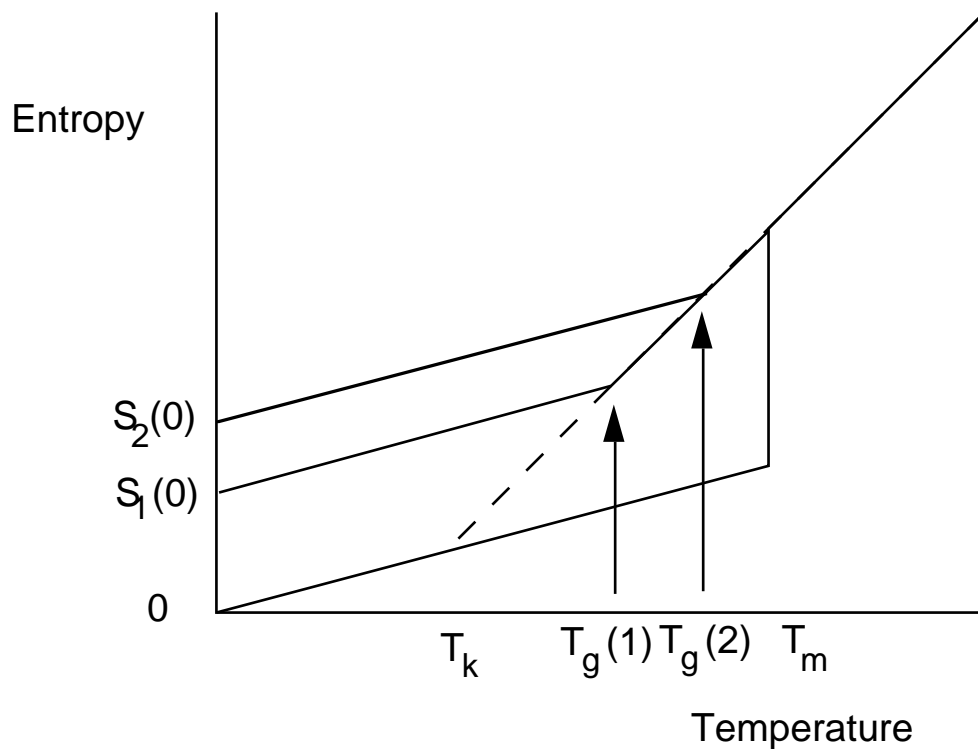
As one lowers the temperature of a liquid below its melting temperature, a glass transition shows itself as a discontinuity in the slope of a plot of volume against temperature. The glass transition temperature depends on the cooling rate; in the diagram above glass (1) is obtained for faster cooling than glass (2).

Often, practically, one measures the heat capacity  $c_p$  as a function of temperature:



Again, the glass transition temperature measured will depend on the cooling rate.

From heat capacity measurements the entropy can be deduced:



## Exercises

1. Calculate the Young modulus for a material with a 6-12 potential. Show that both the Young modulus and the shear modulus are proportional to the total bond energy per unit volume of material.
2. Test the relation we derived for the temperature dependence of viscosity for the case of typical liquids, such as water and benzene.

Data for water:

Temp/ °C	Viscosity/ Pa s
0.0000	0.0017930
10.000	0.0013070
20.000	0.0010020
30.000	0.00079770
40.000	0.00065320
50.000	0.00054700
60.000	0.00046650
70.000	0.00040400
80.000	0.00035440
90.000	0.00031450
100.0	0.00028180

3. For polystyrene,  $B=710$  and  $T_0 = 50$  °C. Plot the function  $h/h_0$  in the temperature range 80 - 150. By what factor does the viscosity and relaxation time vary between the temperatures of 100 °C and 140 °C?

4. List the classes of materials which can form glasses. For each case, give examples of specific glasses, and mention any practical uses.
5. What theories have been proposed to explain glass formation? Describe, compare and criticise the following approaches:
- Mode coupling theory
  - Free volume theory
  - Theories of cooperativity volumes
  - Exactly soluble toy models

## Further Reading

An expanded version of these notes forms the first chapter of  
R.A.L. Jones – Soft Condensed Matter. Oxford, OUP 2002

### Elasticity and viscosity

The basics are covered in many elementary books. My favourite is:  
Tabor, D. (David). - Gases, liquids and solids : and other states of matter. - 3rd ed. -  
Cambridge : Cambridge University Press, 1991  
Main library, [539.1 \(T\)](#)

For a much more sophisticated view, look at the first chapter of  
Chaikin, P. M. and T.C. Lubensky.. - Principles of condensed matter physics - Cambridge :  
Cambridge University Press, 1995.  
Main library [539.2 \(C\)](#)

### Glasses and the glass transition

The best general introduction is in  
Physics of Amorphous Materials, (2<sup>nd</sup> Edition), S.R. Elliott, pp29-49  
(in Main Library and St George's Library)

A comprehensive treatment with an emphasis on inorganic glasses is given in  
Zarzycki, J.. - Glasses and the vitreous state (CUP)  
(in St George's Library)

Most books on polymer physics usually have some discussion of polymer glasses, though  
discussion of theories is usually restricted to the Free Volume theory. Perhaps the best is  
G.R. Strobl, The Physics of Polymers  
(In Main Library)

Two review articles:

A fairly comprehensive overview of glass transition theory. The fact that this article is not  
very much out of date is a depressing commentary on the slow progress of this field!  
MODELS OF THE GLASS-TRANSITION, JACKLE J  
REPORTS ON PROGRESS IN PHYSICS 49: (2) 171-231 FEB 1986  
Available in Main Library

A rather technical review of the mode coupling theory:  
RELAXATION PROCESSES IN SUPERCOOLED LIQUIDS, GOTZE W, SJOGREN L  
REPORTS ON PROGRESS IN PHYSICS 55: (3) 241-376 MAR 1992  
Available on-line at <http://www.iop.org/Journals/rp>