

6 Solid state formation

6.1 Explain why a liquid has to be cooled down below the melting point to become solid. Discuss the possibilities to produce a cast with small grains.

In spite of the second law of thermodynamics, crystallization of pure liquids usually begins at a lower temperature than the melting point, due to high activation energy of homogeneous nucleation. The creation of a nucleus implies the formation of an interface at the boundaries of the new phase. There is an energy cost to form this interface, based on the surface energy of each phase. If a hypothetical nucleus is too small, the energy that would be released by forming its volume is not enough to create its surface, and nucleation does not proceed. Freezing does not start until the temperature is low enough to provide enough energy to form stable nuclei.

The stability of a solid cluster within the melt depends on its surface-volume ratio. The critical nucleus size can be denoted by its radius, and it is at $r=r^*$ (r^* critical radius) that the nucleation proceeds. For example in the classic case of a spherical cluster that liberates $-G_V$ during formation (here G_V is a negative quantity), but which must pay the positive cost of G_i of surface interfacing with the surrounding, the free energy needed to form a spherical cluster of radius r is:

$$\Delta G = -\Delta G_V + \Delta G_i = -\frac{4}{3}\pi r^3 G_v + 4\pi r^2 \sigma$$

so we have nuclei formation. Cooling the system to below the melting point along the G-curve of the liquid, one gains free enthalpy, which can be used for nuclei formation.

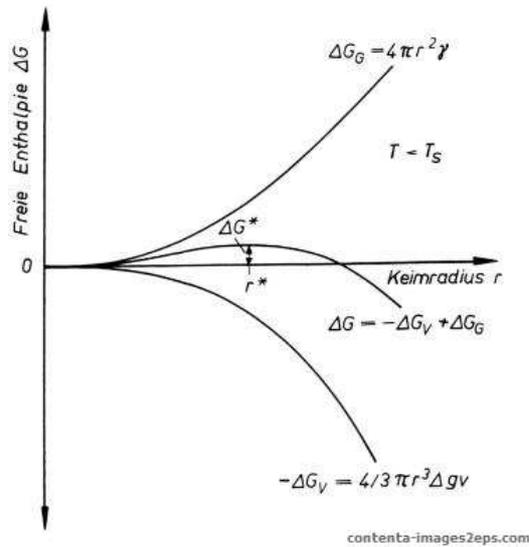


Figure 1: Nucleation: critical radius r^*

What are the possibilities to fabricate metallic casts with **small** grains?

- Use a high supersaturation / undercooling of the melt for the starting of the crystallization (the higher the undercooling, the smaller the critical radius \rightarrow more crystallites start to grow).
- Use heterogeneous nucleation by adding insoluble particles as foreign nuclei.

6.2 The size of the critical nucleus is often considered in 2D. Here, the stability of the nuclei depends on the lattice symmetry. Discuss the differences between 6- and 4-fold symmetry. Why are the magic islands on 4-fold symmetry surfaces monomer, dimer and tetramer, whereby on 6-fold symmetry surfaces one finds monomer, dimer, trimer and heptamer? How can the size of the critical nucleus be determined?

The critical nuclei rather decay or dissociate. They become stable by incorporation of a extra building unit (atom / molecule). Larger number of bonds per atom means higher stability.

- 4-fold-symmetry: square lattice
Magic islands are monomer, dimer, tetramer

The number of bonds needed to break to take one atom off the cluster is 0, 1, and 2, respectively.

b. 6-fold-symmetry: hexagonal lattice

Magic islands are monomer, dimer, trimer and heptamer

The number of bonds needed to take one atom off the cluster is 0, 1, 2, and 3, respectively.

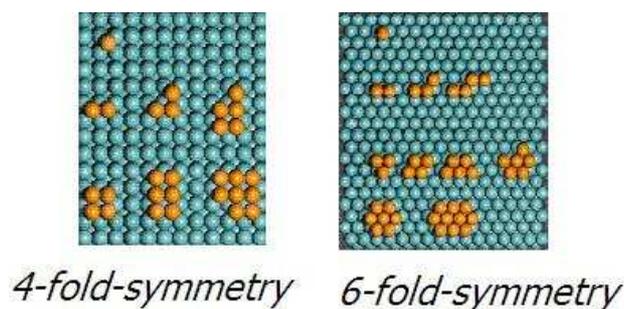


Figure 2: 4-fold and 6-fold symmetry

The critical nucleus can be calculated from the gradient of the slope of an Arrhenius plot of $1/T$ vs n_x per lattice site (on a logarithmic axis).

