Kinetics of nucleation and growth

1.1 Thermodynamics versus kinetics

For much of this course, we have concentrated on the derivation and interpretation of equilibrium phase diagrams, making use of the laws of thermodynamics. Thermodynamics tells us how a material is supposed to behave if sufficient time is allowed for the system to reach equilibrium at any given temperature and pressure. Since, in most cases, this requires long-range diffusion of atomic species through solid and/or liquid phases, equilibrium is rarely achieved in practice. Why then spend so much time studying equilibrium thermodynamics? Basically, any system spends its life continuously trying to reach its equilibrium state as the external conditions of temperature and pressure are changed. The rate at which the system approaches equilibrium (i.e. the kinetics) depends very strongly on how far the system deviates from equilibrium (all other things being equal). The further the system is from equilibrium, the greater the free energy difference between its current state and the equilibrium state (i.e. the greater the free-energy driving force for the transformation). The overall rate of a transformation is often a delicate balance between the free-energy driving force and the rate of diffusion (which in turn is determined by the temperature).

In this practical you will explore how the rates of nucleation and growth of new phases vary with temperature. You will examine crystallization in a commercial soda-lime-silica glass, measure the crystal growth rates and interpret them. We also use the time-temperature-transformation (TTT) diagram of another glass to investigate the effect of different heat treatments on the microstructural development of a glass-ceramic. Throughout the practical, no distinction is made between a glass and an undercooled (or supercooled) liquid. Thus crystallization of the glass is analogous to conventional solidification of a liquid, albeit much slower. The practical is in two parts, A and B. They may be done in either order, but in larger classes it may be necessary to direct you to begin with one or the other.

What you should know by the end of the practical!

i. What factors control the rates of nucleation and growth of a phase

ii. Be able to determine an activation energy for diffusion from growth-rate data

iii. Be familiar with the concept of a TTT diagram

iv. Understand how heat treatment is used to control the microstructure of a glass-ceramic
1.2 Crystal Growth

If ordinary window glass is held for long enough just below its liquidus temperature, crystals will begin to form in the undercooled material (which is a liquid, but rather viscous). This devitrification is undesirable in glass-making, because the crystals scatter light and degrade the optical properties of the glass. In addition, the crystals can have thermal expansion coefficients different from that of the parent glass, resulting in stresses that significantly reduce the strength of the glass. Samples of window glass which have been treated for 17 hours at various temperatures between 800°C and 940°C are available for examination. During these heat treatments, long, thin crystals of a phase known as devitrite (Na$_2$O.3CaO.6SiO$_2$) have formed around the edges.

(a) Examine by eye, with or without a hand lens, one of the samples which has been devitrified at around 900°C. Note that the crystals, though transparent, are visible because their optical properties are different from those of the glass.

(b) Examine the same sample between crossed polars on a light box. Note that the crystals are now much easier to see. The glass is optically isotropic and does not transmit light when viewed between crossed polars. The crystals are optically anisotropic, and allow light to pass through.

(c) Measure the lengths of the longest crystals you can see in samples representative of each heat treatment temperature. Where the crystals are large you may wish to use the x15 magnifiers provided. In other cases, use the graticule in the eyepiece of a microscope and a suitable magnification.

The longest crystals can be presumed to have started growing at the beginning of the heat treatment (others may have started growing later, as further nucleation events occurred). Hence the maximum lengths provide an indication of the growth rate. Use them to plot a graph of crystal growth rate $v$, in $\mu$m/hr, against temperature. The liquidus temperature for this composition is 942 °C, and $v$ must therefore be zero at temperatures at or above this. Observe that the plot has the general form indicated in the lecture handout.
(d) Rate processes commonly obey an Arrhenius-type temperature dependence, in which the rate is proportional to $\exp(-Q/RT)$, where $Q$ is the activation energy of the limiting step. However, if you plot your data from part (c) on a graph of $\ln v$ v. $1/T$, (remember to use $T$ in kelvin) you will see that the simple theory does not hold, and you do not get a straight line.

