N&BM 07-12: Phase Changes (1)

To reiterate:

A phase diagram describes thermal equilibrium, i.e. a static, unchanging situation.

Here we will be interested in phase changes, especially in **melting** and **solidification**. We will keep in mind that for a system to reach equilibrium may take some time. This means that eventually we need to consider the rate at which such changes take place.

We will see that melting/solidification behavior differs greatly between crystalline and amorphous materials because the time scales involved are very different.

Also, for future arguments, we will consider the pressure p to be fixed at 1 atm. The phenomena of interest to us will not depend significantly on the pressure.

N&BM 07-13: Melting (1)

Melting of crystalline solids:

- A crystalline solid has a sharp, well-defined melting point, or melting temperature.
- The molten solid, as a liquid, flows easily and can take on any shape.

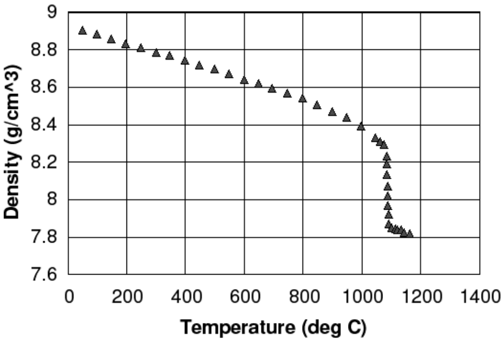
The second point can be expressed more precisely in terms of mechanical properties:

Flowing easily means that the ***liquid*** does not present resistance to shear deformation: Its ***shear modulus is zero***. (This is only an approximation and will be qualified later).

On the other hand, liquids present a great deal of resistance to another type of deformation, namely compression. In general liquids are almost incompressible.

N&BM 07-14: Melting (2)

Another important difference between the solid and liquid state shows up in the density as a function of temperature. Example: Cu.



Experimental data for the density of copper as a function of temperature.

The density drops sharply by about 5% at the melting point of 1088°C.

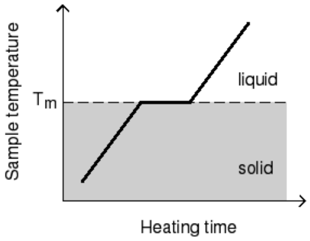
Also note the thermal expansion from room temperature up to the melting point.

N&BM 07-15: Melting (3)

From the point of view of *structure*, melting means that the crystalline solid loses its long-range order and becomes disordered.

From the point of view of *energy*, melting means that the crystalline solid goes from a state of lower to somewhat higher free energy.
Remember: In the disordered state, the average number of nearest neighbors is smaller than in the crystal).

The energy difference between the solid and the melt is supplied by the external heating source:



Schematic plot of sample temperature vs. heating time (very slow heating).

T remains constant at T_m while the solid sample is melting.

N&BM 07-16: Melting (4)

Melting of amorphous solids:

What is the main difference between the melting of a crystal and an amorphous solid (a glass) ?

A glass does not have a distinct melting point. Rather, it gradually becomes softer and softer as its temperature is increased.

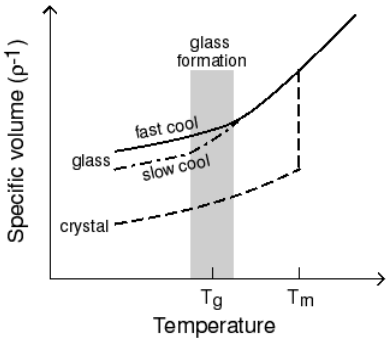
This is not hard to understand:

A glass is disordered even as a solid. There is hardly a difference in structure between a glass in the solid and the liquid state. You can think of a glass as a rigid, frozen-in liquid.

A rising temperature will impart continually increasing mobility to the building blocks of the material, e.g. to the SiO_4 tetrahedra in a silicate glass or polymer chain molecules in a polymer glass. This gradually lowers the resistance of the glass to shear stress and causes it to deform more and more easily.