See "Surface diffusion: Atomic & Collective process", Plenum press, Ny, 1977, Müller et al, p 155.

6.3 Please explain from an experimental point of view, how a DSC-measurement has to be performed. What are the important steps to be performed?

Differential scanning calorimetry or DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The basic principle underlying this technique is that when the sample undergoes a physical transformation such as phase transition, more or less heat will need

to flow to it than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic. For example, as a solid sample melts to a liquid it will require more heat flowing to the sample to increase its temperature at the same rate as the reference. This is due to the absorption of heat by the sample as it undergoes the endothermic phase transition from solid to liquid. Likewise, as the sample undergoes exothermic processes (such as crystallization) less heat is required to raise the sample temperature. By observing the difference in heat flow between the sample and reference, differential scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions. DSC may also be used to observe more subtle phase changes, such as glass transitions.

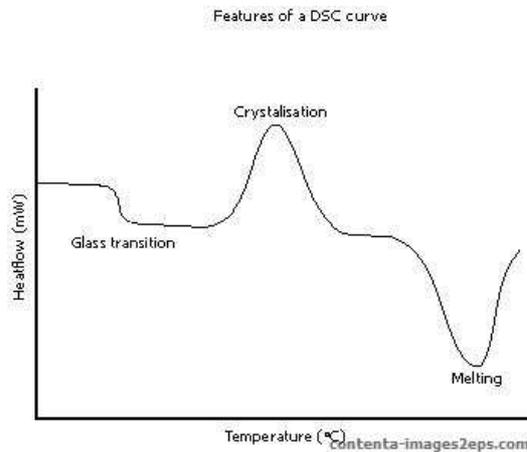


Figure 3: schematic DSC curve demonstrating the appearance of several common features

It is widely used in industrial settings as a quality control instrument due to its applicability in evaluating sample purity and for studying polymer curing. Differential scanning calorimetry can be used to measure a number of characteristic properties of a sample. Using this technique it is possible to observe fusion and crystallization events as well as glass transition temperatures T_g . DSC can also be used to study oxidation, as well as other chemical reactions. Glass transitions may occur as the temperature of an amorphous solid is increased. These transitions appear as a step in the baseline of the recorded DSC signal. This is due to the sample undergoing a change in heat capacity; no formal phase change occurs. As the temperature increases, an

amorphous solid will become less viscous. At some point the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature (T_c). This transition from amorphous solid to crystalline solid is an exothermic process, and results in a peak in the DSC signal. As the temperature increases the sample eventually reaches its melting temperature (T_m). The melting process results in an endothermic peak in the DSC curve. The ability to determine transition temperatures and enthalpies makes DSC a valuable tool in producing phase diagrams for various chemical systems.

6.4 Thermally activated processes show a characteristic behavior. How this behavior can be quantitatively described?

This behavior can be quantitatively described by an Arrhenius plot displays the logarithm of kinetic constants ($\ln(k)$, ordinate axis) plotted against inverse temperature ($1/T$, abscissa). Arrhenius plots are often used to analyze the effect of temperature on the rates of chemical reactions. For a single rate-limited thermally activated process, an Arrhenius plot gives a straight line, from which the activation energy and the pre-exponential factor can both be determined. The Arrhenius equation can be given in the form:

$k = Ae^{-E_a/RT}$ or alternatively $k = Ae^{-E_a/k_B T}$ The only difference is the energy units: the former form uses energy/mole, which is common in chemistry, while the latter form uses energy directly, which is common in physics. The different units are accounted for in using either $R \equiv$ gas constant or Boltzmanns constant k_B . The former form can be written equivalently as: $\ln(k) = \ln(A) - \frac{E_a}{R} \left(\frac{1}{T}\right)$ Where:

k = Rate constant

A = Pre-exponential factor

E_a = Activation energy

R = Gas constant

T = Absolute temperature.