Although the plot in part (d) is not linear, the fundamental atomic mobility in the glass is expected to have an Arrhenius temperature dependence. The growth rate depends not only on the atomic mobility, however, but also on the thermodynamic driving force for crystallization, and has the form:

$$v = C_g \exp\left(-\frac{Q}{RT}\right) \left[1 - \exp\left(-\frac{\Delta G}{RT}\right)\right]$$

where $C_g$ is a constant, $Q$ is the activation energy for atomic motion, and $\Delta G$ is the thermodynamic driving force for crystallization (this is the same as the expression in the lecture handout, except that here $Q$ and $\Delta G$ are molar quantities, so that Boltzmann's constant $k$ is replaced by the gas constant $R$). Remember that $\Delta G$ is a negative quantity - the energy is lower in the final structure.

(e) The driving force is given by $\Delta G = \Delta S \times \Delta T$, where $\Delta T$ is the undercooling below the liquidus temperature. For the present case, the entropy of fusion is $-40 \text{ JK}^{-1}\text{ mol}^{-1}$. Calculate the thermodynamic factor $\langle tf \rangle = [1 - \exp(\Delta G/RT)]$ for each of the temperatures at which the growth rate has been measured, and hence find $v/\langle tf \rangle = C_g \exp(-Q/RT)$. Show that the temperature dependence of the atomic mobility does have an Arrhenius form, by plotting $\ln\{v/\langle tf \rangle\}$ v. $1/T$.

(f) From the plot in (e), estimate the activation energy for atomic motion in the glass.

(g) Look again at a sample devitrified near 900 °C. Where have the crystals nucleated? Is the nucleation likely to have been homogeneous or heterogeneous?

(h) Compare the density of nucleation events seen in the sample treated at 940 °C with the density in any of the other samples. Is this what is expected?
2.1 Time-Temperature-Transformation (TTT) diagrams

You have been introduced to TTT diagrams in the lectures. They are graphs of temperature against log(time), on which various curves corresponding to certain fixed volumes (in %) of the new phase are plotted as a series of ‘C’ curves. Figure 1 is an example of a TTT diagram for a hypothetical glass-ceramic. The numbers beside each C-curve indicate the percentage volume of crystals formed in the glass. For glass-ceramics, the work of nucleation, ΔG*, is high even when heterogeneous nucleation occurs, and so nucleation is favoured at low temperatures and growth at high temperatures. In commercial glass-ceramics, heterogeneous nucleation is induced deliberately by suitable additives such as TiO₂ and ZrO₂.

![TTT curves for crystallisation of a glass](image)

Fig. 1. TTT curves for crystallisation of a glass

(a) From Figure 1, estimate the liquidus temperature of the glass.

(b) Estimate the critical cooling rate for glass formation (i.e. starting at the liquidus temperature, calculate the cooling rate required to prevent any crystals forming).

For the purposes of interpreting TTT diagrams, the glassy phase can be considered to be a liquid. Thus, for example, if the glass were held at 1600 °C to become fully liquid, and then instantly quenched to 1250 °C and held there for 10³ seconds, we would expect there then to be 20% glass (= liquid) and 80% solid (crystal) in the glass-ceramic. This would be retained on quenching instantly to room temperature from 1250°C.
Consider two samples A and B, produced as follows:

(A) Held at 1600°C for two hours, then instantly quenched to 1330°C, held there for 3000 seconds and then quenched to room temperature.

(B) Held at 1600°C for two hours, then instantly quenched to 1150°C, held there for 3000 seconds and then quenched to room temperature.

(c) Calculate the percentage of crystals formed in each sample.

(d) What difference in microstructure would you expect between the two samples?

In commercial glass-ceramics, it is desirable to have a fine-grained microstructure with as little glass as possible. It is also important that the heat-treatment applied to the material should be easy to control.

(e) Explain why either too short a period of heat treatment (e.g. a few seconds) or too long a period (e.g. days or weeks) is undesirable for commercial glass-ceramics.

(f) Giving your reasons, suggest a heat treatment schedule which would result in a desirable microstructure.

{Glass ceramics are used commercially in cooker hobs and oven-to-table ware}