N&BM 07-17: Melting (5)

The difference in the melting behavior between the crystalline and glassy form of a solid can be illustrated by looking at the **specific volume**, which is the inverse of the mass density:



The curve for the crystal is the inverse of the previous curve for Cu, showing the abrupt change in density at the melting temperature T_m.

For the glass there is no abrupt change at T_m. Also, the exact shape of the curve at lower temperature depends on the cooling rate from the melt (to be discussed later).

N&BM 07-18: Melting (6)

Note the following:

1) Above T_m, there is only one curve, for the liquid.

2) Below T_m, the curve for the glass is higher than the curve for the crystal. This is because the glass is less closely packed than the corresponding crystal.

3) For the glass, there is a temperature T_g, or better a small temperature range around T_g, where the curve changes slope. **T_g** is called the **glass transition temperature**.

4) One can say, qualitatively speaking, that upon increasing the temperature, around T_g the glass looses its rigidity. Equivalently, upon decreasing the temperature, below T_g the disordered structure of the glass is frozen in.

5) Similarly, one can say that below T_g the glass will be brittle and above T_g it will be ductile and tough.

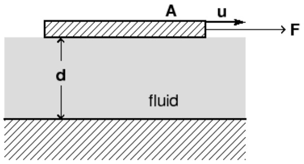
N&BM 07-19: Melting (7)

Typical glass transition and melting temperatures are listed below:

Material	**T_g (°C)**	**T_m (°C)**
Polyethylene	-90	130
Polypropylene	-10	175
Nylon	50	250
Polyvinyl chloride	80	220
Polystyrene	100	240
Polycarbonate	150	265
Soda-lime glass	525	
Borosilicate glass	575	
96% silica	925	
pure silica	1125	~1700

N&BM 07-20: Melting (8)

Since the ease of flow changes continuously with temperature for a glassy material, we need a way to describe this situation quantitatively. We will use the concept of **viscosity** for this purpose.



Consider the setup on the left.

The top plate is being pulled by a horizontal force F at a constant velocity u across a liquid film with thickness d. The area of the plate is A.

Let the direction of u be x, and the vertical direction y.

Experiments show that F is proportional to A and u_x, and inversely proportional to d. Hence we can write:

$$F = \eta A u_x / d$$

where the proportionality constant η is known as the **viscosity**.

N&BM 07-21: Melting (9)

The connection between η and other mechanical properties can be made as follows: Let us write $u_x = \Delta x/\Delta t$. Consequently

$$\frac{u_x}{d} = \frac{1}{d}\frac{\Delta x}{\Delta t} = \frac{1}{\Delta t}\frac{\Delta x}{d} = \frac{\Delta \gamma}{\Delta t}$$

In this equation we have used $\gamma = x/d$ as the shear strain in the fluid induced by the shear stress $\tau = F/A$.

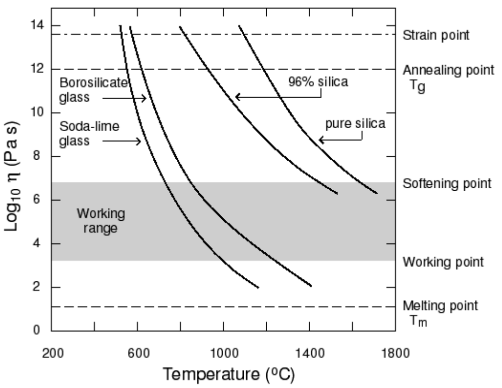
By combining the two equations and solving for η we arrive at

$$\eta = (F/A) / (\Delta\gamma /\Delta t) = \tau / (\Delta\gamma /\Delta t)$$

This means that ***the viscosity η is the ratio of shear stress / shear strain rate.*** For a given shear stress τ, the lower the viscosity, the larger is strain rate of the induced deformation.

N&BM 07-22: Melting (10)

The viscosity is a strong function of temperature:



$1/\eta(T)$ has the usual shape of a thermally activated process. For η itself one can write

$$\log_{10}\eta = C + B/T$$

where B and C are suitable constants.

Strain point:
Built-in strains will relax on the order of hours. At a temperature below the strain point, the glass is essentially rigid.

Annealing point:
This is at around T_g. Built-in strains will relax on the order of minutes.