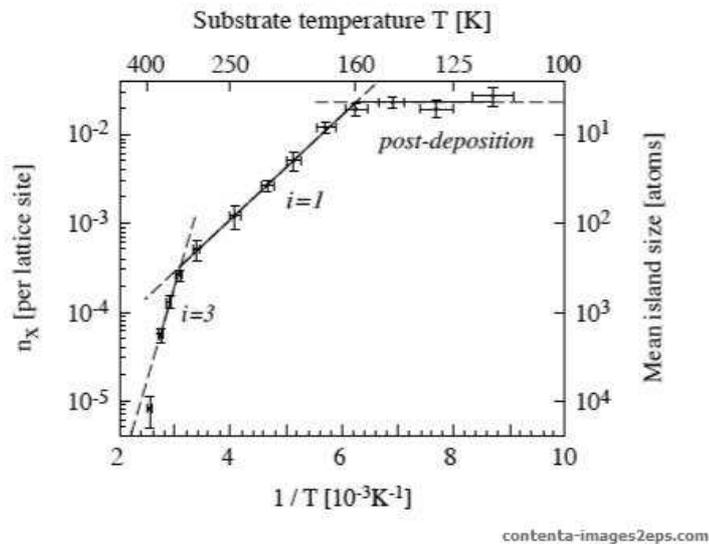


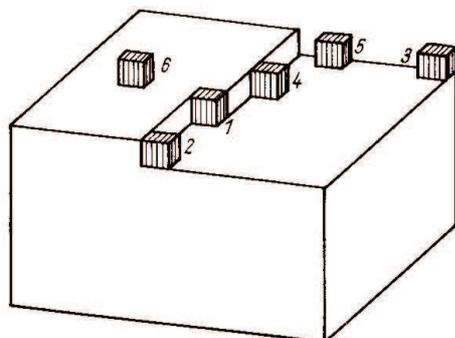
Figure 4: Arrhenius plot of the island density

6.5 Draw a top view of a screw dislocation. Discuss the incorporation of atoms at the edge. Explain the formation of growth spirals and their shape.

The probability of atoms to stick to the surface of a solid state depends on their energetical state, which is related to the possibilities of the atoms to move across the solid state surface and the number of bonds they form with the substrate. Consider a solid state whose surface presents an edge (cp. Fig.5). An atom at position 1 can move in one direction (along the edge) and bonds to the substrate on three sides, and is thus in the most stable state in this configuration. This means it will tend to stay at this position. Atom 2 can move in one direction as well, however it forms bonds on only two sides and has therefore a slightly higher probability to move. An atom that sits on the flat surface (atom 6), on the other hand, has a high mobility and will tend to move (statistically) towards a more stable position. During depositions atoms will tend to stick to edges.

Now consider a screw dislocation on the surface of a solid state (cp. Fig.6), which presents itself as an edge with decreasing height. Similarly as the situation in Fig.5, atoms will tend to stick to the dislocation. Since the height of the dislocation diminishes, a new edge, facing the opposite direction, is

formed when the dislocation is filled up. Simultaneously, atoms will laterally add, extending the area of the growing island. The process repeats with the newly formed edge, yielding the well known spiral growth pattern.



Example NaCl:

1 - growth point (kink site) $E = 0.87$

2 - edge site $E = 0.49$

3 - terrace site $E = 0.25$

4 - edge site $E = 0.18$

5 - terrace site $E = 0.09$

6 - terrace site $E = 0.07$

Units $[e^2/r]$ with ion charge and r shortest distance between different ions.

Figure 5: Energies of atoms on a substrate with an edge.

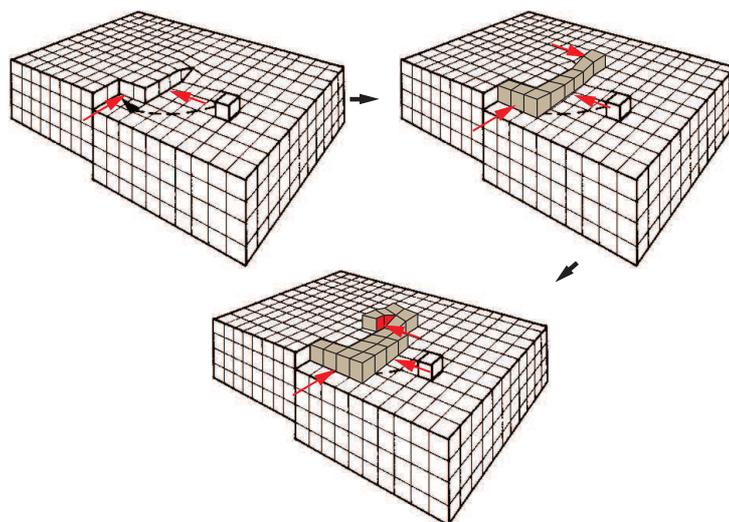


Figure 6: Spiral growth process. The red arrows indicate locations where new atoms tend to stick.